

## CHEMISTRY

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## CHAPTER 1

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## IMPORTANT NOTES

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## CHAPTER 1

## THERMODYNAMICS-01

## 1. INTRODUCTION

Thermodynamics is concerned with energy and its transformation in various forms in different physical and chemical processes.

Thermodynamics     ≡     Thermo + dynamics

Dynamics              ≡     Study of change due to a driving force

Thermo                ≡     Thermal which is related to temperature or energy.

The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change. Laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state. Macroscopic properties like pressure and temperature do not change with time for a system in equilibrium state.

## 2. SOME BASIC DEFINITITIONS (Thermodynamic terms)

## 2.1 SYSTEM :

The macroscopic part of the universe under study is called a **system**. Rest of the universe outside the system is called **surroundings**. The actual or imaginary surface that separates the system from the surroundings is called the **boundary**.

However, the entire universe other than the system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighbourhood of the system constitutes its surroundings.

## 2.1.1 Types of boundary :

- (i) Real or imaginary
- (ii) Rigid (fixed) or movable (flexible)
- (iii) Permeable (allow mass transfer) or impermeable (does not allow mass transfer).
- (iv) Diathermal (allow heat transfer) or Adiabatic (does not allow heat transfer).

## 2.1.2 Types of systems :

- (i) **Isolated system** : A system is said to be isolated if it cannot exchange both matter and energy with the surroundings. Example : coffee in a thermos flask.
- (ii) **Closed system** : A system is said to be closed if it can exchange energy but not matter. Example : Coffee in a closed stainless steel flask.
- (iii) **Open system** : A system is said to be open if it can exchange matter and energy. Example : A thermos flask or a steel flask if not closed.

**Note :** A perfectly isolated system is only a theoretical system.

- 2.2 State of system :** A system is called in a particular state where all the macroscopic properties of the system have definite value.
- 2.3 Properties of system :** The state of a system is defined by a particular set of its measurable quantities called properties. They can be categorised into extensive and intensive properties. Intensive property is one whose value is independent of the size (or mass) of the system. An extensive property is one whose value depends on the size (or mass) of the system.
- \* Extensive properties are additive but intensive properties are non additive.
  - \* Ratio of two extensive property gives an intensive property.

<b>Extensive Properties</b>	<b>Intensive Properties</b>
Volume	Molar volume
Number of moles	Density
Mass	Refractive index
Free Energy (G)	Surface tension
Entropy (S)	Viscosity
Enthalpy (H)	Free energy per mole
Internal energy (E & U)	Specific heat
Heat capacity	Pressure
	Temperature
	Boiling point, freezing point etc

- 2.4 State function or state variable :** Variables like P, V, T are State Functions or State Variables because their values depend only on the present state of a system and not on how the state was reached

**Condition for a function to be a state function :**

(i) If  $\phi$  is state function,  $\int_A^B d\phi = \phi_B - \phi_A$

(ii) If  $\phi$  is a state function,  $\oint d\phi = 0$

- 2.5 Path function :** Function which depends on the path, i.e. how the process is carried out e.g. work & heat.
- 2.6 Thermodynamic process :** A thermodynamic process involves change of a system from one state to another state.

## EXERCISE-I

- 1.** Which of the following are extensive and which are intensive properties ?

Temperature, boiling point, melting point, pressure , density , viscosity , surface tension, refractive index, molar volume, free energy/mole, specific heat, Specific volume , Mass , Volume , number of moles , Heat capacity , internal energy, enthalpy , entropy ,  $\Delta G$ , concentration, dipole moment, pH, gas constant, vapour pressure, specific gravity, E.M.F. of the dry cell, molarity, molality .

**Sol.** **Intensive property :** Temperature, (boiling point, melting point), pressure , density , viscosity, surface tension, refractive index, molar volume, free energy/mole, specific heat, Specific volume, concentration, dipole moment, pH, gas constant, vapour pressure, specific gravity, E.M.F. of the dry cell, molarity, molality.

**Extensive property :** Mass , Volume , number of moles , Heat capacity , internal energy, enthalpy, entropy

- 2.** Which of the following are state function & path function ?

Pressure, Volume, Enthalpy, Work, Heat, Gibbs energy, temperature, Internal energy, Entropy,

**Sol.** **State function :** Pressure, volume , enthalpy, Gibbs energy, temperature, Internal energy, Entropy,

**Path function :** Work , Heat

- 3.** A state function is that :

- (A) which is used in thermochemistry
- (B) which obeys all laws of thermodynamics
- (C) quantity whose value depends only upon the state of the system
- (D) quantity which is used in measuring thermal change

**Ans. (C)**

- 4.** Which amongst the following is an extensive property of the system -

- (A) Temperature
- (B) Volume
- (C) Viscosity
- (D) Refractive index

**Ans. (B)**

- 5.** Which of the following is not a state function of thermodynamic system -

- (A) Internal energy(E)
- (B) Free energy(G)
- (C) Enthalpy(H)
- (D) Work(W)

**Ans. (D)**

- 6.** What is true for a cyclic process [E = internal energy]

- (A)  $W=0$
- (B)  $\Delta E = 0$
- (C)  $\Delta H = 0$
- (D) B & C both

**Ans. (D)**

- 7.** The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy ?

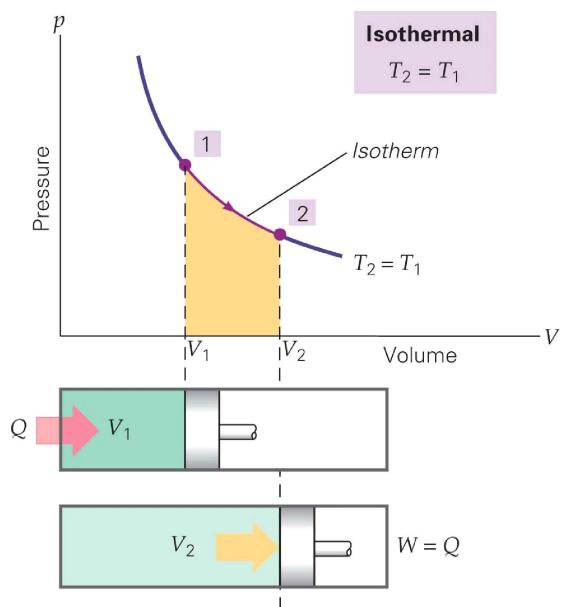
[AIEEE-2003]

- (A)  $< 40 \text{ kJ}$
- (B) Zero
- (C)  $40 \text{ kJ}$
- (D)  $> 40 \text{ kJ}$

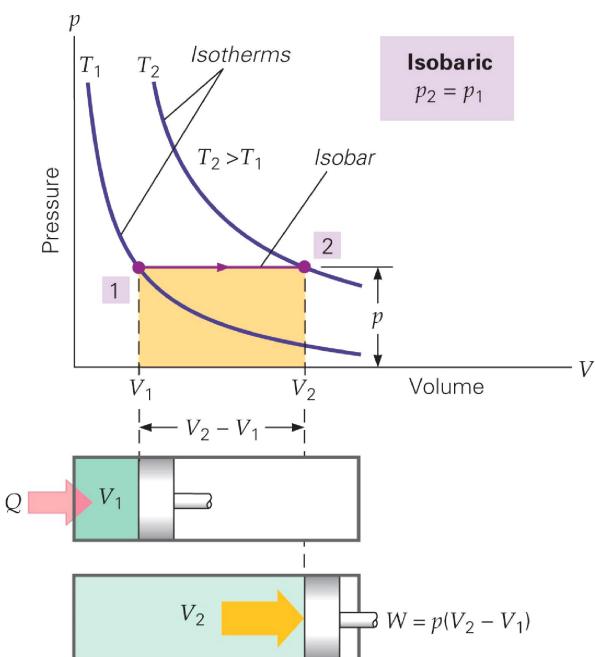
**Ans. (B)**

**Type of process :**
**(i) Isothermal process :**

A process in which temperature of the system remains constant is called isothermal process.


**(ii) Isobaric process :**

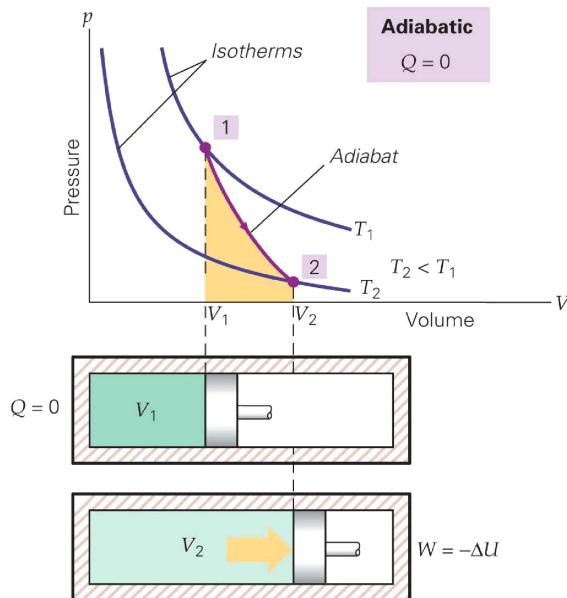
A process in which pressure of the system remains constant is called isobaric process. Temperature and volume of the system may change.



**Ex.** All the reactions or processes taking place in open vessel like boiling of water in open vessel, burning of charcoal, melting of wax take place at constant pressure (1 atm.)

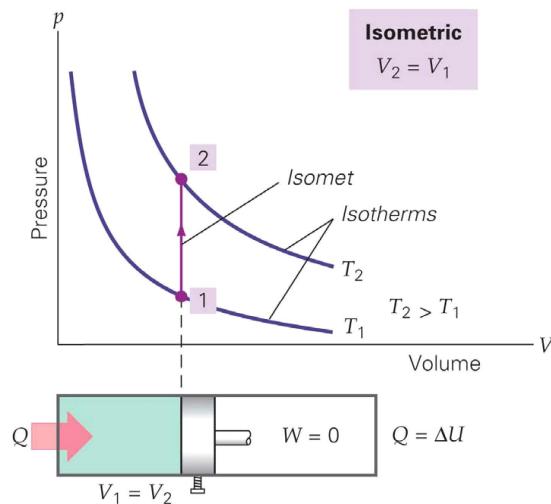
**(iii) Adiabatic process :**

A process in which no heat exchange takes place is called adiabatic process. Adiabatic process occurs in systems with insulated walls.



**(iv) Isochoric process :**

The process for which volume of the system remains constant is called isochoric process i.e., Heating of gas in closed or rigid vessel.



**(v) Cyclic process :** It is combination of two or more process in which the final state of system, becomes identical to the initial. The net change in all thermodynamic properties of system must be zero.

$$\Delta T = \Delta P = \Delta V = \Delta H = \Delta S = \Delta G \dots = 0$$

However  $Q_{\text{net}}$  or  $W_{\text{net}}$  may or may not be zero.

- (vi) **Reversible or Irreversible process :** If the initial state may be received just by reversing the direction of process at any state, process is called reversible. In irreversible process the initial state can never be achieved just by reversing the direction of process.

In the reversible process, the driving force is only infinitesimally greater than the opposing force. In the irreversible process, they differ largely.

A perfectly reversible process is a theoretical process because it takes infinite time but reversible processes are important because it results maximum efficiency in any machine. The actual process occurring in the machine is quasi static which may tend to reversible or irreversible process. During irreversible process, one of the equation of state like  $PV = nRT$ , is valid. Such equation is valid only at initial & final state. However during reversible process such equation are valid throughout the process.

A process is reversible when the system throughout remain in thermodynamic equilibrium with the surrounding.

A system is said in thermodynamic equilibrium when it simultaneously satisfy the following equilibria.

- (a) **Thermal equilibrium:** Same temperature throughout (No heat transfer within the system)
- (b) **Mechanical equilibrium :** Same pressure or force throughout the system (No work should be performed by one part on the other)
- (c) **Material equilibrium :** No change in the composition of system with time. No mass transfer within the system.

If a system is in thermodynamic equilibrium there is no net energy or mass transfer within the system.

### 3. WORK

Thermodynamically, work may be defined as the form of energy which appears only when, there is some change in the boundary of the system. Such work is called mechanical or PV work.

Work may also be non-mechanical like electric work.

Presently, we will discuss only mechanical work.

- (i) It is not thermodynamic property of system.
- (ii) It depends on the quantity of system.
- (iii) Sign convention, work on system = (+)ve.

In physics, work is calculate from the force applied by system, but in chemistry due to external force.

$$W = \int_{V_1}^{V_2} P \cdot dV = - \int_{V_1}^{V_2} P_{\text{ext}} dV$$

Physics	Chemistry
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#### 4. HEAT

Heat is defined as the energy that flows into or out of a system because of a difference in temperature between the system and its surrounding.

According to IUPAC convention

**heat lost by system is expressed with -ive sign**

**heat given to system is expressed with +ive sign**

- \*  $q_v = nC_{v,m} dT$
- \*  $q_p = nC_{p,m} dT$
- \*  $C_{p,m} - C_{v,m} = R$  (for ideal gas)
- \*  $C_v$  &  $C_p$  depends on temperature even for an ideal gas. ( $C = a + bT + cT^2 \dots$ )

**General values of  $C_v$  &  $C_p$  for an ideal gas can be taken as follows.**

Atomicity		$n_{tr}$	$n_{Rot}$	$n_{Vib}$	$C_v$		$C_p$		$\gamma$	
						Incl. Vib	Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib
Mono		3	0	0	$\frac{3}{2}R$	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$	$\frac{5}{3}$
Di		3	2	1	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{2}R$	$\frac{9}{2}R$	$\frac{7}{5}$	$\frac{9}{7}$
Tri	Linear	3	2	4	$\frac{5}{2}R$	$\frac{13}{2}R$	$\frac{7}{2}R$	$\frac{15}{2}R$	$\frac{7}{5}$	$\frac{15}{13}$
	Non Linear	3	3	3	$3R$	$6R$	$4R$	$7R$	$\frac{4}{3}$	$\frac{7}{6}$

#### 5. INTERNAL ENERGY (E & U)

Every system having some quantity of matter is associated with a definite amount of energy, called internal energy.

$$U = U_{\text{Kinetics}} + U_{\text{Potential}} + U_{\text{Electronic}} + U_{\text{nuclear}} + \dots$$

U is a state function & is an extensive property.

$$\Delta U = U_{\text{final}} - U_{\text{initial}}$$

For a given closed system

$$U = f(T, V)$$

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV$$

## 6. ENTHALPY

Chemical reactions are generally carried out at constant pressure (atmospheric pressure) so it has been found useful to define a new state function **Enthalpy** (H) as.

$$H = U + PV$$

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

at constant pressure

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

combining with first law.

$$\Delta H = q_p$$

Hence transfer of heat at constant volume brings about a change in the internal energy of the system whereas that at constant pressure brings about a change in the enthalpy of the system.

### 6.1 RELATIONSHIP BETWEEN $\Delta H$ & $\Delta U$ :

The difference between  $\Delta H$  &  $\Delta U$  becomes significant only when gases are involved (insignificant in solids and liquids)

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

If substance is not undergoing chemical reaction or phase change.

$$\Delta H = \Delta U + nR\Delta T$$

In case of chemical reaction

$$\Delta H = \Delta U + (\Delta n_g)RT$$

## 7. ZEROTH LAW OF THERMODYNAMICS

Two systems in thermal equilibrium with a third system are also in thermal equilibrium with each other. It introduces temperature as a state function.

## 8. FIRST LAW OF THERMODYNAMICS

"Total energy of universe remains constant." It is law of conservation of energy.

Let us consider a system whose internal energy is  $U_1$ . If the system is supplied with heat  $q$ , the internal energy of the system increases to  $U_1 + q$ . If work ( $w$ ) is done on the system, the internal energy in the final state of the system,  $U_2$  is given by

$$U_2 = U_1 + q + w$$

or  $U_2 - U_1 = q + w$

$$\Delta U = q + w$$

According to IUPAC, heat added to the system and work done on the system are assigned positive values as both these modes increase the internal energy of the system.

## EXERCISE - 2

**8.** Represent the following observations in terms of proper IUPAC symbol?

- (a) Heat absorbed by a system is 20 Joule.
- (b) Work done by a system is 40 Joule.
- (c) Work done on a system is 5 Joule.
- (d) Heat given out by system is 50 Joule.

**Ans.** It is standard practice to represent both types of heat and work (in/out or on/by) by single symbols q and w -

- (a)  $q = +20$  Joule.
- (b)  $w = -40$  Joule.
- (c)  $w = +5$  Joule.
- (d)  $q = -50$  Joule.

**9.** For certain processes the heat and work exchanged between system and surrounding is given in standard format. Describe the physical interpretation of each observation.

- (a)  $q = +10$  kJ
- (b)  $w = -20$  kJ

**Ans. (a)  $q = + 10$  kJ :**

Since numerical value of q is positive, this shows heat is absorbed by the system from surrounding resulting in gain of energy by system.

**(b)  $w = - 20$  kJ :**

Since numerical value of work is negative, this shows work is done by the system on surrounding resulting in loss of energy of system.

**10.** Predict sign of work done in following reactions at constant pressure.

<b>Initial state</b>	<b>Final state</b>
(i) $\text{H}_2\text{O(g)}$	$\longrightarrow$
(ii) $\text{H}_2\text{O(s)}$	$\longrightarrow$
(iii) $\text{H}_2\text{O(l)}$	$\longrightarrow$
(iv) $\text{CaCO}_3(\text{s})$	$\longrightarrow$
	$\text{CaO(s)} + \text{CO}_2(\text{g})$

**Ans. (i) + , (ii) - , (iii) - , (iv) -**

**11.** Explain why variation of enthalpy for a process involving an ideal gas is given by  $dH = nC_p dT$ , irrespective of process ?

**Sol.** Because

$H_{\text{ideal gas}} = f(T)$ , independent of pressure or volume

**12.** The heat capacity of a molecule depends upon complexity of the molecule. Explain ?

**Sol.** The heat capacity can be defined as energy needed to raise the temperature of a body by  $1^\circ\text{C}$ . The molecule which have large number of degree's of freedom requires larger quantity of heat to raise the temperature by  $1^\circ\text{C}$ . This is because energy supplied is distributed in each degree of freedom equally.

**13.** If work done by the system is 300 joule when 100 cal heat is supplied to it. The change in internal energy during the process is :-

- (A) - 200 Joule
- (B) 400 Joule
- (C) 720 Joule
- (D) 120 Joule

**Ans. (D)**

14. One mole of a gas absorbs 200J of heat at constant volume. Its temperature rises from 298 K to 308 K. The change in internal energy is :-

**Ans. (A)**

15. A system has internal energy equal to  $U_1$ , 450 J of heat is taken out of it and 600 J of work is done on it. The final energy of the system will be -

(A)  $(U_1 + 150 \text{ J})$       (B)  $(U_1 + 1050 \text{ J})$       (C)  $(U_1 - 150 \text{ J})$       (D)  $(U_1 - 1050 \text{ J})$

**Ans. (A)**

- 16.** The work done by a system is 8J when 40J heat is supplied to it. The change in internal energy of the system during the process :

**Ans. (A)**



**Ans. (A)**

- 18.** 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  $3 \text{ atm}$  is -

**Ans. (A)**

- 19.** Assuming that water vapour is an ideal gas, the internal energy change ( $\Delta U$ ) when 1 mol of water is vapourised at 1 bar pressure and 100°C, (Given : Molar enthalpy of vapourisation of water at 1 bar and 373 K = 41 kJ mol<sup>-1</sup> and R = 8.3 J mol<sup>-1</sup> K<sup>-1</sup> will be) :- [AIEEE-2007]

(A) 4.100 kJ mol<sup>-1</sup>      (B) 3.7904 kJ mol<sup>-1</sup>      (C) 37.904 kJ mol<sup>-1</sup>      (D) 41.00 kJ mol<sup>-1</sup>

**Ans.(3)**

20. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be :- [JEE-MAIN-2013]

(R = 8.314 J/mol K) (ln 7.5 = 2.01)

(A)  $q = + 208 \text{ J}$ ,  $w = - 208 \text{ J}$       (B)  $q = - 208 \text{ J}$ ,  $w = - 208 \text{ J}$

(C)  $q = -208 \text{ J}$ ,  $w = +208 \text{ J}$

$$(B) q = -208 \text{ J}, w = -208 \text{ J}$$

(D)  $q = + 208 \text{ J}$ ,  $w = + 208 \text{ J}$

**Ans.(A)**

**Sol.**  $q = + 208$  Joule

for isothermal process

$$\Delta U = 0$$

from 1<sup>st</sup> law

$$\Delta U = q + w$$

$$0 = q + w$$

$$w = -q = -208 \text{ Joule}$$

## 9. CALCULATION OF $q$ , $w$ , $\Delta U$ & $\Delta H$ IN VARIOUS PROCESS :

### 9.1 ISOTHERMAL EXPANSION OR COMPRESSION OF IDEAL GAS :

For isothermal process :  $\Delta T = 0$

$$\therefore \Delta U = n.C_{p,m} \cdot \Delta T = 0$$

$$\Delta H = n.C_{p,m} \cdot \Delta T = 0$$

$$\text{and } q = \Delta U - w = -w$$

Now,  $w$  depends on path (reversible or irreversible).

#### 9.1.1 Reversible process :

$$w_{\text{rev.}} = - \int_{V_1}^{V_2} P_{\text{ext}} \cdot dV = - \int_{V_1}^{V_2} (P \pm dP) \cdot dV = - \int_{V_1}^{V_2} P \cdot dV = - \int_{V_1}^{V_2} \frac{nRT}{V} \cdot dV$$

$$\therefore w_{\text{rev.}} = -nRT \cdot \ln \frac{V_2}{V_1} = -nRT \cdot \ln \frac{P_1}{P_2}$$

#### 9.1.2 Irreversible process, against a constant external pressure :

$$w_{\text{irr.}} = -P_{\text{ext}} \int_{V_1}^{V_2} dV = -P_{\text{ext}}(V_2 - V_1)$$

#### 9.1.3 Free expansion (or expansion in vacuum) :

$P_{\text{ext}} = 0$  but  $dV = \text{finite}$ , Hence,  $w = 0$

#### 9.1.4 Comparison of magnitude of work :

In expansion, magnitude of work =  $-w_{\text{exp}}$

In compression, magnitude of work =  $w_{\text{comp}}$

$$\text{Now, } w_{\text{rev}} - w_{\text{irr}} = (-P \cdot dV) - (-P_{\text{ext}} \cdot dV) = (P_{\text{ext}} - P) \cdot dV$$

= -ve, always

In expansion,  $P_{\text{ext}} < P$  and  $dV = +ve$

In compression,  $P_{\text{ext}} > P$  and  $dV = -ve$

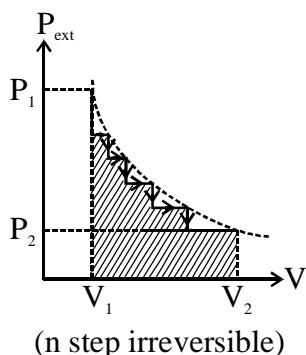
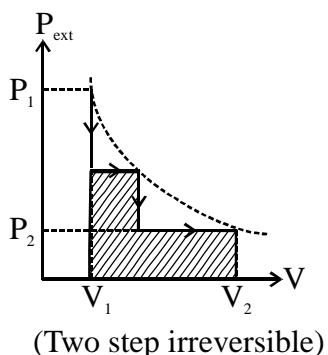
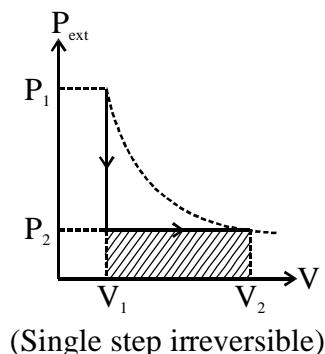
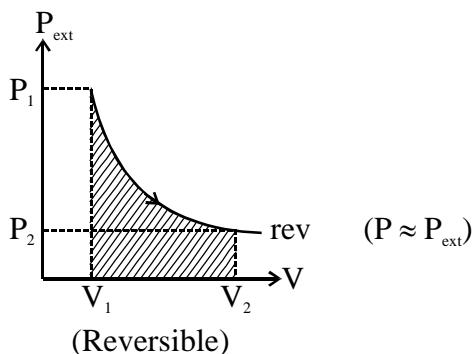
Hence,  $w_{\text{rev}} < w_{\text{irr}}$  (Always, with proper sign).

Now, as magnitude of work in expansion is  $-w_{\text{exp}}$ , hence,  $(-w_{\text{rev, exp}}) > (-w_{\text{irr, exp}})$ , i.e., magnitude of work is greater when expansion is reversible.

And, as magnitude of work in compression is  $w_{\text{comp}}$ , hence,  $(w_{\text{rev, comp}}) < (w_{\text{irr, comp}})$ , i.e., magnitude of work is greater when compression is irreversible.

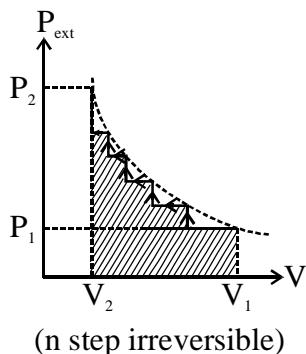
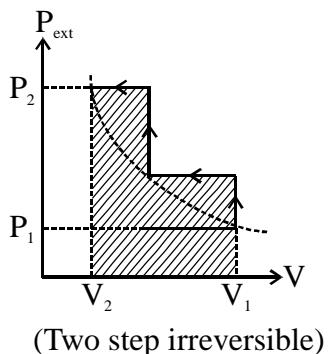
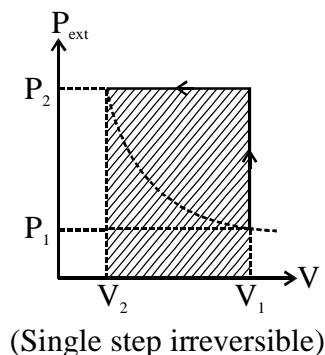
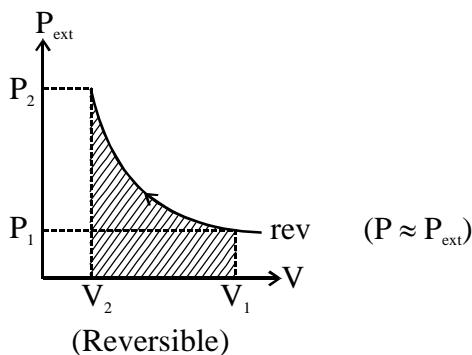
### 9.1.5 Graphical comparison :

#### (a) Expansion :



$(-w_{\text{exp}})$  : Rev > n step > ..... > 2 step > single step

#### (b) Compression :



$(w_{\text{comp}})$  : Rev < n step < ..... < 2 step < single step

**Ex.1 Two moles of an ideal gas undergoes isothermal expansion from 4L to 20L at 27°C.**

**Calculate q, w, ΔU and ΔH, if the process is performed.**

- (i) **reversibly**
- (ii) **irreversibly, against a constant external pressure of 1atm.**
- (iii) **as free expansion**

**Sol.** For isothermal process,  $\Delta T = 0$ . Hence,

$$\Delta U = n \cdot C_{v,m} \cdot \Delta T = 0$$

$$\Delta H = n \cdot C_{p,m} \cdot \Delta T = 0$$

$$(i) \quad w = -nRT \cdot \ln \frac{V_2}{V_1} = -2 \times 8.314 \times 300 \times \ln \frac{20}{4} = -8028.52 \text{ J}$$

$$\text{and } q = -w = 8028.52 \text{ J}$$

$$(ii) \quad w = -P_{\text{ext}} \cdot (V_2 - V_1) = -1 \text{ atm}(20 \text{ L} - 4 \text{ L}) = -16 \text{ L-atm} \\ = -16 \times 101.3 \text{ J} = -1620.8 \text{ J}$$

$$q = -w = 1620.8 \text{ J}$$

$$(iii) \quad w = 0 \text{ and } q = 0$$

## 9.2 ADIABATIC EXPANSION OR COMPRESSION OF IDEAL GAS :

$$q = 0$$

$$\therefore \Delta U = w = n \cdot C_{v,m} \cdot (T_2 - T_1)$$

$$\text{and } \Delta H = n \cdot C_{p,m} \cdot (T_2 - T_1)$$

The change in temperature may be calculated as

$$n \cdot \int_{T_1}^{T_2} C_{v,m} \cdot dT = - \int_{V_1}^{V_2} P_{\text{ext}} \cdot dV$$

- (a) If  $C_{v,m}$  is temperature independent and the process is reversible, then

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

$$\text{or, } P \cdot V^\gamma = \text{constant}$$

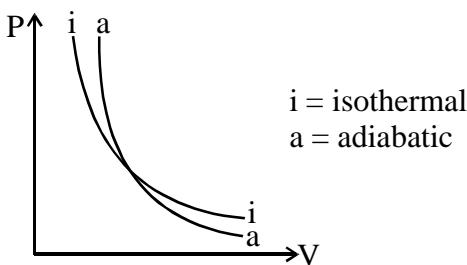
$$\text{or, } T^\gamma P^{1-\gamma} = \text{constant}$$

- (b) If  $C_{v,m}$  is temperature independent and the process is irreversible, then

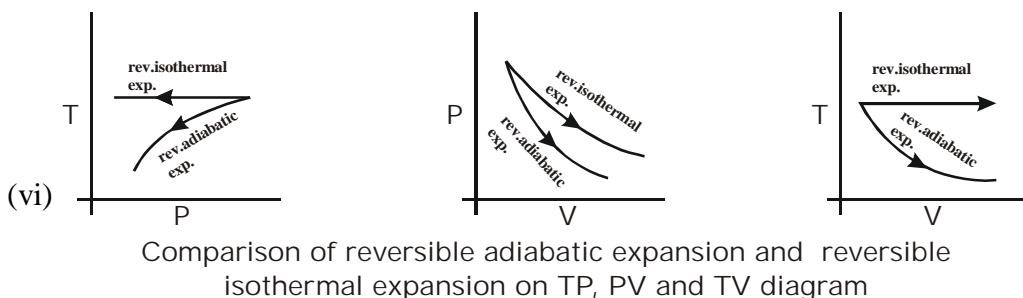
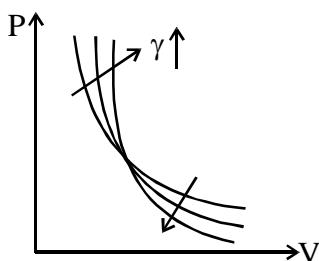
$$n \cdot C_{v,m} \cdot (T_2 - T_1) = -P_{\text{ext}} \cdot (V_2 - V_1)$$

- (i) The temperature of ideal gas decreases in adiabatic expansion (except free expansion, which is isothermal too) and the temperature of ideal gas increases in adiabatic compression.

- (ii) The final temperature of gas is always higher in irreversible process (expansion or compression) relative to reversible process, for the same change in volume.
- (iii) Just like isothermal process, the magnitude of work is maximum when expansion is reversible and compression is irreversible (single step).
- (iv) Work in reversible isothermal and adiabatic processes may be compared graphically.



- (v) Work in reversible adiabatic process may be compared graphically.



- Ex.2. Two moles of an ideal monoatomic gas undergoes adiabatic expansion from 5L, 127°C to 40L. Calculate q, ΔU, w and ΔH, if the process is performed.**
- (i) **reversibly**
  - (ii) **irreversibly, against a constant external pressure of 0.1 atm.**
  - (iii) **as free expansion**

**Sol. :** For adiabatic process,  $q = 0$

$$(i) \quad T \cdot V^{\gamma-1} = \text{constant} \Rightarrow T_1 \cdot V_1^{\gamma-1} = T_2 \cdot V_2^{\gamma-1}$$

$$\therefore T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1} = 400 \times \left( \frac{5}{40} \right)^{\frac{5}{3}-1} = 100 \text{ K}$$

$$\text{Now, } w = \Delta U = nC_v \Delta T = -7482.6 \text{ J}$$

$$\Delta H = \gamma \Delta U = -12471 \text{ J}$$

$$(ii) \quad \Delta U = w = -P_{\text{ext}} \cdot (V_2 - V_1) = -0.1 \times (40 - 5) \times 101.3 = -354.55 \text{ J}$$

$$\text{and } \Delta H = \frac{5}{3} \cdot \Delta U = -590.92 \text{ J}$$

$$(iii) \quad \Delta U = w = 0$$

$$\text{and } \Delta H = 0$$

**Ex.3.** Five moles of an ideal monoatomic gas undergoes adiabatic expansion from 12 atm to 1 atm, against a constant external pressure of 1 atm. If the initial temperature of gas is 27°C, calculate the final temperature. Also calculate  $q$ ,  $\Delta U$ ,  $w$  and  $\Delta H$ .

**Sol. :**  $q = 0$

$$\Delta U = w$$

$$\text{or, } n \cdot C_{v,m} \cdot (T_2 - T_1) = -P_{\text{ext}} \cdot (V_2 - V_1)$$

$$\text{or, } n \cdot \frac{3}{2} R (T_2 - T_1) = -P_2 \left( \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$$

$$\text{or, } \frac{3}{2} (T_2 - 300) = - \left( T_2 - 300 \times \frac{1}{12} \right) \Rightarrow T_2 = 190 \text{ K}$$

$$\text{or, } \Delta U = w = 5 \times \frac{3}{2} R \times (190 - 300) = -6859.05 \text{ J}$$

$$\text{and } \Delta H = \gamma \cdot \Delta U = -11431.75 \text{ J}$$

### 9.3 ISOBARIC PROCESS FOR AN IDEAL GAS :

$$q = \Delta H = n \cdot C_{v,m} \cdot \Delta T$$

$$\therefore \Delta U = n \cdot C_{v,m} \cdot \Delta T$$

$$w = -P \cdot (V_2 - V_1) = -nR \cdot \Delta T$$

**Ex.4.** One mole of an ideal diatomic undergoes isobaric expansion from 27°C to 87°C.  
 Calculate q, ΔU, w and ΔH.

**Sol. :**  $q = \Delta H = n \cdot C_{v,m} \cdot \Delta T = 1 \times \frac{7}{2} R \times 60 = 1745.94 \text{ J}$

$$\Delta U = \frac{\Delta H}{\gamma} = 1247.1 \text{ J}$$

$$\text{and } w = -nR \cdot \Delta T = -1 \times 8.314 \times 60 = -498.84 \text{ J}$$

#### 9.4 ISOCHORIC PROCESS FOR AN IDEAL GAS :

$$w = 0$$

$$q = \Delta U = n \cdot C_{v,m} \cdot \Delta T$$

$$\therefore \Delta U = n \cdot C_{v,m} \cdot \Delta T$$

**Ex.5.** Ten moles of an ideal gas ( $\gamma = 1.2$ ) is heated from 27°C to 47°C at constant volume.  
 Calculate q, ΔU, w and ΔH.

**Sol. :**  $w = 0$

$$q = \Delta U = n \cdot C_{v,m} \cdot \Delta T = 2 \times \frac{R}{1.2-1} \times 20 = 200 R$$

$$\Delta H = \gamma \cdot \Delta U = 240R$$

#### 9.5 POLYTROPIC PROCESS FOR AN IDEAL GAS :

$$\Delta U = n \cdot C_{v,m} \cdot \Delta T$$

$$\therefore \Delta H = n \cdot C_{p,m} \cdot \Delta T$$

For ideal gas is reversible polytropic process and  $C_{v,m}$  temperature independent,

$$P \cdot V^x = \text{constant}$$

$$\text{or, } T \cdot V^{x-1} = \text{constant}$$

where  $x$  = polytropic index

$$w_{\text{rev}} = \frac{P_2 V_2 - P_1 V_1}{1-x} = -\frac{nR(T_2 - T_1)}{1-x} \quad (x \neq 1)$$

$$= -nRT \cdot \ln \frac{V_2}{V_1} \quad (x = 1)$$

$$\text{and } q = n \cdot C_m \cdot \Delta T$$

$$\text{The molar heat capacity, } C_m = C_{v,m} + \frac{P \cdot dV}{n \cdot dT} = C_{v,m} + \frac{R}{1-x}$$

## 9.6 CYCLIC PROCESS :



## 9.7 CHANGE IN PHYSICAL STATE :

Solid  $\rightleftharpoons$  liquid

Liquid  $\rightleftharpoons$  Gas

Solid  $\rightleftharpoons$  Gas

Changes in physical state occurs at constant pressure and temperature conditions.

$$\Delta U = q + w$$

$$q = \Delta H = m.L$$

$$\text{and } w = -P(V_{\text{final state}} - V_{\text{initial state}})$$

**Ex.6.** 90 gm water is completely converted into steam at 100°C and 1 atm. Calculate q,  $\Delta U$ , w and  $\Delta H$ . Latent heat of vaporisation of water at 100°C is 540 cal/gm.

**Sol. :**  $\Delta H = m.L = 90 \times 540 = 48600 \text{ cal}$

$$w = -P(V_{\text{vap}} - V_{\text{water}}) = -P.V_{\text{vap}} = -nRT = -\frac{90}{18} \times 2 \times 373 = -3730 \text{ cal}$$

$$\Delta U = q + w = 48600 + (-3730) = 44870 \text{ cal}$$

## EXERCISE-3

**21.** Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 27°C. ( $\ln 5 = 1.6$ )

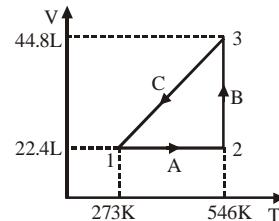
**Ans.  $w = -3.99 \text{ kJ}$**

**22.** Five moles of an ideal gas at 300 K, expanded isothermally from an initial pressure of 4 atm to a final pressure of 1 atm against a constant external pressure of 1 atm. Calculate q, w,  $\Delta U$  &  $\Delta H$ . Calculate the corresponding value of all if the above process is carried out reversibly. ( $\ln 2 = 0.7$ )

**Ans.  $w_{\text{irr}} = -1125 \text{ R}$ ,  $w_{\text{rev}} = -2100 \text{ R}$ ,  $\Delta U = \Delta H = 0$ ,  $q = -w$**

23. One mole of an ideal monoatomic gas is carried through the reversible cycle of the given figure consisting of step A, B and C and involving state 1, 2 and 3. Fill in the blank space in the table given below assuming reversible steps.

Table-1			
State	P	V	T
1			
2			
3			



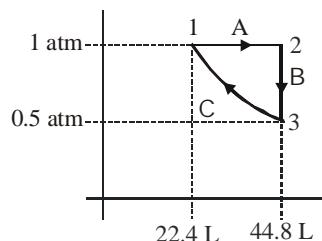
Step	Name of process	q	w	$\Delta U$	$\Delta H$
A					
B					
C					
overall					

Table-1			
State	P	V	T
1	1 atm	22.4	273
2	2 atm	22.4	546
3	1 atm	44.8	546

Step	Name of process	q	w	$\Delta E$	$\Delta H$
A	Isochoric	$3/2 R (273)$	0	$3/2 R (273)$	$5/2 R(273)$
B	Isothermal	$546 R \ln 2$	$-546 R \ln 2$	0	0
C	Isobaric	$-5/2 R(273)$	$R(273)$	$-3/2 R (273)$	$-5/2 R(273)$

24. One mole of an ideal monoatomic gas is put through reversible path as shown in figure. Fill in the blank in the tables given below.

Table-1			
State	P	V	T
1			
2			
3			



Step	Name of process	q	w	$\Delta U$	$\Delta H$
A					
B					
C					
cyclic					

**Ans.**
**Table-1**

<b>State</b>	<b>P</b>	<b>V</b>	<b>T</b>
1	1 atm	22.4	273
2	1	44.8	546
3	0.5	44.8	273

Step	Name of process	q	w	$\Delta E$	$\Delta H$
A	Isobaric	$5/2 R (273)$	$-R(273)$	$3/2 R (273)$	$5/2 R (273)$
B	Isochoric	$-3/2 R (273)$	0	$-3/2 R (273)$	$-5/2 R (273)$
C	Isothermal	$-273 R \ln 2$	$273 R \ln 2$	0	0
	Cyclic	$R(273) - 273 R \ln 2 - R(273) + 273 R \ln 2$	0	0	0

25.  $\frac{1}{22.4}$  mol of an ideal monoatomic gas undergoes a reversible process for which  $PV^2 = C$ . The gas is expanded from initial volume of 1 L to final volume of 2 L starting from initial temperature of 273 K. Find the heat exchanged q during the process. Express your answer in litre atm.

$$R = \frac{22.4}{273} \text{ L atm mole}^{-1} \text{ degree}^{-1}.$$

**Ans. -0.25**

26. An ideal gas is allowed to expand both adiabatic reversibly and adiabatic irreversibly. If  $T_i$  is the initial temperature and  $T_f$  is the final temperature, which of the following statements is correct :-
- $T_f > T_i$  for reversible process but  $T_f = T_i$  for irreversible process [AIEEE-2006]
  - $(T_f)_{\text{rev}} = (T_f)_{\text{irrev}}$
  - $T_f = T_i$  for both reversible and irreversible processes
  - $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$

**Ans.(4)**

27. Which of the following statements/relationships is not correct in thermodynamic changes ?

$$(1) q = -nRT \ln \frac{V_2}{V_1} \text{ (isothermal reversible expansion of an ideal gas)}$$

(2) For a system at constant volume, heat involved merely changes to internal energy.

$$(3) w = -nRT \ln \frac{V_2}{V_1} \text{ (isothermal reversible expansion of an ideal gas)}$$

$$(4) \Delta U = 0 \text{ (isothermal reversible expansion of a gas)}$$

**[JEE-MAINS(online)-2014]**
**Ans.(1)**

## 10. SUMMARY

Process	Expression for w	Expression for q	$\Delta U$	$\Delta H$	Work on PV-graph
Reversible isothermal	$w = -nRT \ln \frac{V_2}{V_1}$ $= -nRT \ln \frac{P_1}{P_2}$	$q = nRT \ln \left( \frac{V_2}{V_1} \right)$ $q = nRT \ln \left( \frac{P_1}{P_2} \right)$	0 process	0	
Irreversible isothermal	$w = -P_{\text{ext}}(V_2 - V_1)$ $= -P_{\text{ext}} \left( \frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$	$q = P_{\text{ext}}(V_2 - V_1)$	0	0	
Isobaric process	$w = -P_{\text{ext}}(V_2 - V_1)$ $= -nR\Delta T$	$q = \Delta H = nC_p \Delta T$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Isochoric process	$w = 0$	$q = \Delta U = nC_v \Delta T$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Reversible adiabatic process	$w = nC_v(T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$	$q = 0$ $PV^\gamma = \text{constant}$ $TV^{\gamma-1} = \text{constant}$ $TP^{1-\gamma/\gamma} = \text{constant}$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Irreversible adiabatic process	$w = nC_v(T_2 - T_1)$ $= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$	$q = 0$ $nC_v(T_2 - T_1) = -P_{\text{ext}} \left( \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Polytropic	$w = \frac{P_2 V_2 - P_1 V_1}{n-1}$ $w = \frac{R(T_2 - T_1)}{(n-1)}$	$q = \int_{T_1}^{T_2} C_v dT$ $w = \frac{R(T_2 - T_1)}{(n-1)}$	$\Delta U = nC_v \Delta T$	$\Delta H = nC_p \Delta T$	
Cyclic Process	Area enclosed in PV-diagram For clockwise -ive For anticlockwise +ive	$q = -w$	0	0	

## 11. LIMITATION OF FIRST LAW :

It can predict the change in energy as a result of change in state or vice-versa, but can not predict the natural direction of change (whether a change can happen on its own or not).

## MISCELLANEOUS PREVIOUS YEARS QUESTION

1. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm<sup>3</sup> to 2.50 dm<sup>3</sup>. Calculate the enthalpy change in this process. C<sub>v,m</sub> for argon is 12.48 JK<sup>-1</sup> mol<sup>-1</sup> [JEE 2000]

**Ans.** ΔH ≈ -115 J

**Sol.** T<sub>1</sub>V<sub>1</sub><sup>γ-1</sup> = T<sub>2</sub>V<sub>2</sub><sup>γ-1</sup>

$$T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1}$$

$$T_2 = 300 (1/2)^{8.3/12.48} \left[ \gamma^{-1} \frac{R}{C_{v,m}} \right]$$

$$T_2 = 189.2 \text{ Kelvin.}$$

$$n = \frac{P_1 V_1}{RT_1} = \frac{(1)(1.25)}{(0.0821)(300)} = 0.507$$

$$\begin{aligned} \Delta H &= nC_{p,m} (T_2 - T_1) \\ &= 0.0507 (20.78) (189.2 - 300) \\ &= -116.732 \text{ Joule.} \end{aligned}$$

2. Which of the following statement is false ? [JEE 2001]
- (A) Work is a state function
  - (B) Temperature is a state function
  - (C) Change of state is completely defined when initial and final states are specified.
  - (D) Work appears at the boundary of the system

**Ans. (A)**

3. One mole of non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) to (4.0 atm, 5.0 L, 245 K) with a change in internal energy (ΔU) = 30.0 L-atm. The change in enthalpy (ΔH) of the process in L-atm. [JEE 2002]
- (A) 40.0
  - (B) 42.3
  - (C) 44.0
  - (D) Not defined, because pressure is not constant

**Ans. (C)**

**Sol.** ΔH = ΔU + P<sub>2</sub>Y<sub>2</sub> - P<sub>1</sub>Y<sub>1</sub>

$$\Delta H = 30 + 20 - 6$$

$$= 44$$

4. One mole of a liquid (1 bar, 100 ml) is taken in an adiabatic container and the pressure increases steeply to 100 bar. Then at a constant pressure of 100 bar, volume decrease by 1 ml. Find  $\Delta U$  and  $\Delta H$ . [JEE 2004]

**Ans.**  $\Delta U = 10 \text{ J}$  ,  $\Delta H = 990 \text{ J}$

$$0 + w = \Delta U$$

$$\Delta U = -P_{ext} (Y_2 - V_1)$$

$$= -100 \left( \frac{-1}{1000} \right)$$

= 0.1 bar litre.

$$\Delta H = \Delta U + P_2 Y_2 - P_1 Y_1$$

$$\Delta H = 0.1 + \left[ \frac{100(99) - (1)(100)}{1000} \right]$$

$$\Delta H = 0.1 + 9.8$$

$$\Delta H = 9.9 \text{ bar, litre}$$

$$\Delta H = 990 \text{ Joules}$$

5. Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in KJ) for the process is :- [JEE 2004]  
 (A) 11.4 kJ              (B) - 11.4 kJ              (C) 0 kJ              (D) 4.8 kJ

**Ans. (C)**

In isothermal process  $\Delta T = 0$

$$\Delta H = nC_{v,m}\Delta T$$

$$\Delta H = 0$$

6. One mole of monoatomic ideal gas expands adiabatically at initial temp. T against a constant external pressure of 1 atm from one litre to two litre. Find out the final temperature.  
 $(R = 0.0821 \text{ litre. atm K}^{-1} \text{ mol}^{-1})$  [JEE 2005]

(a)  $\overline{m}$  (b)  $\overline{m}$  T

$$(C) \quad \text{For } (D) \quad (2)^{\frac{2}{3}-1} \quad (E) \quad 3 \times 0.0821 \quad (F) \quad 3 \times 0.0821$$

D

ext. 2 P v.m. 2 P

$$-1(2 - 1) = 1 \left( \frac{3}{2} R \right) (T_2 - T)$$

$$T_2 = T - \frac{z}{3R}$$

7. The molar heat capacity of a monoatomic gas for which the ratio of pressure and volume is one.

(A)  $\frac{4}{2}R$       (B)  $\frac{3}{2}R$       (C)  $\frac{5}{2}R$       (D) zero

[JEE 2006]

**Ans. (A)**

$$\frac{P}{V} = C$$

$$PV^{-1} = C$$

$$C_m = C_{v.m.} + \frac{R}{1-(-1)}$$

$$= \frac{3}{2}R + \frac{R}{2} = \frac{4R}{2}$$

8. Among the following, the state function(s) is (are)

[JEE 2009]

- (A) Internal energy      (B) Irreversible expansion work  
 (C) Reversible expansion work      (D) Molar enthalpy

**Ans. (A,D)**

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 EXERCISE (S-1)
 

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 BASIC
 

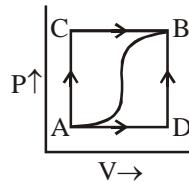
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1. Find the work done in each case :
  - (a) When one mole of ideal gas in 10 litre container at 1 atm is allowed to enter a very large evacuated bulb of capacity 100 litre.
  - (b) When 1 mole of gas expands from 1 litre to 5 litre against constant one atmospheric pressure.
2. Find the work done in atm-litre when 18 mL of water is getting vapourised at 373 K against 1 atm pressure.  
*(Assume the ideal behaviour of water vapour).*
3. Find total degree of freedom and break up as translational, rotational or vibrational degree of freedom in following cases.
 

(i) CO <sub>2</sub>	(ii) SO <sub>2</sub>	(iii) He	(iv) NH <sub>3</sub>
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**Problems related to First law of thermodynamics :**

4. The gas is cooled such that it loses 65 J of heat. The gas contracts as it cools and work done on the system is equal to 20 J. What are q, w and  $\Delta U$  ?
  5. When a system is taken from state A to state B along the path ACB, 80J of heat flows into the system and the system does 30J of work.
    - (a) How much heat flows into the system along path ADB if the work done by the system is 10J ?
    - (b) When the system is returned from state B to A along the curved path, the work done on the system is 20J. Does the system absorb or liberate heat, and how much ?
    - (c) If  $U_D - U_A = 40\text{J}$ , find the heat absorbed in the process AD and DB if work done by system in ADB is 10 Joule.
  6. An ideal gas undergoes expansion from A(10 atm, 1 litre) to B(1 atm, 10 litre), first against 5 atm and then against 1 atm, isothermally. Calculate the amount of heat absorbed (in litre. atm)
  7. 2 moles of an ideal gas is compressed from (1 bar, 2L) to 2 bar isothermally. Calculate magnitude of minimum possible work involved in the change (in Joules).  
 (Given : 1 bar L = 100 J) ( $\ln 2 = 0.7$ )
  8. 2 mole of an ideal gas undergoes isothermal compression along three different paths if its initial state is (2 bar, 4 litre) in all three processes.
    - (i) Reversible compression from till 20 bar.
    - (ii) A single stage compression against a constant external pressure of 20 bar
    - (iii) A two stage compression consisting initially of compression against a constant external pressure of 10 bar until  $P_{\text{gas}} = P_{\text{ext}}$ , followed by compression against a constant pressure of 20 bar until  $P_{\text{gas}} = P_{\text{ext}}$ .
- Calculate the work (in bar. L) for each of these processes and for which of the irreversible processes is the magnitude of the work greater ? [Given : R = 0.08 bar. L/mole.K]



9. A monoatomic ideal gas undergoing irreversible adiabatic compression from 4L to 1L against 1 bar pressure. Calculate the enthalpy change of gas. (Given: 1 bar-L = 100 J)
10. Two mole of ideal diatomic gas ( $C_{V,m} = 5/2 R$ ) at 300K and 5 atm expanded irreversibly & adiabatically to a final pressure of 2 atm against a constant pressure of 1 atm. Calculate q, w,  $\Delta H$  &  $\Delta U$ .
11. Calculate the work done by system in an irreversible (single step) adiabatic expansion of 1 mole of a polyatomic gas ( $\gamma = 4/3$ ) from 400 K and pressure 10 atm to 1 atm.
12. 1 mole of  $\text{CO}_2$  gas at 300 K is expanded under reversible adiabatic condition such that its volume becomes 27 times.
  - What is the final temperature ?
  - What is work done ?

Given  $\gamma = 1.33$  and  $C_V = 25.08 \text{ Jmol}^{-1}\text{K}^{-1}$  for  $\text{CO}_2$ .

13. Molar heat capacity of an ideal gas at constant volume is given by  $C_V = (16.5 + 10^{-2}T) \frac{\text{J}}{\text{K-mol}}$ . If 2 moles of this ideal gas are heated at constant volume from 300K to 400K. Then the change in internal energy (in kJ) will be approximately.
14. Three moles of an ideal gas at 200 K and 2.0 atm pressure undergoes reversible adiabatic compression until the temperature becomes 250 K. For the gas  $C_V$  is  $27.5 \text{ JK}^{-1} \text{ mol}^{-1}$  in this temperature range. Calculate q, w,  $\Delta U$ ,  $\Delta H$  and final V and final P.

$$\text{Given } \left(\frac{5}{4}\right)^{1/0.3} = 2.1, \left(\frac{5}{4}\right)^{35.8/8.3} = 2.61$$

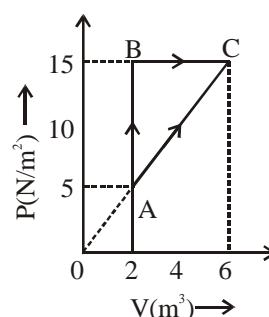
$[R = 8.3 \text{ Joule/mol.K} \text{ or } R = 0.0821 \text{ atm litre/mol.K}]$

#### □ Problem related to cyclic process

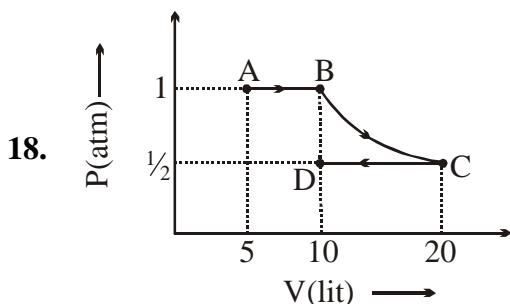
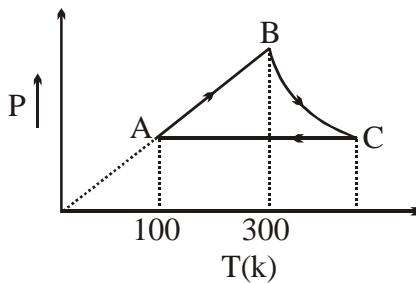
15. One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps :
  - (CA) Isothermal compression from 2 atm and 10 litres to 20 atm and 1 litre.
  - (AB) Isobaric expansion to return the gas to the original volume of 10 litres with T going from  $T_1$  to  $T_2$ .
  - (BC) Cooling at constant volume to bring the gas to the original pressure and temperature. The steps are shown schematically in the figure shown.
  - Calculate  $T_1$  and  $T_2$
  - Calculate  $\Delta U$ , q and w (in calories) for the cycle.

**[Given :  $\ln 10 = 2.3$ ,  $R = 0.0821 \text{ atm.litre/mol-K}$  or  $R = 2 \text{ cal/mol.K}$ ]**

16. The given figure shows a change of state A to state C by two paths ABC and AC for an ideal gas. Calculate the :
  - Path along which magnitude of work done is least ABC or AC
  - Internal energy at C if the internal energy of gas at A is 10 J and amount of heat supplied to change its state to C through the path AC is 200J.
  - Amount of heat supplied to the gas to go from A to B, if internal energy change of gas from A to B is 10 J.



17. Calculate the net work done in the following cycle for one mol of an ideal gas (in calorie), where in process BC, PT = constant. ( $R = 2\text{cal/mol}\cdot\text{K}$ ).



Calculate magnitude of total work done (in atm.lit) for the above process ABCD involving a monoatomic ideal gas.

[Given:  $\ln 2 = 0.7$ ]

**Problem based on polytropic process**

19. For 1 mole of ideal monoatomic gas if  $\frac{P}{V^2} = \text{constant}$  and initial temperature is 100 K. If gas is expanded from 1 L to 2 L then find (a) heat capacity (b) total heat absorbed (c) work (d) change in internal energy.

(Assume  $R = 0.0821 \frac{\text{L} - \text{atm}}{\text{mole} - \text{k}}$ , 1 L-atm = 24 cal)

20. One mole of an ideal monoatomic gas undergoes expansion along a straight line on P-V curve from initial state A(3L, 8 atm) to final state B(7.5 L, 2 atm). Calculate q for the above process in L atm.

**Problems based on change in physical state :**

21. Water expands when it freezes. Determine amount of work done, in joules, when a system consisting of 1.0 L of liquid water freezes under a constant pressure of 1.0 atm and forms 1.1 L of ice.
22. What is  $\Delta U$  when 2.0 mole of liquid water vaporises at 100°C ? The heat of vaporisation,  $\Delta H_{\text{vapour}}$  of water at 100°C is 40.66 kJ mol<sup>-1</sup>.
23. When 1 mole of ice melt at 0°C and at constant pressure of 1 atm, 1440 calories of heat are absorbed by the system. The molar volumes of ice and water are 0.0196 and 0.0180 litre respectively. Calculate  $\Delta H$  and  $\Delta U$  for the reaction.

## EXERCISE (O-1)

## BASIC



Total heat absorbed by the gas in the process is :

- (A) 116J                    (B) 40 J                    (C) 4000 J                    (D) None of these

4. An ideal gas undergoes isothermal expansion from A(10 atm,  $1l$ ) to B(1 atm,  $10 l$ ) either by  
(I) Infinite stage expansion or by  
(II) First against 5 atm and then against 1 atm isothermally

Calculate  $\frac{q_I}{q_{II}}$

- (A)  $\frac{1}{13 \times 2.303}$       (B)  $13 \times 2.303$       (C)  $\frac{13}{23.03}$       (D)  $\frac{23.03}{13}$

5. One mole of ideal gas is allowed to expand reversibly and adiabatically from a temperature of 27°C. If the work done by the gas in the process is 3 kJ, the final temperature will be equal to ( $C_V = 20 \text{ J/K mol}$ )



6. For an adiabatic process, which of the following relation must be correct -

- (A)  $\Delta U = 0$       (B)  $P\Delta V = 0$       (C)  $q = 0$       (D)  $q = +W$

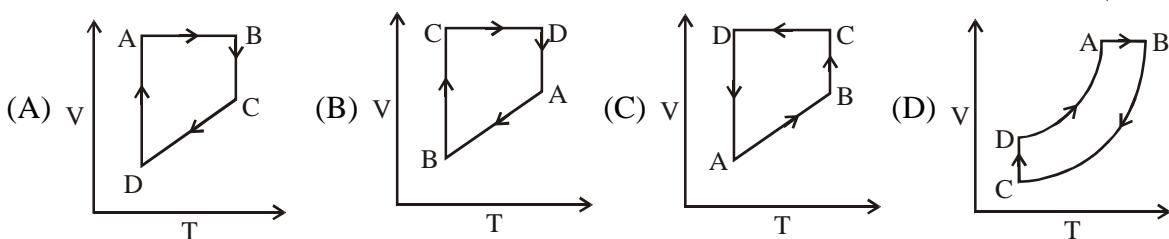
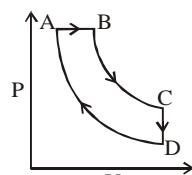
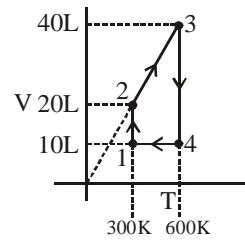
7. A system containing ideal gas is expanded under adiabatic process



8. A gas ( $C_{v,m} = \frac{5}{2}R$ ) behaving ideally was allowed to expand reversibly and adiabatically from 1 litre to 32 litre. Its initial temperature was  $327^\circ C$ . The molar enthalpy change (in J/mole) for the process is :-

(A)  $-1125\text{ R}$       (B)  $-575\text{ R}$       (C)  $-1575\text{ R}$       (D) None of these

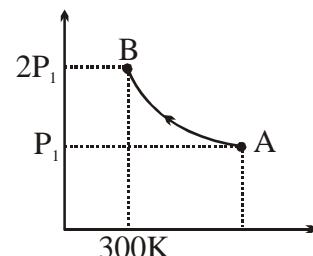
9. Two moles of an ideal gas ( $C_v = \frac{5}{2}R$ ) was compressed adiabatically against constant pressure of 2 atm, which was initially at 350 K and 1 atm pressure. The work involved in the process is equal to -
- (A) 250 R                    (B) 300 R                    (C) 400 R                    (D) 500 R
10. A gas is expanded from volume  $V_1$  to  $V_2$  through three different processes :
- (a) Reversible adiabatic  
 (b) Reversible isothermal  
 (c) Irreversible adiabatic
- The correct statements is -
- (A)  $(T_f)_{\text{Reversible Isothermal}} > (T_f)_{\text{Reversible adiabatic}} > (T_f)_{\text{Irreversible adiabatic}}$   
 (B)  $(T_f)_{\text{Reversible Isothermal}} > (T_f)_{\text{Irreversible adiabatic}} > (T_f)_{\text{Reversible adiabatic}}$   
 (C)  $W_{\text{Reversible Isothermal}} > W_{\text{Irreversible adiabatic}} > W_{\text{reversible adiabatic}}$   
 (D)  $(P_f)_{\text{Reversible Isothermal}} > (P_f)_{\text{Reversible adiabatic}} > (P_f)_{\text{Irreversible adiabatic}}$
11. What is the magnitude of work performed by one mole of an ideal gas when its volume increases eight times in irreversible adiabatic expansion if the initial temperature of the gas is 300 K ?  
 $C_V$  for the gas is 1.5 R. ( $R = 2 \text{ Cal / mol/K}$ )
- (A) 900 Cal                    (B) 450 Cal                    (C) 675 Cal                    (D) 331.58 Cal
12. For a process which follows the equation  $PV^3 = C$ , the work done when one mole of ideal gas was taken from 1 atm to  $2\sqrt{2}$  atm starting from initial temperature of 300 K is
- (A) 300 R                    (B) 150 R                    (C) 600 R                    (D) 900 R
13. What is the net work done (w) when 1 mole of monoatomic ideal gas undergoes in a process described by 1, 2, 3, 4 in given V-T graph  
 Use :  $R = 2 \text{ cal/mole K}$
- In 2 = 0.7**
- (A) -600 cal                    (B) - 660 cal  
 (C) + 660 cal                    (D) + 600 cal
14. A cyclic process ABCD is shown in PV diagram for an ideal gas.  
 which of the following diagram represents the same process ?



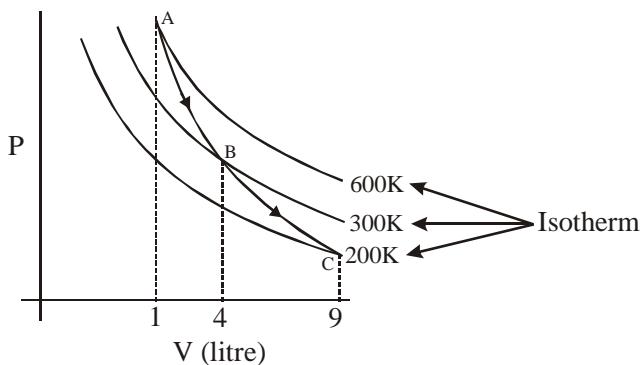
15. 2 moles of an ideal monoatomic gas is taken from state A to state B through a process AB in which  $PT = \text{constant}$ . The process can be represented on a P-T graph as follows:

Select the incorrect option(s):

- (A) Heat evolved by the gas during process AB =  $2100 \text{ R}$
- (B) Heat absorbed by the gas during process AB =  $2100 \text{ R}$
- (C)  $\Delta U = -900 \text{ R}$
- (D)  $W = 1200\text{R}$

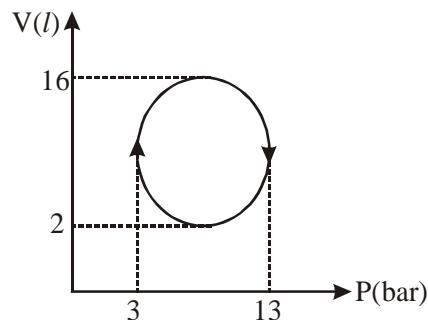


16. The given figure shows a polytropic process ABC for one mole of an ideal gas. Calculate the polytropic index ( $x$ ) for the process-



- (A)  $1/2$
- (B)  $-1/2$
- (C)  $3/2$
- (D) None

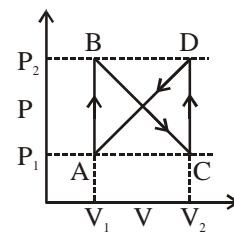
17. Work (in kJ) in the following cyclic process is



- (A)  $-11$
- (B)  $-11000$
- (C)  $11$
- (D)  $11000$

18. An ideal gas is taken around the cycle ABCDA as shown in figure. The net work done during the cycle is equal to :-

- (A) Zero
- (B) Positive
- (C) Negative
- (D) We cannot predict



19. What is  $\Delta U$  for the process described by figure. Heat supplied during the process  $q = 200 \text{ kJ}$ .

(A)  $+50 \text{ kJ}$       (B)  $-50 \text{ kJ}$   
 (C)  $-150 \text{ kJ}$       (D)  $+150 \text{ kJ}$

20. A diatomic ideal gas initially at  $273 \text{ K}$  is given  $100 \text{ cal}$  heat due to which system did  $209 \text{ J}$  work, Molar heat capacity ( $C_m$ ) of gas for the process is [ $1 \text{ cal} = 4.18 \text{ Joule}$ ]

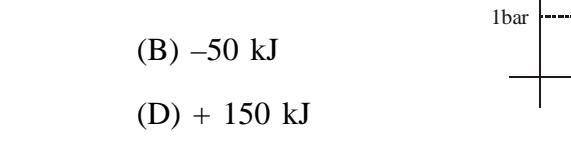
(A)  $\frac{3}{2}R$       (B)  $\frac{5}{2}R$       (C)  $\frac{5}{4}R$       (D)  $5R$

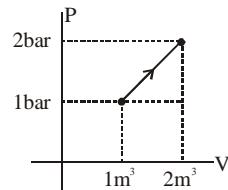
21. For an ideal monoatomic gas during any process  $T = kV$ , find out the molar heat capacity of the gas during the process. (Assume vibrational degree of freedom to be active)

(A)  $\frac{5}{2}R$       (B)  $3R$       (C)  $\frac{7}{2}R$       (D)  $4R$

22. An amount  $Q$  of heat is added to a monoatomic ideal gas in a process in which the gas performs a work  $Q/2$  on its surrounding. The molar heat capacity of gas (in  $\text{cal/K-mol}$ ) for the process is.

(A)  $3R$       (B)  $5R$       (C)  $4R$       (D)  $2R$





## EXERCISE (O-2)

ONE OR MORE THAN ONE MAY BE CORRECT :

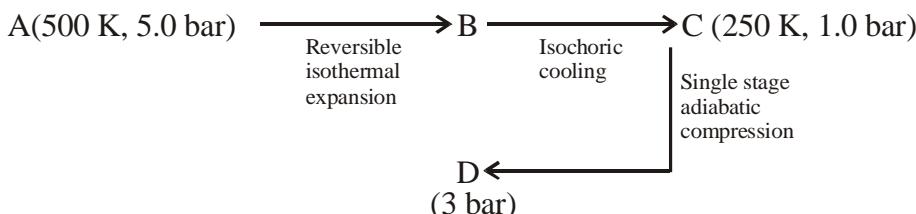
- 1.** An insulated container of gas has two chambers separated by an insulating partition. One of the chambers has volume  $V_1$  and contains ideal gas at pressure  $P_1$  and temperature  $T_1$ . The other chamber has volume  $V_2$  and contains same ideal gas at pressure  $P_2$  and temperature  $T_2$ . If the partition is removed without doing any work on the gas, the final equilibrium temperature of the gas in the container will be :-

$$(A) \frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_2 + P_2 V_2 T_1}$$

$$(B) \frac{P_1 V_1 T_1 + P_2 V_2 T_2}{P_1 V_1 + P_2 V_2}$$

$$(C) \frac{P_1 V_1 T_2 + P_2 V_2 T_1}{P_1 V_1 + P_2 V_2}$$

$$(D) \frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_1 + P_2 V_2 T_2}$$

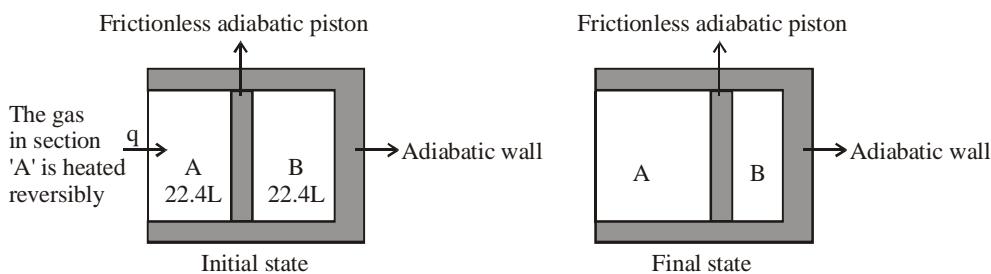


The correct statement is/are

6. Choose the correct statement(s)
- (A) During adiabatic expansion of an ideal gas, magnitude of work obtained is equal to  $\Delta H$  of gas.
  - (B) For same change in temperature of ideal gas through adiabatic process, magnitude of  $W$  will be same in reversible as well as irreversible process
  - (C) During an adiabatic reversible expansion of an ideal gas, temperature of the system increases.
  - (D) For same change in volume of ideal gas,  $\Delta U$  is less in adiabatic expansion than in isobaric expansion if expansion starts with same initial state.
7. Choose the correct statement(s) among the following -
- (A) Internal energy of  $H_2O$  remains constant during conversion of liquid into its vapour at constant temperature.
  - (B) During fusion of ice into water, enthalpy change and internal energy change are almost same at constant temperature
  - (C) Molar heat capacity of gases are temperature dependent
  - (D) During boiling of  $H_2O$  at 1 atm, 100°C, average kinetic energy of  $H_2O$  molecules increases.
8. Suppose that the volume of a certain ideal gas is to be doubled by one of the following processes :
- |   |                                     |
|---|-------------------------------------|
| (A) isothermal expansion                  | (B) adiabatic expansion             |
| (C) free expansion in insulated condition | (D) expansion at constant pressure. |
- If  $E_1, E_2, E_3$  and  $E_4$  respectively are the changes in average kinetic energy of the molecules for the above four processes, then-
- |                 |                 |                 |                 |
|-----------------|-----------------|-----------------|-----------------|
| (A) $E_2 = E_3$ | (B) $E_1 = E_3$ | (C) $E_1 > E_4$ | (D) $E_4 > E_3$ |
|-----------------|-----------------|-----------------|-----------------|
- Assertion / reason :
9. **Statement-1 :** There is no change in enthalpy of an ideal gas during compression at constant temperature.
- Statement-2 :** Enthalpy of an ideal gas is a function of temperature and pressure.
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
  - (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
  - (C) Statement-1 is true, statement-2 is false.
  - (D) Statement-1 is false, statement-2 is true.
10. **Statement-1 :** Due to adiabatic expansion, the temperature of an ideal gas always decreases.
- Statement-2 :** For an adiabatic process,  $\Delta U = w$ .
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
  - (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
  - (C) Statement-1 is true, statement-2 is false.
  - (D) Statement-1 is false, statement-2 is true.

### Paragraph for Q.11 to Q.13

A cylindrical container of volume 44.8 litres is containing equal no. of moles (in integer no.) of an ideal monoatomic gas in two sections A and B separated by an adiabatic frictionless piston as shown in figure. The initial temperature and pressure of gas in both section is 27.3K and 1 atm. Now gas in section 'A' is slowly heated till the volume of section B becomes  $(1/8)^{\text{th}}$  of initial volume.



**Given :**  $R = 2 \text{ cal/mol-K}$ ,  $C_{v,m}$  of monoatomic gas =  $\frac{3}{2}R$ ,

**At 1 atm & 0°C ideal gas occupy 22.4 litre.**

11. What will be the final pressure in container B.  
(A) 2 atm      (B) 8 atm      (C) 16 atm      (D) 32 atm
12. Final temperature in container A will be  
(A) 1638 K      (B) 6988 K      (C) 3274 K      (D) 51 K
13. Change in enthalpy for section A in Kcal  
(A) 48.3      (B) 80.53      (C) 4.83      (D) 8.05

### Paragraph for Q.14 to 16

As a result of the isobaric heating by  $\Delta T = 72\text{K}$ , one mole of a certain ideal gas obtains an amount of heat  $Q = 1.60 \text{ kJ}$ .

14. The work performed by the gas is -  
(A) 8.60 kJ      (B) 0.60 kJ      (C) 16.60 kJ      (D) 4.60 kJ
15. The increment of its internal energy ( in kJ) is  
(A) 1.0      (B) 1.6      (C) 2.2      (D) 2.0
16. The value of  $\gamma$  for the gas is -  
(A) 0.6      (B) 1.4      (C) 1.6      (D) 1.5

**MATCH THE COLUMN :****17.** Match Column-I with Column-II**Column-I (Ideal Gas)**

- (A) Reversible isothermal process
- (B) Reversible adiabatic process
- (C) Irreversible adiabatic process
- (D) Irreversible isothermal process

**Column-II (Related equations)**

- (P)  $W = 2.303 n RT \log(P_2/P_1)$
- (Q)  $W = nC_{V,m} (T_2 - T_1)$
- (R)  $W = -2.303nRT \log(V_2/V_1)$
- (S)  $W = -\int_{V_i}^{V_f} P_{ext.} dV$

**18.** Match the column**Column-I**

- (A) Isothermal vaporisation of water at  $100^{\circ}\text{C}$  & 1 atm
- (B) Isothermal reversible expansion of an ideal gas
- (C) Adiabatic free expansion of ideal gas
- (D) Isochoric heating of an ideal gas

**Column-II**

- (P)  $\Delta T = 0$
- (Q)  $\Delta U = 0$
- (R)  $\Delta H = 0$
- (S)  $q = 0$
- (T)  $w = 0$

**MATCH THE LIST :****19.** Match the following, and select the correct code :-**Column-I**

- (P) Isothermal process (reversible)
- (Q) Adiabatic process (reversible)
- (R) Isochoric process
- (S) Isothermal process (irreversible)

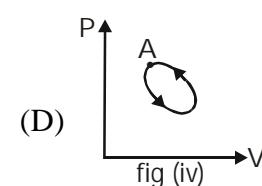
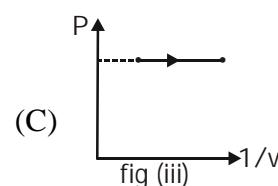
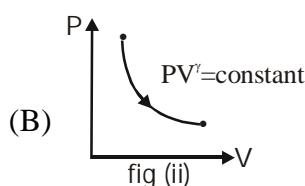
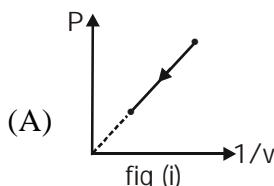
**Column-II**

- (1)  $q = 2.303 nRT \log \frac{P_1}{P_2}$
- (2)  $PV^\gamma = \text{const.}$
- (3)  $q = P_{ext.} (V_2 - V_1)$
- (4) Area under P-V curve is zero

**Code:**

P	Q	R	S
(A) 2	1	4	3
(B) 1	2	4	3
(C) 2	1	3	4
(D) 1	2	3	4

20. The figures given below depict different processes for a given amount of an ideal gas.


**Column-I**

- (P) In Fig (i)
- (Q) In Fig (ii)
- (R) In Fig (iii)
- (S) In Fig (iv)

**Column-II**

- (1) Net heat is absorbed by the system
- (2) Net work is done on the system
- (3) Net heat is rejected by the system
- (4) Net work is done by the system
- (5) Net internal energy change is zero

**Code:**

P	Q	R	S
(A) 1, 4, 5	4	2, 3	2, 3, 5
(B) 1, 4, 5	4	2, 3	2, 3
(C) 1, 2, 4	2	1, 4	2, 3
(D) 1, 2	2	1, 4	3, 5

## EXERCISE (JM)

1. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be :- [JEE-MAIN-2013]

(R = 8.314 J/mol K) ( $\ln 7.5 = 2.01$ )

- (1) q = + 208 J, w = - 208 J
- (2) q = - 208 J, w = - 208 J
- (3) q = - 208 J, w = + 208 J
- (4) q = + 208 J, w = + 208 J

2. Which of the following statements/relationships is not correct in thermodynamic changes ?

(1)  $q = -nRT \ln \frac{V_2}{V_1}$  (isothermal reversible expansion of an ideal gas)

(2) For a system at constant volume, heat involved merely changes to internal energy.

(3)  $w = -nRT \ln \frac{V_2}{V_1}$  (isothermal reversible expansion of an ideal gas)

(4)  $\Delta U = 0$  (isothermal reversible expansion of a gas)

[JEE-MAINS(online)-2014]

3. A gas undergoes change from state A to state B. In this process , the heat absorbed and work done by the gas is 5 J and 8 J, respectively. Now gas is brought back to A by another process during which 3 J of heat is evolved. In this reverse process of B to A:- [JEE-MAINS(online)-2017]

- (1) 10 J of the work will be done by the surrounding on gas.
- (2) 6 J of the work will be done by the surrounding on gas.
- (3) 10 J of the work will be done by the gas.
- (4) 6 J of the work will be done by the gas.

4. The enthalpy change on freezing of 1 mol of water at 5°C to ice at -5°C is :

(Given  $\Delta_{\text{fus}}H = 6 \text{ kJ mol}^{-1}$  at 0°C,  $C_p(H_2O, l) = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $C_p(H_2O, s) = 36.8 \text{ J mol}^{-1} \text{ K}^{-1}$ )

[JEE-MAINS(online)-2017]

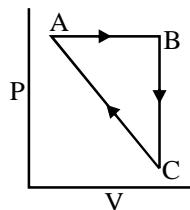
- (1)  $-6.56 \text{ kJ mol}^{-1}$
- (2)  $-5.81 \text{ kJ mol}^{-1}$
- (3)  $-6.00 \text{ kJ mol}^{-1}$
- (4)  $-5.44 \text{ kJ mol}^{-1}$

5.  $\Delta U$  is equal to

[JEE-MAINS(online)-2017]

- (1) Isochoric work
- (2) Isobaric work
- (3) Adiabatic work
- (4) Isothermal work

6. An ideal gas undergoes a cyclic process as shown in figure. [JEE-MAINS(online)-2018]



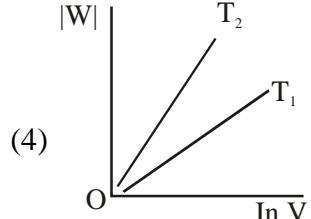
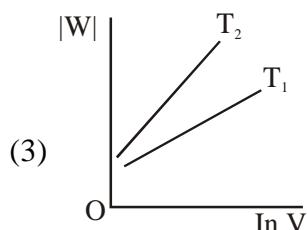
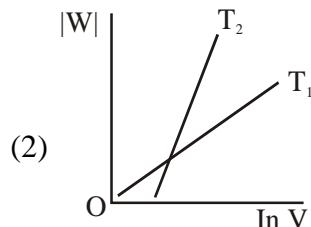
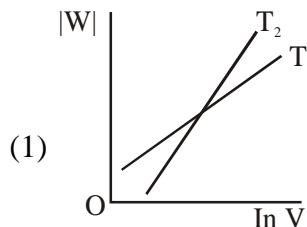
$$\Delta U_{BC} = -5 \text{ kJ mol}^{-1}, q_{AB} = 2 \text{ kJ mol}^{-1}$$

$$W_{AB} = -5 \text{ kJ mol}^{-1}, W_{CA} = 3 \text{ kJ mol}^{-1}$$

Heat absorbed by the system during process CA is :-

- (1) 18  $\text{kJ mol}^{-1}$       (2) +5  $\text{kJ mol}^{-1}$       (3) -5  $\text{kJ mol}^{-1}$       (4) -18  $\text{kJ mol}^{-1}$

7. Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temperatures  $T_1$  and  $T_2$  ( $T_1 < T_2$ ). The correct graphical depiction of the dependence of work done (w) on the final volume (V) is: [JEE-MAINS(online)-2019]

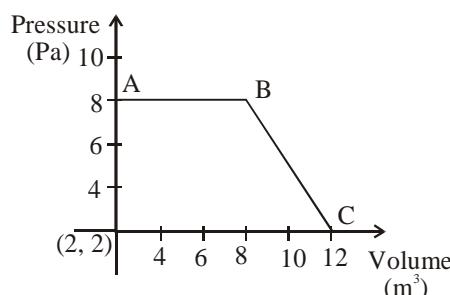


8. An ideal gas undergoes isothermal compression from  $5 \text{ m}^3$  to  $1 \text{ m}^3$  against a constant external pressure of  $4 \text{ Nm}^{-2}$ . Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is  $24 \text{ J mol}^{-1} \text{ K}^{-1}$ , the temperature of Al increases by

[JEE-MAINS(online)-2019]

- (1)  $\frac{3}{2} \text{ K}$       (2)  $\frac{2}{3} \text{ K}$       (3) 1 K      (4) 2 K

9. The magnitude of work done by a gas that undergoes a reversible expansion along the path ABC shown in the figure is \_\_\_\_\_ [JEE-MAINS(online)-2020]

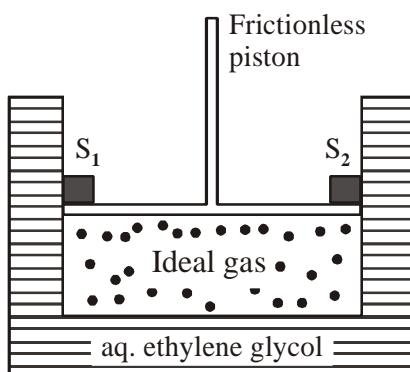


10. At constant volume, 4 mol of an ideal gas when heated from 300 K to 500K changes its internal energy by 5000 J. The molar heat capacity at constant volume is \_\_\_\_\_.

[JEE-MAINS(online)-2020]

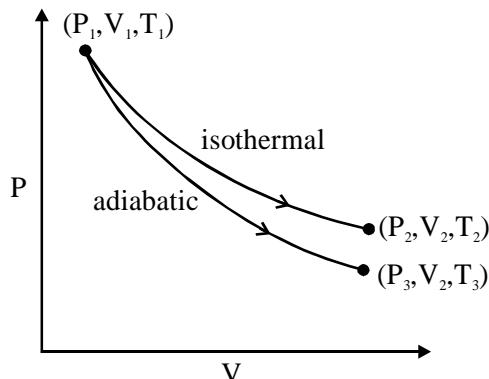
11. A cylinder containing an ideal gas (0.1 mol of 1.0 dm<sup>3</sup>) is in thermal equilibrium with a large volume of 0.5 molal aqueous solution of ethylene glycol at its freezing point. If the stoppers S<sub>1</sub> and S<sub>2</sub> (as shown in the figure) are suddenly withdrawn, the volume of the gas in litres after equilibrium is achieved will be \_\_\_\_\_. (Given, K<sub>f</sub> (water) = 2.0 K kg mol<sup>-1</sup>, R = 0.08 dm<sup>3</sup> atm K<sup>-1</sup> mol<sup>-1</sup>)

[JEE-MAINS(online)-2020]



## EXERCISE (JA)

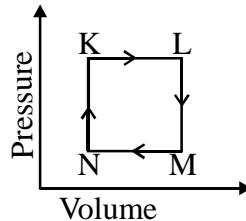
1. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct ? [JEE 2012]





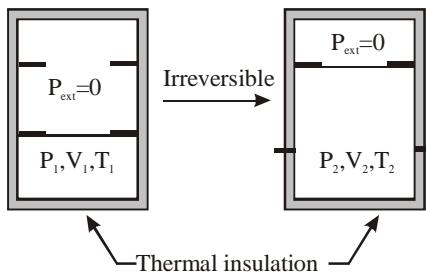

## **Paragraph for Question 2 and 3**

A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure. [JEE 2013]



4. An ideal gas in thermally insulated vessel at internal pressure =  $P_1$ , volume =  $V_1$  and absolute temperature =  $T_1$  expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are  $P_2$ ,  $V_2$  and  $T_2$ , respectively. For this expansion,

[JEE 2014]



(A)  $q = 0$       (B)  $T_2 = T_1$       (C)  $P_2 V_2 = P_1 V_1$       (D)  $P_2 V_2^\gamma = P_1 V_1^\gamma$

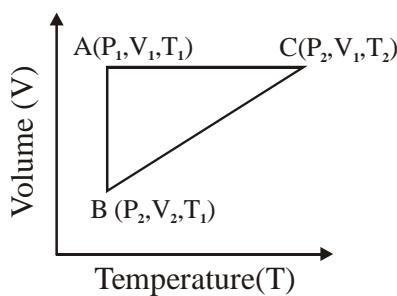
5. An ideal gas is expanded from  $(p_1, V_1, T_1)$  to  $(p_2, V_2, T_2)$  under different conditions. The correct statement(s) among the following is(are) :-

[JEE 2017]

- (A) The work done on the gas is maximum when it is compressed irreversibly from  $(p_2, V_2)$  to  $(p_1, V_1)$  against constant pressure  $p_1$
- (B) The work done by the gas is less when it is expanded reversibly from  $V_1$  to  $V_2$  under adiabatic conditions as compared to that when expanded reversibly from  $V_1$  to  $V_2$  under isothermal conditions.
- (C) The change in internal energy of the gas (i) zero, if it is expanded reversibly with  $T_1 = T_2$ , and (ii) positive, if it is expanded reversibly under adiabatic conditions with  $T_1 \neq T_2$
- (D) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic

6. A reversible cyclic process for an ideal gas is shown below. Here, P, V and T are pressure , volume and temperature , respectively. The thermodynamic parameters q, w, H and U are heat, work, enthalpy and internal energy, respectively.

[JEE 2018]



The correct option(s) is (are)

- (A)  $q_{AC} = \Delta U_{BC}$  and  $w_{AB} = P_2(V_2 - V_1)$       (B)  $w_{BC} = P_2(V_2 - V_1)$  and  $q_{BC} = \Delta H_{AC}$
- (C)  $\Delta H_{CA} < \Delta U_{CA}$  and  $q_{AC} = \Delta U_{BC}$       (D)  $q_{BC} = \Delta H_{AC}$  and  $\Delta H_{CA} > \Delta U_{CA}$

## ANSWER KEY

## EXERCISE (S-1)

1. Ans. (a) 0 (b)  $W = -P\Delta V = -1(5 - 1) = -4$  litre-atm.

2. Ans. -3.1 kJ

3. Ans. (i) 9, 3, 2, 4 (ii) 9, 3, 3, 3 (iii) 3, 3, 0, 0 (iv) 12, 3, 3, 6

4. Ans.  $q = -65$  J;  $w = 20$  J;  $\Delta U = -45$  J

5. Ans. (a) + 60J (b) -70 J (c), + 50 J, + 10 J

6. Ans. (13)

7. Ans. (140)

8. Ans. (i) 18.42 bar.L; (ii) 72 bar.L; (iii) 40 bar.L

9. Ans. (500 J)

10. Ans.  $\Delta U = w = -150$  R,  $\Delta H = -210R$ ,  $q = 0$ . Ans. 2244.78 Joule

12. Ans.  $T_2 = 100K$ ;  $w = -5.016$  kJ

13. Ans. (4)

14. Ans.  $q = 0$ ,  $w = \Delta U = 4.125$  kJ;  $\Delta H = 5.372$  kJ;  $V_f = 11.8$  dm<sup>3</sup>;  $P = 5.22$  atm

15. Ans. (a)  $T_1 = 243.60$  K;  $T_2 = 2436$  K, (b)  $\Delta U = 0$ ;  $q = -w = 3264.24$  cal

16. Ans. (a) AC, (b) 170 J, (c) 10 J

17. Ans. [-800 cal]

18. Ans. (7)

19. Ans. (a)  $\frac{11}{3}$  cal /K-mol. (b) 2566.67 cal (c) -466.67 cal (d) 2100 cal

20. Ans. (9)

21. Ans. -10.13 J

22. Ans.  $\Delta E = 75.12$  kJ

23. Ans.  $\Delta U \approx \Delta H = 1440$  calories

## EXERCISE (O-1)

- |     |         |     |          |     |         |     |         |
|-----|---------|-----|----------|-----|---------|-----|---------|
| 1.  | Ans.(C) | 2.  | Ans.(B)  | 3.  | Ans.(C) | 4   | Ans.(D) |
| 5.  | Ans.(C) | 6.  | Ans.(C)  | 7.  | Ans.(B) | 8.  | Ans.(C) |
| 9.  | Ans.(D) | 10. | Ans. (B) | 11. | Ans.(D) | 12. | Ans.(B) |
| 13. | Ans.(C) | 14. | Ans.(C)  | 15. | Ans.(B) | 16. | Ans.(C) |
| 17. | Ans.(C) | 18  | Ans.(A)  | 19. | Ans.(A) | 20. | Ans.(D) |
| 21. | Ans.(A) | 22. | Ans.(A)  |     |         |     |         |

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### EXERCISE (O-2)

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1. Ans. (A)      2. Ans. (C)      3. Ans. (A,B,C)      4. Ans. (C)  
 5. Ans. (A,B,C,D)    6. Ans. (B, D)    7. Ans. (B,C)    8. Ans. (B,D)  
 9. Ans. (C)      10. Ans. (D)      11. Ans. (D)      12. Ans. (A)  
 13. Ans. (B)      14. Ans. (B)      15. Ans. (A)      16. Ans. (C)  
 17. Ans. (A) → (P,R,S) ; (B) → (Q, S) ; (C) → (Q,S) ; (D) → (S)  
 18. Ans. (A)–P; (B)–P,Q,R ; (C)–P,Q,R,S,T ; D-T  
 19. Ans. (B)      20. Ans. (A)

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### EXERCISE (JM)

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1. Ans. (1)      2. Ans. (1)      3. Ans. (2)      4. Ans. (1)  
 5. Ans. (3)      6. Ans. (2)      7. Ans. (2)      8. Ans. (2)  
 9. Ans. (48.00)    10. Ans. (6.25)    11. Ans. (2.17 to 2.23)

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### EXERCISE (JA)

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1. Ans. (A,D)      2. Ans. (B)      3. Ans. (C)    4. Ans.(A,B,C)  
 5. Ans. (A,B,D)    6. Ans. (B,C)

## CHAPTER 2

**THERMOCHEMISTRY****Chapter  
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## IMPORTANT NOTES

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## CHAPTER 2

# THERMOCHEMISTRY

### 1. INTRODUCTION

Thermocchemistry deals with the energy changes involved in chemical reaction.

### 2. TYPES OF REACTIONS

#### (i) Exothermic reactions :

These are the chemical reactions involving release of heat.

Examples :- Neutralisation reactions, combustion reactions, slaking of lime, etc.

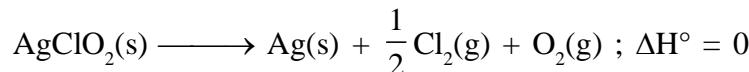
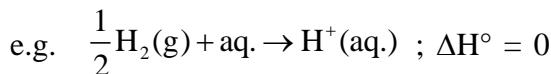
#### (ii) Endothermic reactions :

These are the chemical reactions involving absorption of heat.

Examples :- Decomposition reactions, elemination reaction, etc.

#### (iii) Thermo neutral reactions :

These are chemical reaction in which heat is neither absorbed nor released.



The reason behind release or absorption of heat in the reaction may be defined as difference in internal energy, bond energy, enthalpy, etc.

For exothermic reaction :

(i)  $\sum U_{\text{Reactant}} > \sum U_{\text{Product}}$

(ii)  $\sum H_{\text{Reactant}} > \sum H_{\text{Product}}$

(iii)  $\sum (\text{BE})_{\text{Reactant}} < \sum (\text{BE})_{\text{Product}}$

### 3. REPRESENTATION OF HEAT INVOLVED IN REACTIONS

#### (i) Old convention :

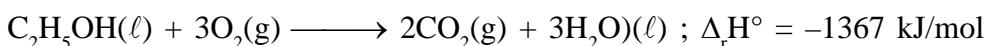


#### (ii) Modern convention :



#### 4. THERMO CHEMICAL EQUATION

It represents a balanced chemical reaction in which the physical state along with allotropic form of all the reaction components as well as heat involved in reaction, are given.



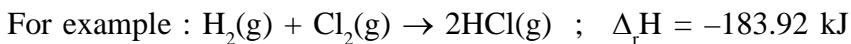
The above equation describes the combustion of liquid ethanol at constant temperature and pressure.

The negative sign of enthalpy change indicates that this is an exothermic reaction.

The coefficients in a balanced thermochemical equation refer to the number of moles (never molecules) of reactants and products in the reaction. Per mole of  $\Delta_r\text{H}^\circ$  defines the mole of reaction. For above reaction per mole means per mole of  $\text{C}_2\text{H}_5\text{OH}(\ell)$ , per 3 moles of  $\text{O}_2(\text{g})$ , per 2 moles of  $\text{CO}_2(\text{g})$  and per 3 moles of  $\text{H}_2\text{O}(\ell)$ .

#### 5. ENTHALPY CHANGE OF REACTION OR REACTION ENTHALPY ( $\Delta_r\text{H}$ )

Enthalpy of reaction is defined as the quantity of heat evolved or absorbed when molar quantities of substances react completely in amounts represented by chemical equation, all components being maintained at same pressure and same temperature conditions.



Thus, when one mole of gaseous hydrogen reacts completely with one mole of gaseous chlorine, 183.92 kJ of heat is evolved.

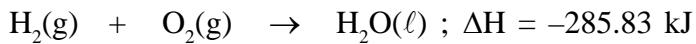
$$\Delta_r\text{H} = \Sigma\text{H}_{\text{products}} - \Sigma\text{H}_{\text{reactants}} = [2 \times \text{H}_m(\text{HCl}, \text{ g})] - [1 \times \text{H}_m(\text{H}_2, \text{ g}) + 1 \times \text{H}_m(\text{Cl}, \text{ g})]$$

where  $\text{H}_m$  = molar enthalpy

#### 5.1 FACTORS AFFECTING HEAT OR ENTHALPY OF REACTION :

The enthalpy change of reaction ( $\Delta\text{H}$ ) depends upon the following factors :

- (i) **Physical state of the reactants and the products :** The  $\Delta\text{H}$  of a reaction depends upon the physical states of reactants and products. For example, when hydrogen and oxygen gases combine to give liquid water, the heat of reaction is different than when they combine to form gaseous water at the same temperature and pressure.



- (ii) **Quantities of reaction components :** The amount of heat evolved or absorbed depends upon the amount of components involved in the reaction. For example, the heat of combustion of 2 moles of carbon is double than heat of combustion of 1 mole of carbon.
- (iii) **Allotropic forms :** The amount of heat evolved or absorbed for different forms of the same substance are different. For example,



- (iv) **Temperature** : The heat of reaction depends upon the temperature of reactants and products.



The dependence of reaction enthalpy on temperature is given by Kirchoff's equation :

$$\Delta_r H_2 - \Delta_r H_1 = \int_{T_1}^{T_2} \Delta_r (C_p) \cdot dT$$

$$\text{and } \Delta_r U_2 - \Delta_r U_1 = \int_{T_1}^{T_2} \Delta_r (C_v) \cdot dT$$

However,  $\Delta_r H$  and  $\Delta_r U$  do not change significantly on changing the temperature.

- (v) **Measurement at constant pressure or volume** : The heat of reaction depends upon the conditions of measurement of heat at constant pressure or volume, as,

$$\Delta_r H = \Delta_r U + \Delta_r (PV)$$

$\Delta H$  may be equal, greater than or less than  $\Delta_r U$ .

For reaction involving gaseous components,

$$\Delta_r H = \Delta_r U + \Delta_r n_g \cdot RT$$

- (vi) **Pressure** : Enthalpy of any component may depend on pressure and  $\Delta_r H$  may change on changing the pressure. As, the enthalpy of an ideal gas is independent from the change in pressure, for the reactions involving ideal gases,  $\Delta_r H$  is pressure independent.

## EXERCISE-I

- Consider the reaction :  $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$  carried out at constant temperature and pressure, if  $\Delta H$  and  $\Delta U$  are the enthalpy and internal energy changes for the reaction, which of the following expressions is true ? [AIEEE-2005]

(A)  $\Delta H = \Delta U$       (B)  $\Delta H = 0$       (C)  $\Delta H > \Delta U$       (D)  $\Delta H < \Delta U$
- For which reaction will  $\Delta H = \Delta U$  ?

(A)  $\text{H}_2(g) + \text{Br}_2(g) \rightarrow 2 \text{HBr}(g)$       (B)  $\text{C}(s) + 2 \text{H}_2\text{O}(g) \rightarrow 2\text{H}_2(g) + \text{CO}_2(g)$   
(C)  $\text{PCl}_5(g) \rightarrow \text{PCl}_3(g) + \text{Cl}_2(g)$       (D)  $2\text{CO}(g) + \text{O}_2(g) \rightarrow 2 \text{CO}_2(g)$
- For which of the following change  $\Delta H \neq \Delta U$  ?

(A)  $\text{H}_2(g) + \text{I}_2(g) \longrightarrow 2\text{HI}(g)$   
(B)  $\text{HCl(aq)} + \text{NaOH(aq)} \longrightarrow \text{NaCl(aq)} + \text{H}_2\text{O}(l)$   
(C)  $\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$   
(D)  $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$

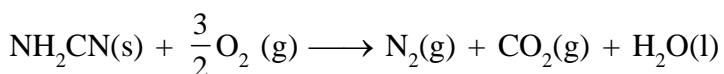
4. A mixture of 2 moles of carbon monoxide and one mole of oxygen in a closed vessel is ignited to get carbon dioxide. If  $\Delta H$  is the enthalpy change and  $\Delta U$  is the change in internal energy, then :-

(A)  $\Delta H > \Delta U$       (B)  $\Delta H < \Delta U$       (C)  $\Delta H = \Delta U$       (D) Not definite

5. For the reaction :  $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ ,  $\Delta H$  is -

(A)  $\Delta U + 2RT$       (B)  $\Delta U - 2RT$       (C)  $\Delta U + RT$       (D)  $\Delta U - RT$

6. When the following reaction was carried out in a bomb calorimeter,  $\Delta U$  is found to be  $-742.7\text{ kJ/mol}$  of  $NH_2CN(s)$  at  $300\text{ K}$ .



Calculate  $\Delta H_{300K}$  for the reaction. ( $R = 8\text{ J/mole-K}$ ).

7. For the reaction :  $2A(g) + 3B(g) \longrightarrow 4C(g) + D(\ell)$  ;  $\Delta H = -20\text{ KJ/mole}$

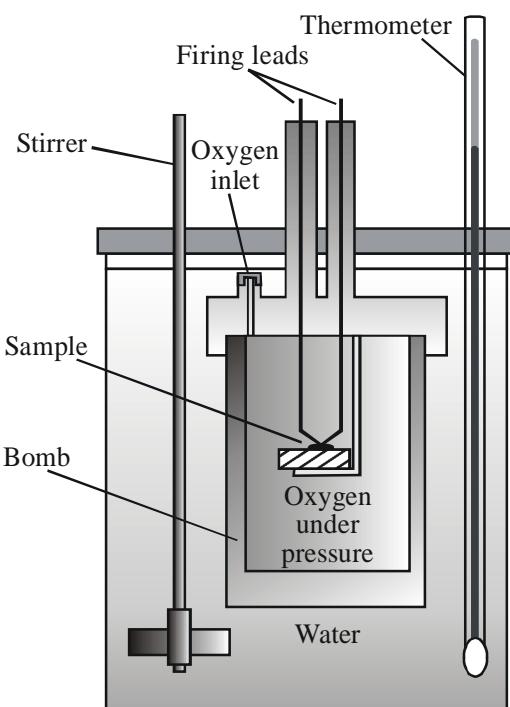
Find the heat exchanged when 0.4 mole of A reacts with excess of B in a closed rigid container. The temperature is constant at  $300\text{ K}$ . [ $R=8.3\text{ J/K mole}$ ]

## 5.2 MEASUREMENT OF $\Delta U$ AND $\Delta H$ : CALORIMETRY :

We can measure energy changes associated with chemical or physical processes by an experimental technique called calorimetry. In calorimetry, the process is carried out in a vessel called calorimeter, which is immersed in a known volume of a liquid. Knowing the heat capacity of the liquid in which calorimeter is immersed and the heat capacity of calorimeter, it is possible to determine the heat evolved in the process by measuring temperature changes. Measurements are made under two different conditions:

- (i) at constant volume,  $q_V$
- (ii) at constant pressure,  $q_p$

(a)  **$\Delta U$  measurements :** For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter (Figure). Here, a steel vessel (the bomb) is immersed in a water bath. The whole device is called calorimeter. The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings. A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb calorimeter is sealed, its volume does not change i.e., the energy changes associated with reactions are measured at constant volume. Under these conditions, no work is

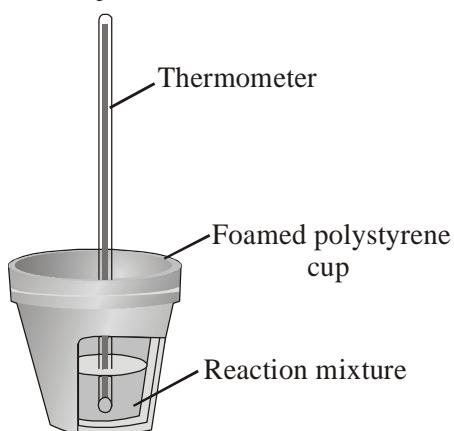


**Figure :** Bomb calorimeter

done as the reaction is carried out at constant volume in the bomb calorimeter. Even for reactions involving gases, there is no work done as  $\Delta V = 0$ . Temperature change of the calorimeter produced by the completed reaction is then converted to  $q_v$ , by using the known heat capacity of the calorimeter with the help of equation 6.11.

- (b)  **$\Delta H$  measurements :** Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a calorimeter shown in figure. We know that  $\Delta H = q_p$  (at constant p) and, therefore, heat absorbed or evolved,  $q_p$  at constant pressure is also called the heat of reaction or enthalpy of reaction,  $\Delta_r H$ .

In an exothermic reaction, heat is evolved, and system loses heat to the surroundings. Therefore,  $q_p$  will be negative and  $\Delta_r H$  will also be negative. Similarly in an endothermic reaction, heat is absorbed,  $q_p$  is positive and  $\Delta_r H$  will be positive.



**Figure :** Calorimeter for measuring heat changes at constant pressure (atmospheric pressure)

**Ex.1.** 1g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation



During the reaction, temperature rises from 298 K to 299 K. If the heat capacity of the bomb calorimeter is 20.7 kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm?

**Sol. :** Suppose  $q$  is the quantity of heat from the reaction mixture and  $C_v$  is the heat capacity of the calorimeter, then the quantity of heat absorbed by the calorimeter.

$$q = C_V \Delta T$$

*Quantity of heat from the reaction will have the same magnitude but opposite sign because the heat lost by the system (reaction mixture) is equal to the heat gained by the calorimeter.*

$$q = -C_V \times \Delta T = -20.7 \text{ kJ/K} \times (299 - 298) \text{ K} = -20.7 \text{ kJ}$$

(Here, negative sign indicates the exothermic nature of the reaction)

Thus,  $\Delta U$  for the combustion of the 1g of graphite = -20.7 kJ

*For combustion of 1 mol of graphite,*

$$\Delta H = \Delta U = \frac{12.0 \text{ g mol}^{-1} \times (-20.7 \text{ kJ})}{1 \text{ g}} = -2.48 \times 10^2 \text{ kJ mol}^{-1}, \quad \text{Since } \Delta n_g = 0$$

## **EXERCISE-II**

## 6. STANDARD ENTHALPY OF REACTION, $\Delta H^\ominus$

Enthalpy of a reaction depends on the conditions under which a reaction is carried out. It is, therefore, necessary that we must specify some standard conditions. **The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.**

**The standard state of a substance at a specified temperature is its pure form at 1 bar.**

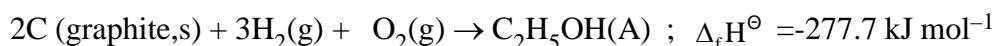
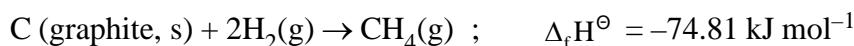
For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 1 bar; standard state of solid iron at 500 K is pure iron at 1 bar. Usually data are taken at 298 K.

Standard conditions are denoted by adding the superscript  $\ominus$  to the symbol  $\Delta H$ , e.g.,  $\Delta H^\ominus$

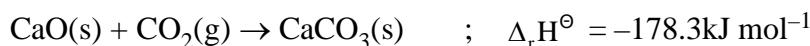
## 7. SOME DIFFERENT KINDS OF $\Delta_r H^\ominus$ :

### 7.1 STANDARD ENTHALPY OF FORMATION, $\Delta_f H^\ominus$ :

The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. The reference state of an element is its most stable state of aggregation at 25° C and 1 bar pressure. For example, the reference state of dihydrogen is  $H_2$  gas and those of dioxygen, carbon and sulphur are  $O_2$  gas,  $C_{\text{graphite}}$  and  $S_{\text{rhombic}}$  respectively. Some reactions with standard molar enthalpies of formation are given below.



It is important to understand that a standard molar enthalpy of formation,  $\Delta_f H^\ominus$ , is just a special case of  $\Delta_r H^\ominus$ , where one mole of a compound is formed from its constituent elements, as in the above three equations, where 1 mol of each, water, methane and ethanol is formed. In contrast, the enthalpy change for an exothermic reaction:



is not an enthalpy of formation of calcium carbonate, since calcium carbonate has been formed from other compounds, and not from its constituent elements. Also, for the reaction given below, enthalpy change is not standard enthalpy of formation,  $\Delta_f H^\ominus$  for  $HBr(g)$ .



Here two moles, instead of one mole of the product is formed from the elements, i.e.,

$$\Delta_r H^\ominus = 2\Delta_f H^\ominus$$

Therefore, by dividing all coefficients in the balanced equation by 2, expression for enthalpy of formation of HBr(g) is written as



- (i)  $\Delta_f H^\ominus = 0$  for all the elements in their reference state.
- (ii) **Standard enthalpy of reaction from standard enthalpy of formation :** The knowledge of standard enthalpy of formation of various substances can be used to calculate the standard enthalpy of reactions under standard conditions. The standard enthalpy of any reaction ( $\Delta H^\ominus$ ) is equal to the difference between the  $\Delta_f H^\ominus$  of all the products and the reactants.

$\Delta H^\ominus = \text{Sum of the standard enthalpy of formation of products} - \text{Sum of the standard enthalpy of formation of reactants.}$

$$\text{i.e., } \Delta_r H^\ominus = \sum \Delta_f H^\ominus_{\text{(products)}} - \sum \Delta_f H^\ominus_{\text{(reactants)}}$$

For a reaction,  $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$

$$\begin{aligned} \Delta_r H^\ominus &= \sum \Delta_f H^\ominus_{\text{(products)}} - \sum \Delta_f H^\ominus_{\text{(reactants)}} \\ &= [c\Delta_f H^\ominus (\text{C}) + d\Delta_f H^\ominus (\text{D})] - [a\Delta_f H^\ominus (\text{A}) + b\Delta_f H^\ominus (\text{B})] \end{aligned}$$

**Ex.2.** Standard enthalpies of formation of CO(g), CO<sub>2</sub>(g), N<sub>2</sub>O(g) and N<sub>2</sub>O<sub>4</sub>(g) are -110, -393, -81 and 10 kJ/mole, respectively. Find the  $\Delta_r H^\ominus$  for the reaction :



$$\begin{aligned} \text{Sol. : } \Delta_r H^\ominus &= \sum \Delta_f H^\ominus_{\text{(products)}} - \sum \Delta_f H^\ominus_{\text{(reactants)}} \\ &= [\Delta_f H^\ominus_{\text{N}_2\text{O}(\text{g})} + 3 \times \Delta_f H^\ominus_{\text{CO}_2(\text{g})}] - [\Delta_f H^\ominus_{\text{N}_2\text{O}_4(\text{g})} + 3 \times \Delta_f H^\ominus_{\text{CO}(\text{g})}] \\ &= [81 + 3 \times (-393)] - [10 + 3 \times (-110)] = -778 \text{ kJ/mol.} \end{aligned}$$

## 7.2 STANDARD ENTHALPY OF COMBUSTION, $\Delta_c H^\ominus$ :

Standard enthalpy of combustion is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the **reactants and products** being in their standard states at the specified temperature.

For example, the standard enthalpy of combustion of methane at 298.15 K is -890.36 kJ mol<sup>-1</sup>.

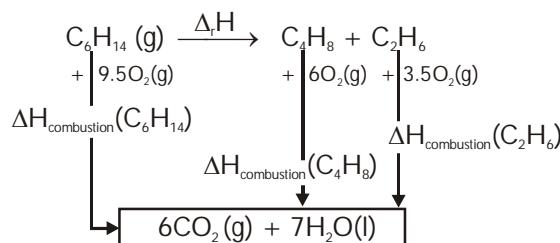
This implies the following reaction :



The standard enthalpy of combustion of methane at 298.15 K may be written as

$$\Delta_c H^\ominus(\text{CH}_4, \text{g}, 298.15 \text{ K}) = -890.36 \text{ kJ mol}^{-1}$$

**7.2.1 Application of enthalpy of combustion :** Consider a reaction of decomposition of  $C_6H_{14}$  into  $C_4H_8$  and  $C_2H_6$ . The following diagram show how enthalpy of combustions can be used to estimate enthalpy of reaction.



From the inspection of the above diagram, it is clear that

$$\Delta H_{\text{reaction}} = \Delta H_{\text{combustion}}(C_6H_{14}) - \Delta H_{\text{combustion}}(C_4H_8) - \Delta H_{\text{combustion}}(C_2H_6)$$

$$\text{Hence } \Delta_r H = \Sigma \Delta_c H(\text{Reactants}) - \Sigma \Delta_c H(\text{Products})$$

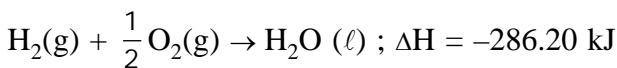
**Ex.3.** Calculate the standard enthalpy of formation of carbon disulphide ( $\ell$ ). Given that the standard enthalpies of combustion of carbon (s) sulphur (s) and carbon disulphide ( $\ell$ ) are 393.3, -293.72 and  $-1108.76 \text{ kJ mol}^{-1}$  respectively.

$$\text{Sol: } C(s) + 2S(s) \longrightarrow CS_2(\ell) ; \quad \Delta_f H^\circ_{CS_2(\ell)} = ?$$

$$\begin{aligned}
 \text{Now, } \Delta_r H^\circ &= \Sigma \Delta_c H^\circ_{(\text{Reactants})} - \Sigma \Delta_c H^\circ_{(\text{Products})} \\
 &= [\Delta_c H^\circ_{C(s)} + 2 \times \Delta_c H^\circ_{S(s)}] - [\Delta_c H^\circ_{CS_2(\ell)}] \\
 &= [(-393.3) + 2 \times (-293.72)] - [-1108.76] \\
 &= -128.02 \text{ kJ/mol}
 \end{aligned}$$

### EXERCISE-III

**11.** On the basis of the following thermochemical data :



The value of enthalpy of formation of  $OH^-$  ion at  $25^\circ\text{C}$  is :-

[AIEEE-2009]

- (A) +228.88 kJ      (B) -343.52 kJ      (C) -22.88 kJ      (D) -228.88 kJ

**12.** The enthalpies of combustion of carbon and carbon monoxide are  $-393.5$  and  $-283 \text{ kJ mol}^{-1}$  respectively. The enthalpy of formation of carbon monoxide per mole :-

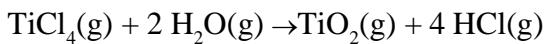
[AIEEE-2004]

- (A) 110.5 kJ      (B) 676.5 kJ      (C) -676.5 kJ      (D) -110.5 kJ

13. For which species  $\Delta H_{\text{formation}} \neq 0$
- (A)  $\text{H}_{(\text{aq.})}^+$       (B)  $\text{Br}_{2(\text{g})}$       (C)  $\text{I}_{2(\text{s})}$       (D)  $\text{C}_{(\text{graphite})}$

14. Which of the following equations represents a reaction that provides the enthalpy of formation of  $\text{CH}_3\text{Cl(g)}$  ?
- (A)  $\text{C(s)} + \text{HCl(g)} + \text{H}_2\text{(g)} \rightarrow \text{CH}_3\text{Cl(g)}$       (B)  $\text{C(s)} + 3/2 \text{H}_2\text{(g)} + 1/2 \text{Cl}_2\text{(g)} \rightarrow \text{CH}_3\text{Cl(g)}$   
 (C)  $\text{C(s)} + 3 \text{H(g)} + \text{Cl(g)} \rightarrow \text{CH}_3\text{Cl(g)}$       (D)  $\text{CH}_4\text{(g)} + \text{Cl}_2\text{(g)} \rightarrow \text{CH}_3\text{Cl(g)} + \text{HCl(g)}$

15. Use the given standard enthalpies of formation to determine the enthalpy of reaction of the following reaction:



$$\Delta H_f^\circ \text{ TiCl}_4\text{(g)} = -763.2 \text{ kJ/mole}$$

$$\Delta H_f^\circ \text{ H}_2\text{O(g)} = -241.8 \text{ kJ/mole}$$

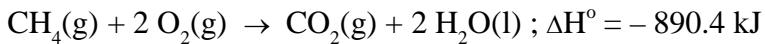
$$(A) -278.1 \text{ kJ} \quad (B) +369.2 \text{ kJ}$$

$$\Delta H_f^\circ \text{ TiO}_2\text{(g)} = -944.7 \text{ kJ/mole}$$

$$\Delta H_f^\circ \text{ HCl(g)} = -92.3 \text{ kJ/mole}$$

$$(C) +67.1 \text{ kJ} \quad (D) -67.1 \text{ kJ}$$

16. Using the following information calculate the enthalpy of formation of  $\text{CH}_4$ .

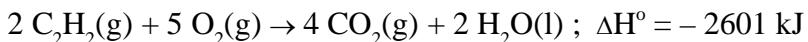


$$\Delta H_f^\circ \text{ CO}_2\text{(g)} = -393.5 \text{ kJ/mole}$$

$$(A) -98.6 \text{ kJ/mole} \quad (B) -65.5 \text{ kJ/mole} \quad (C) -74.9 \text{ kJ/mole} \quad (D) -43.5 \text{ kJ/mole}$$

$$\Delta H_f^\circ \text{ H}_2\text{O(l)} = -285.9 \text{ kJ/mole}$$

17. The heats of formation of  $\text{CO}_2\text{(g)}$  and  $\text{H}_2\text{O(l)}$  are  $-394 \text{ kJ/mole}$  and  $-285.8 \text{ kJ/mole}$  respectively. Using the data for the following combustion reaction, calculate the heat of formation of  $\text{C}_2\text{H}_2\text{(g)}$ .

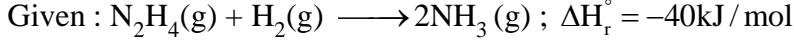


$$(A) -238.6 \text{ kJ/mole} \quad (B) 253.2 \text{ kJ/mole} \quad (C) 238.7 \text{ kJ/mole} \quad (D) 226.7 \text{ kJ/mole}$$

18. The heats of formation of  $\text{CO}_2\text{(g)}$  and  $\text{H}_2\text{O(l)}$  are  $-394 \text{ kJ/mole}$  and  $-285.8 \text{ kJ/mole}$  respectively &  $\Delta H_{\text{Combustion}}^\circ [\text{C}_3\text{H}_8\text{(g)}] = -2221.6 \text{ kJ}$ . Then the heat of formation of  $\text{C}_3\text{H}_8\text{(g)}$  is -

$$(A) 212.2 \text{ kJ/mole} \quad (B) -143.3 \text{ kJ/mole} \quad (C) 185.4 \text{ kJ/mole} \quad (D) -103.6 \text{ kJ/mole}$$

19. The standard enthalpy of formation of ammonia gas is -



$$\Delta H_f^\circ [\text{N}_2\text{H}_4\text{(g)}] = -120 \text{ kJ/mol}$$

$$(A) -60 \text{ kJ/mol} \quad (B) -180 \text{ kJ/mol} \quad (C) 40 \text{ kJ/mol} \quad (D) -80 \text{ kJ/mol}$$

20. Calculate standard enthalpy of formation of carbon-di-sulphide (*l*). Given the standard enthalpy of combustion of carbon (s), sulphur (s) & carbon-di-sulphide (*l*) are :  $-393$ ,  $-293$  and  $-1108 \text{ kJ mol}^{-1}$  respectively.

21. The enthalpy change for the reaction  $\text{C}_3\text{H}_8\text{(g)} + \text{H}_2\text{(g)} \longrightarrow \text{C}_2\text{H}_6\text{(g)} + \text{CH}_4\text{(g)}$  at  $25^\circ \text{ C}$  is  $-55.7 \text{ kJ/mol}$ . Calculate the enthalpy of combustion of  $\text{C}_2\text{H}_6\text{(g)}$ . The enthalpy of combustion of  $\text{H}_2$ ,  $\text{C}_3\text{H}_8$  &  $\text{CH}_4$  are  $-285.8$ ,  $-2220$  &  $-890.0 \text{ kJ/mol}$  respectively.

### 7.3 BOND ENTHALPY, $\Delta_{\text{bond}}H^\ominus$ :

Chemical reactions involve the breaking and making of chemical bonds. Energy is required to break a bond and energy is released when a bond is formed. It is possible to relate heat of reaction to changes in energy associated with breaking and making of chemical bonds. With reference to the enthalpy changes associated with chemical bonds, two different terms are used in thermodynamics.

(i) Bond dissociation enthalpy

(ii) Mean bond enthalpy

Let us discuss these terms with reference to diatomic and polyatomic molecules.

**Diatomeric Molecules:** Consider the following process in which the bonds in one mole of dihydrogen gas ( $H_2$ ) are broken:



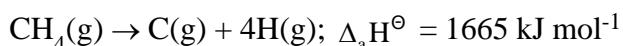
The enthalpy change involved in this process is the bond dissociation enthalpy of H–H bond. The bond dissociation enthalpy is the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gas phase.

Note that it is the same as the enthalpy of atomization of dihydrogen. This is true for all diatomic molecules. For example:

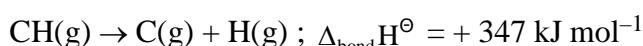
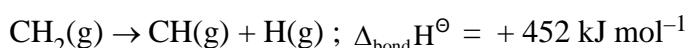
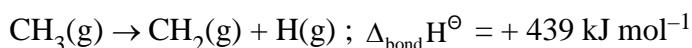
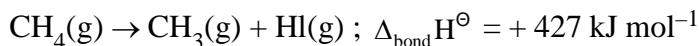


In the case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule.

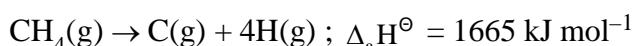
**Polyatomic Molecules:** Let us now consider a polyatomic molecule like methane,  $CH_4$ . The overall thermochemical equation for its atomization reaction is given below:



In methane, all the four C – H bonds are identical in bond length and energy. However, the energies required to break the individual C – H bonds in each successive step differ :



Therefore,



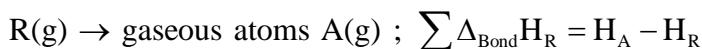
In such cases we use **mean bond enthalpy of C – H bond**.

For example in  $CH_4$ ,  $\Delta_{C-H}H^\ominus$  is calculated as:

$$\Delta_{C-H}H^\ominus = \frac{1}{4} (\Delta_aH^\ominus) = \frac{1}{4} (1665 \text{ kJ mol}^{-1}) = 416 \text{ kJ mol}^{-1}$$

We find that mean C–H bond enthalpy in methane is 416 kJ/mol. It has been found that mean C–H bond enthalpies differ slightly from compound to compound, as in  $\text{CH}_3\text{CH}_2\text{Cl}$ ,  $\text{CH}_3\text{NO}_2$ , etc, but it does not differ in a great deal. Using Hess's law, bond enthalpies can be calculated.

- (i) Mean bond enthalpy may be used to calculate  $\Delta_r H$  of gaseous reaction :  
 Reactants (R, g) —→ Products (P, g), as



$$\Delta_r H = H_p - H_R = \sum \Delta_{\text{bond}} H_R - \sum \Delta_{\text{bond}} H_p$$

$$\boxed{\Delta_r H = \sum \Delta_{\text{bond}} H_{\text{Reactants}} - \sum \Delta_{\text{bond}} H_{\text{Products}}}$$

- (ii) If physical state of any component is different than gaseous, then it should be converted into gaseous atom.  
 (iii)  $\Delta H$  calculated from bond enthalpy give  $\Delta_r H_{\text{theo}}$  because mean enthalpies are used in place of bond dissociation enthalpies. Normally it remain very close to experimental  $\Delta_r H$  but if any reaction component is more or less stable by any effect like resonance, hyperconjugation, strain, etc, the value differs largely. The difference is called energy or enthalpy of the kind responsible for the difference like resonance energy, strain energy, etc. It is given by

$$\Delta_r H_{\text{exp}} - \Delta_r H_{\text{theo}} = \Delta H_{\text{effect}}$$

**Ex.4.** If  $E_{C-C}$  is 344  $\text{kJ mol}^{-1}$  and  $E_{C-H}$  is 415  $\text{kJ mol}^{-1}$ , calculate the enthalpy of formation of propane. The enthalpies of atomization of carbon(s) and hydrogen (g) are 716  $\text{kJ mole}^{-1}$  and 433  $\text{kJ mole}^{-1}$  respectively.

**Sol. :** The enthalpy of formation is the sum of the atomization and bond energies. For propane, the enthalpies of atomization are

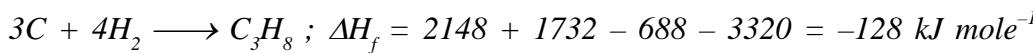


The bond enthalpies are

$$2E_{C-C} = 2 \times -344 = -688 \text{ kJ}$$

$$8E_{C-H} = 8 \times -415 = -3320 \text{ kJ}$$

Adding



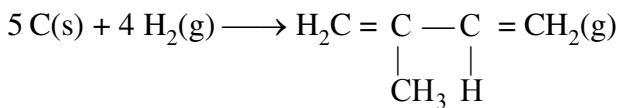
## EXERISE-IV

21. The enthalpy change for the following reaction is 513 kJ. Calculate the average Cl – F bond energy.



- (A) 1542 kJ/mole      (B) 88 kJ/mole      (C) 171 kJ/mole      (D) 514 kJ/mole

22. Using bond enthalpy data, calculate enthalpy of formation of gaseous isoprene .



Given :

$$\text{C} - \text{H} = 98.8 \text{ kcal/mol} ;$$

$$\text{H} - \text{H} = 104 \text{ kcal/mol} ;$$

$$\text{C} - \text{C} = 83 \text{ kcal/mol} ;$$

$$\text{C} = \text{C} = 147 \text{ kcal/mol} \quad \&$$

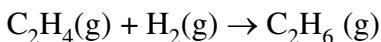
$$\text{C(s)} \rightarrow \text{C(g)} = 171 \text{ kcal/mol}.$$

23. For the reaction :  $\text{N}_2\text{H}_4(\text{g}) \rightarrow \text{N}_2\text{H}_2(\text{g}) + \text{H}_2(\text{g}) ; \Delta_f^{\circ}\text{H} = 109 \text{ kJ /mol}$

Calculate the bond enthalpy of N = N.

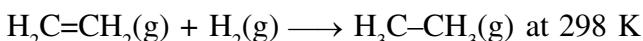
Given : B.E. (N – N ) = 163 kJ/mol, B.E. (N-H) = 391 kJ/mol, B.E. (H-H) = 436 kJ/mol

24. Using the bond enthalpy data given below, calculate the enthalpy change for the reaction.



Bond	C–C	C = C	C–H	H–H
Bond Enthalpy	336 kJ/mol	606 kJ/mol	410 kJ/mol	431 kJ/mol

25. If at 298 K the bond energies of C–H, C–C, C=C and H–H bonds are respectively 414, 347, 615 and 435 kJ mol<sup>-1</sup>, the value of enthalpy change for the reaction : [AIEEE-2003]



will be :-

- (A) +125 kJ      (B) -125 kJ      (C) +250 kJ      (D) -250 kJ

26. The standard enthalphy of formation of  $\text{NH}_3$  is  $-46.0 \text{ kJ mol}^{-1}$ . If the enthalpy of formation of  $\text{H}_2$  from its atoms is  $-436 \text{ kJ mol}^{-1}$  and that of  $\text{N}_2$  is  $-712 \text{ kJ mol}^{-1}$ , the average bond enthalpy of N–H bond in  $\text{NH}_3$  is : [AIEEE-2010]

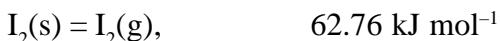
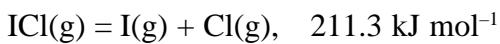
- (A)  $-1102 \text{ kJ mol}^{-1}$       (B)  $-964 \text{ kJ mol}^{-1}$   
(C)  $+352 \text{ kJ mol}^{-1}$       (D)  $+1056 \text{ kJ mol}^{-1}$

27. If the bond dissociation energies of XY,  $\text{X}_2$  and  $\text{Y}_2$  (all gaseous diatomic molecules) are in the ratio of 1 : 1 : 0.5 and  $\Delta_f^{\circ}\text{H}$  for the formation of XY is  $-200 \text{ kJ mol}^{-1}$ . The bond dissociation energy of  $\text{X}_2$  will be [AIEEE-2005]

- (A)  $200 \text{ kJ mol}^{-1}$       (B)  $100 \text{ kJ mol}^{-1}$       (C)  $800 \text{ kJ mol}^{-1}$       (D)  $300 \text{ kJ mol}^{-1}$

28. The enthalpy of atomization of  $\text{PH}_3(\text{g})$  is  $954 \text{ kJ mol}^{-1}$  and that of  $\text{P}_2\text{H}_4(\text{g})$  is  $1485 \text{ kJ mol}^{-1}$ . What is the bond enthalpy of the P-P bond?

29. The enthalpy changes for the following processes are listed below : [AIEEE-2006]



Given that the standard states for iodine and chlorine are  $\text{I}_2(\text{s})$  and  $\text{Cl}_2(\text{g})$ , the standard enthalpy of formation for  $\text{ICl}(\text{g})$  is :-

- (A)  $-16.8 \text{ kJ mol}^{-1}$     (B)  $+16.8 \text{ kJ mol}^{-1}$     (C)  $+244.8 \text{ kJ mol}^{-1}$     (D)  $-14.6 \text{ kJ mol}^{-1}$

30. The standard enthalpy of formation ( $\Delta_f^\circ$ ) at 298K for methane,  $\text{CH}_4(\text{g})$ , is  $-74.8 \text{ kJ mol}^{-1}$ .

The additional information required to determine the average energy for C-H bond formation would be:- [AIEEE-2006]

- (A) Latent heat of vapourization of methane  
 (B) The first four ionization energies of carbon and electron gain enthalpy of hydrogen  
 (C) The dissociation energy of hydrogen molecule  $\text{H}_2$   
 (D) The dissociation energy of  $\text{H}_2$  and enthalpy of sublimation of carbon

31.  $\text{XeF}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow 2\text{HF}(\text{g}) + \text{Xe}(\text{g}) ; \Delta H^\circ = -430 \text{ kJ}$

using the following bond energies :  $\text{H}-\text{H} = 435 \text{ kJ/mol}$ ,  $\text{H}-\text{F} = 565 \text{ kJ/mol}$

Calculate the average bond energy of Xe-F in  $\text{XeF}_2$ .

32. Using the given data calculate enthalpy of formation of acetone (g). [All values in  $\text{kJ mol}^{-1}$ ]

Bond enthalpy of :

$$\text{C}—\text{H} = 415 ; \text{C}—\text{C} = 350 ; (\text{C}=\text{O}) = 730$$

$$(\text{O}=\text{O}) = 495.0 ; \text{H}—\text{H} = 435 ; \Delta_{\text{sub}}\text{H of C} = 720$$

#### 7.4 ENTHALPY OF NEUTRALISATION, $\Delta_{\text{neut}}\text{H}^\ominus$ :

The reaction in which an acid and a base react to give a salt and water is called neutralization reaction. Neutralization reactions are exothermic in nature. The enthalpy change when one gram equivalent of an acid and one gram equivalent of a base neutralise each other completely in dilute aqueous solution, is called enthalpy of neutralization.

For examples :

- (i) Neutralization of  $\text{HCl}$  with  $\text{NaOH}$



- (ii) Neutralization of  $\text{CH}_3\text{COOH}$  with  $\text{NaOH}$

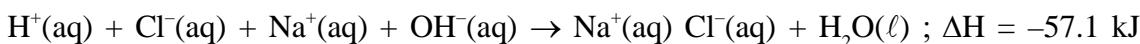


It is important to note that the term gram equivalent is used in the definition of heat of neutralization. This is because neutralization involves 1 mole of  $H^+$  ions and 1 mole of  $OH^-$  ions to form 1 mole of water and 57.1 kJ of heat is liberated.

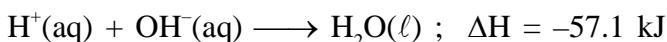


Now, one gram equivalent of various acids on complete dissociation liberates one mole of  $H^+$  ions. But one mole of the acid may produce more than one mole of  $H^+$  ions in solution depending upon its basicity; for example 1 mol of  $H_2SO_4$  gives 2 mol of  $H^+$  ions and 1 mol of  $H_3PO_4$  gives 3 mol of  $H^+$  ions on complete dissociation. But 1 gram equivalent of both ( $H_2SO_4$  or  $H_3PO_4$ ) produces only 1 mol of  $H^+$  ions. Thus, it is more appropriate to use the term gram equivalent in the definition of enthalpy of neutralization.

The average enthalpy of neutralization of any strong acid by a strong base is found to be  $-57.1\text{ kJ}/\text{eq}$ . This is because strong acids and strong bases are completely ionized in aqueous solutions. The aqueous solution of one gram equivalent of all strong acids contain the same number of  $H^+$  ions. Similarly, aqueous solution of one gram equivalent of all strong bases also contain same number of  $OH^-$ . The neutralization reactions between strong acids and strong bases in aqueous solutions involve simply the combination of  $H^+$  ions (from an acid) and  $OH^-$  ions (from a base) to form unionized water molecules. For example, the reaction between hydrochloric acid and sodium hydroxide. The neutralization can be represented as :



Cancelling common ions :



(i)  $\Delta_{neut}H$  for any strong acid by any strong base is almost constant.

$$\Delta_{neut} \Delta(H^+/OH^-) = -57.1\text{ kJ/mole}^{-1} = -13.7\text{ kcal mol}^{-1}$$

It is due to the only enthalpy change occurring in such process which is



(ii) If any of the acid or base is weak, the numerical value of  $\Delta_{neut}H$  decreases from 13.7 kcal by enthalpy of ionization for the weak component. **The weak component is assumed completely unionised in solution.**

**Ex5.** The acids HA, HB & HC are neutralised separately by NaOH. If  $\Delta_{neut}H$  are  $-12.1$ ,  $-3.9$  &  $-7.2\text{ kcal}/\text{eq}$ . Arrange the acids in the increasing order of their acidic strength.

**Sol:** A > C > B

**Ex.6.**  $\Delta_{neut}H$  of  $H_2C_2O_4$  by NaOH is  $-8.7\text{ kcal/mol}$ ,  $\Delta_{ion}H$  of oxalic acid is

**Sol :**  $-27.4 + H_{ion} = -8.7$

$$\therefore \Delta_{ion}H = +18.7\text{ kcal/mol}$$

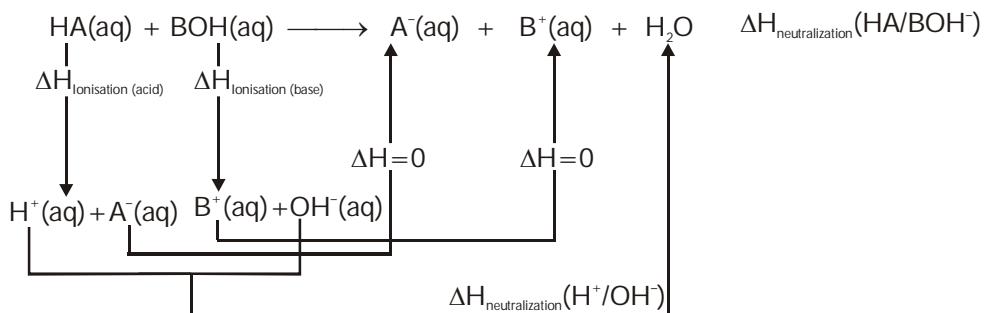
### 7.4.1 The enthalpy of neutralization of weak acid and weak base :

Consider the neutralisation of weak acid HA with weak base BOH.

Where,  $\Delta H_{\text{ionisation}}(\text{HA})$  = Enthalpy of ionization of acid HA = Enthalpy to ionize 1 mole of weak acid in aq. soln.

$\Delta H_{\text{ionisation}}(\text{BOH})$  = Enthalpy of ionization of base BOH

$\Delta H_{\text{neutralisation}}(\text{H}^+/\text{OH}^-)$  = Enthalpy change for the reaction of  $\text{H}^+$  and  $\text{OH}^-$  to form water.



Thus for weak acid :

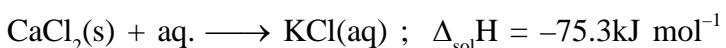
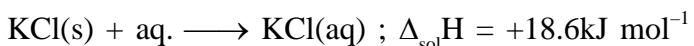
$$\Delta H_{\text{neut}}(\text{BOH/HA}) = \Delta H_{\text{ion.}}(\text{HA}) + \Delta H_{\text{ion}}(\text{BOH}) + \Delta H_{\text{neut}}(\text{H}^+/\text{OH}^-)$$

### EXERCISE-V

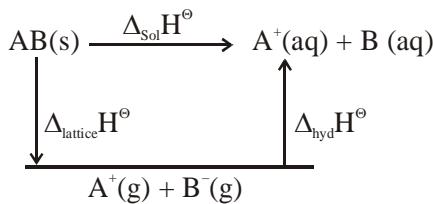
33. Calculate the enthalpy of ionisation of weak acid  $\text{H}_2\text{A}(\text{H}_2\text{A} \rightarrow 2\text{H}^+ + \text{A}^{2-})$  in Kcal/ mol, if enthalpies of neutralisation of  $\text{HCl}$  and  $\text{H}_2\text{A}$  by a strong base are  $-14$  Kcal/eq and  $-11$  Kcal/eq respectively.
34. Enthalpy of neutralization of  $\text{H}_3\text{PO}_3$  acid is  $-106.68$  kJ/mol using  $\text{NaOH}$ . If enthalpy of neutralization of  $\text{HCl}$  by  $\text{NaOH}$  is  $-55.84$  kJ/mol. Calculate  $\Delta H_{\text{ionization}}$  of  $\text{H}_3\text{PO}_3$  into its ions  
 (A)  $50.84$  kJ/mol      (B)  $5$  kJ/mol      (C)  $2.5$  kJ/mol      (D)  $60.84$  kJ/mol

### 7.5 ENTHALPY OF SOLUTION, $\Delta_{\text{sol}}\text{H}^\ominus$ :

When a solute is dissolved in a solvent, a solution is formed. During dissolution of a solute in any solvent, a certain amount of heat is either absorbed or evolved. The change in enthalpy when one mole of a solute is dissolved in a specified quantity of a solvent at a given temperature is called enthalpy of solution. To avoid the amount of solvent, enthalpy of solution is usually defined for an infinite dilute solution. Thus, enthalpy of solution at infinite dilution is the enthalpy change when one mole of a substance is dissolved in such a large quantity of solvent so that further dilution does not give any further enthalpy change.



When an ionic compound dissolves in a solvent, the ions leave their ordered positions on the crystal lattice. These are now more free in solution. But solvation of these ions (hydration in case solvent is water) also occurs at the same time. This is shown diagrammatically, for an ionic compound, AB (s)



The enthalpy of solution of AB(s),  $\Delta_{\text{sol}} H^\ominus$ , in water is, therefore, determined by the selective values of the lattice enthalpy,  $\Delta_{\text{lattice}} H^\ominus$  and enthalpy of hydration of ions,  $\Delta_{\text{hyd}} H^\ominus$  as  

$$\Delta_{\text{sol}} H^\ominus = \Delta_{\text{lattice}} H^\ominus + \Delta_{\text{hyd}} H^\ominus$$

For most of the ionic compounds,  $\Delta_{\text{sol}} H^\ominus$  is positive and the dissociation process is endothermic. Therefore the solubility of most salts in water increases with rise of temperature.

## 7.6 ENTHALPY OF HYDRATION, $\Delta_{\text{Hyd}} H$ :

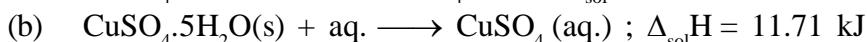
This is defined as the enthalpy change (evolved or absorbed) when one mole of the anhydrous salt combines with the required number of moles of water to form the specific hydrated salt.



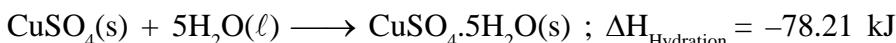
Hydration is generally exothermic change.

If enthalpy of solution of the hydrated and anhydrous salt is known, then heat of hydration can be calculated.

**For example :**

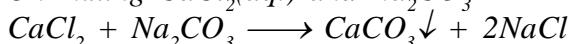


Thus, (a – b) gives

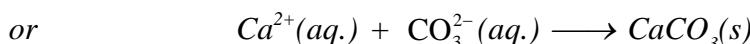
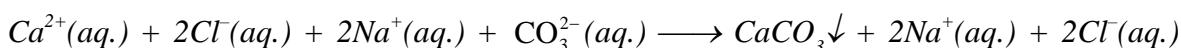


**Ex.7.** Calculate the enthalpy change when infinitely dilute solutions of  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  mixed.  $\Delta H_f^0$  for  $\text{Ca}^{2+}(\text{aq.})$ ,  $\text{CO}_3^{2-}(\text{aq.})$  and  $\text{CaCO}_3(\text{s})$  are  $-129.80$ ,  $-161.65$ ,  $-288.5 \text{ kcal mole}^{-1}$  respectively.

**Sol :** On mixing  $\text{CaCl}_2(\text{aq.})$  and  $\text{Na}_2\text{CO}_3$ ,



Solutions are very dilute and thus 100% dissociation occurs.



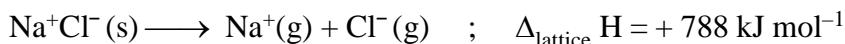
$$\therefore \Delta H = \sum H_{\text{products}}^0 - \sum H_{\text{reactants}}^0$$

$$\text{or} \quad \Delta H = H_{f \text{ CaCO}_3}^0 - [H_{f \text{ Ca}^{2+}}^0 + H_{f \text{ CO}_3^{2-}}^0]$$

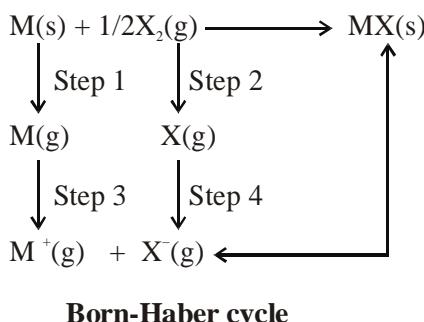
$$\therefore \Delta H^\circ \text{ of a compound} = \Delta H^\circ \text{ formation} = -288.5 - (-129.8 - 161.65) = 2.95 \text{ kcal}$$

## 7.7 LATTICE ENTHALPY ( $\Delta_{\text{lattice}} H$ ) :

The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state under conditions of constant temperature and pressure.

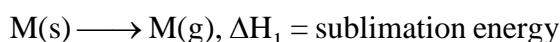


**7.7.1 Determination of lattic energy (Born-Haber cycle) :** Since, it is impossible to find the lattice enthalpies by direct experiment, it is generally calculated by indirect method known as **Born-Haber cycle**.

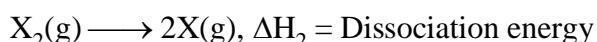


The change in enthalpy that occurs when 1 mole of a solid crystalline substance is formed from its gaseous ions.

**Step 1 :** Conversion of metal to gaseous atoms.



**Step 2 :** Dissociation of  $\text{X}_2$  molecules to X atoms



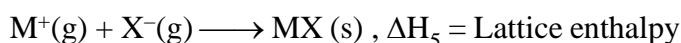
**Step 3 :** Conversion of gaseous metal atom to metal ions by losing electron



**Step 4 :** X(g) atoms gain an electron to form  $\text{M}^-$  ions



**Step 5 :**  $\text{M}^+(\text{g})$  and  $\text{X}^-(\text{g})$  get together and form the crystal lattice



Applying Hess's law we get

$$\Delta H_1 + \frac{1}{2}\Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 = \Delta H_f(\text{MX})$$

On putting the various known values, we can calculate the lattice energy.

**Ex.8.** Calculate the proton affinity of  $\text{NH}_3(g)$  from the following data (in kJ/mole)

$$\Delta H_{\text{dissociation}}^0 : \text{H}_2(\text{g}) = 218$$

$$\Delta H_{\text{formation}}^0 : \text{NH}_3(\text{g}) = -46$$

$$\text{Lattice energy of } \text{NH}_4\text{Cl} = -683$$

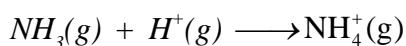
$$\text{Ionisation energy of H} = 1310$$

$$\text{Electron affinity of Cl} = 348$$

$$\text{Bond dissociation energy } \text{Cl}_2(\text{g}) = 124$$

$$\Delta H_{\text{formation}}^0 : \text{NH}_4\text{Cl(s)} = -314$$

**Sol:** We have to calculate  $\Delta H$  for the following equation



$$\text{Given : } \text{H}_2(\text{g}) \longrightarrow 2\text{H}(\text{g}) : \Delta H_1 = 218 \text{ kJ/mole}$$

$$\frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g}) \longrightarrow \text{NH}_3(\text{g}) : \Delta H_2 = -46 \text{ kJ/mole}$$

$$\text{NH}_4\text{Cl(s)} \longrightarrow \text{NH}_4^+(\text{g}) + \text{Cl}^-(\text{g}) : \Delta H_3 = +683 \text{ kJ/mole}$$

$$\text{H}(\text{g}) \longrightarrow \text{H}^+(\text{g}) : \Delta H_4 = 1310 \text{ kJ/mole}$$

$$\text{Cl}(\text{g}) \longrightarrow \text{Cl}^-(\text{g}) : \Delta H_5 = -348 \text{ kJ/mole}$$

$$\text{Cl}_2(\text{g}) \longrightarrow 2\text{Cl}(\text{g}) : \Delta H_6 = 124 \text{ kJ/mole}$$

$$\frac{1}{2}\text{N}_2(\text{g}) + 2\text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{NH}_4\text{Cl(s)} : \Delta H_7 = -314 \text{ kJ/mole}$$

$$\Delta H = -\frac{1}{2}(\Delta H_1) - \Delta H_2 + \Delta H_3 - \Delta H_4 - \Delta H_5 - \frac{1}{2}(\Delta H_6) + \Delta H_7$$

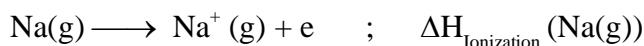
$$= -\frac{1}{2} \times 218 + 46 + 683 - 1310 + 348 - \frac{1}{2} \times 124 - 314$$

$$= -768 \text{ kJ/mole}$$

## 7.8 IONISATION ENTHALPY, $\Delta_i H$ :

Enthalpy change when one mole of gaseous atom is converted into gaseous ion by removing one mole electron from ground state is called ionisation enthalpy.

Example :

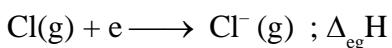


$$\Delta_i H = \text{I.E.} + \frac{5}{2}\text{RT}$$

### 7.9 ELECTRON GAIN ENTHALPY, $\Delta_{eg}H$ :

Enthalpy change when 1 mole electrons are added to valence shell of gaseous atoms is called electron gain enthalpy.

Example :

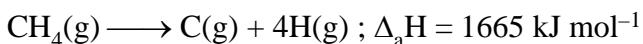


$$\Delta_{eg}H = -E_a - \frac{5}{2}RT$$

### 7.10 ENTHALPY OF ATOMISATION, $\Delta_aH$ :

It is the enthalpy change (always positive) when one mole of a substance is completely dissociated into atoms in the gaseous state, under constant pressure and temperature condition.

For example



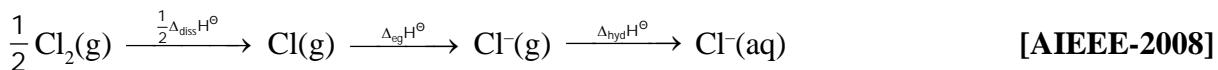
### 7.11 ENTHALPY OF TRANSITION (Enthalpy of allotropic form), $\Delta_{trs}H$ :

It is the enthalpy change when one mole of one allotropic form changes to another under conditions of constant temperature and pressure. For example



## EXERCISE-VI

35. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below:

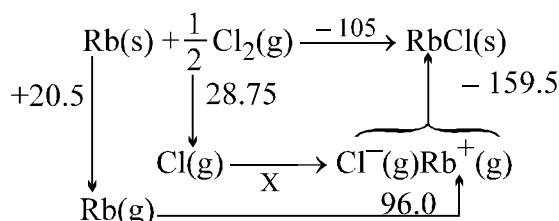


The energy involved in the conversion of  $\frac{1}{2} \text{Cl}_2(\text{g})$  to  $\text{Cl}^-(\text{aq})$

(using the data  $\Delta_{diss}H_{\text{Cl}_2}^\ominus = 240 \text{ kJ mol}^{-1}$ ,  $\Delta_{eg}H_{\text{Cl}}^\ominus = -349 \text{ kJ mol}^{-1}$ ,  $\Delta_{hyd}H_{\text{Cl}^-}^\ominus = -381 \text{ kJ mol}^{-1}$ ) will be:-  
 (A)  $-610 \text{ kJ mol}^{-1}$       (B)  $-850 \text{ kJ mol}^{-1}$       (C)  $+120 \text{ kJ mol}^{-1}$       (D)  $+152 \text{ kJ mol}^{-1}$

36. The lattice enthalpy of solid NaCl is  $772 \text{ kJ mol}^{-1}$  and enthalpy of solution is  $2 \text{ kJ mol}^{-1}$ . If the hydration enthalpy of  $\text{Na}^+$  &  $\text{Cl}^-$  ions are in the ratio of 3:2.5, what is the enthalpy of hydration of chloride ion?  
 (A)  $-140 \text{ kJ mol}^{-1}$       (B)  $-350 \text{ kJ mol}^{-1}$       (C)  $-351.81 \text{ kJ mol}^{-1}$       (D)  $-420 \text{ kJ mol}^{-1}$
37. The enthalpy of solution of anhydrous  $\text{CuSO}_4$  is  $-16 \text{ kcal}$  and that of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is  $3 \text{ kcal}$ . Calculate the enthalpy of hydration of  $\text{CuSO}_4$ .
38. Calculate the electron gain enthalpy of fluorine atom using the following data . (All the values are in  $\text{kJ mol}^{-1}$  at  $25^\circ \text{C}$ ).  $\Delta H_{diss}(\text{F}_2) = 160$ ,  $\Delta_fH(\text{NaF(s)}) = -571$ , I.E.  $[\text{Na(g)}] = 494$ ,  $\Delta H_{sub}[\text{Na(s)}] = 101$  , Lattice enthalpy of  $\text{NaF(s)} = 894$ .

39. The Born–Haber cycle for formation of rubidium chloride (RbCl) is given below (the enthalpies are in k Cal mol<sup>-1</sup>)



Find the value of X.

40. By using the following data, calculate the enthalpy change of hydration of (i) the chloride ion ; (ii) the iodide ion.

enthalpy change of solution of NaCl(s) = - 2 kJ/mol.

enthalpy change of solution of NaI(s) = + 2 kJ/mol.

enthalpy change of hydration of Na<sup>+</sup>(g) = - 390 kJ/mol.

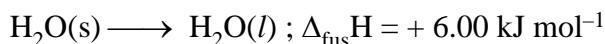
lattice enthalpy of NaCl = - 772 kJ/mol.

lattice enthalpy of NaI = - 699 kJ/mol.

## 7.12 ENTHALPY CHANGES DURING PHASE TRANSFORMATIONS :

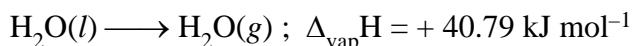
- (i) **Enthalpy of Fusion,  $\Delta_{\text{fus.}}\text{H}$**  : It is the enthalpy change that accompanies melting of one mole of a solid substance at constant temperature (melting point of solid) and pressure.

For example,



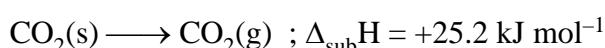
- (ii) **Enthalpy of Vaporisation,  $\Delta_{\text{vap}}\text{H}$**  :

It is the enthalpy change to vapourise one mole of a liquid substance at constant temperature (boiling point of liquid) and pressure for example :



- (iii) **Enthalpy of Sublimation,  $\Delta_{\text{sub}}\text{H}$**  :

It is the amount of enthalpy change to sublime one mole of a solid substance at constant temperature (sublimation temperature of solid) and pressure. For example



## 8. LAWS OF THERMOCHEMISTRY

### (i) Lavoisier and Laplace law :

Heat absorbed or evolved in a process is equal to the heat evolved or absorbed when the process is reversed.



It follows from this law that thermochemical equation may be reversed.

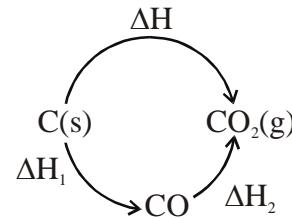
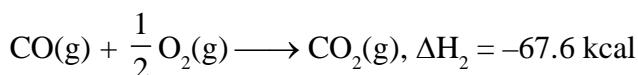
### (ii) Hess's law of constant heat summation :

Heat change of a process is the same whether the process takes place in one step or several steps. It follows from this law that the thermochemical equation may be treated like algebraic equations. Hess's law is helpful in calculating those heat changes which cannot be determined experimentally. It has been experimentally verified and is also a consequence of the law of conservation of energy.

For example : Carbon can be converted into  $\text{CO}_2$  is 1 step



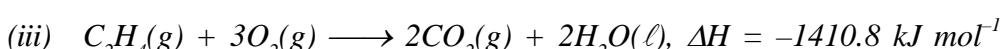
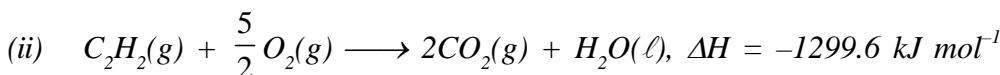
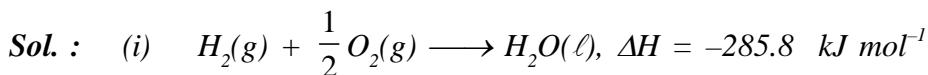
Or in two steps



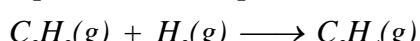
According to Hess's law :  $\Delta H = \Delta H_1 + \Delta H_2 = -26.4 - 67.6 = -94 \text{ kcal}$ .

**Ex.9.** Calculate the heat of reaction for the hydrogenation of acetylene to ethylene at constant volume at  $25^\circ\text{C}$  from the following data.

- (i) Enthalpy of formation of water =  $-285.8 \text{ kJ mol}^{-1}$
- (ii) Enthalpy of combustion of acetylene =  $-1299.6 \text{ kJ mol}^{-1}$
- (iii) Enthalpy of combustion of ethylene =  $-1410.8 \text{ kJ mol}^{-1}$



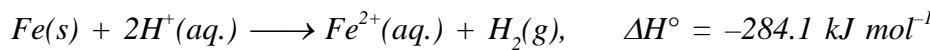
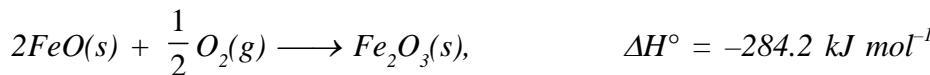
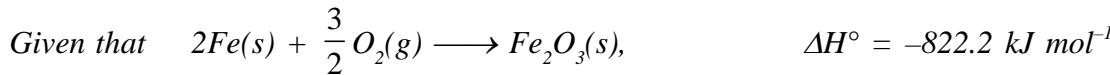
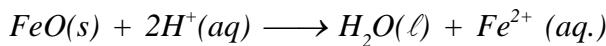
Equation (ii) + equation (i) – equation (iii), we get



$$\Delta H = -1299.6 - 285.8 + 1410.8 = -174.6 \text{ kJ mol}^{-1}$$

$$\Delta E = -174.6 - (-1)(8.314 \times 10^{-3})(298) = -172.12 \text{ kJ mol}^{-1}$$

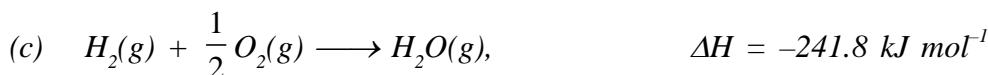
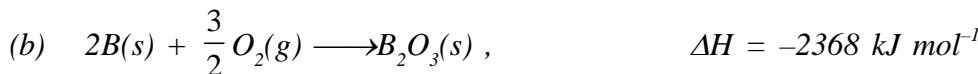
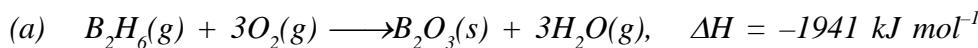
**Ex.10.** Calculate  $\Delta H^\circ$  for the reaction



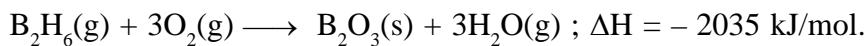
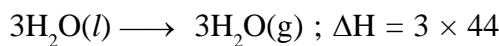
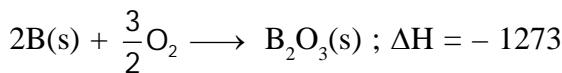
**Sol.** Eq.(iii) + Eq.(iv) -  $\frac{1}{2} \times$  Eq. (i) +  $\frac{1}{2} \times$  Eq.(ii).

$$\Delta H_{\text{required}}^\circ = (-286.0) + (-284.1) - \frac{1}{2}(-822.2) + \frac{1}{2}(-284.2) = -301.1 \text{ kJ/mol.}$$

**Ex.11.** From the following data, determine  $\Delta H_f^0(B_2H_6)$  at 298 K;



**Sol.**  $B_2H_6(g) \longrightarrow 2B(s) + 3H_2(g); \Delta H = -36$



For eq.(a),

$$(-1941) = [(-2368) + 3(-241.8)] - [\Delta_f H_{B_2H_6(g)}^0 + 3 \times 0]$$

$$\therefore [\Delta_f H_{B_2H_6(g)}^0] = -1152.4 \text{ kJ/mol.}$$

## ANSWER KEY

### EXERCISE-I

- |    |                |    |                     |    |          |    |         |
|----|----------------|----|---------------------|----|----------|----|---------|
| 1. | Ans.(D)        | 2. | Ans.(A)             | 3. | Ans. (D) | 4. | Ans.(B) |
| 5. | Ans.(B)        | 6. | Ans. -741.5 kJ/mole |    |          |    |         |
| 7. | Ans. -3.502 kJ |    |                     |    |          |    |         |

### EXERCISE-II

- |     |                                       |    |  |  |  |
|-----|---------------------------------------|----|--|--|--|
| 8.  | Ans. 602.49 kJ                        | 9. | (i) - 885 kJ/mol    (ii) - 889.99 kJ/mol |  |  |
| 10. | $W = 0, \Delta U = -31.723 \text{ J}$ |    |  |  |  |

### EXERCISE-III

- |     |          |     |         |     |                              |     |          |
|-----|----------|-----|---------|-----|------------------------------|-----|----------|
| 11. | Ans.(D)  | 12. | Ans.(D) | 13. | Ans.(B)                      | 14. | Ans. (B) |
| 15. | Ans. (D) | 16. | Ans.(C) | 17. | Ans.(D)                      | 18. | Ans.(D)  |
| 19. | Ans.(D)  | 20. | 129 kJ  | 21. | -1560.1 kJ mol <sup>-1</sup> |     |          |

### EXERCISE-IV

- |     |                    |     |                             |     |         |
|-----|--------------------|-----|-----------------------------|-----|---------|
| 21. | Ans.(C)            | 22. | Ans.(+ 20.6 kcal/mol.)      |     |         |
| 23. | Ans. (400 kJ/mole) | 24. | Ans. - 119 kJ/mol           |     |         |
| 25. | Ans.(B)            | 26. | Ans.(C)                     | 27. | Ans.(C) |
| 28. | 213 kJ / mol       | 29. | Ans.(B)                     | 30. | Ans.(D) |
| 31. | Ans 132.5 kJ/mol   | 32. | -207.5 kJ mol <sup>-1</sup> |     |         |

### EXERCISE-V

- |     |         |     |         |  |  |
|-----|---------|-----|---------|--|--|
| 33. | Ans.(6) | 34. | Ans.(B) |  |  |
|-----|---------|-----|---------|--|--|

### EXERCISE-VI

- |     |  |     |                                |     |                  |
|-----|--|-----|--------------------------------|-----|------------------|
| 35. | Ans.(A)  | 36. | Ans.(B)                        | 37. | - 19 kcal / mole |
| 38. | $-352 \text{ kJ mol}^{-1}$   | 39. | $-90.75 \text{ kcal mol}^{-1}$ |     |                  |
| 40. | for $\text{Cl}^-$ - 384 kJ mol <sup>-1</sup> , for $\text{I}^-$ - 307 kJ mol <sup>-1</sup> |     |                                |     |                  |

## MISCELLANEOUS PREVIOUS YEARS QUESTION

**Q.1** Which of the following is not an endothermic reaction?

- (A) Combustion of methane
- (B) Decomposition of water
- (C) Dehydrogenation of ethene to acetylene
- (D) Conversion of graphite to diamond

[JEE 1999]

**Ans. (A)**

**Sol.** Combustion reaction is always an exothermic reaction

**Q.2** Estimate the average S–F bond enthalpy in SF<sub>6</sub>. The ΔH<sub>f</sub><sup>°</sup> values of SF<sub>6</sub> (g), S(g), and F (g) are – 1100, 275 and 80 kJ/mol respectively. [JEE 99, 5]

**Ans. 309.16 kJ/mol**

**Sol.** SF<sub>6</sub>(g) → S(g) + 6F(g)

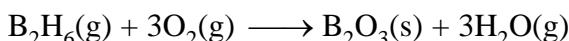
$$\Delta H_{rxn}^0 = \Delta H_f^0[5(g)] + 6\Delta H_f^0[F(g)] - \Delta H_f^0[SF_6(g)]$$

$$\Delta H_{rxn}^0 = 275 + (6 \times 80) + 1100$$

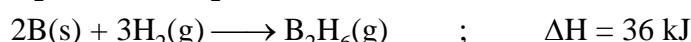
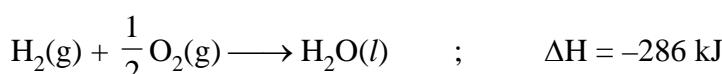
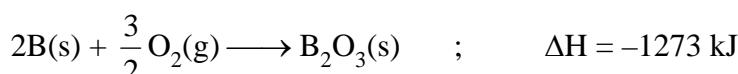
$$\Delta H_{rxn}^0 = 1855$$

$$(S - F) = \frac{\Delta H_{rxn}^0}{6} = \frac{1855}{6} = 309.166 \text{ kJ/mol.}$$

**Q.3** Diborane is a potential rocket fuel which undergoes combustion according to the reaction,



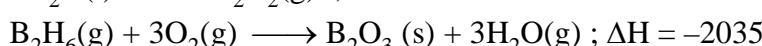
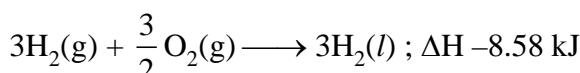
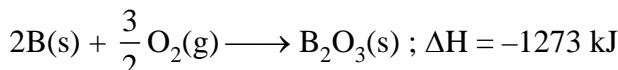
From the following data, calculate the enthalpy change for the combustion of diborane :



[JEE 2000]

**Ans. -2035 kJ mol<sup>-1</sup>**

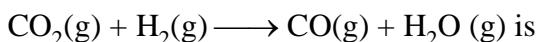
**Sol.** B<sub>2</sub>H<sub>6</sub>(g) → 2B(s) + 3H<sub>2</sub>(g) ; ΔH = -36 kJ



**Q.4**  $\Delta H_f^\circ$  for  $\text{CO}_2(\text{g})$ ,  $\text{CO}(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  are  $-393.5$ ,  $-110.5$  and  $-241.8 \text{ kJ mol}^{-1}$  respectively.

The standard enthalpy change (in kJ) for the reaction

[JEE 2000]



(A) 524.1

(B) 41.2

(C)  $-262.5$

(D)  $-41.2$

**Ans. (B)**

**Sol.**  $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$

$$\Delta H_{\text{rxn}}^0 = (\Delta H_f^0[\text{CO}(\text{g})] + \Delta H_f^0[\text{H}_2\text{O}(\text{g})]) - (\Delta H_f^0[\text{CO}_2(\text{g})] + \Delta H_f^0[\text{H}_2\text{O}(\text{g})])$$

$$\Delta H_{\text{rxn}}^0 = (-110.5 - 241.8) - (-393.5 + 0)$$

$$= + 41.2 \text{ kJ/mol}$$

**Q.5** Which of the following reactions defines  $\Delta H_f^\circ$  ?

[JEE 2003]

(A)  $\text{C}_{(\text{diamond})} + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$

(B)  $1/2 \text{ H}_2(\text{g}) + 1/2 \text{ F}_2(\text{g}) \longrightarrow \text{HF}(\text{g})$

(C)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3$

(D)  $\text{CO}(\text{g}) + 1/2\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$

**Ans. (B)**

**Sol.** In the formation reaction, 1 mole products should be formed from its elements and elements must be in their most abundance state this condition is fulfilled by options (B)

**Q.6** In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is  $2.5 \text{ kJ K}^{-1}$ , the numerical value for the enthalpy of combustion of the gas in  $\text{kJ mol}^{-1}$  is [JEE 2009]

**Ans. (9)**

**Sol.**  $q = (2.5)(0.45) = 1.125$

$$\Delta U_{\text{combination}} = (1.125) \left( \frac{28}{3.5} \right) = -9 \text{ kJ/mol}$$

## EXERCISE (S-1)

### Relationship between $\Delta H$ & $\Delta U$

1. The enthalpy change for the reaction of 50 ml of ethylene with 50.0 ml of  $H_2$  at 1.5 bar pressure is  $\Delta H = - 0.31$  KJ. What is the  $\Delta U$  ?
2. Ethyl chloride ( $C_2H_5Cl$ ), is prepared by reaction of ethylene with hydrogen chloride:  
 $C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(g)$  ;  $\Delta H = - 72.3$  kJ  
What is the value of  $\Delta E$  (in kJ), if 98 g of ethylene and 109.5 g of HCl are allowed to react at 300 K.
3. Determine the amount of heat (in kcal) given off at constant volume when 0.5 mol of  $N_2$  & 1.5 mol of  $H_2$  reacted according to equation at 300 K.  
 $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$  ;  $\Delta_f H_{300} = - 380$  kcal/mol  
(Given :  $R = 2$  cal / mol-K)
4. Ethyl chloride ( $C_2H_5Cl$ ), is prepared by reaction of ethylene with hydrogen chloride :  
 $C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(g)$  ;  $\Delta H = - 72.3$  kJ/mol  
What is the value of  $\Delta U$  (in kJ), if 70 g of ethylene and 73 g of HCl are allowed to react at 300 K.
5. Determine  $\Delta H$  for the following reaction at 500K and constant pressure :  
 $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$   
use the following data :

Substance	$C_p$ (J/mol K)	$\Delta_f H(300K)$ (kJ/mol)
CO (g)	29	-110
$H_2O$ (g)	33	-241
$CO_2$ (g)	37	-393
$H_2$ (g)	29	0

### Enthalpy of formation and combustion

6. When 2 moles of  $C_2H_6(g)$  are completely burnt, 3120 kJ of heat is liberated. Calculate the enthalpy of formation, of  $C_2H_6(g)$  . Given  $\Delta_f H$  for  $CO_2(g)$  &  $H_2O(l)$  are  $- 395$  &  $- 286$  kJ respectively.
7. From the following data at 25°C, Calculate the standard enthalpy of formation of  $FeO(s)$  and of  $Fe_2O_3(s)$ .

Reaction	$\Delta_f H^\circ$ (kJ/mole)
(1) $Fe_2O_3(s) + 3C(\text{graphite}) \rightarrow 2Fe(s) + 3CO(g)$	492
(2) $FeO(s) + C(\text{graphite}) \rightarrow Fe(s) + CO(g)$	155
(3) $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$	-393
(4) $CO(g) + 1/2 O_2(g) \rightarrow CO_2(g)$	-282

8. At 300 K, the standard enthalpies of formation of  $C_6H_5COOH(s)$ ,  $CO_2(g)$  &  $H_2O(l)$  are  $-408$ ,  $-393$  &  $-286\text{ kJ mol}^{-1}$  respectively. Calculate the heat of combustion of benzoic acid at : (i) constant pressure (ii) constant volume.
9. A cylinder of gas is assumed to contain 11.6 kg of butane. If a normal family needs 26,500 kJ of energy per day for cooking, how long will the cylinder last if the enthalpy of combustion,  $\Delta H = -2650\text{ kJ/mole}$  for butane.
10. 0.821 l sample of a mixture of  $CH_4(g)$  &  $O_2(g)$  measured at  $27^\circ C$  & 760 torr was allowed to react at constant pressure in a calorimeter which together with its contents had a heat capacity of 1200 Cal/K. The complete combustion of methane to  $CO_2$  &  $H_2O$  caused a temperature rise, in the calorimeter, of 0.25 K. What was the mole percent of  $CH_4$  in the original mixture?  
 $\Delta H_{\text{comb}}^{\circ}(CH_4) = -200\text{ kcal mol}^{-1}$ .

### Bond Enthalpy

11. Compute the enthalpy of formation of liquid methyl alcohol in  $\text{kJ mol}^{-1}$ , using the following data.  
 Enthalpy of vaporisation of liquid  $CH_3OH = 38\text{ kJ/mol}$ .  
 Enthalpy of formation of gaseous atoms from the elements in their standard states are  
 $H \rightarrow 218\text{ kJ/mol}$  ;  $C \rightarrow 715\text{ kJ/mol}$  ;  $O \rightarrow 249\text{ kJ/mol}$ .

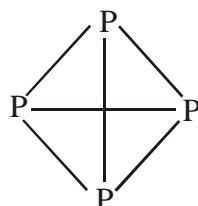
#### Bond Enthalpies



12. Find the enthalpy of S–S bond from the following data.



13. The polymerisation of ethylene to linear polyethylene is represented by the reaction  
 $n CH_2 = CH_2(g) \rightarrow (-CH_2 - CH_2)_n(g)$   
 where  $n$  has a large integral value. Given that the average enthalpies of bond dissociation for  $C=C$  &  $C-C$  at  $298\text{ K}$  are  $+590$  &  $+331\text{ kJ mol}^{-1}$  respectively. Calculate the enthalpy of polymerisation per mole of ethylene at  $298\text{ K}$ .
14. White phosphorus is a tetra-atomic solid  $P_4(s)$  at room temperature.



Find average ( $P - P$ ) bond enthalpy in  $\text{kJ/mol}$ .

Given :  $\Delta H_{\text{sublimation}}$  of  $P_4(s) = 59\text{ kJ/mol}$

$\Delta H_{\text{atomisation}}$  of  $P_4(s) = 1265\text{ kJ/mol}$

15. Calculate enthalpy of combustion of propane [ $\text{C}_3\text{H}_8(\text{g})$ ] in **kJ/mol** at 298 K.

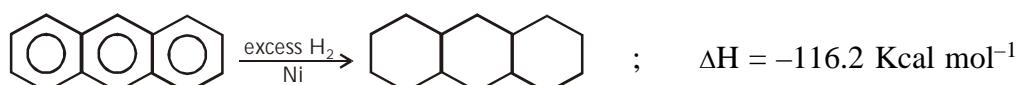
Given : B.E. ( $\text{O} = \text{O}$ ) = 498 kJ/mole ; B.E. ( $\text{C} = \text{O}$ ) = 804 kJ/mole

B.E. ( $\text{C}-\text{H}$ ) = 410 kJ/mole ; B.E. ( $\text{O}-\text{H}$ ) = 464 kJ/mole

B.E. ( $\text{C}-\text{C}$ ) = 345 kJ/mole ; Resonance energy of  $\text{CO}_2(\text{g})$  = – 143 kJ/mole

$\Delta H_{\text{vaporization}}(\text{H}_2\text{O}, l) = 41 \text{ kJ/mol}$

16. Use the following data to answer the questions below :



Calculate the resonance energy of anthracene, 

17. Calculate the magnitude of resonance enthalpy of  $\text{CO}_2(\text{g})$  from following data

$\Delta H^\circ_{\text{combustion}}[\text{C}_{(\text{graphite})}] = -390 \text{ kJ/mol}$

$\Delta H^\circ_{\text{atomisation}}[\text{C}_{(\text{graphite})}] = 715 \text{ kJ/mol}$

$\Delta H^\circ_{\text{B.E.}}[\text{O}=\text{O}] = 500 \text{ kJ/mol}$

$\Delta H^\circ_{\text{B.E.}}[\text{C}=\text{O}] = 800 \text{ kJ/mol}$

### Other types of Enthalpy of reaction

18.  $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O} ; \Delta H^\circ = -57 \text{ kJ/mol}$

$\Delta H_{\text{ionisation}}^0[\text{HCN}] = 45 \text{ kJ/mol}$

If 200 ml , 1/10 M  $\text{Ba}(\text{OH})_2$  solution is mixed with 500 ml , 1/10M HCN, then evolved heat will be.

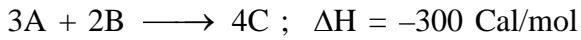
19. The enthalpies of neutralization of  $\text{NaOH}$  &  $\text{NH}_4\text{OH}$  by  $\text{HCl}$  are – 13680 Cal/Eq and – 12270 Cal/Eq. respectively . What would be the enthalpy change if one gram equivalent of  $\text{NaOH}$  is added to one gram equivalent of  $\text{NH}_4\text{Cl}$  in solution ? Assume that  $\text{NH}_4\text{OH}$  and  $\text{NaCl}$  are quantitatively obtained.

20. Two solutions initially at 25°C were mixed in an adiabatic constant pressure calorimeter. One contains 400 ml of 0.2 M weak monoprotic acid solution. The other contain 100 ml of 0.80 M NaOH. After mixing temperature increased to 26.2 °C. How much heat is evolved in the neutralization of 1 mole of acid? Assume density of solution 1.0 g/cm<sup>3</sup>, and specific heat of solution 4.2 J/g-K. Neglect heat capacity of the calorimeter.
21. If the enthalpy of formation of HCl (g) and Cl<sup>-</sup> (aq) are -90 kJ/mole and - 170 kJ/mol, find the enthalpy of solution of hydrogen chloride gas.
22. From the following data of  $\Delta H$  of the following reactions
- $$\text{C(s)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{CO(g)} ; \Delta H = -110 \text{ kJ}$$
- and  $\text{C(s)} + \text{H}_2\text{O(g)} \longrightarrow \text{CO(g)} + \text{H}_2\text{(g)} ; \Delta H = 130 \text{ kJ}$
- Calculate the mole ratio of steam and oxygen on being passed over coke at 1273 K, keeping the reaction temperature constant.

### Miscellaneous

23. Lime is made commercially by decomposition of limestone, CaCO<sub>3</sub>. What is the change in internal energy when 1.00 mole of solid CaCO<sub>3</sub>(V = 34 ml) absorbs 180 kJ of heat and decomposes at certain temperature against a pressure of 1.0 bar to give solid CaO.(Volume = 16 ml) and CO<sub>2</sub>(g)(V = 20 L).
24. One mole of solid Zn is placed in excess of dilute H<sub>2</sub>SO<sub>4</sub> at 27°C in a cylinder fitted with a piston. Find the value of  $\Delta U$ , q and w for the process if the area of piston is 500 cm<sup>2</sup> and it moves out by 50 cm against a pressure of 1 atm during the reaction. The heat given to surrounding is 36.5 kJ.
- $$\text{Zn(s)} + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{H}_2\text{(g)}$$

25. For the gaseous reaction:



If 5 moles of A are mixed with 4 moles of B at 300K, the magnitude of work involved in reaction is.

## EXERCISE (O-1)

Relationship of  $\Delta H$  &  $\Delta U$ 

1. For a reaction,  $2X(s) + 2Y(s) \rightarrow 2C(l) + D(g)$

The  $q_p$  at  $27^\circ C$  is  $-28 \text{ Kcal mol}^{-1}$ , the  $q_v$  is -----  $\text{Kcal mol}^{-1}$

- (A)  $-27.4$  (B)  $+27.4$  (C)  $-28.6$  (D)  $28.6$

2. Consider the reaction at  $300 \text{ K}$



Calculate  $\Delta U$  if 3 mole of  $H_2$  completely react with 3 mole of  $Cl_2$  to form  $HCl$ .

- (A) 0 (B)  $-185 \text{ kJ}$  (C)  $555 \text{ kJ}$  (D)  $-555 \text{ kJ}$

## Enthalpy of formation and combustion

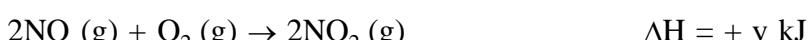
3. Study the following thermochemical equations :



The correct order of enthalpies of formation of A, B and C is -

- (A)  $A < B < C$  (B)  $A < C < B$  (C)  $C < A < B$  (D)  $B < C < A$

4.  $N_2(g) + 2O_2(g) \rightarrow 2NO_2$   $\Delta H = +x \text{ kJ}$



The enthalpy of formation of NO is

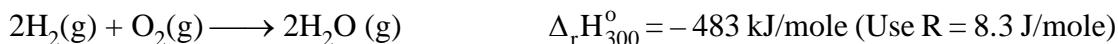
- (A)  $(2x - 2y) \text{ kJ/mol}$  (B)  $(x - y) \text{ kJ/mol}$  (C)  $\frac{1}{2}(y - x) \text{ kJ/mol}$  (D)  $\frac{1}{2}(x - y) \text{ kJ/mol}$

5.  $2NO_2(g) \rightarrow N_2O_4(g) ; \Delta U_f^{\circ} [N_2O_4(g)] = 2 \text{ kcal/mole}$  and  $\Delta U_{\text{reaction}}^{\circ} = -16 \text{ kcal/mol}$  then calculate  $\Delta H_{\text{formation}}^{\circ}$  of  $NO_2$  at  $727^\circ C$

- (A)  $9 \text{ kcal/mol}$  (B)  $4.5 \text{ kcal/mol}$  (C)  $8 \text{ kcal/mol}$  (D)  $10 \text{ kcal/mol}$

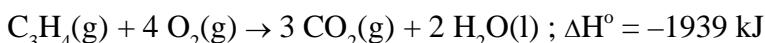
6. Find  $\Delta_r U^{\circ}$  for the reaction  $4HCl(g) + O_2(g) \rightarrow 2Cl_2(g) + 2H_2O(g)$  at  $300 \text{ K}$ . Assume all gases are ideal.

Given :  $H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \quad \Delta_r H_{300}^{\circ} = -184.5 \text{ kJ/mol}$

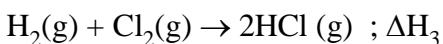
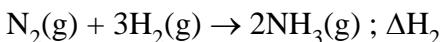
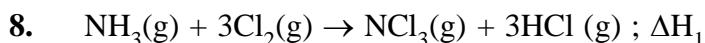


- (A)  $111.5 \text{ kJ/mol}$  (B)  $-109.01 \text{ kJ/mol}$  (C)  $-111.5 \text{ kJ/mol}$  (D)  $-114 \text{ kJ/mol}$

7. What amount of heat energy (kJ) is released in the combustion of  $12.0 \text{ g}$  of  $C_3H_4$  at  $1 \text{ atm}$  constant pressure.



- (A)  $696.3$  (B)  $1939$  (C)  $6463.3$  (D)  $581.7$



The enthalpy of formation of  $\text{NCl}_3(\text{g})$  in the terms of  $\Delta H_1$ ,  $\Delta H_2$  and  $\Delta H_3$  is

(A)  $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

(B)  $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

(C)  $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

(D)  $\Delta H_f = \Delta H_1 + \Delta H_2 - \Delta H_3$

### Bond enthalpy

9. The bond dissociation energy of gaseous  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$  are 104, 58 and 103 kcal mol<sup>-1</sup> respectively. The enthalpy of formation for  $\text{HCl}$  gas will be :-
- (A) -44.0 kcal/mol      (B) -22.0 kcal/mol      (C) 22.0 kcal/mol      (D) 44.0 kcal/mol
10. The reaction  $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g})$  has  $\Delta H = -25$  kcal.

Bond	Bond Enthalpy kCal
$\varepsilon_{\text{C}-\text{Cl}}$	84
$\varepsilon_{\text{H}-\text{Cl}}$	103
$\varepsilon_{\text{C}-\text{H}}$	x
$\varepsilon_{\text{Cl}-\text{Cl}}$	y
$x : y = 9 : 5$	

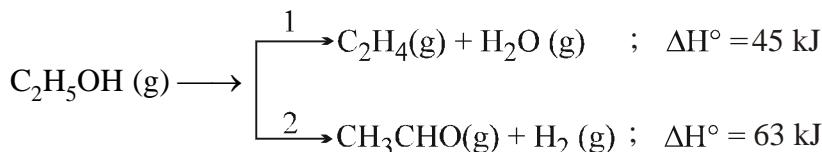
From the given data, what is the bond enthalpy of Cl—Cl bond

(A) 70 kcal/mol      (B) 80 kcal/mol      (C) 67.75 kcal/mol      (D) 57.86 kcal/mol

11. If  $x_1$ ,  $x_2$  and  $x_3$  are enthalpies of H—H, O=O and O—H bonds respectively, and  $x_4$  is the enthalpy of vaporisation of water, estimate the standard enthalpy of combustion of hydrogen

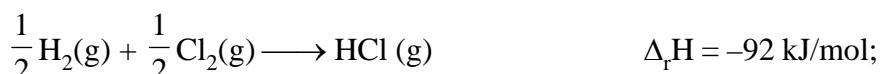
(A)  $x_1 + \frac{x_2}{2} - 2x_3 + x_4$       (B)  $x_1 + \frac{x_2}{2} - 2x_3 - x_4$       (C)  $x_1 + \frac{x_2}{2} - x_3 + x_4$       (D)  $2x_3 - x_1 - \frac{x_2}{2} - x_4$

12. If bond enthalpy of C—C and C=C are 348 kJ /mole and 615 kJ/mole respectively then calculate enthalpy change (in kJ/mole) which occurs during the isomerisation of cyclopropane (g) into propene(g)
- (A) -267      (B) 81      (C) -81      (D) 267

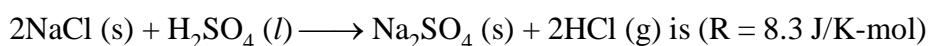


If the molar ratio of  $\text{C}_2\text{H}_4$  to  $\text{CH}_3\text{CHO}$  is 8 : 1 in a set of product gases, then the enthalpy involved in the decomposition of 1 mole of ethanol is

- 18.** The enthalpy changes of the following reactions at 27°C are



from these data, the heat change of reaction at constant volume (in kJ/mol) at 27°C for the process





- 19.** Reactions involving gold have been of particular interest to a chemist . Consider the following reactions.



In an experiment there was an absorption of 0.44 kcal when one mole of  $\text{HAuBr}_4$  was mixed with 4 moles of  $\text{HCl}$ . What is the percentage conversion of  $\text{HAuBr}_4$  into  $\text{HAuCl}_4$ ?

## EXERCISE (O-2)

## Single Correct :

1. What is the ratio of the enthalpy yield on combustion of hydrogen atoms to steam to the yield on combustion of an equal mass of hydrogen molecules to steam?

Given :  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) ; \Delta H = -242 \text{ kJ}$

$$\text{B.E. (H - H)} = 436 \text{ kJ}$$

- (A) 0.80 : 1              (B) 1 : 0.80              (C) 1.80 : 1              (D) 2.80 : 1

2. For the allotropic change represented by the equation C (graphite)  $\rightarrow$  C (diamond),  $\Delta H = 1.9 \text{ kJ}$ . If 6 g of diamond and 6 g of graphite are separately burnt to yield  $\text{CO}_2$ , the heat liberated in first case is

- (A) less than in the second case by 1.9 kJ      (B) more than in the second case by 11.4 kJ  
(C) more than in the second case by 0.95 kJ      (D) less than in the second case by 11.4 kJ

3. (i) Cis-2 - butene  $\rightarrow$  trans - 2 - butene,  $\Delta H_1$

- (ii) Cis – 2 – butene  $\rightarrow$  1 – butene,  $\Delta H,$

(iii) Enthalpy of combustion of 1-butene,  $\Delta H = -649.8$  kcal/mol

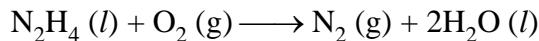
$$(iv) 9\Delta H_1 + 5 \Delta H_2 = 0$$

(v) Enthalpy of combustion of trans 2 – butene,  $\Delta H = -647.0$  kcal/mol.

The value of  $\Delta H_1$  &  $\Delta H_2$  in Kcal/mole are

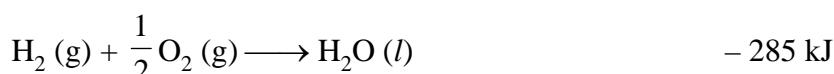
- (A) -1.0, 1.8      (B) 1.8, -1.0      (C) -5, 9      (D) -2, 3.6

4. Hydrazine, a component of rocket fuel, undergoes combustion to yield N<sub>2</sub> and H<sub>2</sub>O.



What is the enthalpy change of combustion of  $\text{N}_2\text{H}_4$  (kJ/mole)

<b>Given Reaction</b>	<b>ΔH/kJ</b>
$2\text{NH}_3(\text{g}) + 3\text{N}_2\text{O}(\text{g}) \longrightarrow 4\text{N}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$	- 1011 kJ
$\text{N}_2\text{O}(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow \text{N}_2\text{H}_4(\text{l}) + \text{H}_2\text{O}(\text{l})$	- 317 kJ
$4\text{NH}_3(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{N}_2\text{H}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l})$	- 286 kJ



- (A) - 620.5      (B) - 622.75      (C) 1167.5      (D) + 622.75

5. The enthalpy change for the reaction,



Calculate the temperature at which  $\Delta_rH$  for the reaction will be zero.

[Given :  $C_{p,m}(\text{CH}_4\text{g}) = 38 \text{ J/K mol}$  ;  $C_{p,m}(\text{CO}, \text{g}) = 31 \text{ J/K mol}$  &  $C_{p,m}(\text{CH}_3\text{CHO}, \text{g}) = 52 \text{ J/K mol}$  ]

- (A)  $1300^\circ\text{C}$       (B)  $1027^\circ\text{C}$       (C)  $700^\circ\text{C}$       (D)  $754^\circ\text{C}$

**More than one may correct**

6. Select the correct option -

- (A)  $\Delta H_f(\text{H(g)})$  is equal to  $\Delta H_{\text{atomisation}}$  of  $\text{H}_2(\text{g})$   
 (B)  $\Delta H_{\text{BE}}(\text{H-H})$  is equal to  $\Delta H_f$  of  $\text{H(g)}$   
 (C)  $\Delta H_{\text{BE}}(\text{H-H})$  is equal to  $\Delta H_{\text{atomisation}}$  of  $\text{H}_2(\text{g})$   
 (D)  $\Delta H_{\text{combustion}}[\text{H}_2(\text{g})]$  is equal to  $\Delta H_f[\text{H}_2\text{O(l)}]$  at  $300\text{K}$

7. Which of the following statement is (are) correct ?

- (A) for any reaction  $\Delta_rH^\circ = \sum \Delta_fH^0_{\text{product}} - \sum \Delta_fH^0_{\text{reactant}}$   
 (B)  $\Delta H_f^\circ$  of  $\text{CO}_2(\text{g})$  is same as the  $\Delta H_{\text{comb.}}^\circ$  of carbon graphite  
 (C) All exothermic gaseous reactions ,  $\sum (\text{B.E.})_{\text{reactants}} > \sum (\text{B.E.})_{\text{products}}$   
 (D) for a reaction  $\text{N}_{2(\text{g})} + \text{O}_{2(\text{g})} \longrightarrow 2\text{NO}_{(\text{g})}$ , the heat at constant pressure and the heat at constant volume at a given temperature are same

8. Which of the following do(es) not represent  $\Delta H^0$  formation of the product.

- (A)  $\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \longrightarrow 2\text{HI(g)}$       (B)  $\frac{2}{3}\text{O}_3(\text{g}) \longrightarrow \text{O}_2(\text{g})$   
 (C)  $\text{NH}_4^+(\text{g}) + \text{Cl}^-(\text{g}) \longrightarrow \text{NH}_4\text{Cl(s)}$       (D)  $\text{P}_4(\text{black}) + 5\text{O}_2(\text{g}) \longrightarrow \text{P}_4\text{O}_{10}(\text{s})$   
 (E) Reaction representing  $\Delta H_{\text{combustion}}$  of C (graphite).

9. From the following data at  $25^\circ\text{C}$

Reaction	$\Delta_rH^\circ \text{ kJ/mol}$
$\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{OH(g)}$	42
$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O(g)}$	-242
$\text{H}_2(\text{g}) \longrightarrow 2\text{H(g)}$	436
$\text{O}_2(\text{g}) \longrightarrow 2\text{O(g)}$	495

Which of the following statement(s) is/are correct:

- (A)  $\Delta_rH^\circ$  for the reaction  $\text{H}_2\text{O(g)} \longrightarrow 2\text{H(g)} + \text{O(g)}$  is  $925.5 \text{ kJ/mol}$   
 (B)  $\Delta_rH^\circ$  for the reaction  $\text{OH(g)} \longrightarrow \text{H(g)} + \text{O(g)}$  is  $502 \text{ kJ/mol}$   
 (C) Enthalpy of formation of  $\text{H(g)}$  is  $-218 \text{ kJ/mol}$   
 (D) Enthalpy of formation of  $\text{OH(g)}$  is  $42 \text{ kJ/mol}$

### Match the column :

**10. Column-I**

- |   |   |
|---|---|
| (A) C(graphite) + O <sub>2</sub> (g) → CO <sub>2</sub> (g)  | (P) ΔH <sub>formation</sub> <sup>0</sup>      |
| (B) C(graphite) → C(gas)  | (Q) ΔH <sub>combustion</sub> <sup>0</sup>     |
| (C) CH <sub>3</sub> COOH(aq) + OH <sup>-</sup> (aq) → CH <sub>3</sub> COO <sup>-</sup> (aq) + H <sub>2</sub> O(l) | (R) ΔH <sub>atomization</sub> <sup>0</sup>    |
| (D) CH <sub>4</sub> (g) → C(g) + 4H(g)  | (S) ΔH <sub>neutralization</sub> <sup>0</sup> |

**Column-II**
**Match list :**

11. Match the enthalpy change (ΔH) mentioned in list-II for 16 gm O<sub>2</sub> with the various reaction in list-I.

**List-I**

- (P) 2C<sub>2</sub>H<sub>2</sub> + 5O<sub>2</sub>(g) → 4CO<sub>2</sub>(g) + 2H<sub>2</sub>O(l), ΔH = -2601 kJ  
 (Q) H<sub>2</sub>(g) + 1/2O<sub>2</sub>(g) → H<sub>2</sub>O(g), ΔH = -285.8 kJ  
 (R) 3FeO(s) + 1/2O<sub>2</sub>(g) → Fe<sub>3</sub>O<sub>4</sub>(s), ΔH = -302.4 kJ  
 (S) C<sub>graphite</sub> + O<sub>2</sub>(g) → CO<sub>2</sub>(g), ΔH = -393.5 kJ

**List-II (ΔH in kJ)**

- (A) -285.8  
 (B) -196.75  
 (C) -260.1  
 (D) -302.4

**Code:**

	P	Q	R	S
(A)	4	1	3	2
(B)	3	1	4	2
(C)	3	4	1	2
(D)	2	3	1	4

### Passage (Q. 12 to Q.13)

Bond dissociation enthalpy of the first H–S bond in hydrogen sulphide is 376 kJ/mole. The enthalpies of formation of H<sub>2</sub>S(g) and S(g) are -20.0 and 277.0 kJ/mole respectively. The enthalpy of formation of gaseous hydrogen atom is 218 kJ/mole. Using above information, answer following questions :

12. The enthalpy of formation of free radical HS is

(A) 138 kJ/mole      (B) -138 kJ/mole      (C) -10 kJ/mole      (D) 357 kJ/mole

13. The bond dissociation enthalpy of the free radical HS is

(A) 138 kJ/mole      (B) 276 kJ/mole      (C) 357 kJ/mole      (D) 376 kJ/mole

### Paragraph for Q.14 to Q.15

Amount of heat evolved during complete combustion of liquid benzene can be calculated from the following data.

(i) 18 gm of graphite on complete combustion evolve 591 kJ heat

(ii)  $\Delta H_f^\circ(H_2O, \ell) = -286 \text{ kJ/mol}$

(iii) The heat of formation of liquid benzene is 50 kJ /mole

**14.** Heat of formation of  $CO_2(g)$  from following data is-

- (A) -286 kJ/mole      (B) -590 kJ/mole      (C) -394 kJ/mole      (D) -3268 kJ/mole

**15.** Find heat evolved from combustion of 78 gm benzene

- (A) 3272 kJ      (B) 6345 kJ      (C) 4536 kJ      (D) 5364 kJ

### Table Type Question :

Column-I  (Reactions)	Column-II  (Characteristics)	Column-III  (Characteristics)
(I) $C(s) + O_2(g) \rightarrow CO_2(g)$	(i) $\Delta H = +ve$	(P) $\Delta H > \Delta E$
(II) $SO_3(g) \rightarrow SO_2(g) + \frac{1}{2} O_2(g)$	(ii) $\Delta n_g = +ve$	(Q) $ \Delta H  >  \Delta E $
(III) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$	(iii) $\Delta n_g = -ve$	(R) $\Delta H < \Delta E$
(IV) $C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$	(iv) $\Delta H = -ve$	(S) $ \Delta H  <  \Delta E $

**16.** Which of the following is only correct match ?

- (A) I , i , P      (B) II , ii , Q      (C) III , iii , S      (D) IV , iv , R

**17.** Which of the following is only incorrect match ?

- (A) II , i , P      (B) III , iv , R      (C) IV , iii , S      (D) II , ii , Q

**18.** Which of the following is only correct match ?

- (A) I , ii , Q      (B) II , iii , Q      (C) III , iv , S      (D) IV , ii , P

## EXERCISE (JM)

1. Consider the reaction :

[AIEEE-2011]

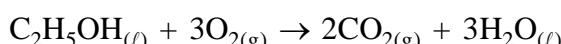


If  $\text{N}_2\text{O}_5(\text{s})$  is formed instead of  $\text{N}_2\text{O}_5(\text{g})$  in the above reaction, the  $\Delta_r\text{H}$  value will be :-

(given,  $\Delta\text{H}$  of sublimation for  $\text{N}_2\text{O}_5$  is  $54\text{ kJ mol}^{-1}$ )

- (1)  $-165\text{ kJ}$       (2)  $+54\text{ kJ}$       (3)  $+219\text{ kJ}$       (4)  $-219\text{ kJ}$

2. The value of enthalpy change ( $\Delta\text{H}$ ) for the reaction



at  $27^\circ\text{C}$  is  $-1366.5\text{ kJ mol}^{-1}$ . The value of internal energy change for the above reaction at this temperature will be :-

[AIEEE-2011]

- (1)  $-1371.5\text{ kJ}$       (2)  $-1369.0\text{ kJ}$       (3)  $-1364.0\text{ kJ}$       (4)  $-1361.5\text{ kJ}$

3. The enthalpy of neutralisation of  $\text{NH}_4\text{OH}$  with  $\text{HCl}$  is  $-51.46\text{ kJ mol}^{-1}$  and the enthalpy of neutralisation of  $\text{NaOH}$  with  $\text{HCl}$  is  $-55.90\text{ kJ mol}^{-1}$ . The enthalpy of ionisation of  $\text{NH}_4\text{OH}$  is:

[JEE-MAINS (online) 2012]

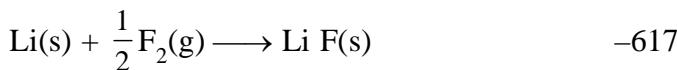
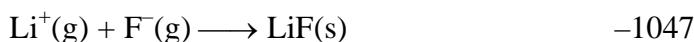
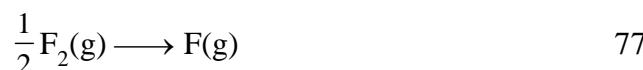
- (1)  $+107.36\text{ kJ mol}^{-1}$       (2)  $-4.44\text{ kJ mol}^{-1}$       (3)  $-107.36\text{ kJ mol}^{-1}$       (4)  $+4.44\text{ kJ mol}^{-1}$

4. Given

[JEE-MAINS (online) 2013]

**Reaction**

**Energy Change (in kJ)**

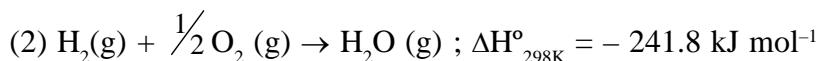
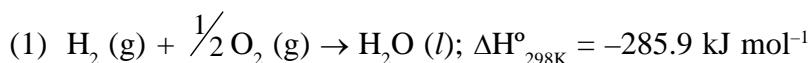


Based on data provided, the value of electron gain enthalpy of fluorine would be :

- (1)  $-300\text{ kJ mol}^{-1}$       (2)  $-328\text{ kJ mol}^{-1}$       (3)  $-350\text{ kJ mol}^{-1}$       (4)  $-228\text{ kJ mol}^{-1}$

5. Given :

[JEE-MAINS (online) 2013]



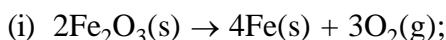
The molar enthalpy of vapourisation of water will be :-

- (1)  $241.8\text{ kJ mol}^{-1}$       (2)  $527.7\text{ kJ mol}^{-1}$       (3)  $44.1\text{ kJ mol}^{-1}$       (4)  $22.0\text{ kJ mol}^{-1}$

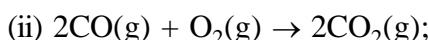
6. The standard enthalpy of formation ( $\Delta_f H^\circ_{298}$ ) for methane,  $\text{CH}_4$  is  $-74.9 \text{ kJ mol}^{-1}$ . In order to calculate the average energy given out in the formation of a C–H bond from this it is necessary to know which one of the following? [JEE-MAINS(online) 2014]
- the dissociation energy of the hydrogen molecule,  $\text{H}_2$ .
  - the dissociation energy of  $\text{H}_2$  and enthalpy of sublimation of carbon (graphite).
  - the first four ionisation energies of carbon and electron affinity of hydrogen.
  - the first four ionisation energies of carbon.
7. For complete combustion of ethanol,  $\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$ , the amount of heat produced as measured in bomb calorimeter, is  $1364.47 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ . Assuming ideality the Enthalpy of combustion,  $\Delta_c H$ , for the reaction will be :- [JEE-MAINS(offline)2014]  
 $(R = 8.314 \text{ J mol}^{-1})$
- |                                    |                                    |
|------------------------------------|------------------------------------|
| (1) $-1460.50 \text{ kJ mol}^{-1}$ | (2) $-1350.50 \text{ kJ mol}^{-1}$ |
| (3) $-1366.95 \text{ kJ mol}^{-1}$ | (4) $-1361.95 \text{ kJ mol}^{-1}$ |
8. The heats of combustion of carbon and carbon monoxide are  $-395.5$  and  $-285.5 \text{ kJ mol}^{-1}$ , respectively. The heat of formation (in kJ) of carbon monoxide per mole is :- [JEE-MAINS(offline)2016]
- |              |             |             |              |
|--------------|-------------|-------------|--------------|
| (1) $-110.5$ | (2) $110.5$ | (3) $676.5$ | (4) $-676.5$ |
|--------------|-------------|-------------|--------------|
9. The enthalpy change on freezing of 1 mol of water at  $5^\circ\text{C}$  to ice at  $-5^\circ\text{C}$  is :  
 (Given  $\Delta_{\text{fus}} H = 6 \text{ kJ mol}^{-1}$  at  $0^\circ\text{C}$ ,  $C_p(\text{H}_2\text{O}, l) = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $C_p(\text{H}_2\text{O}, s) = 36.8 \text{ J mol}^{-1} \text{ K}^{-1}$ ) [JEE-MAINS(online)2017]
- |                                |                                |                                |                                |
|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| (1) $6.56 \text{ kJ mol}^{-1}$ | (2) $5.81 \text{ kJ mol}^{-1}$ | (3) $6.00 \text{ kJ mol}^{-1}$ | (4) $5.44 \text{ kJ mol}^{-1}$ |
|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
10. Given [JEE-MAINS(offline)2017]
- $$\text{C}_{(\text{graphite})} + \text{O}_2(g) \rightarrow \text{CO}_2(g);$$
- $$\Delta_r H^\circ = -393.5 \text{ kJ mol}^{-1}$$
- $$\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l);$$
- $$\Delta_r H^\circ = -285.8 \text{ kJ mol}^{-1}$$
- $$\text{CO}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow \text{CH}_4(g) + 2\text{O}_2(g);$$
- $$\Delta_r H^\circ = +890.3 \text{ kJ mol}^{-1}$$
- Based on the above thermochemical equations, the value of  $\Delta_r H^\circ$  at  $298 \text{ K}$  for the reaction  $\text{C}_{(\text{graphite})} + 2\text{H}_2(g) \rightarrow \text{CH}_4(g)$  will be :-
- |                                 |                                  |                                 |                                  |
|---------------------------------|----------------------------------|---------------------------------|----------------------------------|
| (1) $+74.8 \text{ kJ mol}^{-1}$ | (2) $+144.0 \text{ kJ mol}^{-1}$ | (3) $-74.8 \text{ kJ mol}^{-1}$ | (4) $-144.0 \text{ kJ mol}^{-1}$ |
|---------------------------------|----------------------------------|---------------------------------|----------------------------------|
11. The combustion of benzene (l) gives  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(l)$ . Given that heat of combustion of benzene at constant volume is  $-3263.9 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ ; heat of combustion (in  $\text{kJ mol}^{-1}$ ) of benzene at constant pressure will be - [JEE-MAINS(offline)2018]  
 $(R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1})$
- |               |            |               |              |
|---------------|------------|---------------|--------------|
| (1) $-452.46$ | (2) $3260$ | (3) $-3267.6$ | (4) $4152.6$ |
|---------------|------------|---------------|--------------|

12. Given

[JEE-MAINS(online)2018]

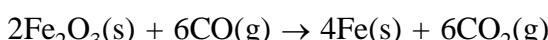


$$\Delta_r G^\circ = +1487.0 \text{ kJ mol}^{-1}$$



$$\Delta_r G^\circ = -514.4 \text{ kJ mol}^{-1}$$

Free energy change,  $\Delta_r G^\circ$  for the reaction



will be :-

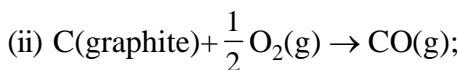
- (1)  $-112.4 \text{ kJ mol}^{-1}$     (2)  $-56.2 \text{ kJ mol}^{-1}$     (3)  $168.2 \text{ kJ mol}^{-1}$     (4)  $208.0 \text{ kJ mol}^{-1}$

13. Given :

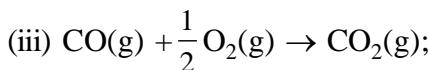
[JEE-MAINS(online)2019]



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



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



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

Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct ?

- (1)  $z = x + y$     (2)  $x = y - z$     (3)  $x = y + z$     (4)  $y = 2z - x$

14. The difference between  $\Delta H$  and  $\Delta U$  ( $\Delta H - \Delta U$ ), when the combustion of one mole of heptane (1) is carried out at a temperature T, is equal to: [JEE-MAINS-(ONLINE)-2019]

- (1)  $3RT$     (2)  $-3RT$     (3)  $-4RT$     (4)  $4RT$

15. Enthalpy of sublimation of iodine is  $24 \text{ cal g}^{-1}$  at  $200^\circ\text{C}$ . If specific heat of  $\text{I}_2(\text{s})$  and  $\text{I}_2(\text{vap})$  are  $0.055$  and  $0.031 \text{ cal g}^{-1}\text{K}^{-1}$  respectively, then enthalpy of sublimation of iodine at  $250^\circ\text{C}$  in  $\text{cal g}^{-1}$  is : [JEE-MAINS(online)2019]

- (1)  $2.85$     (2)  $11.4$     (3)  $5.7$     (4)  $22.8$

16. The standard heat of formation ( $\Delta_f H_{298}^0$ ) of ethane in (kJ/mol), if the heat of combustion of ethane, hydrogen and graphite are  $-1560$ ,  $-393.5$  and  $-286 \text{ kJ/mol}$ , respectively is \_\_\_\_\_

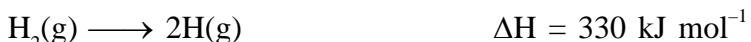
[JEE-MAINS(online)2020]

17. If enthalpy of atomisation for  $\text{Br}_{2(1)}$  is  $x \text{ kJ/mol}$  and bond enthalpy for  $\text{Br}_2$  is  $y \text{ kJ/mol}$ , the relation between them : [JEE-MAINS(online)2020]

- (1) is  $x = y$     (2) is  $x < y$     (3) does not exist    (4) is  $x > y$

## EXERCISE (JA)

1. Using the data provided, calculate the multiple bond energy ( $\text{kJ mol}^{-1}$ ) of a  $\text{C}\equiv\text{C}$  bond in  $\text{C}_2\text{H}_2$ . That energy is (take the bond energy of a  $\text{C}-\text{H}$  bond as  $350 \text{ kJ mol}^{-1}$ ). [JEE 2012]



- (A) 1165                    (B) 837                    (C) 865                    (D) 815

2. The standard enthalpies of formation of  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O(l)}$  and glucose( $\text{s}$ ) at  $25^\circ\text{C}$  are  $-400 \text{ kJ/mol}$ ,  $-300 \text{ kJ/mol}$  &  $-1300 \text{ kJ/mol}$ , respectively. The standard enthalpy of combustion per gram of glucose at  $25^\circ\text{C}$  is - [JEE 2013]

- (A)  $+ 2900 \text{ kJ}$                     (B)  $- 2900 \text{ kJ}$                     (C)  $-16.11 \text{ kJ}$                     (D)  $+ 16.11 \text{ kJ}$

### Paragraph For Questions 3 and 4

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of  $5.7^\circ\text{C}$  was measured for the beaker and its contents.

**(Expt-1).** Because the enthalpy of neutralisation of a strong acid with a strong base is a constant ( $-57.0 \text{ kJ mol}^{-1}$ ), this experiment could be used to measure the calorimeter constant. In a second experiment **(Expt-2)**, 100 mL of 2.0 M acetic acid ( $K_a = 2.0 \times 10^{-5}$ ) was mixed with 100 mL of 1.0M NaOH (under identical conditions to **(Expt-1)**) where a temperature rise of  $5.6^\circ\text{C}$  was measured.

(Consider heat capacity of all solutions as  $4.2 \text{ J g}^{-1}\text{K}^{-1}$  and density of all solutions as  $1.0 \text{ g mL}^{-1}$ ) [JEE 2015]

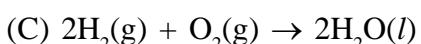
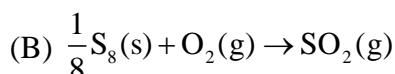
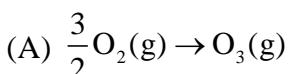
3. Enthalpy of dissociation (in  $\text{kJ mol}^{-1}$ ) of acetic acid obtained from the **Expt-2** is

- (A) 1.0                    (B) 10.0                    (C) 24.5                    (D) 51.4

4. The pH of the solution after **Expt-2**

- (A) 2.8                    (B) 4.7                    (C) 5.0                    (D) 7.0

5. Choose the reaction(s) from the following options, for which the standard enthalpy of reaction is equal to the standard enthalpy of formation. [JEE 2019]



## ANSWER KEY

### EXERCISE (S-1)

- |   |  |
|---|--|
| 1. Ans. – 0.3025 kJ   | 2. Ans. –209.41                            |
| 3. Ans. 189.4 kcal  | 4. –139.6                                  |
| 5. $\Delta H = - 41.2 \text{ kJ}$   | 6. – 88 kJ/mol                             |
| 7. –266 kJ/mol and –825 kJ/mol  | 8. (i) - 3201 kJ/mol (ii) - 3199.75 kJ/mol |
| 9. 20 days  | 10. 4.5%                                   |
| 11. $- 266 \text{ kJ mol}^{-1}$   | 12. 275 kJ/mol                             |
| 13. $- 72 \text{ kJ mol}^{-1}$  | 14. Ans. 201                               |
| 15. Ans. (-2669)  | 16. Ans. (-84 kcal / mol )                 |
| 17. Ans. (5 kJ/mol)   | 18. Ans. (480 J)                           |
| 19. — 1410 Cal  | 20. 31.5 kJ/mole                           |
| 21. – 80 kJ/mole  | 22. 22 : 13                                |
| 23. Ans. 178 kJ   |  |
| 24. Ans. $\Delta U = -39.03 \text{ kJ}$ ; $q = -36.5 \text{ kJ}$ ; $w = -2.53 \text{ kJ}$ |  |
| 25. 1000 Cal  |  |

### EXERCISE (O-1)

- |              |              |              |              |
|--------------|--------------|--------------|--------------|
| 1. Ans.(C)   | 2. Ans.(D)   | 3. Ans.(B)   | 4. Ans.(D)   |
| 5. Ans. (C)  | 6. Ans.(C)   | 7. Ans.(D)   | 8. Ans.(B)   |
| 9. Ans.(B)   | 10. Ans.(D)  | 11. Ans.(B)  | 12. Ans. (B) |
| 13. Ans. (A) | 14. Ans. (A) | 14. Ans. (D) | 16. Ans.(A)  |
| 17. Ans.(B)  | 18. Ans.(B)  | 19. Ans.(C)  |              |

### EXERCISE (O-2)

- |              |   |                  |                  |
|--------------|---|------------------|------------------|
| 1. Ans.(D)   | 2. Ans.(C)                                    | 3. Ans.(A)       | 4. Ans.(A)       |
| 5. Ans.(B)   | 6. Ans.(C, D)                                 | 7. Ans.(A, B, D) | 8. Ans.(A,B,C,D) |
| 9. Ans.(A,D) | 10. Ans. (A) P, Q ; (B) P, R ; (C) S, D - (R) |                  |                  |
| 11. Ans.(B)  | 12. Ans. (A)                                  | 13. Ans.(C)      | 14. Ans.(C)      |
| 15. Ans.(A)  | 16. Ans.(B)                                   | 17. Ans.(C)      | 18. Ans.(D)      |

## EXERCISE (JM)

- |               |             |             |             |
|---------------|-------------|-------------|-------------|
| 1. Ans.(4)    | 2. Ans.(3)  | 3. Ans.(4)  | 4. Ans.(2)  |
| 5. Ans.(3)    | 6. Ans.(2)  | 7. Ans.(3)  | 8. Ans.(1)  |
| 9. Ans.(1)    | 10. Ans.(3) | 11. Ans.(3) | 12. Ans.(2) |
| 13. Ans.(3)   | 14. Ans.(3) | 15. Ans.(4) |             |
| 16. (-192.50) | 17. Ans.(4) |             |             |

## EXERCISE (JA)

- |              |            |             |             |
|--------------|------------|-------------|-------------|
| 1. Ans.(D)   | 2. Ans.(C) | 3. Ans. (A) | 4. Ans. (B) |
| 5. Ans.(A,B) |            |             |             |

## CHAPTER 3

**THERMODYNAMICS-02****Chapter 03**  
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## IMPORTANT NOTES

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**CHAPTER 3****THERMODYNAMICS-02****1. LIMITATION OF FIRST LAW OF THERMODYNAMICS**

The first law of thermodynamics can evaluate the value of  $\Delta U$  and  $\Delta H$  (i.e. energy difference between two states), but can not predict the feasibility of a process. Many processes can take place on their own and many others require an external force to carry out the process. The first law is clueless about why some processes happens on their own and why some others do not.

**❖ Importance of Second law :**

What is the driving force for a process which takes system from one state to other on its own? Why such processes (*called spontaneous process*) take place at all? Answers to these questions are given by second law.

**2. SPONTANEOUS PROCESS**

A spontaneous process is the one which takes place on its own & can drive some other process as well. However, in some cases, initiation may be required.

**Ex :**

- (i) Mixing of two gases.
- (ii) Cooling of a hot object by transferring heat to surrounding.
- (iii) Water flowing down the hill.
- (iv) Rusting of iron.
- (v) Burning of coal, coke, hydrocarbons.
- (vi) Volcanic eruptions.

The synonyms of spontaneous processes are **natural processes** and irreversible processes.

It is a common observation that natural processes occur with finite rate. All spontaneous processes take place due to a finite driving force (which can be temperature difference, height difference, potential energy difference, etc.). Also the change brought about by a spontaneous process can not be restored without making some effort (which brings about permanent change in surrounding). Hence it is quite natural to call these processes as irreversible processes.

**Ex :**

When water flows from a dam, a part of the potential energy is converted into electrical energy and a part is converted into kinetic energy. The kinetic energy part is lost as heat energy. This loss of extra work is the permanent change in universe, because this heat energy lost cannot be completely converted back into P.E. of water.

### 3. DISORDER :

The term 'disorder' is related to randomness. Any macroscopic property of a system is an average of large number of microscopic forces which are random in nature. Greater the randomness associated with microscopic forces, greater is the uncertainty about exact microscopic description of a macroscopic state and greater will be the disorder associated with the macroscopic state.

**As a rule :**

- (i) Greater the number of molecules in which a given energy is distributed, greater is the disorder.
- (ii) Greater the spread of given number of molecules with given energy in space, greater will be the disorder.

### 4. SECOND LAW OF THERMODYNAMICS

The entropy of the universe increases in course of every spontaneous process. The entropy of system is a state function. The change in entropy of a system is given by -

$$dS = \frac{dq_{rev}}{T} \text{ where ; } dq_{rev} = \text{heat exchanged by system in a very small step (reversibly).}$$

#### 4.1 Entropy :

Entropy is a measure of disorder. The entropy is a state function and a basic quantity directly defined by second law. In every spontaneous process, entropy of universe increases.

There are three types of entropy changes :

- (i)  $\Delta S_{\text{System}}$  : Entropy change of system
- (ii)  $\Delta S_{\text{Surrounding}}$  : Entropy change of surrounding
- (iii)  $\Delta S_{\text{Total}}$  : Entropy change of universe

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = \Delta S_{\text{universe}} = \Delta S_{\text{total}} = \Delta S_{\text{isolated}}$$

Normally,  $\Delta S$  means entropy change of system.

#### 4.2 Second law in terms of entropy of universe :

For any spontaneous process (irreversible process) -

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$$

During a reversible process -

$$\Delta S_{\text{universe}} = 0$$

Thus during irreversible process, entropy of universe increases while during reversible process, entropy of universe remains constant.

#### 4.3 Physical significance of quantity $\frac{dq_{rev}}{T}$ :

$dq_{rev}$  = heat absorbed by the system,  $T$  = absolute temperature at which heat is absorbed. Suppose, similar quantity of heat is absorbed at two different temperatures  $T_1$  and  $T_2$  ( $T_2 >> T_1$ ). When heat is supplied at high temperature, the % age increase in kinetic energy is less compared to heat supplied at low temperature. Hence, disorder will increase by greater value, when heat is supplied at lower temperature.

#### 4.4 Determining ' $\Delta S_{\text{surr.}}$ ' for irreversible processes :

The change in entropy is given by : 
$$\frac{\text{heat absorbed by an entity}}{\text{Exact temperature at which heat is absorbed}}$$

The irreversible processes are fast and uncontrolled. The exact temperature of system during exchange of heat cannot be known. Hence, reversible path is needed to evaluate the entropy of system. Along reversible path, the heat exchange and exact temperature both are known.

Surrounding is generally a big entity and heat absorbed by surrounding is comparatively very small as compared to its size. Hence, internal equilibrium of surrounding is not disturbed during exchange of heat.

$\therefore$  Actual heat exchange of system is reversible heat exchange of surroundings

$\therefore (q_{\text{rev}})_{\text{surr}} = -q_{\text{irr}}$  [ $q_{\text{irr}}$  = Actual heat gained by system in a irreversible process.]

Hence, exact temperature and heat exchange both are known as far as surrounding is concerned even for an irreversible process.

$\therefore$  **For irreversible process :**  $\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T}$

	$\Delta S_{\text{system}}$	$\Delta S_{\text{surrounding}}$
(i)	<b>For reversible process :</b> $\Delta S_{\text{system}} = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T}$	<b>For reversible process :</b> $\Delta S_{\text{surr}} = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T} = -\Delta S_{\text{system}}$
(ii)	<b>For irreversible process :</b> $\Delta S_{\text{system}} = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T}$ [Where ; $dq_{\text{rev}}$ = heat gained by system for imaginary reversible path between same states]	<b>For irreversible process :</b> $\Delta S_{\text{surr}} = -\frac{q_{\text{irr}}}{T}$
(iii)	Always evaluated along reversible path (for both reversible and irreversible process)	For reversible process, $\Delta S_{\text{surr}}$ is evaluated along reversible path, while for irreversible process, irreversible heat is used to calculate $\Delta S_{\text{surr}}$ .
(iv)	Since no actual process is reversible, $\Delta S_{\text{system}}$ is always evaluated by hypothetical path.	For hypothetical process, $\Delta S_{\text{surr}}$ is evaluated by hypothetical heat, while for real irreversible process, it is evaluated by heat exchanged in irreversible process.

## 5. SECOND LAW (IN TERMS OF ENGINE)

- (i) No cyclic engine is possible whose only effect is complete conversion of heat into work without making any change in surrounding on its own.
- (ii) Heat can not flow from cold body to hot body on its own without external intervention.
- (iii) Complete conversion of heat (taken from a single source) into work is not possible in a cyclic process while complete conversion of work into heat is possible in a cyclic process. Thus, heat and work are not equivalent from the view point of II law.

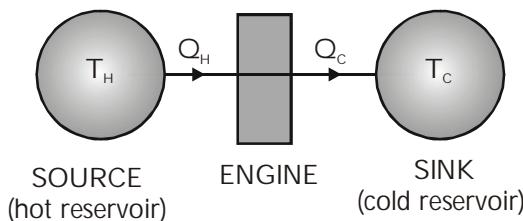
All above statements can be easily justified by realising that heat is a disordered form of energy while work is an ordered form of energy.

Complete conversion of **[Heat → Work]** on its own without any external assistance means **[Disorder → Order]** on its own - which is impossible.

### 5.1 Heat engine :

A heat engine is a device which can work continuously and cyclically without any external help absorbing heat from a source and rejecting a part of heat into sink. The net heat absorbed by engine (heat absorbed from source – heat given out to sink) is converted into work.

⇒ Heat engine must work in cycles , otherwise it can not work continuously.



$Q_H$  = Heat gained by engine per cycle

$Q_c$  = Heat rejected by engine per cycle

$$\text{Efficiency of engine : } \eta = \frac{Q_H - Q_c}{Q_H} = \frac{W_{by}}{Q_H}$$

$W_{by}$  = Work done by engine per cycle.

During operation of heat engine, heat is transferred from source (high temperature reservoir) to sink (low temperature reservoir) thus degrading the quality of energy. Note that net energy of universe remains conserved, but its quality is degraded (i.e. more disordered energy) when heat engine runs spontaneously.

### 5.2 CARNOT ENGINE

A carnot engine (a hypothetical engine) runs in reversible manner. Thus during expansion (work producing process) maximum work is done. However during compression (work requiring process) minimum work need to be done. Thus no engine can be more efficient than carnot engine.

The carnot engine works in following steps. (Assume ideal gas as working material).

- (i) Reversible isothermal expansion
- (ii) Reversible adiabatic expansion
- (iii) Reversible isothermal compression
- (iv) Reversible adiabatic compression

Now :  $Q_{NET} = -W_{NET}$

$$W_{NET} = W_{12} + W_{23} + W_{34} + W_{41}$$

$$W_{12} = -nRT_H \ln\left(\frac{V_2}{V_1}\right)$$

$$W_{23} = nC_V(T_C - T_H)$$

$$W_{34} = -nRT_C \ln\left(\frac{V_4}{V_3}\right)$$

$$W_{41} = -nC_V(T_H - T_C)$$

$$(P_1, V_1, T_2 \rightarrow P_2, V_2, T_2)$$

$$(P_2, V_2, T_2 \rightarrow P_3, V_3, T_1)$$

$$(P_3, V_3, T_1 \rightarrow P_4, V_4, T_1)$$

$$(P_4, V_3, T_1 \rightarrow P_1, V_4, T_2)$$

.....(i)

.....(ii)

.....(iii)

.....(iv)

.....(v)

.....(vi)

.....(vii) for process 2 – 3

.....(viii) for process 1 – 4

Also since process 2 – 3 and 4 – 1 are reversible adiabatic process.

$$T_H V_2^{\gamma-1} = T_C V_3^{\gamma-1}$$

$$T_C V_1^{\gamma-1} = T_H V_4^{\gamma-1}$$

from above equations

$$\left(\frac{V_2}{V_1}\right) = \left(\frac{V_3}{V_4}\right)$$

.....(ix)

Substituting the value of  $\left(\frac{V_4}{V_3}\right)$  in eq.(v) and adding w in individual step.

$$W_{NET} = -nRT_H \ln\left(\frac{V_2}{V_1}\right) + nC_V(T_C - T_H) - nRT_C \ln\left(\frac{V_4}{V_3}\right) - nC_V(T_C - T_H)$$

$$W_{NET} = -nRT_H \ln\left(\frac{V_2}{V_1}\right) - nRT_C \ln\left(\frac{V_1}{V_2}\right)$$

$$W_{NET} = -nR [T_C - T_H] \ln\left(\frac{V_2}{V_1}\right)$$

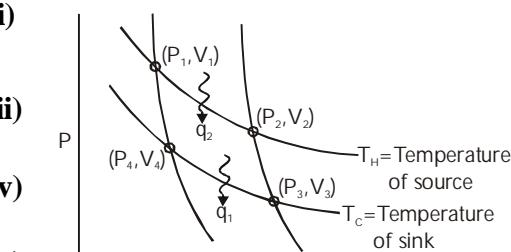
$$\Rightarrow \text{Efficiency } \eta = -\frac{W_{NET}}{q_2}$$

$$\eta = -\frac{nR \ln\left(\frac{V_2}{V_1}\right) [T_H - T_C]}{nRT_H \ln\left(\frac{V_2}{V_1}\right)}$$

$$\therefore \eta = \frac{T_H - T_C}{T_H}$$

Thus efficiency of carnot engine depends only upon temperature of source and sink.

**Note :** If working substance is changed (eg. ideal gas by real gas) efficiency of carnot engine remains unaffeced.



## EXERCISE-1

1. A heat engine absorbs 760 kJ heat from a source at 380K. It rejects (i) 650 kJ, (ii) 560 kJ, (iii) 504 kJ of heat to sink at 280K. State which of these represent a reversible, an irreversible or an impossible cycle.
2. The maximum efficiency of a heat engine operating between 100°C and 25°C is :-  
 (A) 20.11%                    (B) 22.2%                    (C) 25.17%                    (D) None
3. A carnot engine operating between 227°C and 27°C absorbs 2 Kcal of heat from the 227°C reservoir reversibly per cycle. The amount of work done in one cycle is :-  
 (A) 0.4 Kcal                    (B) 0.8 Kcal                    (C) 4 Kcal                    (D) 8 Kcal
4. An ideal gas heat engine operates in carnot's cycle between 227°C and 127°C. It absorbs  $6 \times 10^4$  cal of heat at high temperature. Amount of heat converted to work is :  
 (A)  $2.4 \times 10^4$  cal                    (B)  $4.8 \times 10^4$  cal                    (C)  $1.2 \times 10^4$  cal                    (D)  $6.0 \times 10^4$  cal

### 6. ENTROPY CHANGE OF AN IDEAL GAS

From definition of entropy of system -

$$dS_{\text{system}} = \frac{dq_{\text{rev}}}{T} \quad \dots \dots \dots \text{(i)}$$

from first law,  $dq_{\text{rev.}} = dU + PdV$

For a reversible change involving an ideal gas -

$$dq_{\text{rev}} = nC_{V,m}dT + \frac{nRT}{V}dV \quad \dots \dots \dots \text{(ii)}$$

$$\Rightarrow \int_1^2 \frac{dq_{\text{rev}}}{T} = \int_1^2 \frac{nC_{V,m}dT}{T} + \int_{V_1}^{V_2} nR \frac{dV}{V}$$

$$\Delta S_{\text{system}} = nC_{V,m} \ln \frac{T_2}{T_1} + nR \ell n \left( \frac{V_2}{V_1} \right) = nC_{P,m} \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}$$

**Note :** This formula is applicable to all ideal gas process.

#### 6.1 Ideal gas processes :

##### (i) For isothermal change :

$$\Delta S = \int_1^2 \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int_1^2 dq_{\text{rev}} \quad (\because T = \text{constant})$$

$$\Rightarrow \Delta S = \frac{q_{\text{rev}}}{T} = nR \ell n \frac{V_2}{V_1} \quad \left[ \because q_{\text{rev}} = nRT \ln \left( \frac{V_2}{V_1} \right) \right]$$

##### (ii) For isochoric change :

$$\Delta S = \int \frac{dq_v}{T} = \int_1^2 \frac{nC_{V,m}dT}{T} = nC_{V,m} \int_1^2 \frac{dT}{T} \quad [\because dq_v = nC_{V,m}dT]$$

$$\Rightarrow \Delta S = nC_{V,m} \ell n \frac{T_2}{T_1}$$

**(iii) For isobaric change :**

$$\Delta S = \int \frac{dq_p}{T} = \int_1^2 \frac{nC_{p,m} dT}{T} = nC_{p,m} \int_1^2 \frac{dT}{T} \quad [\because dq_p = nC_{p,m} dT]$$

$$\Rightarrow \Delta S = nC_{p,m} \ln\left(\frac{T_2}{T_1}\right)$$

**(iv) Reversible adiabatic process :**

$$q_{rev} = 0$$

$$\Rightarrow \Delta S = \underbrace{nC_V \ln \frac{T_2}{T_1}}_{\text{entropy change due to change in temperature}} + \underbrace{nR \ln \frac{V_2}{V_1}}_{\text{entropy change due to change in volume}} = 0$$

**(a) During reversible adiabatic expansion :**

$$T_2 < T_1 \text{ and } V_2 > V_1$$

- $\Rightarrow$  Sign of two terms are opposite and magnitudes are same because for reversible adiabatic process -

$$nC_{V,m} \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1}$$

- $\Rightarrow$  +ive and -ive term cancel out each other and hence,  $\Delta S = 0$

Thus, decrease in entropy during expansion due to decrease in temperature is exactly cancelled out by increase in entropy due to increase in volume of system in reversible adiabatic expansion.

**(b) During reversible adiabatic compression :**

$$T_2 > T_1 \text{ and } V_2 < V_1$$

$$\Rightarrow \Delta S_{\text{Total}} = \underbrace{nC_{V,m} \ln \frac{T_2}{T_1}}_{\text{+ive}} + \underbrace{nR \ln \frac{V_2}{V_1}}_{\text{?ive}} = 0$$

Thus, increase in entropy due to increase in temperature is compensated by decrease in entropy due to decrease in volume of system in reversible adiabatic compression.

Hence,  $\Delta S = 0$  for reversible adiabatic compression.

**(v) Irreversible adiabatic process :**

Since process is irreversible,  $\Delta S_{\text{Total}} > 0$ .

$$\Rightarrow \Delta S_{\text{system}} + \Delta S_{\text{surr}} > 0$$

$$\therefore \Delta S_{\text{surr}} = 0$$

$$\therefore \Delta S_{\text{system}} > 0$$

The physical interpretation is -

- (a) During irreversible adiabatic compression, large quantity of heat is produced while decrease in volume is less.

Thus, increase in entropy due to rise in temperature exceeds the decrease in entropy due to decrease in volume. Hence net entropy change is positive.

- (b) During irreversible adiabatic expansion, due to sudden decrease in external pressure, the system remains less challenged during expansion. Hence system do less work-resulting in lesser decrease in temperature.

The increase in volume of system is relatively larger (because system was less challenged)

Thus increase in entropy due to increase in volume exceeds decrease in entropy due to decrease in temperature. The net change in entropy is positive in both processes

$$\Delta S_{\text{surr.}} = 0 \text{ } (\because \text{no heat is exchanged with surrounding}) \text{ and } \Delta S_{\text{total}} > 0.$$

**(vi) Free expansion of an ideal gas against vacuum :**

Free expansion of an ideal gas is an example of irreversible adiabatic as well as irreversible isothermal process.

During free expansion, the  $P_{\text{ext.}} = 0$ . Hence, the ideal gas is not challenged at all during expansion. The kinetic energy of ideal gas remains constant. Hence, no temperature difference is created during expansion between system and surrounding.

$\therefore \Delta T = 0$ , the heat absorbed during the process = 0

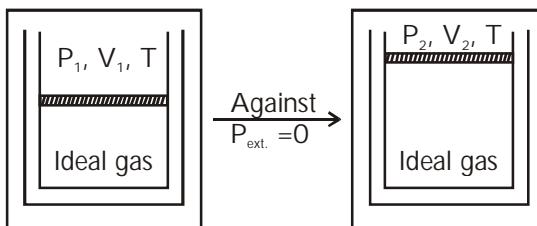
Since,  $V_f > V_i$  and  $T = \text{constant}$ ,  $\Delta S_{\text{system}} > 0$

The free expansion is an example where  $q_{\text{actual}} = 0$ , still  $\Delta S_{\text{system}} > 0$ .

$$\text{This is reasonable, because : } \Delta S_{\text{system}} = \int \frac{dq_{\text{rev.}}}{T}$$

This, example clearly shows that even if  $q_{\text{actual}}$  between two states is zero, this does not means that

$\int_1^2 \frac{dq_{\text{rev.}}}{T}$  between two states is zero. This outlines the importance of reversible path and  $q_{\text{rev.}}$  in calculation of entropy of system.



$$q_{\text{irr}} = 0 ; w_{\text{irr}} = 0$$

$$\Delta S_{\text{system}} = \int_1^2 \frac{dq_{\text{rev.}}}{T} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{\text{surr.}} = \frac{-q_{\text{irr}}}{T} = 0$$

$$\Delta S_{\text{total.}} = nR \ln \frac{V_2}{V_1} > 0$$

## ENTROPY CALCULATION :

Process	$\Delta S_{\text{sys.}}$	$\Delta S_{\text{surr.}}$
Isothermal reversible	$\Delta S_{\text{sys.}} = nR \ln \frac{V_2}{V_1}$	$\Delta S_{\text{surr.}} = -\Delta S_{\text{sys.}}$
Isothermal irreversible	$\Delta S_{\text{sys.}} = nR \ln \frac{V_2}{V_1}$	$\Delta S_{\text{surr.}} = \frac{-q_{\text{sys}}}{T} = \frac{W_{\text{sys}}}{T} = \frac{-P_{\text{ext}}(V_2 - V_1)}{T}$
Adiabatic reversible	$\Delta S_{\text{sys.}} = 0$	$\Delta S_{\text{surr.}} = 0$
Adiabatic irreversible	$\Delta S_{\text{sys.}} = nC_{P,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$	$\Delta S_{\text{surr.}} = 0$
Isochoric reversible	$\Delta S_{\text{sys.}} = nC_{V,m} \ln \frac{T_2}{T_1}$	$\Delta S_{\text{surr.}} = -\Delta S_{\text{sys.}}$
Isochoric irreversible	$\Delta S_{\text{sys.}} = nC_{V,m} \ln \frac{T_2}{T_1}$	$\Delta S_{\text{surr.}} = \frac{-q_{\text{sys}}}{T_{\text{surr}}} = \frac{-nC_{V,m} \Delta T}{T_{\text{final}}}$

**Ex.1** Three moles of an ideal gas is expanded isothermally from 2L to 10L , at 27°C. Calculate  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{surr}}$  and  $\Delta S_{\text{univ.}}$ , if the process is preformed.

(i) Reversibly

(ii) Irreversibly, against a constant external pressure of 1 atm

(iii) As free expansion

**Sol:** (i)  $\Delta S_{\text{univ.}} = 0$ ,  $\Delta S_{\text{surr.}} = -\Delta S_{\text{sys.}}$

$$\text{and } \Delta S_{\text{sys.}} = nR \ln \frac{V_2}{V_1} = 3R \ln \frac{10}{2} = 40.14 \text{ J/K}$$

$$(ii) \Delta S_{\text{sys.}} = 40.14 \text{ J/K}$$

$$\Delta S_{\text{surr.}} = -\frac{P_{\text{ext.}}(V_2 - V_1)}{T} = -\frac{1 \times (10 - 2) \times 101.3}{300} = -2.7 \text{ J/K}$$

$$\text{and } \Delta S_{\text{univ.}} = \Delta S_{\text{sys.}} + \Delta S_{\text{surr.}} = 37.44 \text{ J/K}$$

$$(iii) \Delta S_{\text{sys.}} = 40.14 \text{ J/K}$$

$$\Delta S_{\text{surr.}} = 0 \quad \text{as } P_{\text{ext.}} = 0$$

$$\text{and } \Delta S_{\text{univ.}} = \Delta S_{\text{sys.}} + \Delta S_{\text{surr.}} = 40.14 \text{ J/K}$$

**Ex.2.** Two moles of an ideal monoatomic gas is expanded adiabatically from 10L, 27°C to 80L.

Calculate  $\Delta S_{sys}$ ,  $\Delta S_{surr}$  and  $\Delta S_{univ}$ , if the process is performed.

(i) Reversibly

(ii) Irreversibly, against a constant external pressure of 0.1 atm.

(iii) As free expansion

**Sol.:**  $\Delta S_{surr} = 0$  for all

$$(i) \Delta S_{sys} = \Delta S_{surr} = \Delta S_{univ} = 0$$

$$(ii) n \cdot C_{v,m} \cdot (T_2 - T_1) = -P_{ext}(V_2 - V_1)$$

$$\text{or } 2 \times \frac{3}{2} \times 0.0821 \times (T_2 - 300) = -0.1 \times (80 - 10) \Rightarrow T_2 = 271.58 \text{ K}$$

$$\text{Now, } \Delta S_{sys} = n \cdot C_{v,m} \cdot \ln \frac{T_2}{T_1} + nR \cdot \ln \frac{V_2}{V_1}$$

$$= 2 \times \frac{3}{2} R \times \ln \frac{271.58}{300} \times 2 \times R \times \ln \frac{80}{10} = 32.90 \text{ J/K}$$

$$\text{and } \Delta S_{univ} = \Delta S_{sys}$$

$$(iii) T_1 = T_2 \Rightarrow \Delta S_{sys} = nR \cdot \ln \frac{V_2}{V_1} = 2 \times R \times \ln \frac{80}{10} = 34.58 \text{ J/K}$$

## 6.2 Entropy change of solids and liquids upon heating :

$$\Delta S = \int \frac{dq_{rev}}{T} = \int \frac{mS.dT}{T} = mS \cdot \ln \frac{T_2}{T_1} \quad [S = \text{specific heat of solid/ liquid}]$$

For molar change in entropy,  $m = M(\text{g/mole})$ ; where  $M = \text{molar mass}$ .

Note, for solids and liquids ( $MS \approx C_p \approx C_v$ )

**Ex.3** Two blocks of equal masses and heat capacity but at different temperatures are taken in an adiabatic vessel. Show that total change in entropy when both attain thermal equilibrium is always positive.

**Sol.** Let the temperature of hot body be  $T_H$ , temperature of cold body be  $T_C$  & the final temperature be  $T_F$ .  
Now, net heat exchanged by two bodies must be zero.

$$\Rightarrow mS(T_F - T_H) + mS(T_F - T_C) = 0$$

$$\Rightarrow T_F = \frac{T_H + T_C}{2}$$

Since both bodies are of finite mass, entropy of both bodies are evaluated by reversible paths.

$$\Delta S_{\text{Hot}} = \int_{T_H}^{T_F} mS \cdot \frac{dT}{T} = mS \cdot \ln \frac{T_F}{T_H}$$

$$\Delta S_{\text{Cold}} = \int_{T_C}^{T_F} mS \cdot \frac{dT}{T} = mS \cdot \ln \frac{T_F}{T_C}$$

$$\Rightarrow \Delta S_{\text{total}} = (mS) \ln \left( \frac{T_F^2}{T_H T_C} \right)$$

$$\Rightarrow T_H^2 + T_C^2 + 2T_H T_C - 4T_H T_C = (T_H - T_C)^2 > 0$$

$$\Rightarrow (T_H + T_C)^2 > 4T_H T_C$$

$$\Rightarrow \Delta S_{\text{total}} > 0$$

### 6.3 Reversible phase transitions :

Reversible phase transitions are always isothermal & isobaric.

$$\Delta S_{\text{system, P,T}} = \frac{q_{\text{rev.}}}{T} = \frac{\Delta H_{P,T}}{T_{\text{Transition}}}$$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{P,T}}{T_{\text{Transition}}}$$

$$\Delta S_{\text{total}} = 0$$

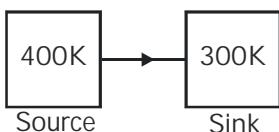
$$\text{Thus, } \Delta S_{\text{vaporisation at boiling point}} = \frac{\Delta H_{\text{vaporisation}}}{T_{\text{vaporisation}}}$$

$$\Delta S_{\text{fusion at melting point}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}}$$

$$\Delta S_{\text{sublimation at sublimation point}} = \frac{\Delta H_{\text{sublimation}}}{T_{\text{sublimation}}}$$

$$\Delta S_{\text{allotropic modification}} = \frac{\Delta H_{\text{allotropic modification}}}{T_{\text{transition}}}$$

**Ex.4** 100 kJ heat is transferred from a larger heat reservoir at 400 K to another large heat reservoir at 300 K. Suppose there is no change in temperature due to exchange of heat :



Find  $\Delta S_{\text{source}}$ ,  $\Delta S_{\text{sink}}$  and  $\Delta S_{\text{total}}$ . Comment on spontaneity of process.

**Ans.** (i)  $\Delta S_{\text{source}} = \frac{\text{heat absorbed by source}}{\text{Temperature of source}}$

$$\Delta S_{\text{source}} = \frac{-100 \text{ kJ}}{400} = -250 \text{ J/K}$$

(ii)  $\Delta S_{\text{sink}} = \frac{\text{heat absorbed by sink}}{\text{Temperature of sink}}$

$$= \frac{+100000 \text{ J}}{300} = 333.33 \text{ J/K}$$

(iii)  $\Delta S_{\text{Total}} = \Delta S_{\text{source}} + \Delta S_{\text{sink}} = +83.33 \text{ J/K}$

**Ex.5** Trouton's rule states that the ratio of the molar heat of vaporisation of a liquid to its normal boiling point is approximately the same for all liquids,  $\frac{\Delta H_{\text{vap}}}{T_{\text{bp}}} = 88 \text{ JK}^{-1} \text{ mol}^{-1} = \Delta S_{\text{vap}}$ . Which of the following liquids do not follow Trouton's rule :  $\text{NH}_3$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{Hg}$ . Explain.

**Ans.**  $\text{NH}_3$ , due to H-bonding :  $\Delta S_{\text{vap}} > 88 \text{ J/K-mol}$

## EXERCISE-2

5. Identify the correct statement regarding a spontaneous process : [AIEEE-2007]
  - (A) For a spontaneous process in an isolated system, the change in entropy is positive
  - (B) Endothermic processes are never spontaneous
  - (C) Exothermic processes are always spontaneous
  - (D) Lowering of energy in the reaction process is the only criterion for spontaneity
6. Find the change in entropy (in cal/k) of 1 mole of  $\text{O}_2$  gas ( $C_V = 5/2 R$ ), when it is
  - (a) heated from 300 K to 400 K isobarically
  - (b) heated from 300 K to 400 K isochorically (Given :  $\ln 3 = 1.1$ ,  $\ln 2 = 0.7$ )
7. One mole of  $\text{NaCl(s)}$  on melting as it's melting point absorbed 32.76 kJ of heat and its entropy is increased by  $30 \text{ JK}^{-1}$ . What is the melting point of sodium chloride ?

8. The entropy change when two moles of ideal monoatomic gas is heated from 200°C to 300°C reversibly and isochorically :-
- (A)  $\frac{3}{2}R \ln\left(\frac{300}{200}\right)$       (B)  $\frac{5}{2}R \ln\left(\frac{573}{273}\right)$       (C)  $3R \ln\left(\frac{573}{473}\right)$       (D)  $\frac{3}{2}R \ln\left(\frac{573}{473}\right)$
9. Predict the sign entropy change for the following processes:
- (A)  $O_2(g) \rightarrow 2O(g)$   
(B)  $2O_3(g) \rightarrow 3O_2(g)$   
(C)  $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$   
(D)  $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$   
(E)  $C_2H_5OH(l) \rightarrow C_2H_5OH(g)$   
(F)  $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
10. 5 mole of an ideal gas expands reversibly from a volume of 8 dm<sup>3</sup> to 80dm<sup>3</sup> at a constant temperature of 27°C. The change in entropy is :-
- (A) 41.57 JK<sup>-1</sup>      (B) - 95.73 JK<sup>-1</sup>      (C) 95.73 JK<sup>-1</sup>      (D) - 41.57 JK<sup>-1</sup>
11. ΔS for the reaction ;  $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$  will be :
- (A) 0      (B) -ve      (C) +ve      (D) ∞
12. Change in entropy is negative for :-
- (A) Bromine (ℓ) → Bromine (g)  
(B) C(s) + H<sub>2</sub>O(g) → CO(g) + H<sub>2</sub>(g)  
(C) (C) N<sub>2</sub>(g, 10 atm, 298 K) → N<sub>2</sub>(g, 1 atm, 298K)  
(D) Fe(at 400 K) → Fe(at 300 K)
13. For which reaction from the following, Δ S will be maximum ?
- (A) Ca(s) +  $\frac{1}{2}O_2(g) \rightarrow CaO(s)$       (B)  $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$   
(C) C(s) + O<sub>2</sub>(g) → CO<sub>2</sub>(g)      (D) N<sub>2</sub>(g) + O<sub>2</sub>(g) → 2NO(g)
14. When two gases are mixed the entropy :-
- (A) Remains constant      (B) Decreases      (C) Increases      (D) Becomes zero
15. For the process,  $CO_2(s) \rightarrow CO_2(g)$  :
- (A) Both ΔH and ΔS are +ve      (B) ΔH is -ve and ΔS is +ve  
(C) ΔH is +ve and ΔS is -ve      (D) Both ΔH and ΔS are -ve

## 7. THIRD LAW OF THERMODYNAMICS

“At absolute zero, the entropy of a perfectly crystalline substance is zero”, which means that at absolute zero, every crystalline solid is in a state of perfect order and its entropy should be zero. By virtue of the third law, the absolute value of entropy (unlike absolute value of enthalpy) for any pure substance can be calculated at room temperature.

$$S_T - S_{0K} = \int_0^T \frac{q_{rev}}{T}$$

Since  $S_{0K} = 0$

$$S_T = \int_0^T \frac{q_{rev}}{T}$$

The variation of entropy of a substance with temperature is given by graph :

At 1, entropy of substance is zero.

- **from 1-2 ;** The temperature of solid increases upon heating -

$$\Rightarrow S_2 - S_1 = \int \frac{C_{P,solid}}{T} dT \quad \dots\dots(i)$$

- **from 2-3 ;** The temperature remains constant during phase transition

$$\Rightarrow S_3 - S_2 = \Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_f} \quad \dots\dots(ii)$$

- **from 3-4 ;** The temperature of liquid increases

$$\Rightarrow S_4 - S_3 = \int_{T_3}^{T_4} \frac{C_{P,liquid} \cdot dT}{T} \quad \dots\dots(iii)$$

- **from 4-5 ;** Reversible vaporisation takes place at constant temperature -

$$\Rightarrow S_5 - S_4 = \Delta S_{vap.} = \frac{\Delta H_{vap.}}{T_b} \quad \dots\dots(iv)$$

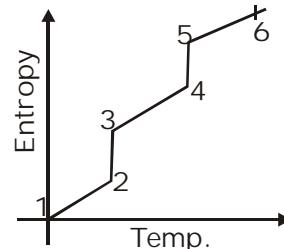
- **from 5-6 ;** The gas is heated -

$$\Rightarrow S_6 - S_5 = \int_{T_5}^{T_6} \frac{C_{P,gas} \cdot dT}{T} \quad \dots\dots(v)$$

$$\Delta S_{1-6} = (S_2 - S_1) + (S_3 - S_2) + (S_4 - S_3) + (S_5 - S_4) + (S_6 - S_5) = S_6 - S_1 \quad [\because S_1 = 0]$$

$\therefore S_6$  = absolute entropy at 6.

$$= \int_{T_1}^{T_2} \frac{C_{P,Solid} dT}{T} + \frac{\Delta H_{fusion}}{T_f} + \int_{T_3}^{T_4} \frac{C_{P,liquid} dT}{T} + \frac{\Delta H_{vap.}}{T_b} + \int_{T_5}^{T_6} \frac{C_{P,gas} dT}{T}$$



Change in entropy of a pure substance with temperature at constant pressure.

- **Comment :** Absolute entropy of a substance can be calculated using third law by reversible path.

### 7.1 Standard absolute molar entropy :

It is the entropy in one mole of substance at standard temperature at 1 bar.

It is calculated assuming that substance is heated isobarically and reversibly at 1 bar from 0 K to standard temperature.

### 7.2 Comparing absolute entropies of substance :

- (i) The absolute entropies of substance follow the order,

$$S(g) \gg S(l) > S(s)$$

- (ii) Entropy increases when solid and liquid is dissolved into solvent,

e.g.	$\text{CH}_3\text{OH}(l)$	$S^\circ = 127 \text{ J/K-mole}$
	$\text{CH}_3\text{OH}(\text{aq})$	$S^\circ = 132.3 \text{ J/K-mole}$
	$\text{NaCl}(s)$	$S^\circ = 72.4 \text{ J/K-mole}$
	$\text{NaCl}(\text{aq.})$	$S^\circ = 115.4 \text{ J/K-mole}$

- (iii) The entropy of dissolved gas is less than pure gas.

e.g.	$\text{HCl}(g)$	$S^\circ = 186.7 \text{ J/K-mole}$
	$\text{HCl}(\text{aq})$	$S^\circ = 55.2 \text{ J/K-mole}$

- (iv) Entropy rises with increasing mass, (if other factors are similar).

e.g.	$\text{F}_2(g)$	$S^\circ = 203 \text{ J/K-mole}$
	$\text{Cl}_2(g)$	$S^\circ = 223 \text{ J/K-mole}$
	$\text{Br}_2(g)$	$S^\circ = 245 \text{ J/K-mole}$

- (v) Entropy is lower in covalently bonded solids, with strong directional bonds, than in solids with partial metallic character.

e.g.	$\text{C}(\text{diamond})$	$S^\circ = 2.44 \text{ J/K-mole}$
	$\text{C}(\text{graphite})$	$S^\circ = 5.69 \text{ J/K-mole}$
	$\text{Sn}(\text{gray})$	$S^\circ = 44.8 \text{ J/K-mole}$
	$\text{Sn}(\text{white})$	$S^\circ = 51.5 \text{ J/K-mole}$

- (vi) Entropy increases with increasing softness and with weakness of bonds between atoms.

e.g.	$\text{C}(\text{diamond})$	$\text{Be}(s)$	$\text{S}_1\text{O}_2(s)$	$\text{Pb}(s)$	$\text{Hg}(l)$
	2.44	9.54	41.8	64.9	77.4
	diamond	hard metal	quartz	soft metal	liquid

- (vii) Entropy increases with chemical complexity

Sub.	$\text{NaCl}$	$\text{MgCl}_2$	$\text{AlCl}_3$
	72.4	89.5	167

For  $\text{CuSO}_4 \cdot n\text{H}_2\text{O}$

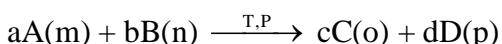
$n = 0$	$n = 1$	$n = 3$	$n = 5$
$S^\circ = 113$	150	225	305

**Note : Above data is given in SI unit.**

### 7.3 Entropy change ( $\Delta_f S$ ) of a chemical reaction :

The change in entropy when reactants turn into products according to a balanced chemical reaction with specified physical state of each reactant and product is called entropy of reaction.

- Consider a reaction :



where m, n, o, p are physical states at temperature T and pressure P.

$$\Delta S_r = \sum S(\text{products}) - \sum S(\text{reactants})$$

$$\Delta r S = cS_C + dS_D - aS_A - bS_B$$

$S_A, S_B, S_C$  and  $S_D$  are absolute molar entropies at temperature T and pressure P (**from third law**)

So,  $\Delta r S$  is evaluated from table of data of third law entropies of various substances.

#### 7.4 $\Delta S_{\text{Surrounding}}$ for chemical reaction :

$\Delta r H = q_p$  = heat absorbed by the system during chemical reaction.

$\Rightarrow -\Delta r H = -q_p = q_{\text{surr}}$  = heat absorbed by the surrounding.

Now,

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = -\frac{\Delta r H}{T}$$

If  $\Delta r H = -$ ive (exothermic) heat is lost by the system and gained by the surrounding.

Hence,  $\Delta S_{\text{surr}}$  increases.

If  $\Delta r H = +$ ive (endothermic process), entropy of surrounding decreases.

$$\therefore \Delta S_{\text{surr}} = -\frac{\Delta r H}{T} = -\text{ive}$$

- We can not comment on entropy change of system from knowledge of  $\Delta r H$ . The entropy change of system ( $\Delta r S$ ) is estimated by third law.

#### 7.5 Driving force of a spontaneous chemical process :

The driving force of a spontaneous chemical process is increase in entropy of universe.

In simple terms, negative value of  $\Delta r H$  and positive value of  $\Delta r S$  favours the chemical process.

If  $\Delta r H$  is positive, the enthalpy factor don't support the forward process. Under these conditions,  $\Delta r S$  should be sufficiently positive to drive the reaction in forward direction. If  $\Delta r H$  is +ive and  $\Delta r S$  is -ive, under a given situation, the process become non-spontaneous because both factors tends to decrease the entropy of the universe.

#### 7.6 Prediction the sign of $\Delta r S$ by inspecting a balanced chemical reaction.

- If more no. of gaseous moles are present on product side,  $\Delta r S$  will be +ive (since gas is more disordered than solid or liquid).

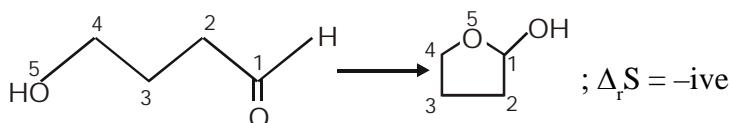
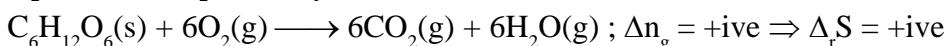
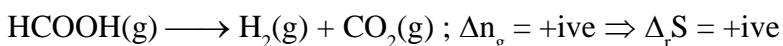
- If
  - solid  $\longrightarrow$  liquid
  - solid  $\longrightarrow$  gas
  - liquid  $\longrightarrow$  gas

then,  $\Delta r S = +$ ive.

- If a molecule is undergoing cyclisation, it's rotational modes of motion are replaced by vibrational modes of motion.

Since quantum energy separation of rotational motion is closely spaced compared to vibrational energy state, rotational energy is more disordered. Hence,  $\Delta r S = -$ ive.

- **Example :**



### 7.7 Table for spontaneity of chemical process and sign of $\Delta_f H$ , $\Delta_f S$ and dependence on temperature.

Sign of $\Delta S^\circ_{298}$	Sign of $\Delta H$	Comment $\Delta S$	Example	$\Delta H^\circ_{298}$	
-	+	Spontaneous at all temperature	$\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{HCl(g)}$ $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$	-185	14.1
-	-	Spontaneous at low temperature	$\text{H}_2\text{(g)} + 1/2 \text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(l)}$ $2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{SO}_3\text{(g)}$	-44	-119
+	+	Spontaneous at high temperature	$\text{NH}_4\text{Cl(s)} \rightarrow \text{NH}_3\text{(g)} + \text{HCl(g)}$ $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO(g)}$	176	284
+	-	Non spontaneous at all temperature	$3\text{O}_2 \rightarrow 2\text{O}_3$ $2\text{H}_2\text{O(l)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O}_2\text{(l)}$	286	-137
				196	-126

### 7.8 State of equilibrium :

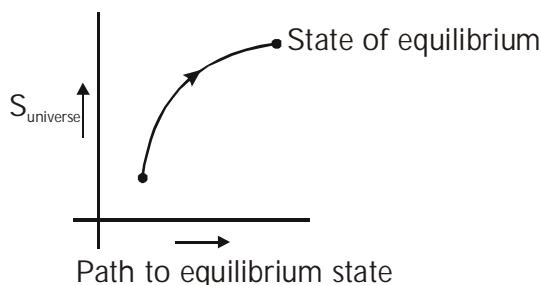
A system at equilibrium is a stable system. Hence, its state variables become constant (do not vary with time) at equilibrium.

If a system is in non-equilibrium state, it moves spontaneously in the direction of equilibrium (because the equilibrium state is stable). During the spontaneous movement towards equilibrium, the entropy of universe increases.

As the system gets closer to equilibrium state, the driving force to attain equilibrium becomes small and so does the increase in disorder of universe. At equilibrium, the driving force to move ahead finishes and entropy of the universe can not increase further.

In nutshell, when a system attains equilibrium, its capacity to increase the disorder of universe is lost.

- At equilibrium, the entropy of universe is maximum.



## 8. GIBB'S FUNCTION

Gibb's function 'G' is defined as  $G = H - TS$ .

Since 'G' is a combination of state variables (a compound state variable), it is a state function. The dimension of Gibb's function is the dimension of energy. 'G' is an extensive quantity.

Gibb's function provide a very useful criteria for spontaneity of a process taking place at constant temperature and pressure (isobaric, isothermal process).

The entropy of universe is also a very useful criteria of spontaneity, but it is based on properties of system as well as surrounding.

The Gibb's function provides criteria for spontaneity based only on the properties of system.

$$\Delta G = \Delta H - \Delta(TS)$$

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

(Isothermal process)

**Ex.6** The thermodynamic stability of a substance is dependent upon the value of Gibb's function. Explain the stability of solid at low temperature and stability of gas at very high temperature.

**Sol.** Any stable state tries to minimise its enthalpy while maximising its entropy.

For solids -  $G_{\text{solid}} = H_{\text{solid}} - TS_{\text{solid}}$  (at certain T & P)

For liquids -  $G_{\text{liquid}} = H_{\text{liquid}} - TS_{\text{liquid}}$  (at certain T & P)

For gas -  $G_{\text{gas}} = H_{\text{gas}} - TS_{\text{gas}}$  (at certain T & P)

At any given T and P,  $H_{\text{solid}} < H_{\text{liquid}} < H_{\text{gas}}$

and  $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$

At very low temperature, TS term contributes very little towards Gibb's function. Hence -

$$G_{\text{solid}} < G_{\text{liquid}} < G_{\text{gas}} \quad (\text{at very low temperature}).$$

This explains why solids are most stable at low temperature.

At very high temperature, TS term is very important. Since  $S_{\text{gas}}$  is large, for gas TS term becomes very large at large temperature. Hence -

$\Rightarrow G_{\text{solid}} > G_{\text{liquid}} > G_{\text{gas}}$  (at very high temperature). Thus, gaseous state is most stable at high temperature.

Hence, the low enthalpies of solid are responsible for stability of solid at low temperature, while high entropy of gas is responsible for stability of gas at high temperature.

### 8.1 $\Delta G_{T,P}$ and $\Delta S_{\text{universe}}$

Decrease in Gibb's function at constant temperature and pressure is related to  $\Delta S_{\text{total}}$  (total entropy change of system and surrounding).

$$-\Delta G = T(\Delta S_{\text{total}})$$

**At constant P, T**

**if  $\Delta G < 0 \Rightarrow$  spontaneous process**

**if  $\Delta G > 0 \Rightarrow$  non-spontaneous process**

**if  $\Delta G = 0 \Rightarrow$  reversible process**

**At constant P, T, Gibbs energy of a system spontaneously decreases.**

## EXERCISE-3

- 16.** Animals operate under conditions of constant pressure and most of the processes that maintain life are electrical (in a broad sense). How much energy is available for sustaining this type of muscular and nervous activity from the combustion of 1 mol of glucose molecules under standard conditions at 37°C (blood temperature) ? The entropy change is + 210 JK<sup>-1</sup> for the reaction as stated.

$$\Delta H_{\text{combustion [glucose]}} = -2808 \text{ kJ / mol.}$$

- 17.** Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction.?
- (A) endothermic and decreasing disorder      (B) exothermic and increasing disorder  
 (C) endothermic and increasing disorder      (D) exothermic and decreasing disorder
- 18.** Standard entropy of X<sub>2</sub>, Y<sub>2</sub> and XY<sub>3</sub> are 60, 40 and 50 JK<sup>-1</sup>mol<sup>-1</sup>, respectively. for the reaction,  
 $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightarrow XY_3$ ,  $\Delta H = -30 \text{ kJ}$  to be at equilibrium, the temperature will be :-
- (A) 1250 K      (B) 500 K      (C) 750 K      (D) 1000 K
- 19.** For a particular reversible reaction at temperature T,  $\Delta H$  and  $\Delta S$  were found to be both +ve. If T<sub>e</sub> is the temperature at equilibrium, then reaction would be spontaneous when :-

**[AIEEE-2010]**

- (A) T = T<sub>e</sub>      (B) T<sub>e</sub> > T      (C) T > T<sub>e</sub>      (D) T<sub>e</sub> is 5 times T
- 20.** For a reaction at 25°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. The reaction is :
- (A) Spontaneous      (B) Non spontaneous  
 (C) At equilibrium      (D) Can't say anything
- 21.** Identify the correct statement for change of Gibbs energy for a system at constant temperature and pressure.
- (A) If  $\Delta G_{\text{system}} > 0$ , the process is spontaneous.  
 (B) If  $\Delta G_{\text{system}} = 0$ , the system has attained equilibrium.  
 (C) If  $\Delta G_{\text{system}} = 0$ , the system is still moving in a particular direction.  
 (D) If  $\Delta G_{\text{system}} < 0$ , the process is non spontaneous.
- 22.** In conversion of lime-stone to lime,  $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$   
 the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  are +179.1 kJ mol<sup>-1</sup> and 160.2 J/K respectively at 298 K and 1 bar.  
 Assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is :-
- [AIEEE-2007]**
- (A) 1008 K      (B) 1200 K      (C) 845 K      (D) 1118 K

## 8.2 CALCULATE AG FOR VARIOUS PROCESSES

(i) Ideal gas subjected to isothermal compression or expansion :

For isothermal process :

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

For ideal gas,  $\Delta H = nC_{p,m}\Delta T = 0$

(As  $\Delta T = 0$ , for isothermal change)

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

(for isothermal change)

$$\therefore \Delta G = -nRT \ln \frac{V_2}{V_1}$$

Hence, during isothermal expansion Gibb's function decreases while during isothermal compression Gibb's function increases.

## **(ii) Isothermal and isobaric phase transitions :**

At transition temperature, the stability (or Gibb's functions) of two phases are equal. Hence, there is no driving force for conversion of one phase into other. This means phase transitions are examples of reversible processes at transition temperature.

Now, for reversible, isothermal and isobaric change,  $\Delta G = 0$

$\Rightarrow \Delta G = 0$ , for phase transitions at transition temperature.

Thus,  $\Delta G_{\text{vap}} = 0$  at boiling point :

$$\Rightarrow \Delta H_{\text{vap}} = T_b \Delta S_{\text{vap}} \Rightarrow T_b = \frac{\Delta H_{\text{vap}}}{\Delta S_{\text{vap}}}$$

Also,  $\Delta G_{\text{fusion}} = 0$  at melting point :

$$\Rightarrow \Delta H_{\text{fusion}} = T_f \Delta S_{\text{fusion}}$$

$$T_f = \frac{\Delta H_{\text{fusion}}}{\Delta S_{\text{fusion}}}$$

**Ex.7** The enthalpy of vaporization of a liquid is  $30 \text{ kJ mol}^{-1}$  and entropy of vaporization is  $75 \text{ J mol}^{-1} \text{ K}^{-1}$ . The boiling point of the liquid at 1 atm is :

- (A)  $250\text{ K}$       (B)  $400\text{ K}$       (C)  $450\text{ K}$       (D)  $600\text{ K}$

Ans. [B]

$$\text{Sol. } T = \frac{\Delta H_{\text{vap}}}{\Delta S_{\text{vap}}} = \frac{30 \times 10^3}{75} = 400 \text{ K}$$

**Ex.8 At what minimum temperature would a given reaction become spontaneous if  $\Delta H = +119 \text{ kJ}$  and  $\Delta S = +263 \text{ J/K}$ ?**

- (A)  $452\text{ K}$       (B)  $2210\text{ K}$       (C)  $382\text{ K}$       (D)  $2.21\text{ K}$

**Ans. [A]**

$$\text{Sol. } T = \frac{\Delta H}{\Delta S} = \frac{119 \times 10^3}{263} = 452.47 \text{ K}$$

### iii. $\Delta_r G$ for a chemical reaction.

Consider a reaction :  $aA + bB \xrightarrow{T,P} cC + dD$

The change in Gibb's function for a chemical reaction is change in  $\Delta G$  when reactants react according to a given balanced chemical reaction with specified physical state of each reactant and product at given temperature and pressure.

$$\Delta_r G = cG_C + dG_D - aG_A - bG_B \quad \dots\dots\dots (i)$$

Where  $G_A$ ,  $G_B$ ,  $G_C$  and  $G_D$  are molar Gibb's function of A,B,C and D respectively at given T and P. also,

$$\left. \begin{array}{l} G_A = H_A - TS_A \\ G_B = H_B - TS_B \\ G_C = H_C - TS_C \\ G_D = H_D - TS_D \end{array} \right\} \quad \dots\dots\dots (ii)$$

Substituting (ii) in (i)

$$\Delta_r G = (cH_C + dH_D - aH_A - bH_B) - T(cS_C + dS_D - aS_A - bS_B)$$

$$\Rightarrow \boxed{\Delta_r G = \Delta_r H - T\Delta_r S}$$

$(\Delta H)_{T,P}$	$(\Delta S)_{T,P}$	$(\Delta G)_r$
- ve	+ ve	Always -ve
+ ve	- ve	Always +ve
+ ve	+ ve	At low temperature, $\Delta G = +$ ve At high temperature, $\Delta G = -$ ve
- ve	- ve	At low temperature, - ve
- ve	- ve	At high temperature, + ve

#### Remarks

- Reaction is spontaneous
- Reaction non-spontaneous
- Non-spontaneous
- Spontaneous
- Spontaneous
- Non spontaneous

### (iv) Gibb's functions of pure substances :

Consider a pure substance having a Gibb's function as follows :

$$G = H - TS = U + PV - TS$$

Let, the pressure and temperature are varied by infinitesimally small value :

$$dG = dU + PdV + VdP - TdS - SdT$$

$$\text{As, } dU = dq - PdV \text{ and } TdS = dq$$

[Assume only PV- work and reversible process.]

$$\boxed{dG = VdP - SdT}$$

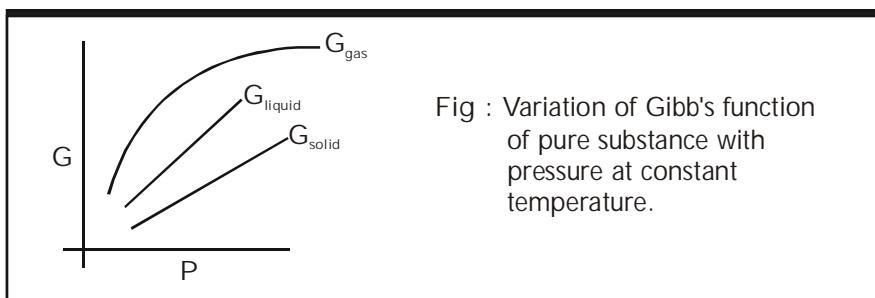
**(a)** If pressure is varied keeping temperature constant -

$$dG = VdP \Rightarrow \left( \frac{dG}{dP} \right)_T = V$$

The physical significance of above relation is when pressure over a substance is increased, it's Gibb's function increases & the increase is proportional to molar volume. Since molar volume of gas, liquid and solid are in order, as follows :

$$V_{\text{Gas}} > V_{\text{Liquid}} > V_{\text{Solid}}$$

Hence, Gibb's function of gases increases most rapidly on increasing pressure. That's why, gas phase becomes unstable at high pressure.



- (b) If temperature is changed keeping pressure constant -

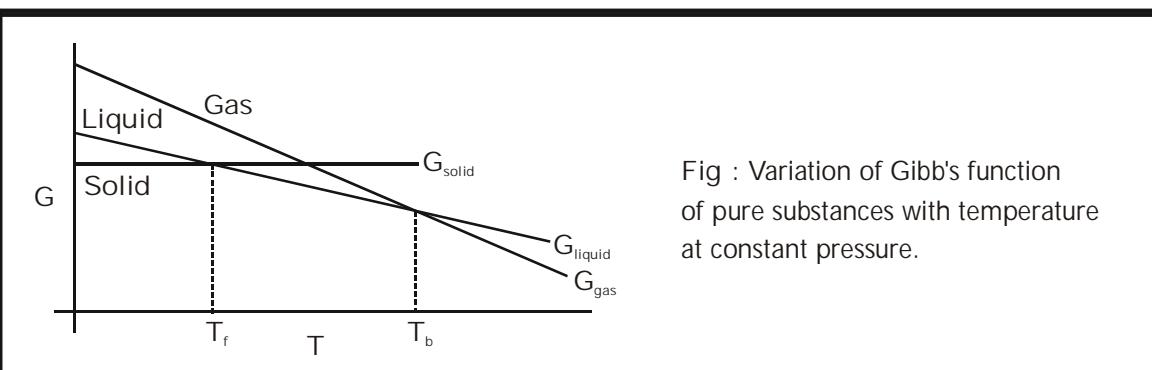
$$dG = -SdT \Rightarrow \left( \frac{dG}{dT} \right)_P = -S$$

Since entropy of pure substances are always positive, the slope of G vs T curve is negative. Also since,

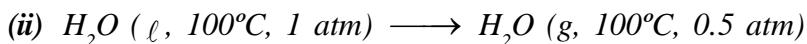
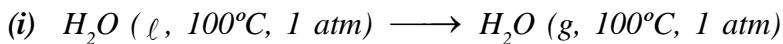
$$S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$$

$\Rightarrow$  the slope is more negative for gas.

Thus, on increasing temperature, the Gibb's function of pure substances decreases, but this decrement is maximum for gaseous phase. Thus, gas phase acquire stability on increasing temperature.



**Ex. 9.** Calculate  $\Delta G_m$  for the following process:



**Sol. :** (i)  $\Delta G = 0$  (Equilibrium condition)



$$\Delta G_1 = 0$$

$$\Delta G_2 = nRT \cdot \ln \frac{P_2}{P_1} = 1 \times R \times 373 \times \ln \frac{0.5}{1} = -2149.5 \text{ J}$$

$$\therefore \Delta G = \Delta G_1 + \Delta G_2 = -2149.5 \text{ J}$$

### 8.3 APPLICATION OF GIBB'S ENERGY (AS MEASURE OF NON-PV WORK)

For a pure substance

$$dG = d(H - TS) = dH - TdS - SdT$$

also  $dH = dU + PdV + VdP$

also  $dU = dq - PdV - w_{\text{non-PV}}$

$(w_{\text{non-PV}} = \text{non-PV work done by system})$

$$\Rightarrow dG = dq - PdV - w_{\text{non-PV}} + PdV + VdP - TdS - SdT$$

for a reversible change at constant T and P.

$dq = TdS$ ; and  $SdT$  and  $VdP$  term vanishes.

$$\Rightarrow dG = TdS - w_{\text{non-PV}} - TdS$$

$$(dG)_{T,P} = - w_{\text{non-PV}}$$

$$\Rightarrow -(dG)_{T,P} = w_{\text{non-PV}}$$

Thus decrease in Gibb's function at constant temperature and pressure is equal to maximum non-PV work obtainable from system.

### 9. Chemical equilibrium :

The state of chemical equilibrium is characterised by constant value of temperature, pressure and composition of a closed system. The state of equilibrium represent most stable state acquired by chemical system under given conditions.

The characteristics of state of equilibrium are :

- (i) The equilibrium is attained in closed system.
- (ii) At equilibrium, the chemical system is at minimum value of Gibb's function possible under given conditions.
- (iii) A state of equilibrium is attained spontaneously.
- (iv) At equilibrium, the rate of change of Gibb's function with progress of reaction under given conditions becomes zero  $\Rightarrow \Delta_r G = 0$ .
- (v) At state of equilibrium, the total Gibb's function of products becomes equal to total Gibb's function of reactants.

## ANSWER KEY

## EXERCISE-1

1. Ans. (i) irreversible, (ii) reversible, (iii) impossible
2. Ans.(A)                    3. Ans.(B)                    4. Ans.(C)

## EXERCISE-2

5. Ans.(A)
6. Ans. (a) 2.1 cal/K , (b) 1.5 cal/K
7. Ans 819°C
8. Ans.(C)
9. Ans.  
(A) (+ive)                    (B) (+ive)                    (C)  $\approx 0$                     (D) (+ive)  
(E) (+ive)                    (F) (-ive)
10. Ans.(C)                    11. Ans.(C)                    12. Ans.(D)                    13. Ans.(B)
14. Ans.(C)                    15. Ans.(A)

## EXERCISE-3

16. Ans. -2873.1 kJ            17. Ans. (B)                    18. Ans.(C)                    19. Ans.(C)
20. Ans.(B)                    21. Ans.(B)                    22. Ans.(D)

# MISCELLANEOUS SOLVED QUESTION

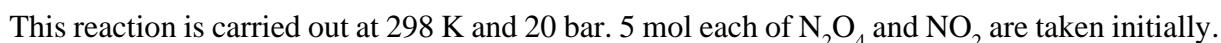
1. When 1-pentyne(A) is treated with 4N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne(B) & 3.5% of 1, 2-pentadiene (C). The equilibrium was maintained at 175°C. Calculate  $\Delta G^\circ$  for the following equilibria.



From the calculated value of  $\Delta G_1^\circ$  &  $\Delta G_2^\circ$  indicate the order of stability of A, B & C. Write a reasonable reaction mechanism sharing all intermediate leading to A, B & C. [JEE 2001]

2. Show that the reaction  $\text{CO(g)} + \frac{1}{2} \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)}$  at 300 K is spontaneous and exothermic, when the standard entropy is  $-0.094 \text{ kJ mol}^{-1} \text{ K}^{-1}$ . The standard Gibbs free energies of formation for  $\text{CO}_2$  and  $\text{CO}$  are  $-394.4$  and  $-137.2 \text{ kJ mol}^{-1}$ , respectively. [JEE 2001]

3.  $\text{N}_2\text{O}_4\text{(g)} \rightleftharpoons 2\text{NO}_2\text{(g)}$



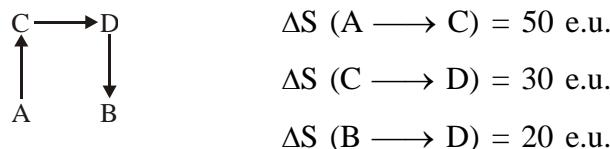
Given :  $(\Delta G_f^0)_{N_2O_4} = 100 \text{ kJ mol}^{-1}$ ;  $(\Delta G_f^0)_{NO_2} = 50 \text{ kJ mol}^{-1}$

(i) Find  $\Delta G$  for reaction at 298 K under given condition.

(ii) Find the direction in which the reaction proceeds to achieve equilibrium. [JEE 2004]

4. The enthalpy of vapourization of a liquid is  $30 \text{ kJ mol}^{-1}$  and entropy of vapourization is  $75 \text{ J mol}^{-1} \text{ K}^{-1}$ . The boiling point of the liquid at 1 atm is :- [JEE 2004]  
(A) 250 K (B) 400 K (C) 450 K (D) 600 K

5. A process A  $\longrightarrow$  B is difficult to occur directly instead it takes place in three successive steps.



[JEE 2006]

Where e.u. is entropy unit.

Then the entropy change for the process  $\Delta S$  ( $A \rightarrow B$ ) is :-

- (A) + 100 e.u.      (B) - 60 e.u.      (C) - 100 e.u.      (D) + 60 e.u.

7. **Statement-1 :** There is a natural asymmetry between converting work to heat and converting heat to work.

**Statement-2 :** No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. [JEE 2008]

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.

8. **Statement-1 :** For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.

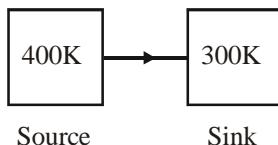
**Statement-2 :** At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. [JEE 2008]

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.

## EXERCISE (S-1)

## □ Carnot Cycle

1. The efficiency of a carnot cycle is  $1/6$ . On decreasing the temperature of the sink by  $65^{\circ}\text{C}$ , the efficiency increases to  $1/3$ . Calculate the temperature of source and sink.
  2. A carnot cycle has an efficiency of  $40\%$ . Its low temperature reservoir is at  $9^{\circ}\text{C}$ . What is the temperature of source ?
  3. A diatomic ideal gas is expanded isothermally to  $32$  times of it's initial volume then it is cooled to restore to initial entropy at constant volume. Calculate ratio of intial temperature to final temperature
  4. One mole of an ideal monoatomic gas was taken through reversible isochoric heating from  $100\text{ K}$  to  $1000\text{ K}$ . Calculate  $\Delta S_{\text{system}}$ ,  $\Delta S_{\text{surr}}$  and  $\Delta S_{\text{total}}$ 
    - (i) when the process is carried out reversibly
    - (ii) when the process is carried out irreversibly (one step)
  5.  $100\text{ kJ}$  heat is transferred from a large heat reservoir at  $400\text{ K}$  to another large heat reservoir at  $300\text{ K}$ . Suppose there is no change in temperature due to exchange of heat and combinedly source and sink form isolated system.



Find (a)  $\Delta S_{\text{source}}$ , (b)  $\Delta S_{\text{sink}}$  and (c)  $\Delta S_{\text{total}}$ . Also comment on spontaneity of process.

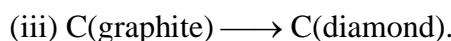
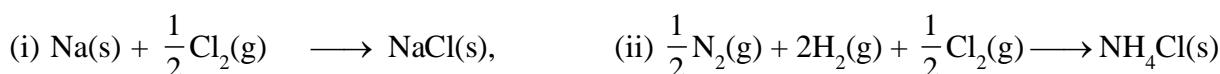
6. A system of 100 kg mass undergoes a process in which its specific entropy increases from  $0.3 \text{ kJkg}^{-1}\text{K}^{-1}$  to  $0.4\text{kJkg}^{-1}\text{K}^{-1}$ . At the same time, the entropy of the surrounding decreases from  $80 \text{ kJK}^{-1}$  to  $75 \text{ kJK}^{-1}$ . Find the  $(\Delta S)_{\text{universe}}$  in  $\text{kJK}^{-1}$ .

7. Calculate  $(\Delta S)_{\text{universe}}$  (in cal/K) when 1kg water at 300K is brought into contact with a heat reservoir at 600K. Specific heat capacity of water is  $1\text{cal/gm}^{\circ}\text{C}$ . Assume no change in physical state of water. ( $\ln 2 = 0.7$ )

8. 1 mole of ideal monoatomic gas is heated by supplying 5 kJ heat from a reservoir maintained at 400 K from 300 K to 400 K. In the process volume of gas increased from 1 L to 10 L. Find  $\Delta S_{\text{total}}$  (in  $\text{J/K mol}$ ) in the process

Use :  $\ln \left( \frac{4}{3} \right) = 0.3$ ,  $\ln 10 = 2.3$ ,  $R = 8.3 \text{ J/K-mol}$  and  $\ln x = 2.3 \log x$

- 9.** Calculate  $\Delta S^\circ$  at 298K of



The values of  $S^\circ$  of Na,  $\text{Cl}_2$ , NaCl,  $\text{NH}_4\text{Cl}$ ,  $\text{N}_2$ ,  $\text{H}_2$  diamond & graphite are 51, 223, 72, 95, 192, 131, 2.43 &  $5.69 \text{ J K}^{-1} \text{ mol}^{-1}$  respectively.

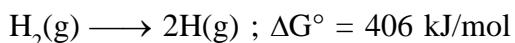
- 10.** Identify the substance in each of the following pairs of samples that has the higher entropy?

## □ Gibb's Function

11. Calculate the  $\Delta G^\circ$  change at 300 K for the reaction;

$\text{Br}_2(\ell) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{BrCl}(\text{g})$ . For the reaction  $\Delta H^\circ = 29.3 \text{ kJ}$  & the standard entropies of  $\text{Br}_2(\ell)$ ,  $\text{Cl}_2(\text{g})$  &  $\text{BrCl}(\text{g})$  at the 300 K are 150, 220, 240  $\text{J mol}^{-1}\text{K}^{-1}$  respectively.

- 12.** The standard entropies of  $\text{H}_2(\text{g})$  and  $\text{H}(\text{g})$  are 130 and 115  $\text{J mol}^{-1}\text{K}^{-1}$  respectively at 300K.  
Using the data given below calculate the bond energy of  $\text{H}_2$ (in kJ/mol) :-



13. 5 mole  $\text{H}_2\text{O}(\ell)$  at 373K and 1 atm is converted into  $\text{H}_2\text{O(g)}$  at 373K and 5 atm. Calculate  $\Delta G$  for this process. [Given : R = 2Cal/K-mol,  $\ln 5 = 1.6$ ]

- 14.** Calculate  $\Delta G$  (in bar-L) when a definite mass of a monoatomic ideal gas at 1 bar & 27°C is expanded adiabatically against vacuum from 10 L to 20 L ( $\ln 2 = 0.7$ )

- 15.** Find  $(\Delta S)_{\text{universe}}$  (in Joule/mole/K) at 1 bar for a chemical reaction at 300 K if  $\Delta H^{\circ}_{300\text{ K}} = 75 \text{ kJ / mol}$   
 $\Delta S^{\circ}_{300\text{ K}} = 300 \text{ J/K}$

16. A liquid freezes into a solid ( $\Delta H = -1000 \text{ J/mole}$ ) at 200 K and 1 atm. (it's normal melting point).

(j) What is the value of  $\Delta G$  at 200 K?

(ii) What is the  $\Delta S$  value at 200 K?

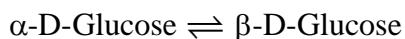
(iii) Will the freezing be spontaneous at 150 K and 1 atm? Calculate  $\Delta S_{\text{total}}$ :

(iv) What is the value of  $\Delta G$  at 250 K and 1 atm?

(And it is assumed that  $\Delta S$  and  $\Delta H$  do not depend on temperature)

#### Thermodynamic and equilibrium constant

17.  $\alpha$ -D Glucose undergoes mutarotation to  $\beta$ -D-Glucose in aqueous solution. If at 300K there is 60% conversion. Calculate  $\Delta G^\circ$  of the reaction. ( $\ln 2 = 0.7$ ,  $\ln 3 = 1.1$ )



- 18.** The equilibrium constant of the reaction  $2\text{C}_3\text{H}_6(\text{g}) \rightleftharpoons \text{C}_2\text{H}_4(\text{g}) + \text{C}_4\text{H}_8(\text{g})$  is found to fit the expression

$$\ln K = -1.04 - \frac{1088K}{T}$$

Calculate the standard reaction enthalpy and entropy at 400 K.

- 19.** For the reaction  $\text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$ ;  $\Delta H^\circ_{300} = -95 \text{ kJ/mole}$ ,  
 $\Delta S^\circ_{300} = -95.0 \text{ J/K mole}$ . Find the value of  $\ln k_p$  for this reaction at 300 K.

## EXERCISE (O-1)

- 1.** A reversible heat engine A (based on carnot cycle) absorbs heat from a reservoir at 1000 K and rejects heat to a reservoir at  $T_2$ . A second reversible engine B (based on carnot cycle) absorbs the same amount of heat as rejected by the engine A, from the reservoir at  $T_2$  and rejects energy to a reservoir at 360K.  
 If the efficiencies of engines A and B are the same then the temperature  $T_2$  is :-  
 (A) 680 K                    (B) 640 K                    (C) 600 K                    (D) 670 K

**2.** Which of the following is incorrect for a closed system in which an irreversible process is occurring?  
 (A)  $Q_{\text{sys}} + Q_{\text{surr}} = 0$                     (B)  $W_{\text{sys}} + W_{\text{surr}} = 0$                     (C)  $\Delta U_{\text{sys}} + \Delta U_{\text{surr}} = 0$                     (D)  $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$

**3.** For conversion C(graphite)  $\rightarrow$  C(Diamond), the  $\Delta S$  is :-  
 (A) Zero                    (B) Positive                    (C) Negative                    (D) Can not be predicted

**4.** Considering entropy (S) as a thermodynamic parameter, the criteria for the spontaneity of any process is :-  
 (A)  $\Delta S_{\text{system}} - \Delta S_{\text{surroundings}} > 0$                     (B)  $\Delta S_{\text{system}} > 0$  only  
 (C)  $\Delta S_{\text{surroundings}} > 0$  only                    (D)  $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$

**5.** If  $\Delta H_{\text{vapourisation}}$  of substance X( $\ell$ ) (molar mass = 30 g/mol) is 300 J/g at it's boiling point 300 K, then molar entropy change for reversible condensation process is :-  
 (A) 30 J/mol.K                    (B) -300 J/mol.K                    (C) -30 J/mol.K                    (D) -10 J/mol.K

**6.** For 1 mole of an ideal monoatomic gas on moving from one state to other, the temperature is doubled but pressure becomes  $\sqrt{2}$  times. Then entropy change in the process will be  
 $(R = 2 \text{ Cal/mol-K})$   
 (A)  $R \ln 2$                     (B)  $2R \ln 2$                     (C)  $3R \ln 2$                     (D)  $\frac{R}{2} \ln 2$

**7.** If  $S^0$  for  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$  are 0.13, 0.22 and  $0.19 \text{ kJ K}^{-1} \text{ mol}^{-1}$  respectively. The total change in standard entropy for the reaction,  $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$  is :  
 (A)  $30 \text{ JK}^{-1} \text{ mol}^{-1}$                     (B)  $40 \text{ JK}^{-1} \text{ mol}^{-1}$                     (C)  $60 \text{ JK}^{-1} \text{ mol}^{-1}$                     (D)  $20 \text{ JK}^{-1} \text{ mol}^{-1}$

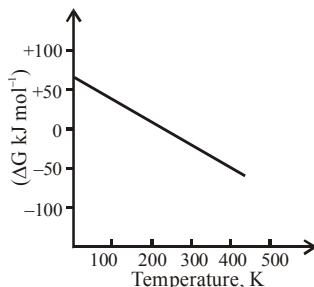
**8.** For a perfectly crystalline solid  $C_{\text{p,m}} = aT^3$ , where a is constant. If  $C_{\text{p,m}}$  is  $0.42 \text{ J/K-mol}$  at 10 K, molar entropy at 10 K is  
 (A)  $0.42 \text{ J/K-mol}$                     (B)  $0.14 \text{ J/K-mol}$                     (C)  $4.2 \text{ J/K-mol}$                     (D) Zero

**9.** Identify the correct statement regarding entropy.  
 (A) At absolute zero, the entropy of perfectly crystalline substance is taken to be +ve  
 (B) At absolute zero, entropy of perfectly crystalline substance is taken to be zero.  
 (C) At  $0^\circ\text{C}$ , the entropy of a perfectly crystalline substance is taken to be zero.  
 (D) At absolute zero, the entropy of all crystalline substances is taken to be zero.

10. In which of the following reactions do you expect to have a decrease in entropy?

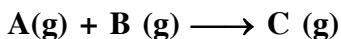


11. What can be concluded about the values of  $\Delta H$  and  $\Delta S$  from this graph?



- (A)  $\Delta H > 0, \Delta S > 0$    (B)  $\Delta H > 0, \Delta S < 0$    (C)  $\Delta H < 0, \Delta S > 0$    (D)  $\Delta H < 0, \Delta S < 0$

12. For the reaction at 300 K



$$\Delta U = -3.0 \text{ kcal} \quad ; \quad \Delta S = -10.0 \text{ cal/K}$$

value of  $\Delta G$  is ?

- (A) -600 cal      (B) -6600 cal      (C) -6000 cal      (D) none

13. For the reaction that taking place at certain temperature  $\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S(g)}$ , if equilibrium pressure is X bar, then  $\Delta_r G^\circ$  would be :-

- (A)  $-2 \text{ RT ln } X$       (B)  $-\text{RT} (\ln X - \ln 2)$   
 (C)  $-2 \text{ RT} (\ln X - \ln 2)$       (D)  $-0.5 \text{ RT} (\ln X - \ln 2)$

14. What is the free energy change ( $\Delta G$ ) when 1.0 mole of water at  $100^\circ\text{C}$  and 1 atm pressure is converted into steam at  $100^\circ\text{C}$  and 1 atm pressure ?

- (A) 80 cal      (B) 540 cal      (C) 620 cal      (D) zero

15. What is the free energy change ( $\Delta G$ ) when 1.0 mole of water at  $100^\circ\text{C}$  and 1 atm pressure is converted into steam at  $100^\circ\text{C}$  and 2 atm pressure ?

- (A) Zero      (B) 540 cal      (C) 517.13 cal      (D) 510 cal

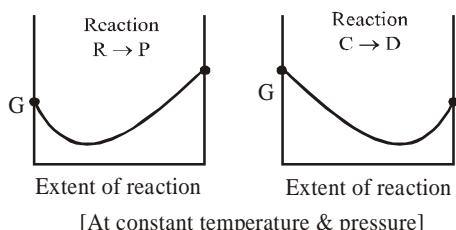
16. If  $\Delta G^\circ > 0$  for a gaseous reaction then :

- (A)  $K_p > 1$   
 (B)  $K_p < 1$   
 (C) The products predominate in the equilibrium mixture  
 (D) Mole of product must be less than mole of reactant

17. Heat liberated for an ideal gas undergoing reversible isothermal process is 1200 cal at 300 K.  
 What will be Gibb's free energy change for the process ?

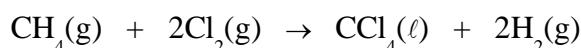
- (A) 1200 cal      (B) -1200 cal      (C) 400 cal      (D) -400 cal

18. With the help of given curves select the correct statement.



- (A) C will partially convert into D.      (B) R will not convert into P  
 (C) R will be completely converted into P.      (D) C will be completely converted in D.

19. Evaluate  $\Delta S^\circ$  for the reaction below at 25°C.



Given :

	$\text{CH}_4(\text{g})$	$\text{Cl}_2(\text{g})$	$\text{CCl}_4(\text{l})$	$\text{H}_2(\text{g})$
$\Delta H_f^\circ$ (kJ/mol)	-74.81	0	-135.4	0
$\Delta G_f^\circ$ (kJ/mol)	-50.75	0	-65.27	0
(A) -360 J/K	(B) -66.9 J/K	(C) -155 J/K	(D) -487 J/K	

20. All of the following have  $\Delta G_f^\circ = 0$ , except -

- (A)  $\text{O}_2(\text{g})$       (B)  $\text{Br}_2(\text{g})$       (C)  $\text{H}_2(\text{g})$       (D)  $\text{Ca}(\text{s})$

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 EXERCISE (O-2)
 

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## Single correct :

1. When two equal sized pieces of the same metal at different temperatures  $T_h$  (hot piece) and  $T_c$  (cold piece) are brought into thermal contact and isolated from its surrounding. The total change in entropy of system is given by ? Suppose heat capacity of each piece is C.

$$(A) C \ln \frac{T_c + T_h}{2T_c} \quad (B) C \ln \frac{T_2}{T_1} \quad (C) C \ln \frac{(T_c + T_h)^2}{2T_h \cdot T_c} \quad (D) C \ln \frac{(T_c + T_h)^2}{4T_h \cdot T_c}$$

2. The change in entropy of 2 moles of an ideal gas upon isothermal expansion at 243.6 K from 20 litre until the pressure becomes 1 atm, is :-

$$(A) 1.385 \text{ cal/K} \quad (B) -1.2 \text{ cal/K} \quad (C) 1.2 \text{ cal/K} \quad (D) 2.77 \text{ cal/K}$$

3. For the hypothetical reaction ,  $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ ,  $\Delta_r G$  and  $\Delta_r S$  are 20 kJ/mole and  $-20 \text{ JK}^{-1} \text{ mol}^{-1}$  respectively at 200 K. If  $\Delta_r C_p$  is  $20 \text{ JK}^{-1} \text{ mol}^{-1}$  then  $\Delta_r H$  at 400 K is :-

$$(A) 20 \text{ kJ/mole} \quad (B) 7.98 \text{ kJ/mole} \quad (C) 28 \text{ kJ/mole} \quad (D) 16 \text{ kJ/mole}$$

4. 1 mole of ice at  $0^\circ\text{C}$  is converted in steam at  $100^\circ\text{C}$  then calculated  $\Delta S$ , in the process. enthalpy of vapourisation and fusion are  $540 \text{ cal gm}^{-1}$  and  $80 \text{ cal gm}^{-1}$  respectively. Use the average heat capacity of liquid water as  $1 \text{ cal gm}^{-1}$  degree.

$$(A) 18 \left( \frac{80}{373} + \frac{540}{373} + \ln \frac{373}{273} \right) \quad (B) 18 \left( \frac{80}{273} + \frac{540}{373} + \ln \frac{373}{273} \right)$$

$$(C) 18 \left( \frac{80}{273} + \frac{540}{373} + \ln \frac{273}{373} \right) \quad (D) 18 \left( \frac{80}{273} + \frac{540}{373} + 100 \right)$$

5. The value of  $\Delta G_f^\circ$  of gaseous mercury is 38 kJ/mole. At what total external pressure mercury start boiling at  $27^\circ\text{C}$ . ( $R \cdot \ln 10 = 19 \text{ J/K-mol}$ )

$$(A) 10^{-6.67} \quad (B) 10^{-1.67} \quad (C) 10^{-13.33} \quad (D) 10^{-3.33}$$

6. If molar internal energy for a gas in a closed rigid vessel given by

$$U = a + bT + cT^2$$

find the entropy change (in J/K) at constant volume when 1 mol of gas are heated from 200 K to 400K. [Given :  $a = 20 \text{ J/mol}$ ;  $b = 10 \text{ J/K-mol}$ ;  $c = 2 \times 10^{-2} \text{ J/K}^2\text{-mol}$ ] ( $\ln 2 = 0.7$ )

$$(A) 15 \quad (B) 30 \quad (C) 60 \quad (D) 9.78$$

7. Statement -1 : When process  $H_2O(s) \rightleftharpoons H_2O(l)$ , reaches equilibrium in a closed system at constant temperature and pressure, Gibb's function of  $H_2O(s)$  &  $H_2O(l)$  become same.

Statement - 2 : For reversible phase change at constant temperature & pressure, change in Gibb's free energy will be zero.

(A) Statement-1 is true, statement- 2 is true and statement- 2 is correct explanation for statement-1.

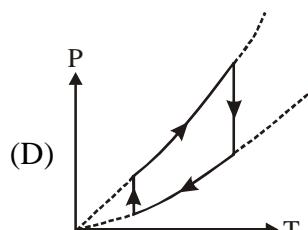
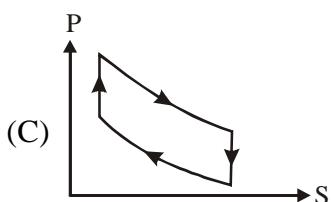
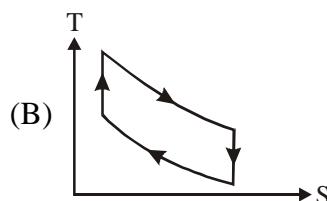
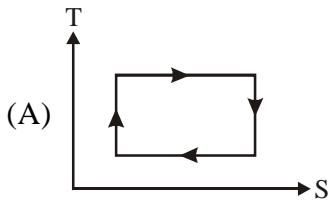
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false

(D) Statement-1 is false, statement-2 is true.

8. **Statement- 1 :** Absolute entropy of an ion in aqueous solution at 298 K may be negative.  
**Statement -2 :** Absolute entropy at 298 K of any substance can never be negative.
- (A) Statement-1 is true, statement- 2 is true and statement- 2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false  
(D) Statement-1 is false, statement-2 is true.
9. **Statement-1 :** Net heat absorbed in a cyclic process must be always equal to net work done by the system in the cyclic process.  
**Statement-2 :** Internal energy of system is a function of state.
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.
10. **Statement-1 :** Entropy change in reversible adiabatic expansion of an ideal gas is zero.  
**Statement-2 :** The increase in entropy due to volume increase just compensate the decrease in entropy due to fall in temperature.
- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.
- MORE THAN ONE MAY BE CORRECT :**
11. Select the correct statement(s).
- (A) In a reversible process,  $\Delta G$  is always zero in a closed system.  
(B) In a reversible process,  $\Delta S_{\text{univ}}$  is always zero in a closed system.  
(C) In a reversible process,  $\Delta S_{\text{sys}}$  is always zero in a closed system.  
(D) In a reversible process,  $\Delta S_{\text{sys}}$  is always zero in an isolated system.
12. Which of the following statement (s) is/ are correct ?
- (A) The quantities E, H and G have the same dimension  
(B) Gibb's free energy of 10 gm ice at 0° C and 1.0 atm is less than the Gibb's free energy of 10 gm water at 0° C and 1 atm.  
(C)  $\Delta S_{\text{sys}} = 0$  for every adiabatic process in a closed system.  
(D) For every reversible process in a closed system,  $\Delta S_{\text{sys}} = \frac{\Delta H_{\text{sys}}}{T}$

13. Which of the following represents the carnot cycle-



14. The normal boiling point of a liquid 'A' is 350 K.  $\Delta H_{\text{vap}}$  at normal boiling point is 35 kJ/mole.

Pick out the correct statement(s). (Assume  $\Delta H_{\text{vap}}$  to be independent of pressure).

(A)  $\Delta S_{\text{vaporisation}} > 100 \text{ J/K mole}$  at 350 K and 0.5 atm

(B)  $\Delta S_{\text{vaporisation}} < 100 \text{ J/K mole}$  at 350 K and 0.5 atm

(C)  $\Delta S_{\text{vaporisation}} < 100 \text{ J/K mole}$  at 350 K and 2 atm

(D)  $\Delta S_{\text{vaporisation}} = 100 \text{ J/K mole}$  at 350 K and 2 atm

15. In isothermal ideal gas compression :

(A)  $w$  is + ve      (B)  $\Delta H$  is zero      (C)  $\Delta S_{\text{gas}}$  is + ve      (D)  $\Delta G$  is + ve

16. Which of the following statement (s) is/are false :

(A)  $\Delta_r S$  for  $\frac{1}{2} \text{N}_2(\text{g}) \longrightarrow \text{N}(\text{g})$  is positive

(B)  $\Delta G_{\text{system}}$  is always zero for a reversible process in a closed system

(C)  $\Delta G^\circ$  for an ideal gas is a function of temperature and pressure

(D) Entropy of a closed system is always maximized at equilibrium

17. Which of the following processes are spontaneous ?

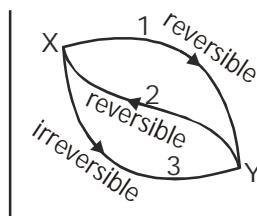
(A) Burning of fossil fuel

(B) Decomposition of water into  $\text{H}_2$  and  $\text{O}_2$  gas at room temperature

(C) Spreading of perfume in a room

(D) Diffusion of gas from high pressure to low pressure

18. Suppose a system make a transition from state X to state Y.



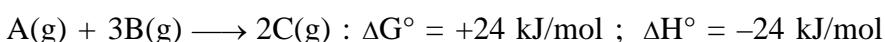
Given :  $\Delta S_{XY} = 10 \text{ J/K}$

- (A) The state Y is more disordered than state X.  
 (B)  $\Delta S_{XY}$  for path 1 and 3 is same.  
 (C)  $\Delta S_{YX} = -10 \text{ J/K}$   
 (D) The transition  $X \rightarrow Y$  must be spontaneous.
19. In which of the following processes involving an ideal gas, entropy of system remains constant?  
 (A) Reversible isothermal expansion      (B) Irreversible adiabatic expansion  
 (C) Reversible adiabatic expansion      (D) Free expansion
20. In which of the following process involving ideal gas, entropy of surrounding remains constant ?  
 (A) Reversible isobaric heating      (B) Reversible adiabatic expansion  
 (C) Irreversible adiabatic compression      (D) Free expansion

#### Paragraph for Question 21 to 22

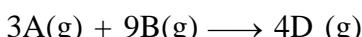
The reactions whose  $\Delta G^\circ$  are positive can not take place under standard state conditions. However another reaction whose  $\Delta G^\circ$  is negative can be coupled with the former type of reaction to give overall spontaneous process.

Consider the given reactions whose  $\Delta G^\circ$  at 300 K are provided to answer following questions.



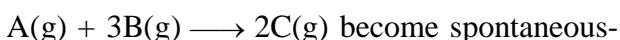
All data at 300 K temperature.

21. What is  $\Delta S^\circ$  at 300 K of reaction (in J/Kmole) :



- (A) -640      (B) -480      (C) +640      (D) -240

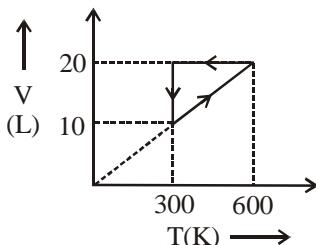
22. Assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  do not vary with temperature. At what minimum temperature reaction



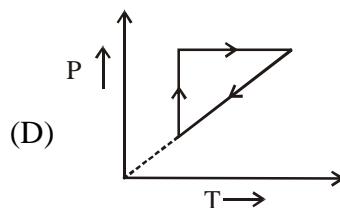
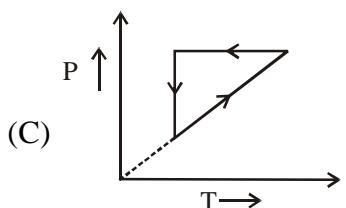
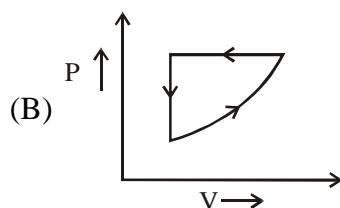
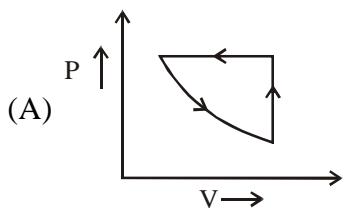
- become spontaneous-  
 (A) 6250 K      (B) 625 K      (C) 150 K      (D) 1000 K

### **Paragraph for Q.23 to Q.24**

One mol of ideal monoatomic gas undergo the state change as shown in the following graph  
 $(\ln 2 = 0.7)$



23. Correct graph for the process in paragraph is -



- 24.** Efficiency of the cycle will be -



## Table type question :

<b>Column-I</b>	<b>Column-II</b>	<b>Column-III</b>
(A) Combustion of butane gas at S.T.P.	(P) Entropy change of universe constant	(I) Low temperature conditions favourable
(B) Dissolution of sodium chloride in water at STP	(Q) Entropy change of system positive	(II) More spontaneous at high temperature
(C) Adding carbon dioxide gas to water to form carbonated water at high pressure and 298K	(R) Enthalpy change of system negative	(III) High pressure condition favourable
(D) Vaporisation of liquid water at 1 atm and 373K	(S) Entropy change of universe positive	(IV) More spontaneous at low pressure

- 25.** Which of following option is incorrect -

- (A) A – S – I              (B) B – Q – IV              (C) C – R – I              (D) D – P – IV

26. In column-I (A) if the reaction was carried at 400 K which option would be correct -  
 (A) A – P – II      (B) A – Q – III      (C) A – S – IV      (D) A – R – III
27. In column-I (D), if vaporisation is carried out at 15 atm which option is correct -  
 (A) D – P – IV      (B) D – S – II      (C) D – R – I      (D) D – Q – II

### MATCH THE LIST :

28. Match the Column :

#### Column-I

- (P)  $\text{H}_2\text{O} (\ell, 1 \text{ atm}, 363 \text{ K})$   
 $\rightarrow \text{H}_2\text{O} (\text{g}, 1 \text{ atm}, 363 \text{ K})$
- (Q)  $\text{H}_2\text{O} (\text{s}, 1 \text{ atm}, 373 \text{ K})$   
 $\rightarrow \text{H}_2\text{O} (\text{g}, 1 \text{ atm}, 373 \text{ K})$
- (R)  $\text{H}_2\text{O} (\ell, 1 \text{ atm}, 273 \text{ K})$   
 $\rightarrow \text{H}_2\text{O} (\text{s}, 1 \text{ atm}, 273 \text{ K})$
- (S)  $\text{H}_2\text{O} (\text{s}, 1 \text{ atm}, 353 \text{ K})$   
 $\rightarrow \text{H}_2\text{O} (\ell, 1 \text{ atm}, 353 \text{ K})$

#### Column-II

- (1)  $\Delta_r S > 0$
- (2)  $\Delta_r G > 0$
- (3)  $\Delta_r H < 0$
- (4)  $\Delta_r U > 0$

### Code:

P	Q	R	S
(A) 2	4	1	3
(B) 4	2	3	1
(C) 2	1	3	4
(D) 4	3	1	2

### MATCH THE COLUMN :

29. Column-I

- (A) Reversible adiabatic compression
- (B) Reversible vaporisation
- (C) Adiabatic free expansion of ideal gas  
in vacuum
- (D) Dissociation of  
 $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

#### Column-II

- (P)  $\Delta S_{\text{system}} > 0$
- (Q)  $\Delta S_{\text{system}} < 0$
- (R)  $\Delta S_{\text{surrounding}} < 0$
- (S)  $\Delta S_{\text{surrounding}} = 0$

30. Column-I

#### (Related to process)

- (A) Fusion at melting point
- (B) Vapourisation at boiling point
- (C) Condensation at triple point
- (D) Melting at normal boiling point

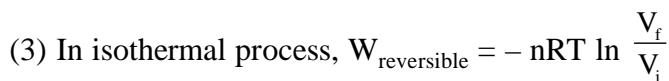
#### Column-II

- #### (Related to system)
- (P)  $\Delta G = 0$
- (Q)  $\Delta G < 0$
- (R)  $\Delta S > 0$
- (S)  $\Delta H \approx \Delta U$

## EXERCISE (JM)

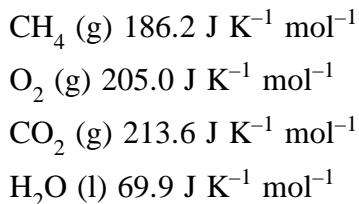
1. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of  $10 \text{ dm}^3$  to a volume of  $100 \text{ dm}^3$  at  $27^\circ\text{C}$  is :- [AIEEE-2011]  
 (1)  $32.3 \text{ J mol}^{-1} \text{ K}^{-1}$    (2)  $42.3 \text{ J mol}^{-1} \text{ K}^{-1}$    (3)  $38.3 \text{ J mol}^{-1} \text{ K}^{-1}$    (4)  $35.8 \text{ J mol}^{-1} \text{ K}^{-1}$
2. The incorrect expression among the following is :- [AIEEE-2012]  
 (1)  $K = e^{-\Delta G^\circ/RT}$

(2) 
$$\frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$$



(4) 
$$\ln K = \frac{\Delta H^\circ - T\Delta S^\circ}{RT}$$

3. The entropy ( $S^\circ$ ) of the following substances are : [JEE-MAINS-(online) 2014]



The entropy change ( $\Delta S^\circ$ ) for the reaction



- (1)  $-312.5 \text{ JK}^{-1} \text{ mol}^{-1}$    (2)  $-37.6 \text{ JK}^{-1} \text{ mol}^{-1}$   
 (3)  $-108.1 \text{ JK}^{-1} \text{ mol}^{-1}$    (4)  $-242.8 \text{ JK}^{-1} \text{ mol}^{-1}$

4. The molar heat capacity ( $C_p$ ) of  $\text{CD}_2\text{O}$  is 10 cals at 1000 K. The change in entropy associated with cooling of 32 g of  $\text{CD}_2\text{O}$  vapour from 1000 K to 100 K at constant pressure will be  
 (D = deuterium, at. mass = 2u) [JEE-MAINS-(online) 2014]

- (1)  $-23.03 \text{ cal deg}^{-1}$    (2)  $2.303 \text{ cal deg}^{-1}$    (3)  $23.03 \text{ cal deg}^{-1}$    (4)  $-2.303 \text{ cal deg}^{-1}$

5.  $\Delta_f G^\circ$  at 500 K for substance 'S' in liquid state and gaseous state are  $+100.7 \text{ kcal mol}^{-1}$  and  $+103 \text{ kcal mol}^{-1}$ , respectively. Vapour pressure of liquid 'S' at 500 K is approximately equal to :  
 ( $R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$ ) - [JEE-MAINS-(online) 2018]

- (1) 0.1 atm   (2) 10 atm   (3) 100 atm   (4) 1 atm

6. For which of the following processes,  $\Delta S$  is negative? [JEE-MAINS-(online) 2018]
- |   |  |
|---|--|
| (1) $\text{C(diamond)} \rightarrow \text{C(graphite)}$<br>(3) $\text{H}_2(\text{g}) \rightarrow 2\text{H(g)}$ | (2) $\text{N}_2(\text{g}, 273 \text{ K}) \rightarrow \text{N}_2(\text{g}, 300 \text{ K})$<br>(4) $\text{N}_2(\text{g}, 1 \text{ atm}) \rightarrow \text{N}_2(\text{g}, 5 \text{ atm})$ |
|---|--|

7. At 320 K, a gas  $A_2$  is 20% dissociated to A(g). The standard free energy change at 320 K and 1 atm in J mol<sup>-1</sup> is approximately : [JEE-MAINS-(online) 2018]

( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ;  $\ln 2 = 0.693$ ;  $\ln 3 = 1.098$ )



8. Two blocks of the same metal having same mass and at temperature  $T_1$  and  $T_2$ , respectively. are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy,  $\Delta S$ , for this process is : [JEE-MAINS-(online) 2019]

$$(1) \quad 2C_p \ln\left(\frac{T_1 + T_2}{4T_1 T_2}\right) \quad (2) \quad 2C_p \ln\left[\frac{(T_1 + T_2)^{\frac{1}{2}}}{T_1 T_2}\right] \quad (3) \quad C_p \ln\left[\frac{(T_1 + T_2)^2}{4T_1 T_2}\right] \quad (4) \quad 2C_p \ln\left[\frac{T_1 + T_2}{2T_1 T_2}\right]$$

9. For the chemical reaction  $X \rightleftharpoons{} Y$ , the standard reaction Gibbs energy depends on temperature T (in K) as : [JEE-MAINS-(online) 2019]

$$\Delta_r G^\circ \text{ (in kJ mol}^{-1}\text{)} = 120 - \frac{3}{8}T$$

The major component of the reaction mixture at T is :

- 10.** For the equilibrium, [JEE-MAINS-(online) 2019]

$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ , the value of  $\Delta G^\circ$  at 298 K is approximately :-

- (1) -80 kJ mol<sup>-1</sup>      (2) -100 kJ mol<sup>-1</sup>      (3) 100 kJ mol<sup>-1</sup>      (4) 80 kJ mol<sup>-1</sup>

11. The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by

$$\Delta_r G^\circ = A - BT$$

Where A and B are non-zero constants. Which of the following is TRUE about this reaction ?

- (1) Exothermic if  $B < 0$  [JEE-MAINS-(online) 2019]  
(2) Exothermic if  $A > 0$  and  $B < 0$   
(3) Endothermic if  $A < 0$  and  $B > 0$   
(4) Endothermic if  $A > 0$

12. The reaction,  $\text{MgO(s)} + \text{C(s)} \rightarrow \text{Mg(S)} + \text{CO(g)}$ , for which  $\Delta_rH^\circ = + 491.1 \text{ kJ mol}^{-1}$  and  $\Delta_rS^\circ = 198.0 \text{ JK}^{-1} \text{ mol}^{-1}$ , is not feasible at 298 K. Temperature above which reaction will be feasible is :- [JEE-MAINS-(online) 2019]

- (1) 1890.0 K      (2) 2480.3 K      (3) 2040.5 K      (4) 2380.5 K

13. A process has  $\Delta H = 200 \text{ Jmol}^{-1}$  and  $\Delta S = 40 \text{ JK}^{-1}\text{mol}^{-1}$ . Out of the values given below, choose the minimum temperature above which the process will be spontaneous :

[JEE-MAINS-(online) 2019]



14. The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is : [JEE-MAINS-(online) 2019]

[JEE-MAINS-(online) 2019]

(Specific heat of water liquid and water vapour are  $4.2 \text{ kJ K}^{-1} \text{ kg}^{-1}$  and  $2.0 \text{ kJ K}^{-1} \text{ kg}^{-1}$ ; heat of liquid fusion and vapourisation of water are  $344 \text{ kJ kg}^{-1}$  and  $2491 \text{ kJ kg}^{-1}$ , respectively).

( $\log 273 = 2.436$ ,  $\log 373 = 2.572$ ,  $\log 383 = 2.583$ )

- (1) 7.90 kJ kg<sup>-1</sup> K<sup>-1</sup>    (2) 2.64 kJ kg<sup>-1</sup> K<sup>-1</sup>    (3) 8.49 kJ kg<sup>-1</sup> K<sup>-1</sup>    (4) 9.26 kJ kg<sup>-1</sup> K<sup>-1</sup>

- 15.** The process with negative entropy change is : [JEE-MAINS-(online) 2019]

- ### (1) Dissolution of iodine in water

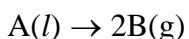
- ## (2) Synthesis of ammonia from N<sub>2</sub> and H<sub>2</sub>

- (3) Dissolution of  $\text{CaSO}_4(\text{s})$  to  $\text{CaO}(\text{s})$  and  $\text{SO}_3(\text{g})$

- #### (4) Sublimation of dry ice

- 16.** For the reaction ;

[JEE-MAINS-(online) 2020]

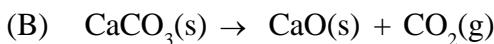
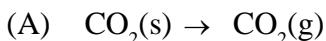


$\Delta U = 2.1 \text{ kcal}$ ,  $\Delta S = 20 \text{ cal K}^{-1}$  at 300 K

Hence  $\Delta G$  in kcal is \_\_\_\_\_.

## EXERCISE (JA)

1. Match the transformations in **Column-I** with appropriate option in **Column-II** [JEE 2011]

**Column-I**

**Column-II**

(p) phase transition

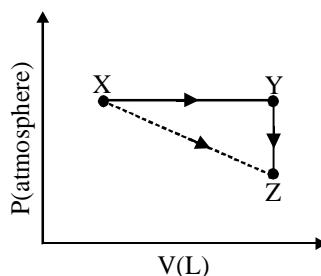
(q) allotropic change

(r)  $\Delta H$  is positive

(s)  $\Delta S$  is positive

(t)  $\Delta S$  is negative

2. For an ideal gas, consider only P-V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is (are) correct ? [take  $\Delta S$  as change in entropy and w as work done] [JEE 2012]



(A)  $\Delta S_{x \rightarrow z} = \Delta S_{x \rightarrow y} + \Delta S_{y \rightarrow z}$

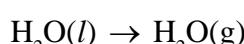
(B)  $W_{x \rightarrow z} = W_{x \rightarrow y} + W_{y \rightarrow z}$

(C)  $W_{x \rightarrow y \rightarrow z} = W_{x \rightarrow y}$

(D)  $\Delta S_{x \rightarrow y \rightarrow z} = \Delta S_{x \rightarrow y}$

3. For the process

[JEE 2014]



at  $T = 100^\circ\text{C}$  and 1 atmosphere pressure, the correct choice is

(A)  $\Delta S_{\text{system}} > 0$  and  $\Delta S_{\text{surroundings}} > 0$

(B)  $\Delta S_{\text{system}} > 0$  and  $\Delta S_{\text{surroundings}} < 0$

(C)  $\Delta S_{\text{system}} < 0$  and  $\Delta S_{\text{surroundings}} > 0$

(D)  $\Delta S_{\text{system}} < 0$  and  $\Delta S_{\text{surroundings}} < 0$

4. Match the thermodynamic processes given under Column-I with the expressions given under Column-II. [JEE 2015]

**Column - I**

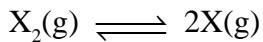
- (A) Freezing of water at 273 K and 1 atm
  - (B) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions
  - (C) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container
  - (D) Reversible heating of H<sub>2</sub>(g) at 1 atm from 300 K to 600 K followed by reversible cooling to 300 K at 1 atm
- (P)  $q = 0$
  - (Q)  $w = 0$
  - (R)  $\Delta S_{sys} < 0$
  - (S)  $\Delta U = 0$
  - (T)  $\Delta G = 0$

5. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings ( $\Delta S_{surr}$ ) in J K<sup>-1</sup> is - [JEE 2016]

- (1 L atm = 101.3 J)
- (A) 5.763
  - (B) 1.013
  - (C) -1.013
  - (D) -5.763

**Paragraph for Q.6 & Q.7**

Thermal decomposition of gaseous X<sub>2</sub> to gaseous X at 298 K takes place according to the following equation : [JEE 2016]



The standard reaction Gibbs energy,  $\Delta_r G^\circ$ , of this reaction is positive. At the start of the reaction, there is one mole of X<sub>2</sub> and no X. As the reaction proceeds, the number of moles of X formed is given by  $\beta$ . Thus,  $\beta_{equilibrium}$  is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally.

(Given : R = 0.083 L bar K<sup>-1</sup> mol<sup>-1</sup>)

6. The equilibrium constant K<sub>p</sub> for this reaction at 298 K, in terms of  $\beta_{equilibrium}$ , is

- (A)  $\frac{8\beta_{equilibrium}^2}{2-\beta_{equilibrium}}$
- (B)  $\frac{8\beta_{equilibrium}^2}{4-\beta_{equilibrium}^2}$
- (C)  $\frac{4\beta_{equilibrium}^2}{2-\beta_{equilibrium}}$
- (D)  $\frac{4\beta_{equilibrium}^2}{4-\beta_{equilibrium}^2}$

7. The **INCORRECT** statement among the following for this reaction is
- (A) Decrease in the total pressure will result in formation of more moles of gaseous X
- (B) At the start of the reaction, dissociation of gaseous  $X_2$  takes place spontaneously
- (C)  $\beta_{\text{equilibrium}} = 0.7$
- (D)  $K_c < 1$
8. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at  $T = 298 \text{ K}$  are

[JEE 2017]

$$\Delta_f G^\circ [\text{C(graphite)}] = 0 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ [\text{C(diamond)}] = 2.9 \text{ kJ mol}^{-1}$$

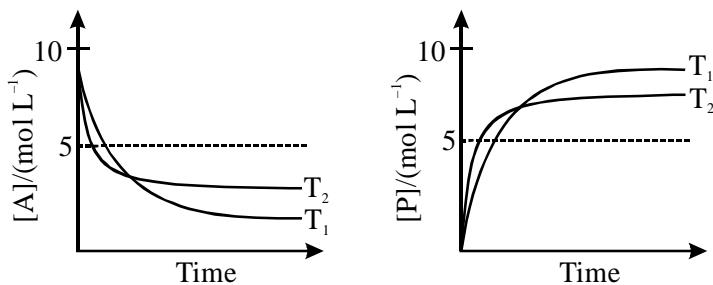
The standard state means that the pressure should be 1 bar , and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by  $2 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ . If C(graphite) is converted to C(diamond) isothermally at  $T = 298 \text{ K}$ , the pressure at which C(graphite) is in equilibrium with C(diamond), is

[Useful information :  $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ ;  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$ ;  $1 \text{ bar} = 10^5 \text{ Pa}$ ]

- (A) 14501 bar      (B) 29001 bar      (C) 58001 bar      (D) 1405 bar

9. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by
- (A) With increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive
- (B) With increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases
- (C) With increase in temperature, the value of K for exothermic reaction decreases because favourable change in entropy of the surroundings decreases
- (D) With increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system negative

10. For a reaction,  $A \rightleftharpoons P$ , the plots of  $[A]$  and  $[P]$  with time at temperatures  $T_1$  and  $T_2$  are given below. [JEE 2018]



If  $T_2 > T_1$ , the correct statement(s) is (are)

(Assume  $\Delta H^\theta$  and  $\Delta S^\theta$  are independent of temperature and ratio of  $\ln K$  at  $T_1$  to  $\ln K$  at  $T_2$  is

greater than  $\frac{T_2}{T_1}$ . Here H, S, G and K are enthalpy, entropy, Gibbs energy and equilibrium

constant, respectively.)

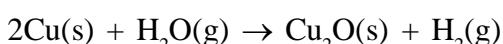
(A)  $\Delta H^\theta < 0, \Delta S^\theta < 0$

(B)  $\Delta G^\theta < 0, \Delta H^\theta > 0$

(C)  $\Delta G^\theta < 0, \Delta S^\theta < 0$

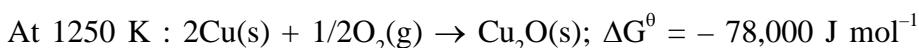
(D)  $\Delta G^\theta < 0, \Delta S^\theta > 0$

11. The surface of copper gets tarnished by the formation of copper oxide.  $N_2$  gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the  $N_2$  gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below

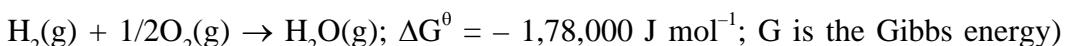


$p_{\text{H}_2}$  is the minimum partial pressure of  $\text{H}_2$  (in bar) needed to prevent the oxidation at 1250 K. The value of  $\ln(p_{\text{H}_2})$  is \_\_\_\_.

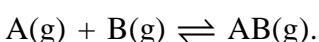
(Given : total pressure = 1 bar, R (universal gas constant) =  $8 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\ln(10) = 2.3$ . Cu(s) and  $\text{Cu}_2\text{O(s)}$  are mutually immiscible.



[JEE 2018]



12. Consider the following reversible reaction, [JEE 2018]



The activation energy of the backward reaction exceeds that of the forward reaction by  $2RT$  (in  $\text{J mol}^{-1}$ ). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of  $\Delta G^\theta$  (in  $\text{J mol}^{-1}$ ) for the reaction at 300 K is \_\_\_\_.

(Given ;  $\ln(2) = 0.7$ ,  $RT = 2500 \text{ J mol}^{-1}$  at 300 K and G is the Gibbs energy)

## ANSWER KEY

### EXERCISE (S-1)

1. Ans. **117°C, 52°C**
2. Ans. **197°C**
3. Ans. **(4)**
4. Ans. (i)  $\Delta S_{\text{syst}} = 28.72 \text{ J/K}$ ;  $\Delta S_{\text{surr}} = -28.72 \text{ J/K}$ ;  $\Delta S_{\text{total}} = 0$   
(ii)  $\Delta S_{\text{sys}} = 28.72 \text{ J/K}$ ;  $\Delta S_{\text{surr}} = -11.22 \text{ J/K}$ ,  $\Delta S_{\text{total}} = 17.50 \text{ J/K}$
5. Ans. (a) **-250 J/K** (b) **333.33 J/K** (c) **+83.33 J/K**. Process is spontaneous.
6. Ans. **(5)**
7. Ans **(200)**
8. Ans. **10.325**
9. Ans. (i) **-90.5** (ii) **-374.5** (iii) **-3.26** (all in  $\text{J mol}^{-1} \text{ K}^{-1}$ )
10. Ans. [A] - II ; [B] - II ; [C] - II ; [D] - II
11. Ans. **-3.7 kJ**
12. Ans **436 kJ**
13. Ans. **5.968 kcal**
14. Ans. **(-7)**
15. Ans. **(50)**
16. Ans.  
(i)  $\Delta G = 0$   
(ii)  $\Delta S = -5 \text{ J/mole.K}$   
(iii)  $\Delta S_{\text{total}} = +1.66 \text{ J/ mole. K}$ ; process in spontaneous  
(iv)  $\Delta S_{\text{total}} = - \text{J/mole. K} = \Delta G = +250 \text{ J/mole. K}$  ]
17. Ans. **-997.68 J/mol**
18. Ans.  $\Delta H^\circ = 9.04 \text{ kJ/mol}$ ;  $\Delta S^\circ = -8.64 \text{ J/mol}^{-1} \text{ K}^{-1}$
19. Ans. **26.7**

### EXERCISE (O-1)

- |             |              |              |             |
|-------------|--------------|--------------|-------------|
| 1. Ans.(C)  | 2. Ans.(D)   | 3. Ans.(C)   | 4. Ans.(D)  |
| 5. Ans.(C)  | 6. Ans.(B)   | 7. Ans.(A)   | 8. Ans.(B)  |
| 9. Ans.(B)  | 10. Ans.(B)  | 11. Ans.(A)  | 12. Ans.(A) |
| 13. Ans.(C) | 14. Ans.(D)  | 15. Ans.(C)  | 16. Ans.(B) |
| 17. Ans.(A) | 18. Ans. (A) | 19. Ans. (C) | 20. Ans.(B) |

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### EXERCISE (O-2)

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- |  |                 |                 |              |
|--|-----------------|-----------------|--------------|
| 1. Ans.(D)   | 2. Ans.(D)      | 3. Ans.(A)      | 4. Ans.(B)   |
| 5. Ans.(A)   | 6. Ans.(A)      | 7. Ans.(A)      | 8. Ans.(C)   |
| 9. Ans.(A)   | 10. Ans.(A)     | 11. Ans.(B,D)   | 12. Ans.(A)  |
| 13. Ans (A,C,D)  | 14. Ans.(A,C)   | 15. Ans.(A,B,D) |              |
| 16. Ans.(B,C,D)  | 17. Ans.(A,C,D) | 18. Ans.(A,B,C) | 19. Ans. (C) |
| 20. Ans.(B,C,D)  | 21. Ans.(A)     | 22. Ans.(C)     | 23. Ans.(D)  |
| 24. Ans.(D)  | 25. Ans.(B)     | 26. Ans.(C)     | 27. Ans.(D)  |
| 28. Ans.(C)  |                 |                 |              |
| 29. Ans. (A) - S ; (B) - P,R ; (C) - P, S (D) - P, R     |                 |                 |              |
| 30. Ans. (A) - P,S,R ; (B) - P,R ; (C) - P (D) - Q, R, S |                 |                 |              |

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### EXERCISE (JM)

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- |                          |             |             |             |
|--------------------------|-------------|-------------|-------------|
| 1. Ans.(3)               | 2. Ans.(4)  | 3. Ans.(4)  | 4. Ans.(1)  |
| 5. Ans.(1)               | 6. Ans.(4)  | 7. Ans.(2)  | 8. Ans.(3)  |
| 9. Ans.(1)               | 10. Ans.(4) | 11. Ans.(4) | 12. Ans.(2) |
| 13. Ans.(1)              | 14. Ans.(4) | 15. Ans.(2) |             |
| 16. Ans.(-2.70 to -2.71) |             |             |             |

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### EXERCISE (JA)

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- |   |               |                 |                |
|---|---------------|-----------------|----------------|
| 1. Ans.(A)→(p, r, s) ; (B)→(r, s) ; (C)→(t) ; (D)→(p, q, t)           |               |                 |                |
| 2. Ans.(A) , (C)  |               | 3. Ans. (B)     |                |
| 4. Ans. (A) → R, T ; (B) → P, Q, S ; (C) → P, Q, S ; (D) → P, Q, S, T |               |                 |                |
| 5. Ans. (C)   | 6. Ans.(B)    | 7. Ans.(C)      | 8. Ans.(A)     |
| 9. Ans.(BC)   | 10. Ans.(A,C) | 11. Ans.(-14.6) | 12. Ans.(8500) |

## CHAPTER 4

**CHEMICAL EQUILIBRIUM****Chapter Contents** 04

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## IMPORTANT NOTES

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## CHAPTER 4

## CHEMICAL EQUILIBRIUM

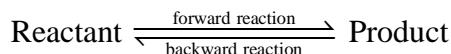
## 1. TYPES OF CHEMICAL REACTION :

The chemical reactions are classified on the basis of the extent to which they proceed, into the following two classes ;

- I. Reversible reactions :** Reaction in which entire amount of the reactants is not converted into products is termed as reversible reaction.

**(i) Characteristics of reversible reactions :**

- (a) These reactions can be started from either side.
- (b) These reactions are never complete.
- (c) This sign ( $\rightleftharpoons$ ) represents the reversibility of the reaction.



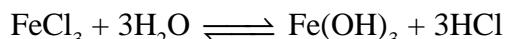
- (d) These reactions attain equilibrium and all the times, reaction mixture contains both reactant and product molecules. When reaction attains equilibrium the concentrations of reactants and product become constant (not same necessarily).

**(ii) Examples of reversible reactions :**

- (a) Neutralisation between an acid and a base either one or both are weak.



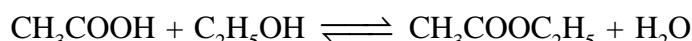
- (b) Salt hydrolysis



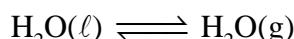
- (c) Thermal decomposition



- (d) Esterification



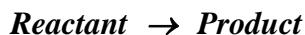
- (e) Evaporation of water in a closed vessel



- II. Irreversible reactions :** Reaction in which entire amount of the reactants is converted into products is termed as irreversible reaction.

**(i) Characteristics of irreversible reactions :**

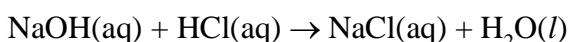
- (a) These reactions proceed only in one direction (forward direction)
- (b) These reactions can proceed to completion and reactant is completely converted into product.
- (c) The arrow ( $\rightarrow$ ) is placed between reactants and products



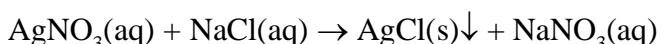
- (d) These reactions never attain equilibrium.

**(ii) Examples of irreversible reactions :**

- (a) Neutralisation between strong acid and strong base



- (b) Precipitation reactions

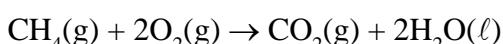


- (c) Thermal decomposition



However, if the above reaction is carried out in closed container, i.e., leaving no scope for gas to escape out, the reaction shows reversible nature.

- (d) Combustion reactions

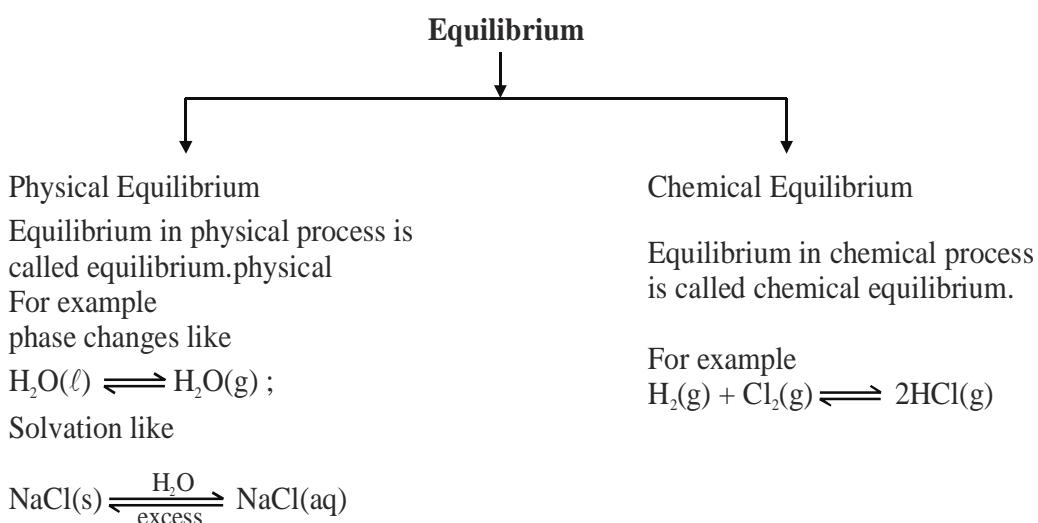


## 2. EQUILIBRIUM :

In the state of equilibrium, system loses its tendency for a change and all the properties associated with system like pressure, temperature, composition, etc become constant and do not vary without external stimulation. On the basis of nature of process in which state of equilibrium is attained, it may be of two types :

(A) Physical equilibrium

(B) Chemical equilibrium

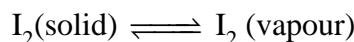


### 2.1 Physical equilibrium :

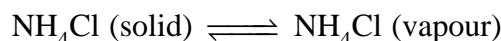
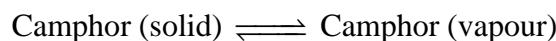
If in a system only physical state (phase) is changed and equilibrium is established, (i.e. there is no chemical change), the equilibrium is called **physical equilibrium**. Ex : Fusion of ice, evaporation of water, dissolution of salts , absorption of gases in liquid, etc.

Following are the types of common physical equilibria :

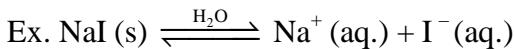
- (i) **Liquid-Vapour equilibria** : In a closed vessel, the vapours above the liquid are in equilibrium at given temperature.  
Ex.  $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}(g)$
- (ii) **Solid-Liquid equilibria** : This equilibrium can be established only at melting point of solid. At this stage solid and liquid phases exist simultaneously in equilibrium.  
Ex.  $\text{H}_2\text{O}(s) \rightleftharpoons \text{H}_2\text{O}(\ell)$  at melting point
- (iii) **Solid-Vapour equilibria** : Let us now consider the systems where solids sublime to vapour phase. If we place solid iodine in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of colour increases with time. After certain time the intensity of colour becomes constant and at this stage equilibrium is attained. Hence solid iodine sublimes to give iodine vapour and the iodine vapour condenses to give solid iodine. The equilibrium can be represented as,



Other examples showing this kind of equilibrium are,



- (iv) **(Solute-Solvent) Saturated solution equilibria** : If the rate of dissolution of solids in liquid is equal to the rate of crystallization of solid from solution i.e. solution is saturated with respect to solid then saturated solution equilibria established, provided temperature is constant.



- (v) **(Gas + Solvent) Saturated solution equilibria** : In such equilibriums, solvents is saturated with respect to gas i.e. rate of entering of gas molecules in solvent is equal to rate of escaping of gas molecules from solvents. Above phenomenon can be observed in closed container at definite temperature.

Ex : Dissolved  $\text{CO}_2$  in cold drinks, dissolved  $\text{O}_2$  in water, etc.

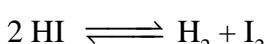
- Note:**
- (i) The solubilities of gases in liquid is a function of pressure of gas over liquid.
  - (ii) **Henry's law** can be applied on such system, that states, the mass of gas dissolved in a given mass of solvent at any temperature is proportional to the pressure of the gas above the solvent.
  - (iii) One should not compare it with liquid vapour equilibria.

## 2.2 Chemical equilibrium :

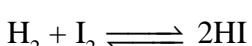
Analogous to the physical systems, chemical reactions also attain a state of equilibrium. These reactions can occur both in forward and backward directions. When the rates of the forward and reverse reactions become equal, the concentrations of the reactants and the products become constant. This is the stage of chemical equilibrium. This equilibrium consists of a forward reaction in which the reactants give product(s) and reverse reaction in which product(s) gives the original reactants.

### 2.2.1 Characteristics of Chemical equilibrium :

- (i) It is attained in reversible chemical reactions only.
- (ii) Equilibrium is possible only in closed system.
- (iii) In this state, all the measurable properties of the system like temperature, concentration, colour, density etc. don't undergo any change with time, i.e. constant.
- (iv) Equilibrium is dynamic in nature i.e., at microscopic level reaction is not stopped. It appears that no change is occurring but both the opposing reactions are proceeding at the same rate. So there is no net change. Thus equilibrium is not static in nature.
- (v) Chemical equilibrium can be approached from both sides



or

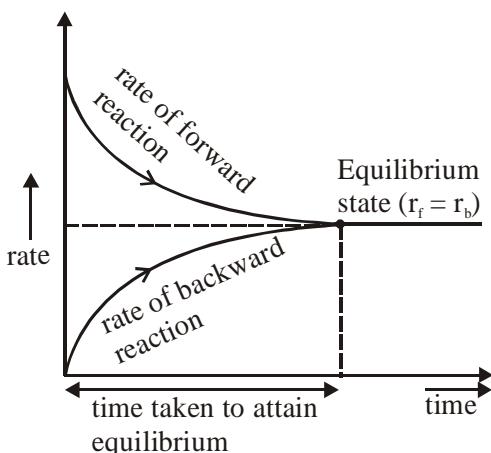


At equilibrium, reactants and products have fixed composition and this is independent of the fact whether the reaction starts with the reactant or with the product.

- (vi) Equilibrium is not affected by the presence of catalyst. The catalyst only helps in attaining equilibrium rapidly.
- (vii) At equilibrium, opposing reactions (i.e., forward and backward) proceed with equal rates.  
i.e., rate of forward reaction = rate of backward reaction.

- Note:**
- (i) Whenever question doesn't ask about direction, then we take forward direction only.
  - (ii) In a reversible reaction if forward reaction is exothermic then the backward reaction will be endothermic and vice versa.

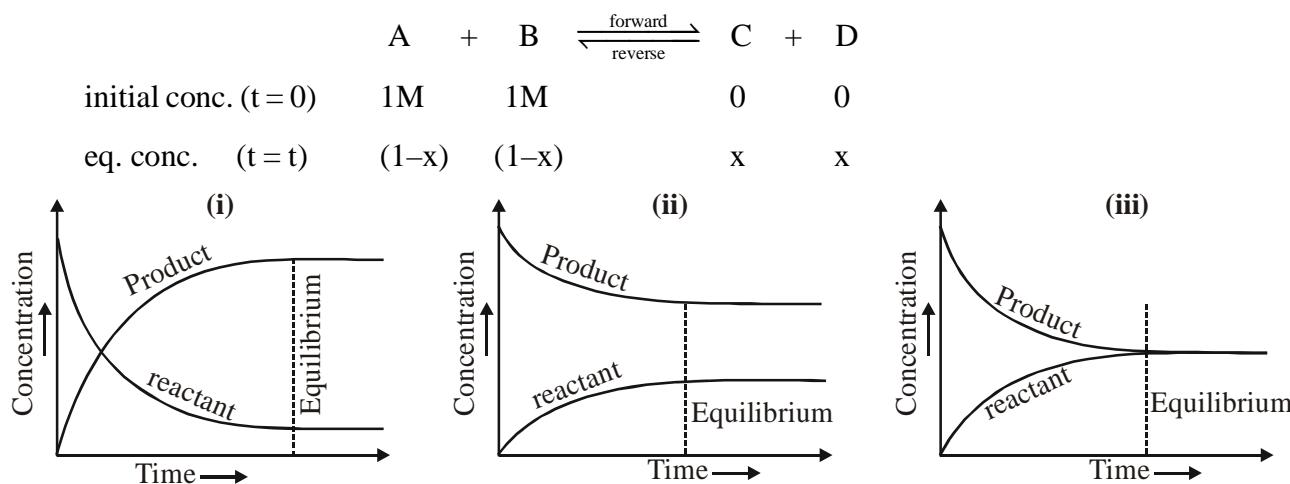
### 2.2.2 Variation of Rate v/s Time :



From above graph, initially rate of forward reaction decreases and the rate of backward reaction increases. At certain stage, rate of forward reaction becomes equal to rate of backward reaction called **equilibrium state**.

### 2.2.3 Variation of Concentration v/s Time :

Let us consider a reversible reaction,



In the begining (at time  $t = 0$ ), the container has only the reacting molecules A and B while the products C and D are nil. With the passage of time, the reactants A and B will be used up or consumed to form the products , C and D. It means that the concentration or molar concentration of the reactants will decrease while those of the products will increase. A stage will be ultimately reached when their concentration becomes constant i.e., their will be no further change in concentration of either of the reactants A and B or of the products C and D. This represents a state of equilibrium.

**Note:** At equilibrium, the concentration of reactant and product will be constant. It means, it may be different as above graph (i) & (ii) or same as above graph (iii) but the rate of forward reaction and the backward reaction will be always same.

#### Ex.1 Chemical equilibrium is a condition :

- (A) where all species have same concentration
- (B) where all species have constant concentration with respect to time.
- (C) where all species have unit concentration
- (D) all of above

**Sol. (B)**

#### Ex.2 Example of physical equilibria, is :

- (A)  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
- (B)  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- (C)  $\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\ell)$
- (D)  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

**Sol. (C)**

Physical equilibria does not include any chemical change.

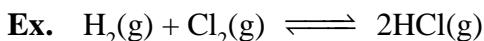
### 3. TYPES OF CHEMICAL EQUILIBRIUM :

I. Homogeneous equilibrium

II. Heterogeneous equilibrium

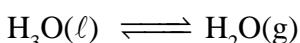
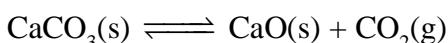
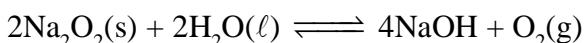
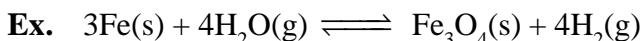
#### I. Homogeneous equilibrium :

It is the equilibrium when all reactants and products are in same phase.



#### II. Heterogeneous equilibrium :

It is the equilibrium the reactants and the products are present in different phases. All physical equilibria are heterogeneous.



### 4. ACTIVE MASS :

The mass of a substance which effect the rate of reaction i.e. mass of substance which take a part actively in a reaction. Active mass depends on state of substance.

(i) **Solution state :** In this state, active mass of a substance is represented by concentration (molarity). Active mass is usually expressed in concentration by enclosing the symbol of the reactant in square bracket [ ].

$$\text{Active mass} = \frac{\text{moles}}{\text{Volume in litres}} = \frac{\text{grams(w)}}{\text{mol.wt.}(M_w) \times \text{Volume in litres(V)}} = \frac{w \times 1000}{M_w \times V(\text{mL})}$$

(ii) **Gaseous state :** In this state, active mass of a substance may be represented as concentration (molarity) or partial pressure.

(iii) **Pure solid & pure liquid :** In this state, active mass of solids , pure liquids and solvents in large excess is a constant quantity because there is no change in activity with the change in quantity or volume of system.

$$\text{Molar concentration (M)} = \frac{w}{M \times V} = \frac{d}{M} = \frac{\text{density of the substance}}{\text{molar mass of the substance}} = \text{constant}$$

as density of pure solids and liquids is constant and molar mass is also constant.

## 5. LAW OF MASS ACTION AND LAW OF EQUILIBRIUM CONSTANT :

The law of mass action is given by **Guldberg** and **Waage**. According to it, "the rate of a chemical reaction at a particular temperature is proportional to the product of active masses of reactants raised to the powers equal to their stoichiometric coefficients".

Consider a reversible reaction :  $m_1 A + m_2 B \rightleftharpoons n_1 C + n_2 D$

According to law of mass action

$$\text{rate of forward reaction } (r_f) \propto (a_A)^{m_1} (a_B)^{m_2}$$

$$r_f = k_f (a_A)^{m_1} (a_B)^{m_2}$$

$$\text{rate of backward reaction } (r_b) \propto (a_C)^{n_1} (a_D)^{n_2}$$

$$r_b = k_b (a_C)^{n_1} (a_D)^{n_2}$$

At equilibrium  $r_f = r_b$

$$k_f (a_A)^{m_1} (a_B)^{m_2} = k_b (a_C)^{n_1} (a_D)^{n_2}$$

$$K_{eq} = \frac{k_f}{k_b} = \frac{(a_C)^{n_1} (a_D)^{n_2}}{(a_A)^{m_1} (a_B)^{m_2}}$$

where,  $K_{eq}$  = equilibrium constant

$k_f$  = forward rate (velocity) constant

$k_b$  = backward rate (velocity) constant

$a_A$ ,  $a_B$  = active mass of reactant A & B

$a_C$ ,  $a_D$  = active mass of product C & D

$m_1$ ,  $m_2$  = stoichiometry coefficient of reactant A & B

$n_1$ ,  $n_2$  = stoichiometry coefficient of product C & D

At a given temperature, the product of molar concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of molar concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the **Equilibrium Law or Law of Chemical Equilibrium**.

### 5.1 Types of equilibrium constant ( $K_{eq}$ ) :

- (i) **Equilibrium constant in terms of concentration ( $K_C$ )** :  $K_C$  is defined for reactions in gas phase & solution phase. Molar concentrations are used to express amounts.
- (ii) **Equilibrium constant in terms of partial pressure ( $K_P$ )** :  $K_P$  is defined for reactions in gas phase. Partial pressures are used to express amounts.

**Ex.** Consider a reversible reaction in gas phase :  $m_1 A + m_2 B \rightleftharpoons n_1 C + n_2 D$

$$K_C = \frac{[C]^{n_1} [D]^{n_2}}{[A]^{m_1} [B]^{m_2}}$$

$$K_P = \frac{(P_C)^{n_1} (P_D)^{n_2}}{(P_A)^{m_1} (P_B)^{m_2}}$$

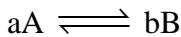
here,

$[A]$ ,  $[B]$ ,  $[C]$ ,  $[D]$  = Molar concentration of A, B, C, D respectively at equilibrium .

$(P_A)$ ,  $(P_B)$ ,  $(P_C)$ ,  $(P_D)$  = partial pressure of A, B, C, D respectively at equilibrium .

## 5.2 Units of equilibrium constant :

**5.2.1** The value of equilibrium constant  $K_c$  can be calculated by substituting the concentration terms in mol/L or M and for  $K_p$  partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same. For general reactions,



$$(i) \quad K_c = \frac{[B]^b}{[A]^a}$$

$$\text{unit of } K_c = \left( \frac{\text{mol}}{\text{L}} \right)^{b-a} = [M]^{b-a} = M^{\Delta n_g}$$

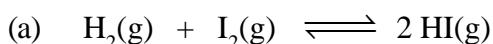
here,  $\Delta n_g = b - a$  = moles of (Product – Reactant)

$$(ii) \quad K_p = \frac{(P_B)^b}{(P_A)^a}$$

$$\text{unit of } K_p = (\text{atm})^{b-a} = (\text{atm})^{\Delta n_g} \text{ or } (\text{Pa})^{\Delta n_g} \text{ or } (\text{bar})^{\Delta n_g}$$

here,  $\Delta n_g = b - a$  = moles of (Product – Reactant)

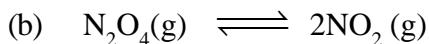
**Ex.3** Write down the expression and unit for following reaction :



$$K_c = \frac{[HI]^2}{[H_2][I_2]} \quad \left( \frac{\text{mol}}{\text{L}} \right)^0$$

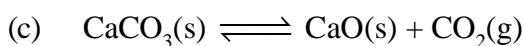
$$K_p = \frac{P_{HI}^2}{P_{H_2} P_{I_2}} \quad (\text{atm})^0$$

∴  $K_c$  and  $K_p$  have no unit.



$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \quad \left( \frac{\text{mol}}{\text{L}} \right)^1$$

$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}} \quad (\text{atm})^1$$



$$K_c = [CO_2] \quad \left( \frac{\text{mol}}{\text{L}} \right)^1$$

$$K_p = P_{CO_2} \quad (\text{atm})^1$$

**5.2.2** Equilibrium constants is expressed in standard state that is called standard state equilibrium constant or thermodynamic equilibrium constant, which is dimensionless quantity. It is denoted by  $K_c^0$  and  $K_p^0$ . For a pure gas, the standard state is 1 bar. Therefore a pressure of 4 bar in standard state can be expressed as  $4 \text{ bar}/1 \text{ bar} = 4$ , which is a dimensionless number and concentration of

3 M solution in standard state can be expressed as  $\frac{3\text{M}}{1\text{M}} = 3$ , which is a dimensionless number.

The numerical value of equilibrium constant depends on the standard state chosen. Thus, in this system both  $K_c^0$  and  $K_p^0$  are dimensionless quantities but have different numerical values due to different standard states. For example,



$$K_C = [C] \quad (\text{mol/L})$$

$$\text{but } K_C^0 \text{ is a dimensionless quantity so } K_C^0 = \frac{[C]}{1\text{M}}$$

$$K_p = P_C \quad (\text{bar})^1$$

$$\text{but } K_p^0 \text{ is a dimensionless quantity so } K_p^0 = \frac{P_C}{1\text{ bar}}$$

### 5.3 Relation between $K_p$ & $K_c$ :

For the reaction ,  $aA + bB \rightleftharpoons cC + dD$

we can write

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \dots\dots\dots \text{(i)}$$

Assuming the gaseous components to behave ideally ,

$$P_i V_i = n_i RT$$

$$P_i = (n_i/V_i) RT = C_i RT = [i] RT$$

where [i] is the molar concentration of the species 'i'.

$$P_A = [A]RT, P_B = [B]RT, P_C = [C]RT, P_D = [D]RT$$

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} = \frac{([C]RT)^c \cdot ([D]RT)^d}{([A]RT)^a \cdot ([B]RT)^b} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} \times (RT)^{(c+d)-(a+b)}$$

from eq..(i)

$$K_p = K_C (RT)^{(c+d)-(a+b)}$$

$$K_p = K_C (RT)^{\Delta n_g}$$

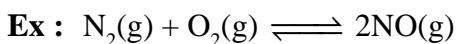
$\Delta n_g = (\text{Number of moles of gaseous products}) - (\text{Number of moles of gaseous reactants})$ .

$$\Delta n_g = (c + d) - (a + b)$$

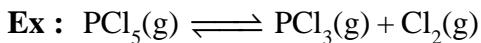
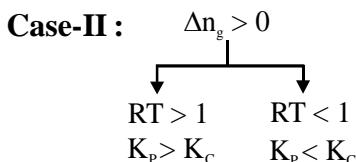
The units of  $K_p$  &  $K_c$  are not fixed and depend on stoichiometry of the reaction. In case the number of moles of the reactant & that of the product are same  $K_p$  &  $K_c$  do not have any unit.

### 5.4 Different cases for $K_p = K_c (RT)^{\Delta n_g}$ :

**Case-I :** If  $\Delta n_g = 0$  then  $K_p = K_c$



$K_p$  = unit less ;  $K_c$  = unit less ;

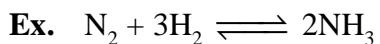
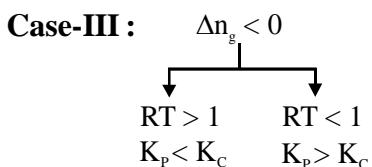


$$\Delta n_g = 2 - 1 = 1 \text{ then } K_p = K_c (RT)^1$$

if  $RT > 1$  then  $K_p > K_c$

if  $RT < 1$  then  $K_p < K_c$

Unit :  $K_p = \text{atm}^1$  ;  $K_c = \text{conc.}^1$



$$\Delta n_g = 2 - 4 = -2 \text{ then } K_p = K_c (RT)^{-2}$$

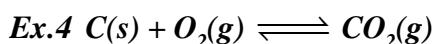
if  $RT > 1$  then  $K_p < K_c$

if  $RT < 1$  then  $K_p > K_c$

$K_p = \text{atm}^{-2}$  ;  $K_c = \text{conc.}^{-2}$

**Case-IV :** If  $T = \frac{1}{R} = \frac{1}{0.821} \approx 12.2\text{K}$

$[K_p = K_c ; \text{for any value of } \Delta n_g]$



**Mole of O<sub>2</sub> and CO<sub>2</sub> are 5 mole and 10 mole at equilibrium respectively, then find K<sub>p</sub> & K<sub>c</sub> for above reaction.**

**Sol.** Partial pressure = Mole fraction × Total pressure

$$P_{\text{CO}_2} = X_{\text{CO}_2} \cdot P_T = \frac{n_{\text{CO}_2}}{n_T} \times P_T = \frac{10}{15} \times P_T$$

$$P_{\text{O}_2} = X_{\text{O}_2} \cdot P_T = \frac{n_{\text{O}_2}}{n_T} \times P_T = \frac{5}{15} \times P_T$$

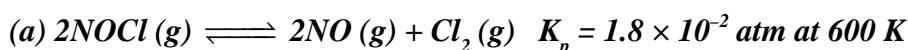
$$K_p = \frac{P_{\text{CO}_2}}{P_{\text{O}_2}}$$

$$K_p = \frac{\frac{10}{15} \times P_T}{\frac{5}{15} \times P_T} = 2$$

$$\therefore K_p = K_c (RT)^{\Delta n_g}$$

$$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{2}{(RT)^0} = 2$$

**Ex.5 Find the values of K<sub>c</sub> for each of the following equilibria from the value of K<sub>p</sub>.**

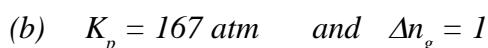


**Sol.** (a)  $2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g)$

$$K_p = 1.8 \times 10^{-2} \text{ atm} \quad \text{and} \quad \Delta n_g = 3 - 2 = 1$$

$$K_p = K_c (RT)^{\Delta n_g} = K_c \times (RT)$$

$$\therefore K_c = \frac{K_p}{RT} = \frac{1.8 \times 10^{-2}}{0.0821 \times 600} = 3.65 \times 10^{-4} \text{ M}$$



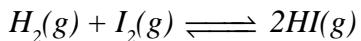
$$K_p = K_c (RT)^{\Delta n_g} = K_c \times (RT)$$

$$\therefore K_c = \frac{K_p}{RT} = \frac{167}{0.0821 \times 1173} = 1.734 \text{ M}$$

**Ex.6** In the reaction,  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$  the concentration of  $H_2$ ,  $I_2$  and  $HI$  at equilibrium are 10.0, 6.0 and 28 moles per litre respectively. What will be the equilibrium constant?



Sol.(B)



*Applying law of mass action,*

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

Given [H<sub>3</sub>] = 10 mol L<sup>-1</sup>

$$[I_2] = 6.0 \text{ mol L}^{-1}$$

$$[HI] = 28.0 \text{ mol L}^{-1}$$

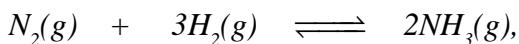
$$So, \quad K_c = \frac{(28.0)^2}{(10) \times (6.0)} = 13.066$$

**Ex.7 For a gas phase reaction at equilibrium,**

$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$ , the partial pressures of  $H_2$  and  $N_2$  are 0.4 and 0.8 atmosphere respectively. The total pressure of the entire system is 2.4 atmosphere. What will be the value of  $K_p$  if all the pressures are given in atmosphere ?

- (A)  $32 \text{ atm}^{-2}$       (B)  $20 \text{ atm}^{-2}$       (C)  $28.125 \text{ atm}^{-2}$       (D)  $80 \text{ atm}^{-2}$

Sol.(C)



## *Partial pressures at equilibrium*

$$0.8 \qquad \qquad 0.4 \qquad \qquad [2.4 - (0.8 + 0.4) = 1.2]$$

*Applying law of mass action,*

$$K_p = \frac{[\text{P}_{\text{NH}_3}]^2}{[\text{P}_{\text{N}_2}][\text{P}_{\text{H}_2}]^3} = \frac{1.2 \times 1.2}{0.8 \times 0.4 \times 0.4 \times 0.4} \Rightarrow K_p = 28.125 \text{ atm}^{-2}$$

**Ex.8.**  $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ ; *Correct option for reaction is/are :*

- (a)  $K_p = K_c$
  - (b)  $K_p > K_c$
  - (c)  $K_p < K_c$
  - (d) any of these, depending on temperature.

## Sol.(D)

If (d) option is not given, then the answer is (b) because  $\frac{1}{R} \approx 12.2\text{K}$  which is very low relative to room temperature.

**Ex.9.** For which of the following reactions,  $K_p > K_c$  at  $25^\circ\text{C}$  ( $298\text{K}$ )

- $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
- $\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \rightleftharpoons 2\text{HI}(\text{g})$
- $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_2(\text{g})$
- $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
- $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

**Sol.** (b, d, e)

**Ex.10.** For a gaseous reaction  $K_p = 0.4 \text{ atm}^3$  at  $27^\circ\text{C}$ . Calculate  $K_c$ .

$$\text{Sol. } K_p = K_c (RT)^{(3)}$$

$$0.4 = K_c (0.0821 \times 300)^3$$

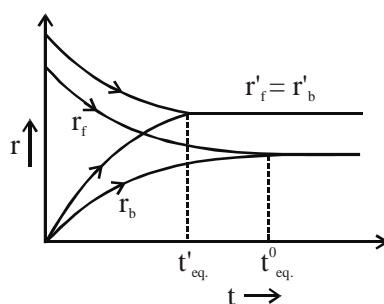
$$K_c = 2.6 \times 7 \times 10^{-8} \text{ M}^3$$

## 6. Characteristics of equilibrium constant :

- The expression for equilibrium constant K is applicable only when concentrations of the reactants and products have attained their equilibrium values and do not change with time.
- The value of equilibrium constant is independent of initial concentration of the reactants and product.
- Equilibrium constant has one unique value for a particular reaction represented by a balanced equation at a given temperature.
- Value of equilibrium constant is not affected by catalyst. Catalyst simply helps in attaining equilibrium earlier. The relative increase in the rate of forward as well as backward reaction remains same on using the catalyst.

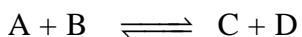
$$K_{\text{eq. uncatalyst}} = \frac{K_f}{K_b}$$

$$K_{\text{eq. catalyst}} = \frac{K_f \times x}{K_b \times x} = \frac{K_f}{K_b} = K_{\text{eq. (uncatalyst)}}$$



## 6.1 Factor affecting the equilibrium constant :

### (A) Mode of representation of the reaction :



The equilibrium constant for the reaction

$$K_c = \frac{[C][D]}{[A][B]}$$

If the reaction is reversed



$$\text{then, } K'_c = \frac{[A][B]}{[C][D]}$$

The two equilibrium constant related as ;  $K_c = \frac{1}{K'_c}$

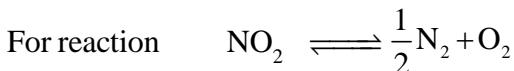
*If the reaction is reversed, the value of the equilibrium constant is inverted.*

### (B) Stoichiometry of the reaction :

When a reversible reaction can be written with the help of two or more stoichiometric equation, the value of equilibrium constant will be numerically different.

- (i) For reaction,  $2\text{NO}_2 \rightleftharpoons \text{N}_2 + 2\text{O}_2$

$$K_c = \frac{[\text{N}_2][\text{O}_2]^2}{[\text{NO}_2]^2}$$

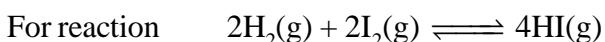


$$K'_c = \frac{[\text{N}_2]^{\frac{1}{2}}[\text{O}_2]}{[\text{NO}_2]}$$

The two constants are related as  $K'_c = \sqrt{K_c}$

- (ii) For reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

$$K_p = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} \cdot P_{\text{I}_2}}$$



$$K'_p = \frac{P_{\text{HI}}^4}{P_{\text{H}_2}^2 \cdot P_{\text{I}_2}^2}$$

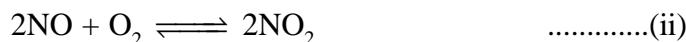
The two constants are related as  $K'_p = K_p^2$ .

In general,  $n\text{H}_2(\text{g}) + n\text{I}_2(\text{g}) \rightleftharpoons 2n\text{HI}(\text{g})$

$$K' = K^n$$

*When the coefficient of a balanced equation are multiplied by a common factor 'n', the equilibrium constant must be raised to the respective factor,  $K_{\text{eq}}^n$ .*

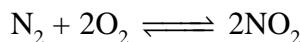
**(C) Addition the reaction :**



For the 1<sup>st</sup> step,  $K_1 = \frac{[NO]^2}{[N_2][O_2]}$

For the 2<sup>nd</sup> step,  $K_2 = \frac{[NO_2]^2}{[NO]^2 [O_2]}$

from eq. (i) + (ii)



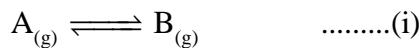
For this reaction,  $K = \frac{[NO_2]^2}{[N_2][O_2]^2}$

the above reaction is related as

$$\therefore K_1 \times K_2 = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K$$

*If there is addition of two reaction then the equilibrium constant is multiplied.*

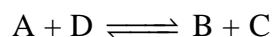
**(D) Subtract the reaction :**



For the (i) step,  $K_1 = \frac{[B]}{[A]}$

For the (ii) step,  $K_2 = \frac{[D]}{[C]}$

from eq. (i)–(ii)



For this reaction,  $K = \frac{[B][C]}{[A][D]}$

the above reaction is related as ,  $K = \frac{K_1}{K_2} = \frac{[B]}{[A]} \times \frac{[C]}{[D]} = K$

*If we subtract of two reaction, then the equilibrium constant will be divided.*

**Ex.11** What should be the equilibrium constant for the reaction  $\text{HI} \rightleftharpoons \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{I}_2$  if the equilibrium constant for the reaction  $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$  at  $444^\circ\text{C}$  is 64?



**Sol.**  $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$      $\text{HI} \rightleftharpoons \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{I}_2$

$$K_1 = \frac{[HI]^2}{[H_2][I_2]} \quad K_2 = \frac{[H_2]^{1/2}[I_2]^{1/2}}{[HI]}$$

$$\text{Therefore, } K_2 = \frac{1}{\sqrt{K_1}} = \frac{1}{\sqrt{64}} = \frac{1}{8} = 0.12$$

**(E) Equilibrium constant depends upon the temperature.**

The equilibrium constant of a particularly balanced reaction depends only on temperature. It is independent from all other factor like amount of components, concentration, pressure, volume etc.

$$K_{eq.} = \frac{K_f}{K_b}$$

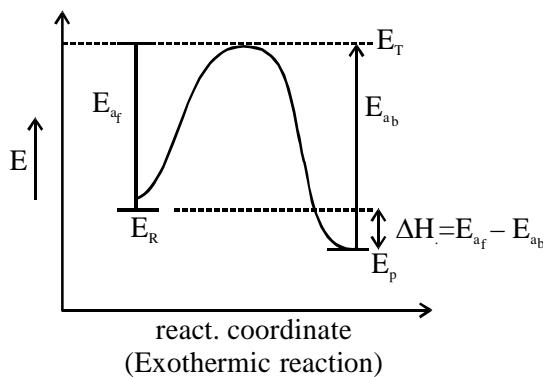
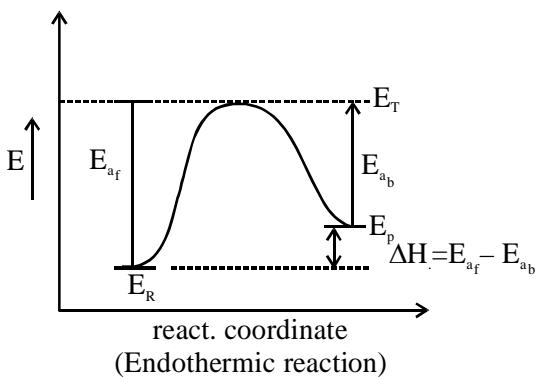
And rate constant,  $K \equiv A \cdot e^{-E_a/RT}$

$$\text{Now, } K_{\text{eq.}} = \frac{K_f}{K_b} = \frac{A_f \cdot e^{-E_{af}/RT}}{A_b \cdot e^{-E_{ab}/RT}} = \frac{A_f}{A_b} \cdot e^{-(E_{af} - E_{ab})/RT}$$

$$K_{eq.} = A \cdot e^{-\Delta H / RT} \quad (\text{Van't Hoff's equation})$$

where  $A = \frac{A_f}{A_b} = \text{constant}$

and  $\Delta H = E_{a_f} - E_{a_b}$



If  $K_1$  and  $K_2$  be the equilibrium constants of a reaction at absolute temperatures  $T_1$  and  $T_2$ , then

$$\ell n \frac{K_2}{K_1} = \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

On increasing the temperature the rate constant of reaction increases. But the reaction with higher activation energy is more sensitive towards temperature change. For the reaction of higher activation energy the value of rate contact increases largely on increasing temperature as well as the rate constant decreases largely as decrease in temperature.

For endothermic reaction

$$\Delta H = E_{a_f} - E_{a_b} = +ve$$

$$\Rightarrow T \uparrow ; K_{eq.} = \frac{K_f}{K_b} \uparrow \quad (K_f \text{ larger increasing and hence } K_{eq.} \text{ increase})$$

For exothermic reaction

$$\Delta H = E_{a_f} - E_{a_b} = -ve$$

$$\Rightarrow T \uparrow ; K_{eq.} = \frac{K_f}{K_b} \uparrow \quad (K_b \text{ larger increasing and hence } K_{eq.} \text{ decreases})$$

**Ex.12** The equilibrium constant for the reaction  $H_2(g) + S(s) \rightleftharpoons H_2S(g)$ ; is 18.5 at 925 K and 9.25 at 1000 K respectively. The enthalpy of the reaction will be :

- |                                    |                                    |
|------------------------------------|------------------------------------|
| (A) - 68000.05 J mol <sup>-1</sup> | (B) - 71080.57 J mol <sup>-1</sup> |
| (C) - 80071.75 J mol <sup>-1</sup> | (D) 57080.75 J mol <sup>-1</sup>   |

**Sol.(B)**

Using the relation,

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{9.25}{18.5} = \frac{\Delta H}{2.303 \times 8.314} \times \frac{75}{925 \times 1000}$$

$$-0.301 = \frac{\Delta H \times 75}{2.303 \times 8.314 \times 925 \times 1000} \Rightarrow \Delta H = -71080.57 \text{ J mol}^{-1}$$

**Ex.13.** The equilibrium  $2A + B_2 \rightleftharpoons 2AB$  involves the two component equilibria,

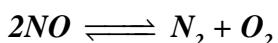
$A + B_2 \rightleftharpoons AB + B$  and  $A + B \rightleftharpoons AB$  with respective equilibrium constants  $K_1$  and  $K_2$ ,

How is the equilibrium constant,  $K$ , for the overall equilibrium related to  $K_1$  and  $K_2$ ?

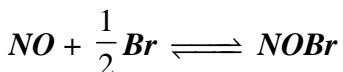
- |                     |                   |                   |                     |
|---------------------|-------------------|-------------------|---------------------|
| (A) $K = K_1 + K_2$ | (B) $K = K_1 K_2$ | (C) $K = K_1/K_2$ | (D) $K_2 = K_1 K_2$ |
|---------------------|-------------------|-------------------|---------------------|

**Sol.** (B)

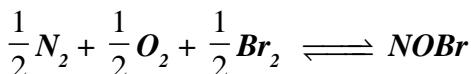
**Ex.14. For the reactions :**



$$KC_1 = 2.4 \times 10^{30}$$



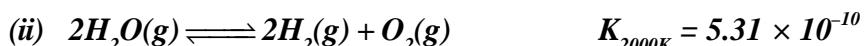
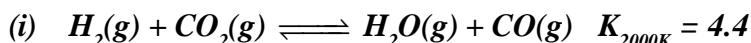
$$KC_2 = 1.4$$



$$K_{C_3} = x \text{ Find the value of } x.$$

Sol.  $9.04 \times 10^{-16}$

**Ex.15. From the following data :**



State whether the reaction (iii) is exothermic or endothermic?

Sol. Equation (iii) =  $-[2 \times (i) + (ii)]$

$$\therefore K_{2000(iii)} = \frac{1}{K_1^2 K_2} = \frac{1}{(4.4)^2 \times 5.31 \times 10^{-10}} = 9.7 \times 10^7$$

$$\therefore T \uparrow K \downarrow \Rightarrow \text{reaction is exothermic.}$$

## 7. APPLICATION OF EQUILIBRIUM CONSTANT :

- (I) Predicting the extent of a reaction
- (II) Predicting the direction of the reaction and
- (III) Calculating equilibrium composition.

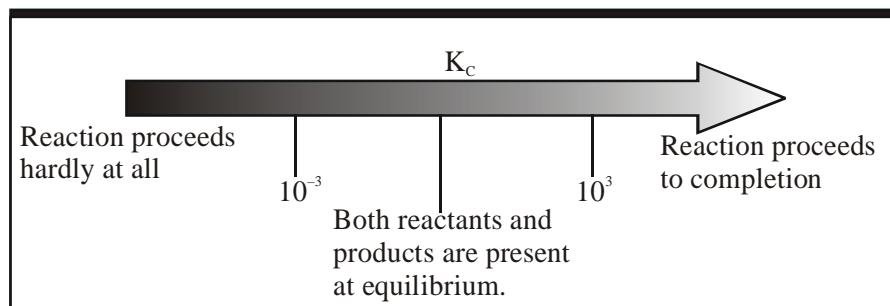
### 7.1 Predicting the extent of reaction :

The numerical value of the equilibrium constant for a reaction indicates the extent of the reaction. But it is important to note that an equilibrium does not give any information about the rate at which the equilibrium is reached. The magnitude of  $K_c$  or  $K_p$  is directly proportional to the concentrations of products (as these appear in the numerator of equilibrium constant expression) and inversely proportional to the concentrations of the reactants (these appear in the denominator). This implies that a high value of  $K$  is suggestive of a high concentration of products and vice-versa.

We can make the following generalisations concerning the composition of equilibrium mixtures:

- (i) If  $K_c > 10^3$ , products predominate over reactants. If  $K_c$  is very large, the reaction proceeds almost all the way to completion.
- (ii) If  $K_c < 10^{-3}$ , reactants predominate over products. If  $K_c$  is very small, the reaction proceeds hardly at all.

- (iii) If  $K_c$  is in the range  $10^{-3}$  to  $10^3$ , appreciable concentration of both reactants and products are present.



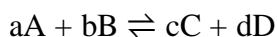
**Ex.16** In the following cases which is predominant (reactant or product) for the given value of  $K_c$ .

- (a)  $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ , at 300K has  $K_c = 4.0 \times 10^{31}$ .  
 (b)  $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ , at 298 K has  $K_c = 4.8 \times 10^{-31}$ .  
 (c)  $N_2O_4 \rightleftharpoons 2NO_2$ , at 298 K has  $K_c = 4.64 \times 10^{-3}$ .

- Sol.** (a) If  $K_c > 10^3$ , products predominate over reactants. If  $K_c$  is very large, the reaction proceeds almost all the way to completion.  
 (b) If  $K_c < 10^{-3}$ , reactants predominate over products. If  $K_c$  is very small, the reaction proceeds hardly at all.  
 (c) Also, gas phase decomposition of  $N_2O_4$  to  $NO_2$  is another reaction with a value of  $K_c = 4.64 \times 10^{-3}$  at 25°C which is neither too small nor too large. Hence, equilibrium mixtures contain appreciable concentrations of both  $N_2O_4$  and  $NO_2$ .

## 7.2 Predicting the direction of the Reaction :

The equilibrium constant is also used to find in which direction, the reaction mixture of reactants and products will proceed. For this purpose, we calculate the reaction quotient, Q. The reaction quotient is defined in the same way as the equilibrium constant (with molar concentrations to give  $Q_C$ , or with partial pressure to give  $Q_P$ ) at any stage of reaction. For a general reaction:



$$Q_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Then, if  $Q_C > K_c$ , the reaction will proceed in the direction of reactants (reverse reaction).

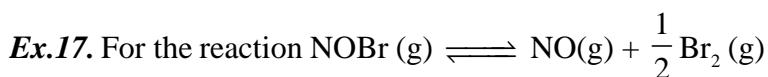
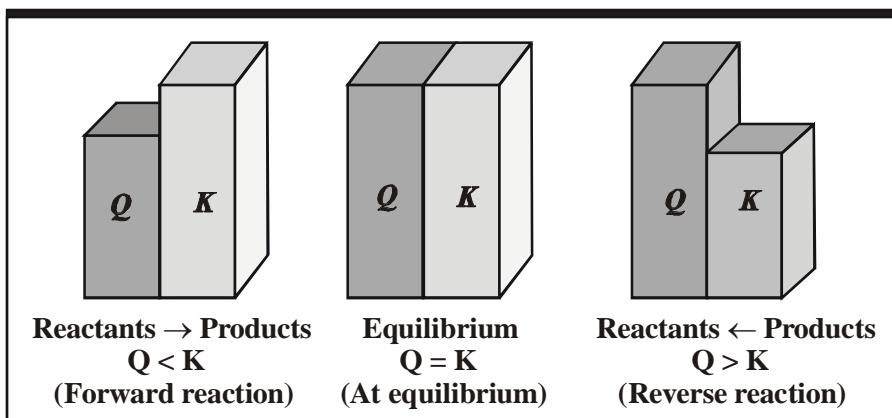
- if  $Q_C < K_c$ , the reaction will move in the direction of the products  
 if  $Q_C = K_c$ , the reaction mixture is already at equilibrium.

In the reaction,  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ , if the molar concentrations of  $\text{H}_2$ ,  $\text{I}_2$  and  $\text{HI}$  are 0.1 M, 0.2 M and 0.4 M, respectively at 783 K, then reaction quotient at this stage of the reaction is

$$Q_C = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.4)^2}{(0.1)(0.2)} = 8$$

$K_C$  for this reaction at 783 K is 46 and we find that  $Q_C < K_C$ . The reaction, therefore, will move to right i.e. more  $\text{H}_2(\text{g})$  and  $\text{I}_2(\text{g})$  will react to form more  $\text{HI}(\text{g})$  and their concentration will decrease till  $Q_C = K_C$ .

Thus, a reaction has a tendency to form products if  $Q < K$  and to form reactants if  $Q > K$ .



$K_p = 0.15$  atm at  $90^\circ\text{C}$ . If  $\text{NOBr}$ ,  $\text{NO}$  and  $\text{Br}_2$  are mixed at this temperature having partial pressures 0.5 atm, 0.4 atm and 2.0 atm respectively, will  $\text{Br}_2$  be consumed or formed?

**Sol.**  $Q_p = \frac{[\text{P}_{\text{Br}_2}]^{1/2}[\text{P}_{\text{NO}}]}{[\text{P}_{\text{NOBr}}]} = \frac{[0.20]^{1/2}[0.4]}{[0.50]} = 0.36$

$$\therefore K_p = 0.15$$

Hence, reaction will shift in backward direction

$\therefore \text{Br}_2$  will be consumed



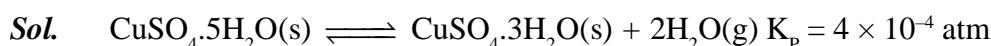
$$Q = \frac{\text{P}_{\text{CO}_2}}{1} = \text{P}_{\text{CO}_2} = X_{\text{CO}_2} \cdot 1_{\text{total}}$$

$$\frac{1}{100} \times 1 \text{ atm} = 0.01 \text{ atm.} < K_p$$

It will go in forward direction

0.1%  $\text{CO}_2$  is not sufficient

**Ex.19.** Predict whether  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s)$  be efflorescent or  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}(s)$  be hydroscopic and vapour pressure of  $\text{H}_2\text{O}$  at  $25^\circ\text{C} = 0.04 \text{ atm}$ .



Partial pressure of  $\text{H}_2\text{O}$  at eq. =  $P_{\text{H}_2\text{O}}$

$$K_p = P_{\text{H}_2\text{O}}^2$$

$$P_{\text{H}_2\text{O}} = \sqrt{4 \times 10^{-4}} = 2 \times 10^{-2} \text{ atm}$$

$$Q = 4 \times 10^{-2} \text{ atm}$$

So,  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  be hydroscopic in this condition.

**Ex.20.** In above problem what maximum humidity for which  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s)$  work as efflorescent.

**Sol.**  $\left(0.04 \times \frac{x}{100}\right)^2 < 4 \times 10^{-4}$

$$0.16 \times 1.0^{-4} \times \frac{x^2}{10000} < 4 \times 10^{-4}$$

$$x^2 < 50$$

$$x < 50\%$$

$$\text{Max. R.H.} = 50\% \text{ Ans.}$$

**Ex.21.** Study the following reaction



(i) Which of the following is best dehydrating drying agent.

(A) A.  $2\text{H}_2\text{O}(g)$  (D) A(s)

(B) B.  $3\text{H}_2\text{O}(g)$  (E) B(s)

(C) C.  $4\text{H}_2\text{O}(g)$  (F) C(s)

$$A \rightarrow K_p = P_{\text{H}_2\text{O}}^2 \Rightarrow P_{\text{H}_2\text{O}} = 0.02 \text{ atm}$$

$$B \rightarrow K_p = P_{\text{H}_2\text{O}}^3 \Rightarrow P_{\text{H}_2\text{O}} = 0.03 \text{ atm}$$

$$C \rightarrow K_p = P_{\text{H}_2\text{O}}^4 \Rightarrow P_{\text{H}_2\text{O}} = 0.04 \text{ atm}$$

For the best dehydrating agent the moisture remained must be minimum.

(ii) If A(s), B(s) and C(s) are placed in a room where  $P_{\text{H}_2\text{O}}(g) = 0.025 \text{ atm}$ , which will act as dehydrating agent.

(A) A(s) (B) B(s) & C(s) (C) B(s) (D) All

(iii) Which of the following will be efflorescent at 7.5% R.H. if aqueous term = 0.04 atm.

(a) Only A.  $2\text{H}_2\text{O}(s)$  (b) Only B.  $3\text{H}_2\text{O}(s)$

(c) Only C.  $4\text{H}_2\text{O}(s)$

(d) Only A.  $2\text{H}_2\text{O}(s)$  & B.  $3\text{H}_2\text{O}(s)$

(e) Only B.  $3\text{H}_2\text{O}(s)$  & C.  $4\text{H}_2\text{O}(s)$

**Sol.** (i) D (ii) A (iii) C

### 7.3 Calculating equilibrium concentrations :

In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed :

**Step 1.** Write the balanced equation for the reaction.

**Step 2.** Under the balanced equation, make a table that lists for each substance involved in the reaction :

- (a) the initial concentration,
- (b) the change in concentration on going to equilibrium, and
- (c) the equilibrium concentration.

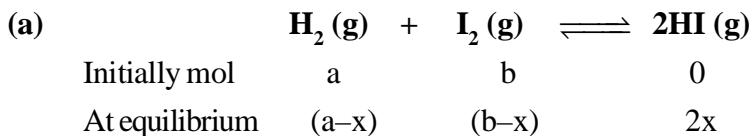
In constructing the table, define  $x$  as the concentration (mol/L) of one of the substances that reacts on going to equilibrium, then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of  $x$ .

**Step 3.** Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for  $x$ . If you are to solve a quadratic equation choose the mathematical solution that makes chemical sense.

**Step 4.** Calculate the equilibrium concentrations from the calculated value of  $x$ .

**Step 5.** Check your results by substituting them into the equilibrium equation.

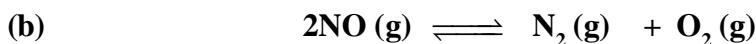
#### 7.3.1 Some General Equilibrium Expressions :



$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = \frac{4x^2}{(a-x)(b-x)}$$

$$K_p = \frac{(p_{\text{HI}})^2}{p_{\text{H}_2} \times p_{\text{I}_2}} = \frac{\frac{(2x)^2}{(a+b)^2} P^2}{\left(\frac{a-x}{a+b} \cdot P\right) \left(\frac{b-x}{a+b} \cdot P\right)} = \frac{4x^2}{(a-x)(b-x)}$$

$$\text{So } K_c = K_p \quad (\Delta n_g = 0)$$



Initially mol a 0 0

At equilibrium (a-x) x/2 x/2

$$K_c = \frac{[\text{N}_2][\text{O}_2]}{[\text{NO}]^2} = \frac{x/2 \times x/2}{(a-x)^2} = \frac{x^2}{4(a-x)^2} = K_p \quad (\Delta n_g = 0)$$

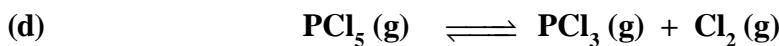


Initially mol a b 0 0

At equilibrium (a-x) (b-x) x x

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{x^2}{(a-x)(b-x)}$$

$K_p$  should not be given for this reaction ,



Initially mol a 0 0

At equilibrium (a-x) x x

Active mass  $\frac{(a-x)}{v}$   $\frac{x}{v}$   $\frac{x}{v}$

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{\frac{x}{v} \times \frac{x}{v}}{\frac{(a-x)}{v}} = \frac{x^2}{(a-x)v}$$

$$K_p = \frac{p_{\text{PCl}_3} \times p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{\left(\frac{x}{a+x} \cdot P\right) \times \left(\frac{x}{a+x} \cdot P\right)}{\left(\frac{a-x}{a+x}\right)P} = \frac{x^2 P}{(a+x)(a-x)} = \frac{x^2 P}{a^2 - x^2}$$



Initially mol a b 0

At equilibrium (a-x) (b-3x) 2x

Active mass  $\frac{(a-x)}{v}$   $\left(\frac{b-3x}{v}\right)$   $\left(\frac{2x}{v}\right)$

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-3x}{v}\right)^3} = \frac{4x^2 V^2}{(a-x)(b-3x)^3}$$

$$K_p = \frac{(p_{\text{NH}_3})^2}{p_{\text{N}_2} \times (p_{\text{H}_2})^3} = \frac{\left[\frac{2xP}{a+b-2x}\right]^2}{\left[\frac{(a-x)P}{a+b-2x}\right] \left[\frac{(b-3x)P}{a+b-2x}\right]^3} = \frac{4x^2(a+b-2x)^2}{(a-x)(b-3x)^3 P^2}$$

**(g) Equilibrium constant expressions in term of 'α'**

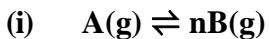


Initial moles	1	—	—
---------------	---	---	---

At. Eq.	1- $\alpha$	$\alpha$	$\alpha$
---------	-------------	----------	----------

$$K_C = \frac{\alpha^2}{1-\alpha} \left( \frac{1}{V} \right) \quad \text{and} \quad K_P = \frac{\alpha^2}{1-\alpha^2} P_T$$

**(h) Degree of dissociation in terms of molar mass and vapour density**



$$\alpha = \frac{M_T - M_O}{M_O(n-1)} \quad \text{or} \quad \alpha = \frac{D_T - D_O}{D_O(n-1)}$$

$M_T$  = Theoretical molar mass of reactant

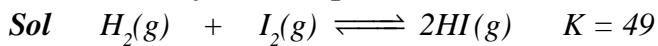
$M_O$  = Observed molar mass of mixture

$$D_T = \frac{M_T}{2} \quad \text{and} \quad D_O = \frac{M_O}{2}$$



$$\alpha = \frac{M_T - M_O}{M_O \left( \frac{1}{n} - 1 \right)}$$

**Ex.22 5 moles  $H_2$  gas and 5 moles iodine-vapours are taken in vessel of 10 L capacity. Determine the moles of each at equilibrium.**



$$49 = \frac{(2x)^2 v^2}{(5-x)(5-x)v^2}$$

$$49 = \frac{(2x)^2}{(5-x)^2}$$

$$7 = \frac{2x}{5-x}$$

$$35 - 7x = 2x$$

$$35 = 9x$$

$$x = \frac{35}{9}$$

$$\text{Moles at equilibrium} = \frac{10}{9}, \frac{10}{9}, \frac{70}{9}$$

**Ex.23 How many moles of  $H_2(g)$  should be mixed with each mole  $I_2$  vapours in order to convert 90% of it into  $HI$ .**

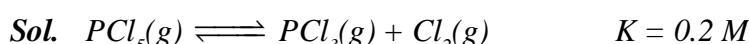


$$\begin{array}{ccc} x & & 1 \\ x-a & & 0.1 \end{array}$$

$$1.8$$

$$50 = \frac{3.24}{(x-0.9)(0.1)} \Rightarrow x = 1.548$$

**Ex.24 2 moles of  $PCl_5(g)$  is taken in 10 ℥ vessel. Calculate its concentration at equilibrium.**



$$\begin{array}{ccc} 2-x & & x \\ x & & x \end{array}$$

$$\begin{array}{ccc} \frac{2-x}{v} & & \frac{x}{v} \\ \frac{x}{v} & & \frac{x}{v} \end{array}$$

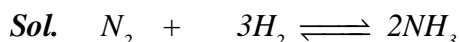
$$0.2 = \frac{\left(\frac{x}{v}\right)^2}{\left(\frac{2-x}{v}\right)} \Rightarrow x = 1.24$$

$$[PCl_5] = 0.076 M$$

$$[PCl_3] = 0.124 M$$

$$[Cl_2] = 0.124 M$$

**Ex.25 1 : 3 molar ratio mixture of  $N_2$  and  $H_2$  yields 20% by mole  $NH_3$  at 30 atm; calculate  $K_p$  for the equilibrium represented by**



$$\begin{array}{cccc} 0 & a & 3a & 0 \end{array}$$

$$\begin{array}{cccc} t & (a-x) & 3(a-x) & 2x \end{array}$$

$$Total \ moles = 4a - 2x$$

$$X_{NH_3} = 0.2 = \frac{2x}{4a - 2x} \Rightarrow 2x = 0.8a - 0.4x \Rightarrow x = a/3$$

$$P_{NH_3} = 0.2 \times 30 = 6 \text{ atm}$$

$$P_{NH_3} = X_{N_2} \times P_T = \frac{a-x}{4a-2x} \times 30 = 0.2 \times 30 = 6 \text{ atm}$$

$$P_{H_2} = \frac{3(a-x)}{4a-2x} = 0.6 \times 30 = 18 \text{ atm}$$

$$\therefore K_p = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = \frac{6}{6 \times (18)^2} = 1.03 \times 10^{-3} \text{ atm}^{-2}$$

**Ex.26** An air sample containing 21:79 (mole ratio) of  $O_2$  &  $N_2$  is heated to  $2400^\circ C$ . If the mole percent of NO at equilibrium is 1.8%, calculate  $K_p$  for the reaction  $N_2 + O_2 \rightleftharpoons 2NO$ .



$$X_{NO} = 0.018$$

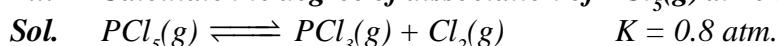
$$P_{NO} = 0.018 \times P_T$$

$$2P = 0.018 \times P_T \quad [\because \Delta n = 0 \Rightarrow P_T = 1 \text{ atm}]$$

$$P = \frac{0.018 \times 1}{2} = 0.009$$

$$K_p = \frac{[P_{NO}]^2}{P_{N_2} \times P_{O_2}} = \frac{(0.018)^2}{(0.781)(0.201)} = 2.06 \times 10^{-3}$$

**Ex.27** Calculate the degree of dissociation of  $PCl_5(g)$  at 20 atm.



$x$	$0$	$0$
$x - a$	$a$	$a$

$$\text{Total mole} = x + a$$

$$\frac{x-a}{x+a}(20) = \frac{a}{x+a}20 = \frac{a}{x+a}20$$

$$0.8 = \frac{\left(\frac{a}{x+a}\right)^2 (20)^2}{\left(\frac{x-a}{x+a}\right)20} \Rightarrow 0.04 = \frac{a^2}{x^2 - a^2}$$

$$\frac{x}{a} = \frac{1}{\sqrt{26}} = 0.2$$

$$\alpha = 0.2$$

**Ex.28** The vapour density a sample of  $N_2O_4(g)$  is 40 at 10 atm. Calculate  $K_p$  for the reaction.



Initial	$a$	$0$
$a - x$	$2x$	

$$\text{Total mole} = (a - x) + 2x = a + x$$

$$\frac{a-x}{a+x}P = \frac{2x}{a+x}P$$

$$V.D. = \frac{M_{avg}}{2}$$

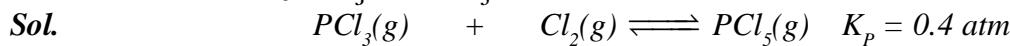
$$M_{avg} = 2 \times 40 = 80$$

$$M_{avg} = \frac{\text{Total mass}}{\text{Total moles}} = \frac{92a}{a+x} = 80$$

$$x = \frac{12}{80}a = 0.15a$$

$$K_p = \frac{4x^2}{a^2 - x^2} = 9.2 \times 10^{-2}$$

**Ex.29 At what pressure an equimolar mixture of  $PCl_5(g)$  and  $Cl_2(g)$  should be taken in order to convert 75% of  $PCl_3$  into  $PCl_5$ .**



Initial	$a$	$0$
Final	$a - 0.75a$	$a - 0.75a \quad 0.75a$
	$= 0.25a$	$= 0.25a$

$$\text{Total mole} = 1.25a$$

Equ. par. pr.	$\frac{0.25a \times P}{1.25a}$	$\frac{0.25a \times P}{1.25a}$	$\frac{0.75a \times P}{1.25}$
	$\frac{P}{5}$	$\frac{P}{5}$	$\frac{3P}{5}$

$$K_p = \frac{P_{PCl_5}}{P_{PCl_3} P_{Cl_2}} \Rightarrow 0.4 = \frac{\frac{3P}{5}}{\frac{P}{5} \times \frac{P}{5}} \Rightarrow P = 37.5$$

But this is pressure at equilibrium but we have to find initial pressure

Now, from  $PV = nRT$

$$\frac{P_1}{P_2} = \frac{n_1}{n_2} \Rightarrow \frac{P_1}{37.5} = \frac{2}{1.25} \Rightarrow P = 60 \text{ atm}$$

**Alternate method :**

Initial partial pressure	$PCl_3(g)$	$+ Cl_2(g) \rightleftharpoons PCl_5(g)$	$P_o \quad 0$
E.P.P.	$P_o - 0.75P_o$	$P_o - 0.75P_o \quad 0.75P_o$	
	$= 0.25P_o$	$= 0.25P_o$	
	$0.4 = \frac{0.75P_o}{0.25P_o \times 0.25P_o}$		$\Rightarrow P_o = 30 \text{ atm}$

$\therefore$  Initial total pressure of mixture  $= P_o + P_o = 60 \text{ atm}$

**Note :** In any problem related with relative extent of reaction, initial mole may be taken as 1 but the initial pressure or concentration should not be taken as 1.

**Ex.30 100 gm  $CaCO_3$  is taken in 30 ℥ empty vessel and the vessel is sealed and the sample is heated to  $627^\circ C$ . Calculate the mass % of  $CaCO_3$  decomposed.**



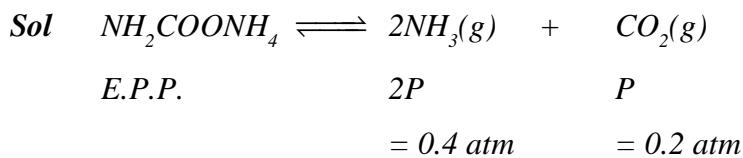
Initial 1 mole	$0$	$0$
Final	$1-x$	$x \quad x$
Total mole	$1+x$	

$$K_p = \frac{P_{CO_2}}{1} = P_{CO_2} \Rightarrow P_{CO_2} = \frac{n \cdot RT}{V}$$

$$0.821 = \frac{x \times 0.0821 \times 900}{30} \Rightarrow x = \frac{1}{3}$$

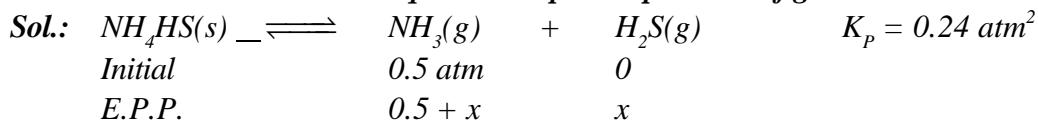
$$\% \text{ of } CaCO_3 \text{ decomposed} = \frac{1}{3} \times 100 = \frac{100}{3} \%$$

**Ex.31** Some solid ammonium carbamate  $\text{NH}_4\text{COONH}_4$  is taken in an evacuated vessel and the vessel is sealed after a very long time a constant pressure of 0.6 atm is observed due to dissociation of the solid into  $\text{NH}_3$  and  $\text{CO}_2$  gas. Calculate the dissociation constant of solid.



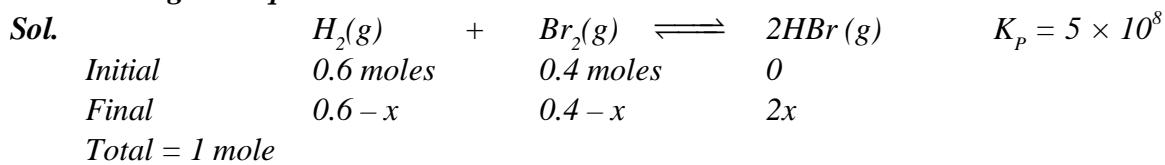
$$K_p = \frac{[0.4]^2[0.2]}{1} = 0.032 \text{ atm}^3$$

**Ex.32** Some solid ammonium hydrogen sulphide  $\text{NH}_4\text{HS}$  is taken in a vessel containing ammonium gas at 0.5 atm. Calculate the equilibrium partial pressure of gas.



$$K_p = \frac{P_{\text{NH}_3} \cdot P_{\text{H}_2\text{S}}}{1} \Rightarrow 0.24 = (0.5 + x)x \Rightarrow x = 0.3 \text{ atm.}$$

**Ex.33** 0.6 moles of  $\text{H}_2(g)$  and 0.4 moles of  $\text{Br}_2$  vapour are allowed to react. Calculate the moles of each gas at equilibrium.



$$K_p = \frac{(2x)^2}{(0.6-x)(0.4-x)} = \frac{4x^2}{x^2 - x + 0.24}$$

$$(5 \times 10^8 - 4)x^2 - 5 \times 10^8x + 1.2 \times 10^8 = 0$$

$$5 \times 10^8x^2 - 5 \times 10^8x + 1.2 \times 10^8 = 0$$

$$8x^2 - x + 0.24 = 0$$

$$x = 0.4, 0.6 (\text{Not acceptable})$$

As  $K_p$  is much larger than 1000 the reaction almost completes.

$$\text{Final moles of HBr} = 0.8$$

$$\text{Final moles of H}_2 = 0.2$$

But Final moles of  $\text{Br}_2 \neq 0$

**Note :**

The final moles of  $Br_2$  may be calculated by first completing the reaction in forwards direction and then achieving equilibrium from backward direction.

	$H_2(g)$	+	$Br_2(g)$	$\rightleftharpoons$	$2HBr(g)$
Initial	0.6		0.4		0
Final	0.2		0		0.8

	$2HBr$	$\rightleftharpoons$	$H_2$	+	$Br_2(g)$	$K' = \frac{1}{K} = 2 \times 10^{-9} \ll 10^{-3}$
	0.8		0.2		0	
Final	$0.8 - y$		$0.2 + \frac{y}{2}$		$\frac{y}{2}$	

$$K' = \frac{[H_2][Br_2]}{[HBr]^2} = 2 \times 10^{-9} = \frac{\left(0.2 + \frac{y}{2}\right)y}{(0.8 - y)^2}$$

As  $K'$  is very small we may assume that  $0.8 - y \approx 0.8$

$$\text{and, } 0.2 + \frac{y}{2} \approx 0.2$$

$$\therefore 2 \times 10^{-9} = \frac{0.2 \times \frac{y}{2}}{0.64}$$

$$y = 1.28 \times 10^{-8}$$

$$\text{Final moles HBr} = 0.8 - y \approx 0.8$$

$$H_2 = 0.2 + \frac{y}{2} \approx 0.2$$

$$Br_2 = \frac{y}{2} = 6.4 \times 10^{-9}$$

**Ex.34 Calculate concentration of A at equilibrium for a reaction,  $A(g) \rightleftharpoons B(g)$  ;  $K_C = 10^{50}$ , if the initial concentration of A is 2 M.**

**Sol.**  $A(g) \rightleftharpoons B(g)$

initial conc.	2	0
Change in conc.	-x	x
equib. conc.	$2-x$	$0+x$

$K_C$  is very-very high so maximum reactant converted into product.

$$\therefore \frac{K_C}{\text{initial conc.}} \geq 10^3 \text{ then } \frac{10^{50}}{2} \geq 10^3.$$

So  $2-x \approx 0 \Rightarrow x \approx 2$  but reactant never zero.

$$\text{equib. conc.} \quad 2-x \approx y \quad x \approx 2$$

$$K_c = \frac{[B]}{[C]}$$

$$10^{50} = \frac{x}{2-x}$$

$$10^{50} = \frac{2}{y} \Rightarrow y = 2 \times 10^{-50} \text{ M}$$

$$[A] = 2 \times 10^{-50} \text{ M}$$

## 8. LE CHATELIER'S PRINCIPLE :

Le Chatelier's principle is applicable for any system in equilibrium which states as :

When a system in equilibrium is disturbed by external agency, the system tends to attain again an equilibrium by adjusting itself. These are these some factors by which a system in equilibrium can be disturbed.

- (i) Changing the concentration of reactant and product.
- (ii) Changing the pressure (or volume) of the system.
- (iii) Changing the temperature.

For a chemical reaction in equilibrium, Le Chatelier's principle can be stated as,

**If we change concentration, pressure or temperature of a chemical reaction in equilibrium, the equilibrium will shift to the right or the left so as to minimise the change.**

### 8.1 Effect of a change in concentration :

- (a) If more reactant is added or some product is removed from an equilibrium mixture having equilibrium constant K then the reaction moves in the forward direction (as  $Q_c < K_c$ ) to give a new equilibrium and more products are produced.
- (b) If more product are added to or some reactant are removed from an equilibrium mixture, the reaction moves in the reverse direction (as  $Q_c > K_c$ ) to give a new equilibrium and more reactant are produced.

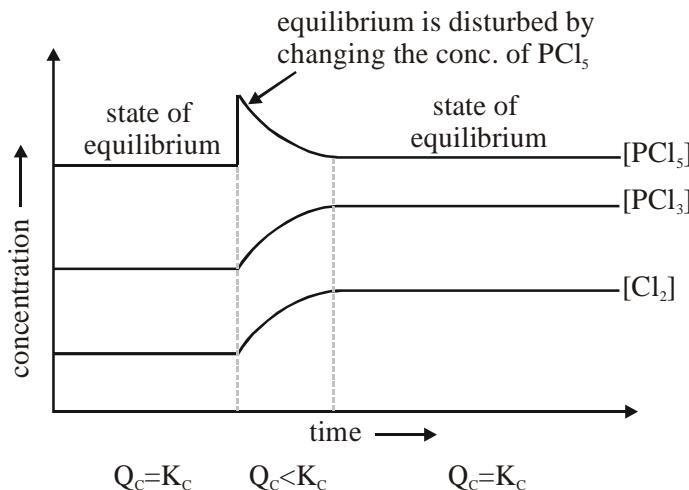
**Ex.** The decomposition of gaseous  $\text{PCl}_5$  is a reversible reaction,  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ . Let the equilibrium concentrations of  $\text{PCl}_5$ ,  $\text{PCl}_3$  and  $\text{Cl}_2$  are respectively  $[\text{PCl}_5]$ ,  $[\text{PCl}_3]$  and  $[\text{Cl}_2]$ . The  $K_c$  for this reaction can be written as :

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \text{ Also we know that at equilibrium } K_c = Q_c.$$

**Case-I :** Let the concentration of  $\text{PCl}_5$  is doubled to disturb the equilibrium. This will change the reaction quotient,  $Q_c$  to :

$$Q_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[2\text{PCl}_5]} = \frac{1}{2} \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{K_c}{2}$$

After disturbing the equilibrium, the value of  $Q_C$  becomes less than  $K_C$ . In order to restore the  $Q_C$  value to  $K_C$ , the concentration of  $\text{PCl}_5$  must be decreased while the concentrations of  $\text{PCl}_3$  and  $\text{Cl}_2$  are to be increased. This is achieved by favoring the forward reaction.

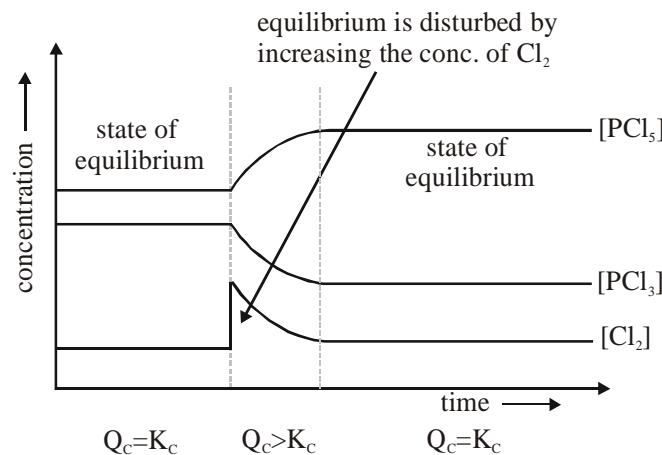


The forward reaction is also favored by removing the products from the reaction mixture (decrease in the concentration of products). Upon removal of products, the rate of forward reaction becomes greater than that of backward reaction momentarily. This will also decrease the reaction quotient. Hence the system tries to reestablish the equilibrium by converting more reactants to products so as to make the rates of both forward and backward reactions become equal again.

**Case-II :** For example, in case of the decomposition of  $\text{PCl}_5$ , if the concentration of  $\text{Cl}_2$  is increased by two times at equilibrium, the  $Q_C$  value becomes greater than the  $K_C$  value.

$$Q_C = \frac{[\text{PCl}_3][2\text{Cl}_2]}{[\text{PCl}_5]} = 2 \times \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = 2K_C$$

Hence the system tries to restore the value of  $Q_C$  to  $K_C$  again. The backward reaction is favored to decrease the concentration of  $\text{Cl}_2$ . However the concentration of  $\text{PCl}_3$  also decreases automatically while the concentration of  $\text{PCl}_5$  increases while doing so.



## 8.2 Effect of a change in pressure :

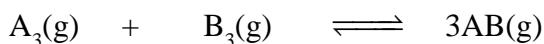
We know that, if we increase the volume of container then the pressure of the container decreases and if we decrease the volume of container then the pressure of the container increases.

$$\text{i.e., } \text{Pressure (P)} \propto \frac{1}{\text{Volume (V)}}$$

Hence, if the pressure is decreased by increasing the volume of a reaction mixture, the reaction shifts in the direction of more moles of gas while if the pressure is increased by decreasing the volume of a reaction mixture, the reaction shifts in the direction of fewer moles of gas.

Here moles of reactant or product means co-efficients of reactant or product.

- (a) Suppose a general equation



at equi :      a M                  b M                  c M

For this reaction, moles of product > moles of reactant i.e.,  $[\Delta n = (3 - 2) > 0]$

$$K_C = \frac{(c)^3}{a \times b}$$

If we increase the pressure of the system from 0.5 atm pressure to 1 atm pressure by decreasing the volume of container from 5 litre to 2.5 litre. Hence, concentration of all the reactant and product will change and it will be greater than the initial value. Hence we can say that,

If pressure becomes double then volume becomes half and hence concentration becomes double

as (Concentration  $\propto \frac{\text{Moles}}{\text{Volume}}$ )

$\therefore$  Concentration  $\propto$  Pressure

$$Q_C = 2 \times \frac{c^3}{a \times b} > K_C$$

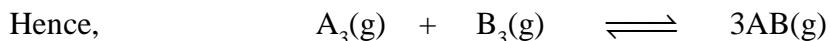
Hence reaction will move from right to left i.e., in the backward direction.

Hence,       $A_3(g) + B_3(g) \rightleftharpoons 3AB(g)$

Moles at equi.       $2a+x$        $2b+x$        $2c-3x$

It can be simply said that, reaction will move from right to left by increasing the pressure of the system as moles of product > moles of reactant i.e., move in the direction of fewer moles.

- (b) If pressure decreases from 1 atm to 0.5 atm. Volume will increase by factor 2 concentration will decrease by factor 1/2



changed conc.  $a/2$   $b/2$   $c/2$

at equi. conc.  $a/2-x$   $b/2-x$   $c/2+3x$

$$Q_C = \frac{(c/2)^3}{a/2 \times b/2} = \frac{1}{2} \frac{c^3}{a \times b} < K_C$$

i.e.,  $Q_C < K_C$

Therefore, reaction will move from left to right and as moles of product > moles of reactants, therefore reaction will move from left to right by decreasing the pressure of the system i.e. move in the direction of greater moles.

- (c) If moles of reactant = moles of product i.e.,  $\Delta n = 0$  then change in pressure of equilibrium mixture has no effect i.e. at this position  $Q_C = K_C$  will always exist.

### 8.3 Effect of a change in temperature :

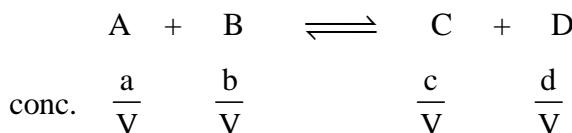
On increasing the temperature equilibrium shifts in the direction of absorption of heat (endothermic direction)

### 8.4 EFFECT OF INERT GAS AT THE EQUILIBRIUM :

#### (i) Effect of inert gas at constant volume :

When the addition of inert gas (non-reacting gas) is carried out at constant volume (V), the equilibrium remains unaffected for reactions whether they have  $\Delta n = 0$  or  $\Delta n \neq 0$ .

Let us consider a general equation at temperature T K, and a, b, c and d are the moles of A, B, C and D respectively,



Since, V = constant, so addition of inert gas has no effect on equilibrium

$\therefore \frac{a}{V}, \frac{b}{V}, \frac{c}{V}$  and  $\frac{d}{V}$  will not change

$$Q_C = K_C \quad \text{or} \quad Q_p = K_p$$

#### (ii) Effect of inert gas at constant pressure :

- (a) The addition of an inert gas at constant pressure to an equilibrium, the equilibrium shifts in the direction of greater number of moles.

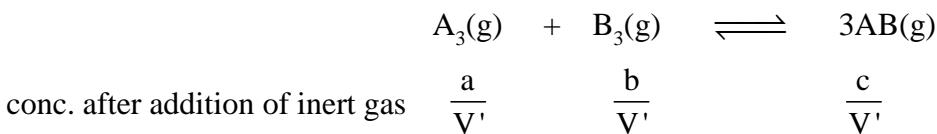
At constant pressure, addition of inert gas or non-reacting gas means increase in volume of the system.

Suppose a reaction having  $\Delta n > 0$  and a, b, c and d are the moles of A, B, C and D respectively and V be the volume before addition of inert gas.



$$\frac{a}{V} \quad \frac{b}{V} \quad \frac{c}{V} \quad [\text{equilibrium conc. before addition of inert gas}]$$

Let us consider  $V'$  be the total volume of the system after addition of inert gas So,  $V' > V$



$$\therefore \frac{a}{V'} < \frac{a}{V}, \frac{b}{V'} < \frac{b}{V} \text{ and } \frac{c}{V'} < \frac{c}{V}$$

$$\text{Now, } K_c = \frac{\left(\frac{c}{V}\right)^3}{\left(\frac{a}{V}\right)\left(\frac{b}{V}\right)} = \frac{1}{V} \times \frac{c^3}{a \times b} \text{ and } Q_c = \frac{\left(\frac{c}{V'}\right)^3}{\left(\frac{a}{V'}\right)\left(\frac{b}{V'}\right)} = \frac{1}{V'} \times \frac{c^3}{a \times b}$$

$K_c > Q_c$ , hence reaction will move from left to right (forward direction) as  $\Delta n > 0$  and similarly we can prove that for a reaction having  $\Delta n < 0$

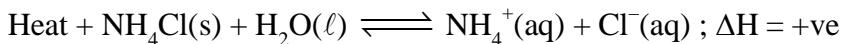


For this reaction  $K_c < Q_c$ , after addition of inert gas. Hence, reaction will move from right to left (reverse direction) as  $\Delta n < 0$ .

## 8.5 APPLICATION OF LE-CHATELIER'S PRINCIPLE :

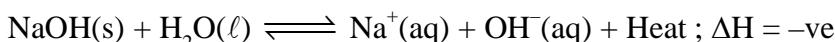
The principle is applicable not only to chemical equilibria but also to physical equilibria in similar way.

- (a) Dissolution of ammonium chloride in water



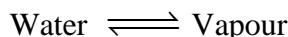
With rise in temperature, equilibrium will shift in direction which will lower the temperature counteract the effect. So, equilibrium shifts in forward direction which is endotherm reaction. Hence, solubility of  $\text{NH}_4\text{Cl}$  increases with rise in temperature.

- (b) Dissolution of sodium hydroxide in water



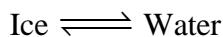
Sodium hydroxide dissolve in water with evolution of heat. Therefore, a rise in temperature will decrease its solubility. On the other hand, a decrease in temperature will increase the solubility of sodium hydroxide and reaction will shift in forward direction.

- (c) Effect of pressure on boiling point :



An increase in pressure will favour backward reaction i.e., the reaction in which volume decreases ( $V_{\text{vap.}} > V_w$ ). thus more water will exist at equilibrium (B.pt of solvent increase with increase in pressure). So decrease in pressure will shift the reaction forward.

- (d) Effect of pressure on melting point :

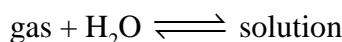


Increase in pressure will favour forward reaction because  $V_{\text{ice}} > V_{\text{water}}$ . Thus more ice melt or the m.pt of ice is lowered with pressure.



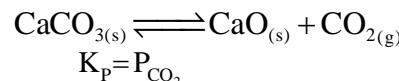
An increase in pressure will favour backward reaction because volume of liquid is more than solid thus more solid will exist at equilibrium (m.pt of solid increases with pressure).

- (e) Effect of pressure on solubility of gases :



Increase in pressure favour forward reaction. [Henry's law]

- (f) In solid reactants equilibrium will not shift to the right side even if the more reactants are added.

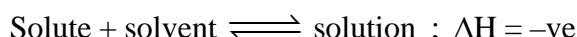


Equilibrium will not be affected by adding CaO or  $\text{CaCO}_3$  at that temperature. But if volume is increased the equilibrium will shift to the right side to keep the pressure of  $\text{CO}_2$  constant.

- (g) Effect of temperature on solubility



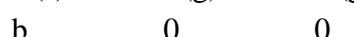
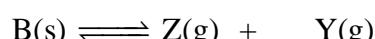
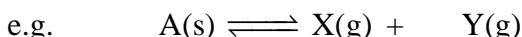
An increase in temperature favours endothermic or forward reaction i.e., solubility increases (urea, glucose).



In exothermic dissolution solubility decreases with temperature i.e., reaction will be in backward direction.

## 9. SIMULTANEOUS EQUILIBRIUM

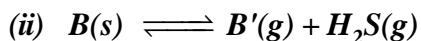
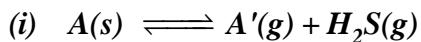
If in any container there are two or more equilibria existing simultaneously involving one or more than one common species, then in both/all the equilibrium, the concentration of common species is the total concentration of that species due to all the equilibria under consideration.



$$K_{C_1} = t(u + t)$$

$$K_{C_2} = (u + t)u$$

**Ex.35 Two solid compounds A and B dissociate into gaseous products at 20°C as**



**At 20°C, pressure over excess solid A is 50 mm and that over excess solid B is 68 mm find**

**(a) The dissociation constant of A and B**

**(b) Relative no. of moles of A and B in the vapour phase over a mixture of solid A and B.**

**(c) Show that the total pressure of the gas over the solid mixture would be 84.4 mm**



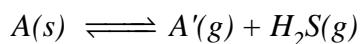
$$A(s) \rightleftharpoons A'(g) + H_2S(g) \quad P = 50 \text{ mm} \quad \Rightarrow \quad P_{H_2S} = P_{A'} = \frac{P}{2} = 25 \text{ mm}$$

$$B(s) \rightleftharpoons B'(g) + H_2S(g) \quad P = 68 \text{ mm} \quad \Rightarrow \quad P_{H_2S} = P_{B'} = \frac{P}{2} = 34 \text{ mm}$$

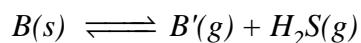
$$(i) \quad K_{P_1} = (25)^2 = 625 \text{ mm}^2$$

$$K_{P_2} = (34)^2 = 1156 \text{ mm}^2$$

**(ii) Ratio of moles is same as that of partial pressure so,**



$$P_1 \quad P_1 + P_2$$



$$P_2 \quad P_2 + P_1$$

$$K_{P_1} = P_{A'} \times P_{H_2S} = P_1(P_1 + P_2) \quad \dots(i)$$

$$K_{P_2} = P_{B'} \times P_{H_2S} = P_2(P_1 + P_2) \quad \dots(ii)$$

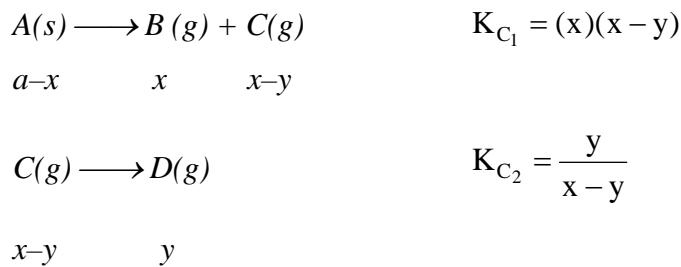
$$\frac{K_{P_1}}{K_{P_2}} = \frac{P_1}{P_2} = \frac{625}{1156}$$

$$(iii) \quad \text{total pressure} = P_1 + P_2 + (P_1 + P_2) = 2(P_1 + P_2)$$

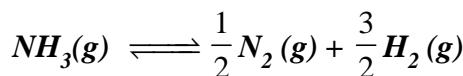
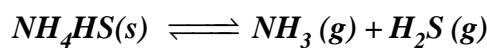
$$(i) + (ii) = (P_1 + P_2)^2$$

$$\sqrt{K_{P_1} + K_{P_2}} = P_1 + P_2 \quad \Rightarrow \quad P_T = \sqrt[3]{K_{P_1} + K_{P_2}} = 84.4 \text{ mm}$$

## 10. SEQUENTIAL EQUILIBRIUM



**Ex36.** 102 g of solid  $NH_4HS$  is taken in the 2L evacuated flask at 57°C. Following two equilibrium exist simultaneously

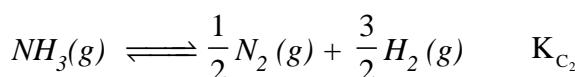


one mole of the solid decomposes to maintain both the equilibrium and 0.75 mole of  $H_2$  was found at the equilibrium then find the equilibrium concentration of all the species and  $K_C$  for both the reaction.

**Sol.** Moles of  $NH_4HS = \frac{102}{51} = 2$



2	1	0
$1-x$	0	1



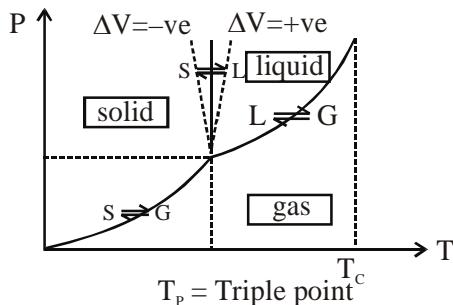
$1-x$	$\frac{x}{2}$	$\frac{3x}{3}$
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Given that moles of  $H_2 = \frac{3x}{3} = 0.75 \Rightarrow x = \frac{1}{2}$

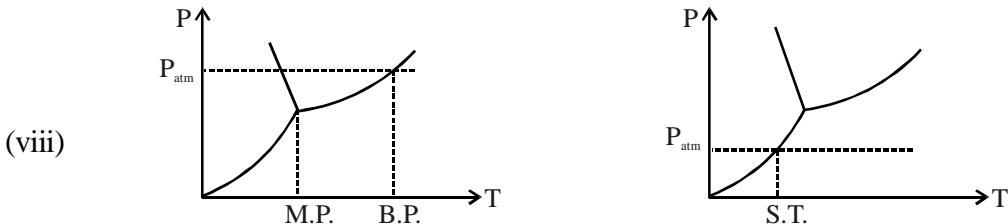
$$K_{C_1} = \frac{1}{2} \frac{(1-x)}{2} = \frac{1}{8} \quad [Since V = 2 L]$$

$$K_{C_2} = \frac{\left(\frac{3x}{4}\right)^{3/2} \left(\frac{x}{4}\right)^{1/2}}{\left(\frac{1-x}{2}\right)} = \frac{\left(\frac{3}{8}\right)^{3/2} \left(\frac{1}{4}\right)^{1/2}}{\left(\frac{1}{4}\right)} = (3)^{3/2} \frac{1}{64} \times \frac{4}{1} = \frac{(3)^{3/2}}{16}$$

## 11. PHYSICAL EQUILIBRIUM



- (i) The combination of temperature and pressure at which all the three physical state of matter co-exist is called triple point of that matter.
- (ii) The vapour pressure of solid is minimum (0) at absolute zero and maximum at triple point.
- (iii) The vapour pressure of liquid is minimum at triple point and maximum at critical temperature.
- (iv) On each line in the graph, the matter exist in two physical states is equilibrium.
- (v) In between two lines, the matter exist in only one physical state.
- (vi) The melting point of solid and the triple point of matter differs slightly.
- (vii) Any solid may be directly converted into gasous state or through liquid state by adjusting the external pressure relative to triple point pressure.



## 12. EQUILIBRIUM CONSTANT & $\Delta G^\circ$

### Gas phase reactions :

Consider a reaction :  $aA(g) + bB(g) \longrightarrow cC(g) + dD(g)$

Now molar Gibb's functions of A, B, C and D are given by :

$$G_A = G_A^\circ + RT \ln\left(\frac{P_A}{P_0}\right)$$

$$G_B = G_B^\circ + RT \ln\left(\frac{P_B}{P_0}\right)$$

$$G_C = G_C^\circ + RT \ln\left(\frac{P_C}{P_0}\right)$$

$$G_D = G_D^\circ + RT \ln\left(\frac{P_D}{P_0}\right)$$

$$\text{Now, } \Delta_r G = cG_C + dG_D - aG_A - bG_B$$

Substituting value of  $G_A$ ,  $G_B$ ,  $G_C$  and  $G_D$  in above equation :

$$\Delta_r G = (cG_C^\circ + dG_D^\circ - bG_B^\circ - aG_A^\circ) + RT \ln \left[ \frac{\left( \frac{P_C}{P_0} \right)^c \left( \frac{P_D}{P_0} \right)^d}{\left( \frac{P_A}{P_0} \right)^a \left( \frac{P_B}{P_0} \right)^b} \right]$$

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

$$\text{Where , } Q = \left( \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \right) \left( \frac{1}{P_0} \right)^{(c+d-a-b)}$$

$$\text{At equilibrium, } \Delta_r G = 0 \text{ and } Q = K_p = \left( \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \right) \left( \frac{1}{P_0} \right)^{\Delta n_g}$$

$$\Delta_r G^\circ = -RT \ln K_p$$

**Note :** Q contains partial pressures at any given moment but  $K_p$  contain partial pressures at equilibrium.

### 13. RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANT & $\Delta G^\circ$ , $\Delta H^\circ$ , $\Delta S^\circ$

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$\Delta H^\circ - T\Delta S^\circ = -RT \ln K_{eq}$$

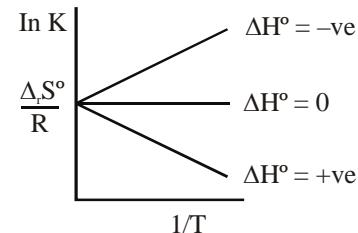
$$\ln K_{eq} = \frac{-\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R}$$

$$\ln K_1 = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{RT_1}$$

$$\ln K_2 = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{RT_2}$$

[where  $K_1$  &  $K_2$  are values of  $K_p$  at temperature  $T_1$ K &  $T_2$ K respectively]

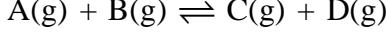
$$\ln \left( \frac{K_2}{K_1} \right) = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (\text{Van't Hoff's equation})$$



### EXERCISE

1. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant  $K_C$  is :- [AIEEE-2003]  
(A)  $\Delta G^\circ = RT \ln K_C$     (B)  $-\Delta G^\circ = RT \ln K_C$     (C)  $\Delta G = RT \ln K_C$     (D)  $-\Delta G = RT \ln K_C$

2. For the reaction at 298 K



$$\Delta H^\circ = -29.8 \text{ kcal}; \Delta S^\circ = -0.1 \text{ kcal/K}$$

Calculate  $\Delta G^\circ$  and  $K$ .

3. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K is :-  
(A)  $-\Delta G^\circ = RT \ln K$     (B)  $\Delta G = RT \ln K$     (C)  $-\Delta G = RT \ln K$     (D)  $\Delta G^\circ = RT \ln K$

### Answer Key

1. Ans.(B)

2. Ans. $\Delta G^\circ = 0$ ;  $K = 1$

3. Ans.(A)

## MISSLENIOS PREVIOUS YEARS QUESTION

1. For the reaction  $\text{CO}_{(\text{g})} + 2\text{H}_{2(\text{g})} \rightleftharpoons \text{CH}_3\text{OH}_{(\text{g})}$ ;  $\text{H}_2$  is introduced into a five litre flask at  $327^\circ\text{C}$ , containing 0.2 mole of  $\text{CO}_{(\text{g})}$  and a catalyst till the pressure is 4.92 atmosphere. At this point 0.1 mole of  $\text{CH}_3\text{OH}_{(\text{g})}$  is formed. Calculate  $K_c$  and  $K_p$ . [JEE 1990]

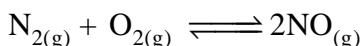
**Ans.**  $K_c = 279.64 \text{ litre}^2 \text{ mole}^{-2}$ ;  $K_p = 0.115 \text{ atm}^{-2}$

2. At temperature  $T$ , a compound  $\text{AB}_{2(\text{g})}$  dissociates according to the reaction  $2\text{AB}_{2(\text{g})} \rightleftharpoons 2\text{AB}_{(\text{g})} + \text{B}_{2(\text{g})}$ ; with a degree of dissociation ' $x$ ', which is small compared to unity. Deduce the expression for ' $x$ ' in terms of the equilibrium constant  $K_p$  and the total pressure  $P$ .

[JEE 1994]

$$\text{Ans. } x = \sqrt[3]{\frac{2K_p}{P}}$$

3. A sample of air consisting of  $\text{N}_2$  and  $\text{O}_2$  was heated to 2500 K until the equilibrium



was established with an equilibrium constant  $K_c = 2.1 \times 10^{-3}$ . At equilibrium, the mole% of NO was 1.8. Estimate the initial composition of air in mole fraction of  $\text{N}_2$  and  $\text{O}_2$ .

[JEE 1997]

**Ans.** 79%, 21%

4. The degree of dissociation is 0.4 at 400K & 1.0 atm for the gasoeus reaction  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2(\text{g})$ . Assuming ideal behaviour of all gases. Calculate the density of equilibrium mixture at 400K & 1.0 atm pressure. [JEE 1999]

**Ans.** Ans.  $4.54 \text{ g dm}^{-3}$

$$\begin{array}{rcl} \text{Sol. } \text{PCl}_5 & = & \text{PCl}_3 + \text{Cl}_2 \\ & 1 & - \\ & 1-0.4 & 0.4 \\ & 0.6 & 0.4 \end{array}$$

$$M_{av} = \frac{208.5}{1.4}$$

$$PM = dRT$$

$$1 \times \frac{208.5}{1.4} = d \times 0.0821 \times 400$$

5. For the reversible reaction :

[JEE 2000]

$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  at  $500^\circ\text{C}$ . The value of  $K_p$  is  $1.44 \times 10^{-5}$ , when partial pressure is measured in atmospheres. The corresponding value of  $K_c$  with concentration in mol L<sup>-1</sup> is :

- (A)  $1.44 \times 10^{-5} / (0.082 \times 500)^2$       (B)  $1.44 \times 10^{-5} / (8.314 \times 773)^2$   
 (C)  $1.44 \times 10^{-5} / (0.082 \times 500)^2$       (D)  $1.44 \times 10^{-5} / (0.082 \times 773)^{-2}$

**Ans.** (D)

$$\text{Sol. } K_p = K_c (RT)^{-2}$$

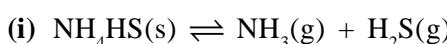
**Ans. (D)**

**Sol.** O increases at initial steps

7. When 3.06g of solid  $\text{NH}_4\text{HS}$  is introduced into a two litre evacuated flask at  $27^\circ\text{C}$ , 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. [JEE 2000]

  - Calculate  $K_C$  &  $K_P$  for the reaction at  $27^\circ\text{C}$ .
  - What would happen to the equilibrium when more solid  $\text{NH}_4\text{HS}$  is introduced into the flask?

Ans. (i)  $K_c = 8.1 \times 10^{-5} \text{ mol}^2 \text{ L}^2$ ;  $K_p = 4.91 \times 10^{-2} \text{ atm}^2$  (ii) No effect;



$$\frac{0.06}{2} \text{ mole} \quad - \quad -$$

$$\frac{0.042}{2} \text{ mole} \quad \frac{0.018}{2} \quad \frac{0.018}{2}$$

$$K_c = \frac{0.018}{2} \times \frac{0.018}{2}$$

$$K_C = 8.1 \times 10^{-5}$$

$$K_p = (8.1 \times 10^{-5}) \times (RT)^2$$

(ii) When more of  $\text{NH}_4\text{H}_5(\text{s})$  is added then no-effect will occur on equilibrium.



**Ans. (D)**

**Sol.**  $K_p$  depends only on temperature.

9. Consider the following equilibrium in a closed container :  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ .

At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant ( $K_p$ ) and degree of dissociation ( $\alpha$ ) : [JEE 2002]

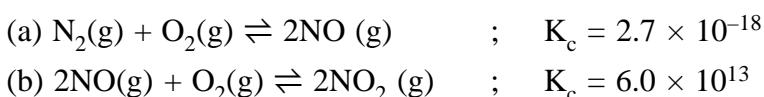


**Ans. (D)**

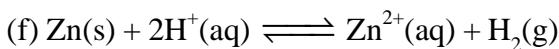
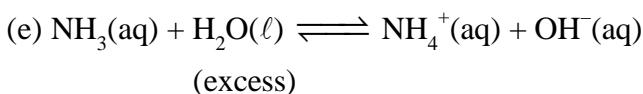
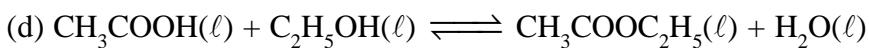
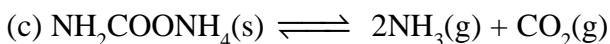
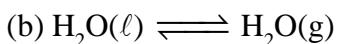
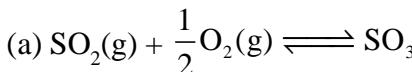
**Sol.**  $K_p$  is independent of volume of container

## EXERCISE (S-1)

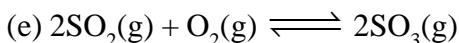
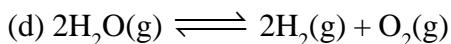
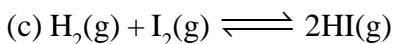
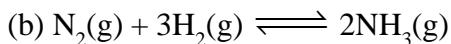
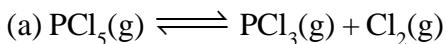
1. Which of the following reactions goes almost all the way to completion, and which proceeds hardly at all?



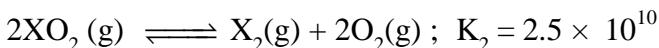
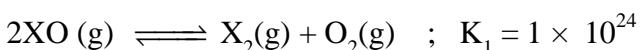
2. Write down the expression for equilibrium constant  $K_p$  and  $K_c$  for the following reactions :



3. Write the relationship between  $K_p$  and  $K_c$  for the following reactions :

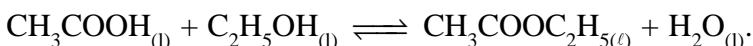


4. Find stability of reactants for the given equilibrium reaction :



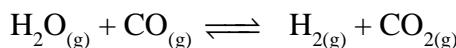
5. The value of  $K_c$  for the reaction  $2\text{A} \rightleftharpoons \text{B} + \text{C}$  is  $2 \times 10^{-3}$ . At a given time, the composition of reaction mixture is  $[\text{A}] = [\text{B}] = [\text{C}] = 3 \times 10^{-4}$  M. In which direction the reaction will proceed ?

6. The ester or ethyl acetate is formed by the reaction between ethanol and acetic acid and equilibrium is represented as :



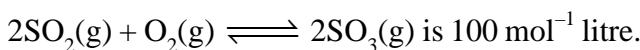
- (a) Write the concentration ratio (reaction quotient),  $Q_c$  for this reaction. (Note that water is not in excess and is not a solvent in this reaction).
- (b) At 293 K, if starts with 1.00 mole of acetic acid and 0.180 moles of ethanol, there is 0.171 moles of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.
- (c) Starting with 0.500 moles of ethanol and 1.000 mole of acetic acid and maintaining it at 293 K, 0.214 moles of ethyl acetate is found after some time. Has equilibrium been reached ?

7. If  $K_c = 0.5 \times 10^{-9}$  at 1000 K for the reaction  $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ , what is  $K_c$  at 1000 K for the reaction  $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$ ?
8. An equilibrium mixture of  $PCl_5$ ,  $PCl_3$  and  $Cl_2$  at a certain temperature contains  $0.5 \times 10^{-3}$  M  $PCl_5$ ,  $1.5 \times 10^{-2}$  M  $PCl_3$ , and  $3 \times 10^{-2}$  M  $Cl_2$ . Calculate the equilibrium constant  $K_c$  for the reaction  $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ .
9. A sample of  $HI$  ( $9.6 \times 10^{-3}$  mol) was placed in an empty 2.00 L container at 1000 K. After equilibrium was reached, the concentration of  $I_2$  was  $4 \times 10^{-4}$  M. Calculate the value of  $K_c$  at 1000 K for the reaction  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ .
10. The vapour pressure of water at  $27^\circ C$  is 0.2463 atm. Calculate the values of  $K_p$  and  $K_c$  at  $27^\circ C$  for the equilibrium  $H_2O(l) \rightleftharpoons H_2O(g)$ .
11. The value of  $K_c$  for the reaction  $3O_2(g) \rightleftharpoons 2O_3(g)$  is  $8 \times 10^{-55}$  at  $25^\circ C$ . Do you expect pure air at  $25^\circ C$  to contain much  $O_3$  (ozone) when  $O_2$  and  $O_3$  are in equilibrium? If the equilibrium concentration of  $O_2$  in air at  $25^\circ C$  is  $8 \times 10^{-3}$  M, what is the equilibrium concentration of  $O_3$ ?
12. One mole of  $H_2O$  and one mole of  $CO$  are taken in a 10 L vessel and heated to 725 K. At equilibrium 40 percent of water (by mass) reacts with carbon monoxide according to the equation.



Calculate the equilibrium constant for the reaction.

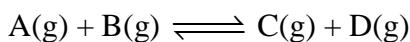
13. A vessel at 1000 K contains  $CO_2$  with a pressure of 0.6 atm. some of the  $CO_2$  is converted into  $CO$  on addition of graphite. Calculate the value of  $K$ , if total pressure at equilibrium is 0.9 atm.
14. Calculate the equilibrium concentration of  $H_2$ ,  $I_2$  and  $HI$  at 300 K if initially 2 mol of  $H_2$  and  $I_2$  are taken in a closed container of having volume 10 lit. [Given :  $H_2 + I_2 \rightleftharpoons 2HI$ ;  $K = 100$  at 300 K]
15. A mixture of  $SO_3$ ,  $SO_2$  and  $O_2$  gases is maintained at equilibrium in 10 litre flask at a particular temperature in which  $K_c$  for the reaction,



At equilibrium,

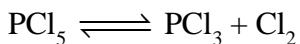
- If number of mole of  $SO_3$  and  $SO_2$  in flask are same, how many mole of  $O_2$  are present ?
- If number of mole of  $SO_3$  in flask are twice the number of mole of  $SO_2$ , how many mole of  $O_2$  are present ?

16. For the given reaction,



the number of moles at equilibrium was found to be 4, 4, 2 & 8 respectively in 1 L container. Find the new equilibrium concentration if 18 moles of D are added to above 1 L container.

17. For the given reaction,



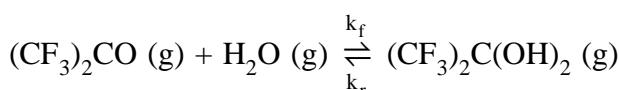
the number of moles at equilibrium was found to be 2, 6 & 4 respectively at 10 atm pressure. Find the new equilibrium moles & partial pressure, if it is restablished at an equilibrium pressure 50 atm.

18. For the dissociation reaction  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$  derive the expression for the degree of dissociation in terms of  $K_p$  and total pressure P.
19. For the reaction  $2\text{SO}_{3(\text{g})} \rightleftharpoons 2\text{SO}_{2(\text{g})} + \text{O}_{2(\text{g})}$   
 Initially 5 moles of  $\text{SO}_3$  is taken and at equilibrium 4 moles of  $\text{SO}_3$  is dissociated then find out  $\alpha$  and the value of  $K_C$  (Volume = 2 litre)
20. 1.1 mole of A mixed with 2.2 mole of B and the mixture is kept in a 1 litre flask at the equilibrium,  $\text{A} + 2\text{B} \rightleftharpoons 2\text{C} + \text{D}$  is reached. At equilibrium 0.2 mole of C is formed then the value of  $K_C$  will be.
21. The air pollutant NO is produced in automobile engines from the high temperature reaction  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ ;  $K_c = 16$  at 2300 K. If the initial concentrations of  $\text{N}_2$  and  $\text{O}_2$  at 2300 K are both 1.5 M, what are the concentrations of NO,  $\text{N}_2$ , and  $\text{O}_2$  when the reaction mixture reaches equilibrium?
22. At 700 K,  $K_p = 0.2$  for the reaction  $\text{ClF}_3(\text{g}) \rightleftharpoons \text{ClF}(\text{g}) + \text{F}_2(\text{g})$ . Calculate the equilibrium partial pressure of  $\text{ClF}_3$ ,  $\text{ClF}$ , and  $\text{F}_2$  if only  $\text{ClF}_3$  is present initially, at a partial pressure of 0.150 atm.
23. The degree of dissociation of  $\text{N}_2\text{O}_4$  into  $\text{NO}_2$  at 1.5 atmosphere and 40°C is 0.25. Calculate its  $K_p$  at 40°C. Also report degree of dissociation at 10 atmospheric pressure at same temperature.
24. At 46°C,  $K_p$  for the reaction  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$  is 0.667 atm. Compute the percent dissociation of  $\text{N}_2\text{O}_4$  at 46°C at a total pressure of 380 Torr.
25.  $2\text{NOBr}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Br}_2(\text{g})$ . If nitrosyl bromide ( $\text{NOBr}$ ) is 33.33% dissociated at 25°C & a total pressure of 0.28 atm. Calculate  $K_p$  for the dissociation at this temperature.
26. The system  $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$  maintained in a closed vessel at 60°C & a pressure of 5 atm has an average (i.e. observed) molecular weight of 69, calculate  $K_p$ . At what pressure at the same temperature would the observed molecular weight be (230/3) ?
27. In the esterification  $\text{C}_2\text{H}_5\text{OH}(\text{l}) + \text{CH}_3\text{COOH}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \text{H}_2\text{O}(\text{l})$  an equimolar mixture of alcohol and acid taken initially yields under equilibrium, the water with mole fraction = 0.333. Calculate the equilibrium constant.
28. The equilibrium constant for the reaction is 9 at 900°C  $\text{S}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons \text{CS}_2(\text{g})$ . Calculate the pressure of two gases at equilibrium, when 2 atm of  $\text{S}_2$  and excess of  $\text{C}(\text{s})$  come to equilibrium.

29. A sample of  $\text{CaCO}_3(\text{s})$  is introduced into a sealed container of volume 0.821 litre & heated to 1000K until equilibrium is reached. The equilibrium constant for the reaction  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  is  $4 \times 10^{-2}$  atm at this temperature. Calculate the mass of CaO present at equilibrium.
30. Anhydrous calcium chloride is often used as a dessicant. In the presence of excess of  $\text{CaCl}_2$ , the amount of the water taken up is governed by  $K_p = 6.4 \times 10^{85}$  for the following reaction at room temperature,  $\text{CaCl}_2(\text{s}) + 6\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})$ . What is the equilibrium vapour pressure of water in a closed vessel that contains  $\text{CaCl}_2(\text{s})$ ?
31. 20.0 grams of  $\text{CaCO}_3(\text{s})$  were placed in a closed vessel, heated & maintained at  $727^\circ\text{C}$  under equilibrium  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  and it is found that 75 % of  $\text{CaCO}_3$  was decomposed. What is the value of  $K_p$ ? The volume of the container was 15 litres.
32. (a) Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and additional hydrogen at high temperature and pressure in the presence of a suitable catalyst. Write the expression for the equilibrium constant for the reversible reaction.  

$$2\text{H}_2(\text{g}) + \text{CO}(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g}) \quad \Delta H = -90.2 \text{ kJ}$$
- (b) Assume that equilibrium has been established and predict how the concentration of  $\text{H}_2$ , CO and  $\text{CH}_3\text{OH}$  will differ at a new equilibrium if (1) more  $\text{H}_2$  is added. (2) CO is removed. (3)  $\text{CH}_3\text{OH}$  is added. (4) the pressure on the system is increased. (5) the temperature of the system is increased. (6) more catalyst is added.
33. Ammonia is a weak base that reacts with water according to the equation  

$$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+ + \text{OH}^- (\text{aq})$$
  
 Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?  
 (a) Addition of NaOH. (b) Addition of HCl. (c) Addition of  $\text{NH}_4\text{Cl}$ .
34. Consider the gas-phase hydration of hexafluoroacetone,  $(\text{CF}_3)_2\text{CO}$ :



At  $76^\circ\text{C}$ , the forward and reverse rate constants are  $k_f = 0.15 \text{ M}^{-1}\text{s}^{-1}$  and  $k_r = 6 \times 10^{-4}\text{s}^{-1}$ . What is the value of the equilibrium constant  $K_c$ ?

35. Listed in the table are forward and reverse rate constants for the reaction  $2\text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$

Temperature (K)	$k_f (\text{M}^{-1}\text{s}^{-1})$	$k_r (\text{M}^{-1}\text{s}^{-1})$
1400	0.29	$1.1 \times 10^{-6}$
1500	1.3	$1.4 \times 10^{-5}$

Is the reaction endothermic or exothermic? Explain in terms of kinetics.

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 EXERCISE (O-1)
 

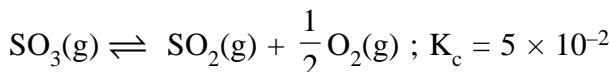
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Only one is correct

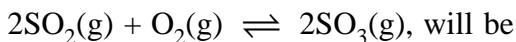
1.  $x \rightleftharpoons{ } y$  reaction is said to be in equilibrium, when :-  
 (A) Only 10% conversion of x to y takes place  
 (B) Complete conversion of x to y has taken place  
 (C) Conversion of x to y is only 50% complete  
 (D) The rate of change of x to y is just equal to the rate of change of y to x in the system
2. For which reaction is  $K_p = K_c$  :-  
 (A)  $2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g)$       (B)  $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$   
 (C)  $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$       (D)  $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$
3. For the reaction  

$$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s) \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O}_{(s)} + 2\text{H}_2\text{O}_{(g)}$$
 Which one is correct representation :-  
 (A)  $K_p = (P_{(\text{H}_2\text{O})})^2$       (B)  $K_c = [\text{H}_2\text{O}]^2$       (C)  $K_p = K_c(RT)^2$       (D) All
4.  $\log \frac{K_p}{K_c} + \log RT = 0$  is true relationship for the following reaction:-  
 (A)  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$       (B)  $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$   
 (C)  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$       (D) (B) and (C) both
5. For a reaction  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ , the value of  $K_c$  does not depends upon :-  
 (a) Initial concentration of the reactants      (b) Pressure  
 (c) Temperature      (d) Catalyst  
 (A) Only c      (B) a, b, c      (C) a, b, d      (D) a, b, c, d
6. If some He gas is introduced into the equilibrium  $\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$  at constant pressure and temperature then equilibrium constant of reaction:  
 (A) Increase      (B) Decrease      (C) Unchange      (D) Nothing can be said

7. The equilibrium constant for the given reaction :

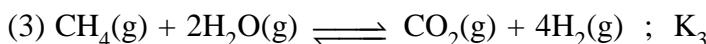
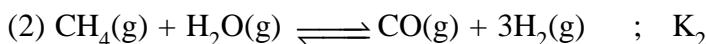
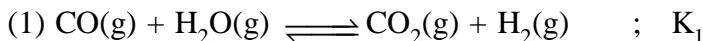


The value of  $K_c$  for the reaction :





- 8.** For the following three reactions, 1, 2 and 3 equilibrium, constants are given :



Which of the following relations is correct ?

- $$(A) K_1 \sqrt{K_2} = K_3 \quad (B) K_2 K_3 = K_1 \quad (C) K_3 = K_1 K_2 \quad (D) K_3 = K_2^3 K_1^2$$

9. Sulfide ion in alkaline solution reacts with solid sulfur to form polysulfide ions having formulas  $S_2^{2-}$ ,  $S_3^{2-}$ ,  $S_4^{2-}$  and so on. The equilibrium constant for the formation of  $S_2^{2-}$  is 12 ( $K_1$ ) & for the formation of  $S_3^{2-}$  is 132 ( $K_2$ ), both from S and  $S^{2-}$ . What is the equilibrium constant for the formation of  $S_3^{2-}$  from  $S_2^{2-}$  and S?



- 10.** If 0.5 mole  $\text{H}_2$  is reacted with 0.5 mole  $\text{I}_2$  in a ten-litre container at  $444^\circ \text{C}$  and at same temperature value of equilibrium constant  $K_c$  is 49, the ratio of  $[\text{HI}]$  and  $[\text{I}_2]$  will be :-





- 12.** How many moles per litre of  $\text{PCl}_5$  has to be taken to obtain 0.1 mole  $\text{Cl}_2$ , if the value of equilibrium constant  $K_c$  is 0.04 ?

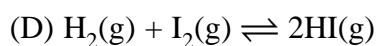
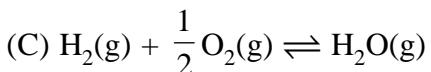
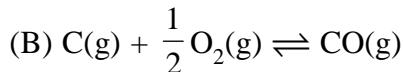
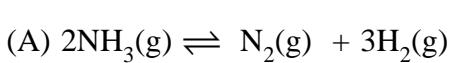


- 13.** In the beginning of the reaction,  $A \rightleftharpoons B + C$ , 2 moles of A are taken, out of which 0.5 mole gets dissociated. What is the degree of dissociation of A ?

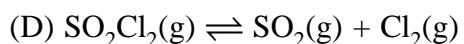
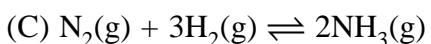
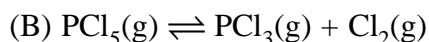
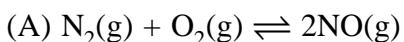
14. In the reaction,  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ , the amount of each  $\text{PCl}_5$ ,  $\text{PCl}_3$  and  $\text{Cl}_2$  is 2 mole at equilibrium and total pressure is 3 atmosphere. The value of  $K_p$  will be  
 (A) 1.0 atm.      (B) 3.0 atm.      (C) 2.9 atm.      (D) 6.0 atm.
15. 4 moles of  $\text{PCl}_5$  are heated at constant temperature in closed container. If degree of dissociation for  $\text{PCl}_5$  is 0.5 calculate total number of moles at equilibrium :-  
 (A) 4.5      (B) 6      (C) 3      (D) 4
16. For the reaction  $\text{A} + 2\text{B} \rightleftharpoons 2\text{C} + \text{D}$ , initial concentration of A is  $a$  and that of B is 1.5 times that of A. Concentration of A and D are same at equilibrium. What should be the concentration of B at equilibrium ?  
 (A)  $\frac{a}{4}$       (B)  $\frac{a}{2}$       (C)  $\frac{3a}{4}$       (D) All of the above.
17. For the reaction  $3\text{A(g)} + \text{B(g)} \rightleftharpoons 2\text{C(g)}$  at a given temperature,  $K_c = 9.0$ . What must be the volume of the flask, if a mixture of 2.0 mol each of A, B and C exist in equilibrium?  
 (A) 6L      (B) 9L      (C) 36 L      (D) None of these
18. For the following gases equilibrium.  
 $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$   
 $K_p$  is found to be equal to  $K_c$ . This is attained when temperature is  
 (A) 0°C      (B) 273 K      (C) 1 K      (D) 12.19 K
19. The degree of dissociation of  $\text{SO}_3$  is  $\alpha$  at equilibrium pressure  $p^0$ .  
 $K_p$  for  $2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$   
 (A)  $\frac{p^0\alpha^3}{2(1-\alpha)^3}$       (B)  $\frac{p^0\alpha^3}{(2+\alpha)(1-\alpha)^2}$       (C)  $\frac{p^0\alpha^2}{2(1-\alpha)^2}$       (D) None of these
20. For the reaction :  $2\text{HI(g)} \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ , the degree of dissociated ( $\alpha$ ) of  $\text{HI(g)}$  is related to equilibrium constant  $K_p$  by the expression  
 (A)  $\frac{1+2\sqrt{K_p}}{2}$       (B)  $\sqrt{\frac{1+2K_p}{2}}$       (C)  $\sqrt{\frac{2K_p}{1+2K_p}}$       (D)  $\frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$
21. The equilibrium constant for the reaction  
 $\text{A(g)} + 2\text{B(g)} \rightleftharpoons \text{C(g)}$   
 is  $0.25 \text{ dm}^6 \text{ mol}^{-2}$ . In a volume of  $5 \text{ dm}^3$ , what amount of A must be mixed with 4 mol of B to yield 1 mol of C at equilibrium.  
 (A) 3 moles      (B) 24 moles      (C) 26 moles      (D) None of these

22. A 20.0 litre vessel initially contains 0.50 mole each of  $H_2$  and  $I_2$  gases. These substances react and finally reach an equilibrium condition. Calculate the equilibrium concentration of HI if  $K_{eq} = 49$  for the reaction  $H_2 + I_2 \rightleftharpoons 2HI$ .
- (A) 0.78 M      (B) 0.039 M      (C) 0.033 M      (D) 0.021 M
23. At 675 K,  $H_2(g)$  and  $CO_2(g)$  react to form  $CO(g)$  and  $H_2O(g)$ ,  $K_p$  for the reaction is 0.16. If a mixture of 0.25 mole of  $H_2(g)$  and 0.25 mol of  $CO_2$  is heated at 675 K, mole % of  $CO(g)$  in equilibrium mixture is :
- (A) 7.14      (B) 14.28      (C) 28.57      (D) 33.33
24. The vapour density of  $N_2O_4$  at a certain temperature is 30. What is the % dissociation of  $N_2O_4$  at this temperature?
- (A) 53.3%      (B) 106.6%      (C) 26.7%      (D) None
25. The equilibrium constant  $K_p$  (in atm) for the reaction is 9 at 7 atm and 300 K.
- $$A_2(g) \rightleftharpoons B_2(g) + C_2(g)$$
- Calculate the average molar mass (in gm/mol) of an equilibrium mixture.
- Given :** Molar mass of  $A_2$ ,  $B_2$  and  $C_2$  are 70, 49 & 21 gm/mol respectively.
- (A) 50      (B) 45      (C) 40      (D) 37.5
26. Vapour density of the equilibrium mixture of the reaction
- $$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$
- is 6.0  
Percent dissociation of ammonia gas is:
- (A) 13.88      (B) 58.82      (C) 41.66      (D) None of these
27. The equilibrium concentration of B [ $(B)_e$ ] for the reversible reaction  $A \rightleftharpoons B$  can be evaluated by the expression:-
- (A)  $K_C [A]_e^{-1}$       (B)  $\frac{k_f}{k_b} [A]_e^{-1}$       (C)  $k_f k_b^{-1} [A]_e$       (D)  $k_f k_b [A]^{-1}$
28. The equilibrium  $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$  shifts forward if :-
- (A) A catalyst is used.  
 (B) An adsorbent is used to remove  $SO_3$  as soon as it is formed.  
 (C) Small amounts of reactants are removed.  
 (D) None of these
29. In manufacture of NO, the reaction  $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ ,  $\Delta H +ve$  is favourable if :-
- (A) Pressure is increased      (B) Pressure is decreased  
 (C) Temperature is increased      (D) Temperature is decreased

30. In which of the following reactions, increase in the pressure at constant temperature does not affect the moles at equilibrium :



31. Change in volume of the system does not alter the number of moles in which of the following equilibrium



32. The conditions favourable for the reaction :



are :

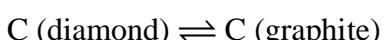
(A) low temperature, high pressure

(B) any value of T and P

(C) low temperature and low pressure

(D) high temperature and high pressure

33. Densities of diamond and graphite are 3.5 and 2.3 gm/mL.



$$\Delta_r H = -1.9 \text{ kJ/mole}$$

favourable conditions for formation of diamond are

(A) high pressure and low temperature

(B) low pressure and high temperature

(C) high pressure and high temperature

(D) low pressure and low temperature

34. The equilibrium  $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$  is attained at  $25^\circ\text{C}$  in a closed rigid container and an inert gas, helium is introduced. Which of the following statements is/are correct.

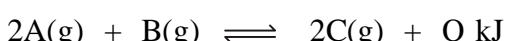
 (A) concentrations of  $\text{SO}_2$ ,  $\text{Cl}_2$  and  $\text{SO}_2\text{Cl}_2$  do not change

(B) more chlorine is formed

 (C) concentration of  $\text{SO}_2$  is reduced

 (D) more  $\text{SO}_2\text{Cl}_2$  is formed

35. The yield of product in the reaction



would be lower at :

(A) low temperature and low pressure

(B) high temperature &amp; high pressure

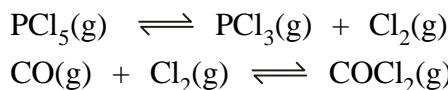
(C) low temperature and to high pressure

(D) high temperature &amp; low pressure

## EXERCISE (O-2)

More than one may be correct

1. Following two equilibrium is simultaneously established in a container



If some Ni(s) is introduced in the container forming  $\text{Ni}(\text{CO})_4(\text{g})$  then at new equilibrium

- (A)  $\text{PCl}_3$  concentration will increase      (B)  $\text{PCl}_3$  concentration will decrease  
 (C)  $\text{Cl}_2$  concentration will remain same      (D) CO concentration will remain same

2. For the reaction  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ , the forward reaction at constant temperature is favoured by

- (A) introducing an inert gas at constant volume  
 (B) introducing chlorine gas at constant volume  
 (C) introducing an inert gas at constant pressure  
 (D) introducing  $\text{PCl}_5$  at constant volume.

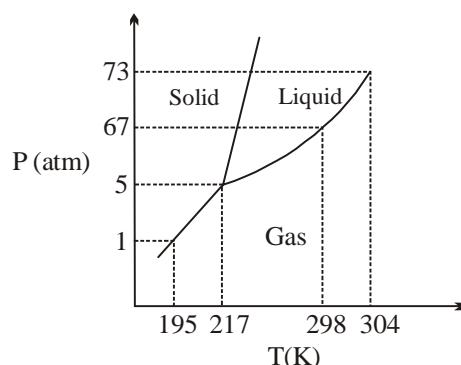
3. When  $\text{NaNO}_3$  is heated in a closed vessel, oxygen is liberated and  $\text{NaNO}_2$  is left. At equilibrium

- (A) addition of  $\text{NaNO}_2$  favours reverse reaction  
 (B) addition of  $\text{NaNO}_3$  favours forward reaction  
 (C) increasing temperature favours forward reaction  
 (D) increasing pressure favours reverse reaction

4. For the gas phase reaction,  $\text{C}_2\text{H}_4 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6$  ( $\Delta H = -32.7 \text{ kcal}$ ), carried out in a closed vessel, the equilibrium moles of  $\text{C}_2\text{H}_4$  can be increased by

- (A) increasing the temperature      (B) decreasing the pressure  
 (C) removing some  $\text{H}_2$       (D) adding some  $\text{C}_2\text{H}_6$

5. Phase diagram of  $\text{CO}_2$  is shown as following

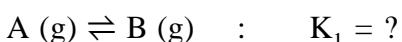


Based on above find the correct statement(s)

- (A) 298K is the normal boiling point of liquid  $\text{CO}_2$   
 (B) At 1 atm & 190 K  $\text{CO}_2$  will exist as gas.  
 (C)  $\text{CO}_2(\text{s})$  will sublime above 195K under normal atmospheric pressure  
 (D) Melting point & boiling point of  $\text{CO}_2$  will increase on increasing pressure

6. The equilibrium between, gaseous isomers A, B and C can be represented as

<b>Reaction</b>	<b>Equilibrium constant</b>
-----------------	-----------------------------



If one mole of A is taken in a closed vessel of volume 1 litre, then

(A)  $[A] + [B] + [C] = 1$  M at any time of the reactions

(B) Concentration of C is 4.1 M at the attainment equilibrium in all the reactions

(C) The value of  $K_1$  is  $\frac{1}{0.24}$

(D) Isomer [A] is least stable as per thermodynamics.

7. For the gas phase exothermic reaction,  $A_2 + B_2 \rightleftharpoons C_2$ , carried out in a closed vessel, the equilibrium moles of  $A_2$  can be increased by

(A) increasing the temperature

(B) decreasing the pressure

(C) adding inert gas at constant pressure

(D) removing some  $C_2$

8. Consider the equilibrium  $HgO(s) + 4I^-(aq) + H_2O(l) \rightleftharpoons HgI_4^{2-}(aq) + 2OH^-(aq)$ , which changes will decrease the equilibrium concentration of  $HgI_4^{2-}$

(A) Addition of 0.1 M HI (aq)

(B) Addition of HgO (s)

(C) Addition of  $H_2O(l)$

(D) Addition of KOH (aq)

9. Decrease in the pressure for the following equilibria :  $H_2O(s) \rightleftharpoons H_2O(l)$  result in the :

(A) formation of more  $H_2O(s)$

(B) formation of more  $H_2O(l)$

(C) increase in melting point of  $H_2O(s)$

(D) decrease in melting point of  $H_2O(s)$

### Assertion Reason

10. **Statement -1 :** Total number of moles in a closed system at new equilibrium is less than the old equilibrium if some amount of a substance is removed from a system

(consider a reaction  $A(g) \rightleftharpoons B(g)$  ) at equilibrium.

**Statement -2 :** The number of moles of the substance which is removed, is partially compensated as the system reached to new equilibrium.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is false, statement-2 is true.

(D) Statement-1 is true, statement-2 is false.

- 11.** **Statement-1 :** Ammonia at a pressure of 10 atm and  $\text{CO}_2$  at a pressure of 20 atm are introduced into an evacuated chamber. If  $K_p$  for the reaction  $\text{NH}_2\text{COONH}_4(s) \rightleftharpoons 2\text{NH}_3(g) + \text{CO}_2(g)$  is 2020  $\text{atm}^3$ , the total pressure after a long time is less than 30 atm.  
**Statement-2 :** Equilibrium can be attained from both directions.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.

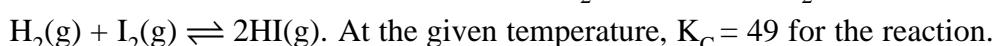
**12.** **Statement-1 :** Catalyst does not alter the equilibrium constant  
**Statement-2 :** Because for the catalysed reaction and uncatalysed reaction  $\Delta H$  remain same an equilibrium constant depend on  $\Delta H$ .  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.

**13.** **Statement-1 :** Equilibrium constant may show higher or lower values with increase in temperature  
**Statement-2 :** The change depend on heat of reaction.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.

## Comprehension :

**Paragraph for Question Nos. 14 to 16**

In a 7.0 L evacuated chamber, 0.50 mol H<sub>2</sub> and 0.50 mol I<sub>2</sub> react at 427°C.



**Paragraph for Question Nos. 18 to 20**

Influence of pressure, temperature, concentration and addition of inert gas on a reversible chemical reaction in equilibrium can be explained by formulating the expression for equilibrium constant  $K_c$  or  $K_p$  for the equilibrium. On the other hand Le Chatelier principle can be theoretically used to explain the effect of P, T or concentration on the physical or chemical equilibrium both.

- 18.** For the reaction :  $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$  increase of pressure shows :
- An increase in degree of dissociation and a decrease in  $K_c$
  - A decrease in degree of dissociation and a decrease in  $K_c$
  - An increase in degree of dissociation but  $K_c$  remains constant
  - A decrease in degree of dissociation but  $K_c$  remains constant
- 19.** For the reaction :  $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ ;  $\Delta H = -ve$ , An increase in temperature shows :
- More dissociation of  $\text{SO}_3$  and a decrease in  $K_c$
  - Less dissociation of  $\text{SO}_3$  and an increase in  $K_c$
  - More dissociation of  $\text{SO}_3$  and an increase in  $K_c$
  - Less dissociation of  $\text{SO}_3$  and an decrease in  $K_c$
- 20.** For the reaction :  $\text{Fe}^{3+}(\text{aq.}) + \text{SCN}^-(\text{aq.}) \rightleftharpoons \underset{\text{Yellow}}{[\text{Fe}(\text{NCS})]^{2+}}(\text{aq.})$  ; in equilibrium if little more aqueous solution of  $\text{FeCl}_3$  is added, than :
- Forward reaction becomes more and red colours is deepened
  - Backward reaction becomes more and red colour faintens
  - Solution becomes colourless
  - None of these

**Match the column :**

**21. Column I**

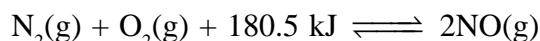
- $K_p < K_c$
- Introduction of inert gas at constant pressure will decrease the concentration of reactants
- $K_p^o$  is dimensionless
- Temperature increase will shift the reaction on product side.

**Column II**

- $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$
- $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
- $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$
- $\text{NH}_3(\text{g}) + \text{HI}(\text{g}) \rightleftharpoons \text{NH}_4\text{I}(\text{s})$

**22. Column-I**
**(Reactions)**

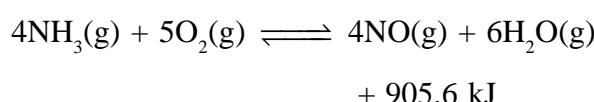
(A) Oxidation of nitrogen



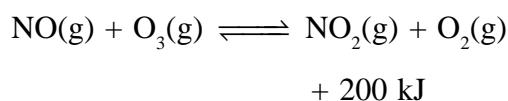
(B) Dissociation of  $N_2O_4(g)$



(C) Oxidation of  $NH_3(g)$



(D) Formation of  $NO_2(g)$


**Column-II**
**(Favourable conditions)**

(p) Addition of inert gas at constant pressure

(q) Decrease in pressure

(r) Decrease in temperature

(s) Increase in temperature

**Matching list type :**

Answer Q.No. 23, 24 and 25 by appropriately matching the information given in the three columns of the following table.

**Column-I**
**(Reaction)**
**Column-II**
**(If  $\alpha$  is negligible w.r.t. 1)**
**Column-III**

(A)  $2X(g) \rightleftharpoons Y(g) + Z(g)$ ,  $\Delta H = -ve$

(P)  $\alpha = 2 \times \sqrt{K_p}$

(I) K increase with increase in temperature

(B)  $X(g) \rightleftharpoons Y(g) + Z(g)$ ,  $\Delta H = +ve$

(Q)  $\alpha = 3 \times \sqrt{K_p \cdot P}$

(II) K decrease with increase in temperature

(C)  $3X(g) \rightleftharpoons Y(g) + Z(g)$ ,  $\Delta H = +ve$

(R)  $\alpha = \left( \frac{2K_p}{P} \right)^{1/3}$

(III) Pressure has no effect

(D)  $2X(g) \rightleftharpoons Y(g) + 2Z(g)$ ,  $\Delta H = +ve$

(S)  $\alpha = \sqrt{K_p / P}$

(IV) Addition of inert gas at constant pressure shift equilibrium in forward direction

**23. Which of the following option is correctly matched?**

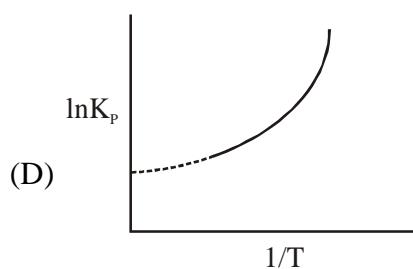
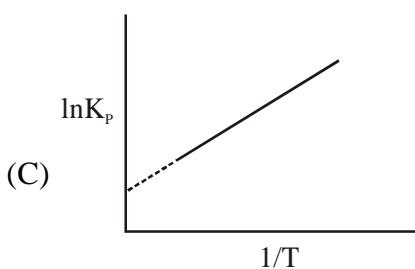
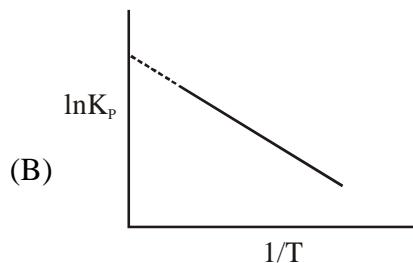
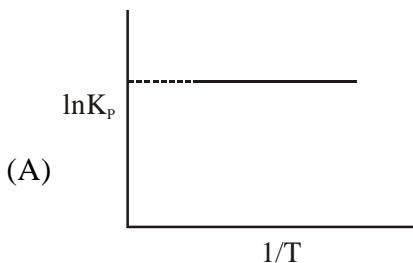
(A) A-Q-III

(B) B-S-II

(C) C-Q-II

(D) D-R-IV

- 24.** Correct representation of reaction in option (A) is represented by graph



25. For the reaction of option (B) if degree of dissociation varies inversely as square root of pressure of the system. Suppose at constant temperature volume is increased 16 times of its initial volume the degree of dissociation ( $\alpha$ ) for this reaction will become :

(A) 4 times

(B) 2 times

(C) 1/4 times

(D) 1/2 times

## EXERCISE (JM)

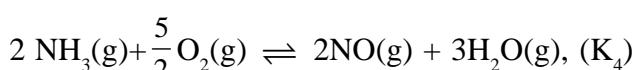
1. A vessel at 1000 K contains  $\text{CO}_2$  with a pressure of 0.5 atm. Some of the  $\text{CO}_2$  is converted into  $\text{CO}$  on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of  $K$  is :- [AIEEE-2011]  
(1) 0.3 atm      (2) 0.18 atm      (3) 1.8 atm      (4) 3 atm
2. The equilibrium constant ( $K_C$ ) for the reaction  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$  at temperature T is  $4 \times 10^{-4}$ . The value of  $K_C$  for the reaction  $\text{NO}(\text{g}) \rightarrow \frac{1}{2}\text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$  at the same temperature is :- [AIEEE-2012]  
(1) 50.0      (2) 0.02      (3)  $2.5 \times 10^2$       (4)  $4 \times 10^{-4}$
3. 8 mol of  $\text{AB}_3(\text{g})$  are introduced into a 1.0  $\text{dm}^3$  vessel. If it dissociates as  $2\text{AB}_3(\text{g}) \rightleftharpoons \text{A}_2(\text{g}) + 3\text{B}_2(\text{g})$  At equilibrium, 2mol of  $\text{A}_2$  are found to be present. The equilibrium constant of this reaction is :- [JEE-MAINS(online)-12]  
(1) 36      (2) 3      (3) 27      (4) 2
4. The value of  $K_p$  for the equilibrium reaction  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$  is 2. The percentage dissociation of  $\text{N}_2\text{O}_4(\text{g})$  at a pressure of 0.5 atm is [JEE-MAINS(online)-12]  
(1) 71      (2) 50      (3) 88      (4) 25
5.  $K_1$ ,  $K_2$  and  $K_3$  are the equilibrium constants of the following reactions (I), (II) and (III), respectively  
(I)  $\text{N}_2 + 2\text{O}_2 \rightleftharpoons 2\text{NO}_2$       (II)  $2\text{NO}_2 \rightleftharpoons \text{N}_2 + 2\text{O}_2$   
(III)  $\text{NO}_2 \rightleftharpoons \frac{1}{2}\text{N}_2 + \text{O}_2$  [JEE-MAINS(online)-12]

The correct relation from the following is :

$$(1) K_1 = \sqrt{K_2} = K_3 \quad (2) K_1 = \frac{1}{K_2} = \frac{1}{K_3} \quad (3) K_1 = \frac{1}{K_2} = K_3 \quad (4) K_1 = \frac{1}{K_2} = \frac{1}{(K_3)^2}$$

6. One mole of  $\text{O}_2(\text{g})$  and two moles of  $\text{SO}_2(\text{g})$  were heated in a closed vessel of one litre capacity at 1098 K. At equilibrium 1.6 moles of  $\text{SO}_3(\text{g})$  were found. The equilibrium constant  $K_C$  of the reaction would be :- [JEE-MAINS(online)-12]  
(1) 60      (2) 80      (3) 30      (4) 40
7.  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ ,  $K_1$       (1)  
 $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ ,  $K_2$       (2)  
 $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$ ,  $K_3$       (3)

The equation for the equilibrium constant of the reaction



in terms of  $K_1$ ,  $K_2$  and  $K_3$  is :

$$(1) \frac{K_1 K_3^2}{K_2} \quad (2) \frac{K_2 K_3^3}{K_1} \quad (3) \frac{K_1 K_2}{K_3} \quad (4) K_1 K_2 K_3$$

### [JEE-MAINS(online)-13]

- 9.** For the decomposition of the compound, represented as

[JEE-MAINS(online)-14]



the  $K_p = 2.9 \times 10^{-5}$  atm<sup>3</sup>.

If the reaction is started with 1 mol of the compound, the total pressure at equilibrium would be

- $$(1) 38.8 \times 10^{-2} \text{ atm} \quad (2) 1.94 \times 10^{-2} \text{ atm} \quad (3) 5.82 \times 10^{-2} \text{ atm} \quad (4) 7.66 \times 10^{-2} \text{ atm}$$

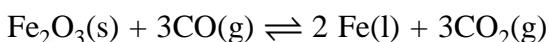
10. For the reaction  $\text{SO}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \rightleftharpoons \text{SO}_{3(g)}$ , if  $K_p = K_C (RT)^x$  where the symbols have usual meaning then the value of x is : (assuming ideality) [JEE-MAINS-14]

- (1)  $\frac{1}{2}$       (2) 1      (3) -1      (4)  $-\frac{1}{2}$

11. The equilibrium constants at 298 K for a reaction  $A + B \rightleftharpoons C + D$  is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in mol L<sup>-1</sup>) will be : [JEE-MAINS-16]

- (1) 1.182      (2) 0.182      (3) 0.818      (4) 1.818

- 12.** The following reaction occurs in the Blast Furnace where iron ore is reduced to iron metal:

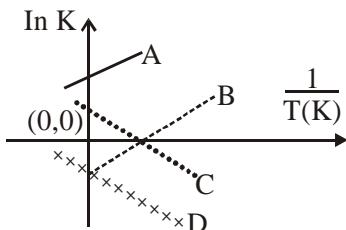


[JEE-MAINS(online)-17]

Using the Le Chatelier's principle, predict which one of the following will **not** disturb the equilibrium?

- (1) Removal of  $\text{CO}_2$     (2) Addition of  $\text{Fe}_2\text{O}_3$     (3) Addition of  $\text{CO}_2$     (4) Removal of CO

13. Which of the following lines correctly show the temperature dependence of equilibrium constant, K, for an exothermic reaction ? [JEE-MAINS(offline)-18]



- (1) B and C      (2) C and D      (3) A and D      (4) A and B

14. In which of the following reactions, an increase in the volume of the container will favour the formation of products ? [JEE-MAINS(online)-18]

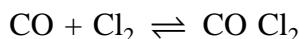
- $$(1) \text{2NO}_2(\text{g}) \rightleftharpoons \text{2NO}(\text{g}) + \text{O}_2(\text{g})$$

- $$(2) \text{ } 3\text{O}_2(\text{g}) \rightleftharpoons 2\text{O}_3(\text{g})$$

- $$(3) \text{ H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$$

- $$(4) \text{4NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{l})$$

15. At a certain temperature in a 5 L vessel, 2 moles of carbon monoxide and 3 moles of chlorine were allowed to reach equilibrium according to the reaction, [JEE-MAINS(online)-18]



At equilibrium, if one mole of CO is present then equilibrium constant ( $K_c$ ) for the reaction is :-

- (1) 4 (2) 3 (3) 2 (4) 2.5

16. At 320 K, a gas  $\text{A}_2$  is 20% dissociated to  $\text{A(g)}$ . The standard free energy change at 320 K and 1 atm in  $\text{J mol}^{-1}$  is approximately : [JEE-MAINS(online)-18]

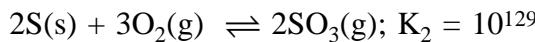
$$(\mathbf{R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}; \ln 2 = 0.693; \ln 3 = 1.098})$$

- (1) 4281 (2) 4763 (3) 2068 (4) 1844

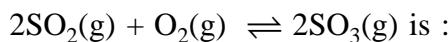
17. The gas phase reaction  $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$  is an exothermic reaction. The decomposition of  $\text{N}_2\text{O}_4$ , in equilibrium mixture of  $\text{NO}_2(\text{g})$  and  $\text{N}_2\text{O}_4(\text{g})$ , can be increased by :-

- (1) Addition of an inert gas at constant volume. [JEE-MAINS(online)-18]  
 (2) Increasing the pressure.  
 (3) Lowering the temperature.  
 (4) Addition of an inert gas at constant pressure.

18. For the following reactions, equilibrium constants are given : [JEE-MAINS(online)-19]

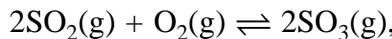


The equilibrium constant for the reaction,



- is : (1)  $10^{181}$  (2)  $10^{154}$  (3)  $10^{25}$  (4)  $10^{77}$

19. For the reaction, [JEE-MAINS(online)-19]



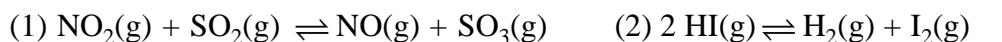
$$\Delta H = -57.2 \text{ kJ mol}^{-1} \text{ and}$$

$$K_c = 1.7 \times 10^{16}.$$

Which of the following statement is INCORRECT?

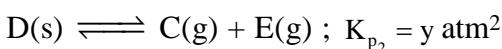
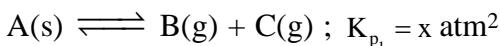
- (1) The equilibrium constant is large suggestive of reaction going to completion and so no catalyst is required.  
 (2) The equilibrium will shift in forward direction as the pressure increase.  
 (3) The equilibrium constant decreases as the temperature increases.  
 (4) The addition of inert gas at constant volume will not affect the equilibrium constant.

20. In which one of the following equilibria,  $K_p \neq K_c$ ? [JEE-MAINS(online)-19]



21. Two solids dissociate as follows

[JEE-MAINS(online)-19]



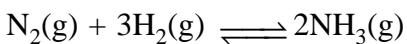
The total pressure when both the solids dissociate simultaneously is :-

- (1)  $(x + y)$  atm      (2)  $x^2 + y^2$  atm      (3)  $2(\sqrt{x+y})$  atm      (4)  $\sqrt{x+y}$  atm

22. In a chemical reaction,  $A + 2B \xrightleftharpoons{K} 2C + D$ , the initial concentration of B was 1.5 times of the concentration of A, but the equilibrium concentrations of A and B were found to be equal. The equilibrium constant(K) for the aforesaid chemical reaction is : [JEE-MAINS(online)-19]

- (1) 16      (2) 4      (3) 1      (4)  $\frac{1}{4}$

23. Consider the reaction,

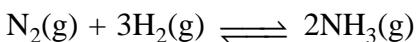
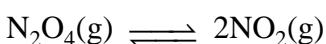
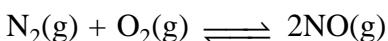


The equilibrium constant of the above reaction is  $K_p$ . If pure ammonia is left to dissociate, the partial pressure of ammonia at equilibrium is given by (Assume that  $P_{NH_3} \ll P_{\text{total}}$  at equilibrium)

- (1)  $\frac{\frac{3}{2} K_p^2 P^2}{4}$       (2)  $\frac{\frac{3}{2} K_p^2 P^2}{16}$       (3)  $\frac{K_p^2 P^2}{16}$       (4)  $\frac{K_p^2 P^2}{4}$

24. The value of  $K_p/K_C$  for the following reactions at 300K are, respectively :

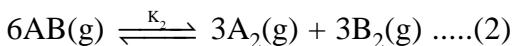
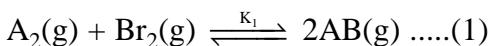
(At 300K,  $RT = 24.62 \text{ dm}^3 \text{ atm mol}^{-1}$ )



- (1) 1,  $24.62 \text{ dm}^3 \text{ atm mol}^{-1}$ ,  $606.0 \text{ dm}^6 \text{ atm}^2 \text{ mol}^{-2}$   
 (2) 1,  $4.1 \times 10^{-2} \text{ dm}^{-3} \text{ atm}^{-1} \text{ mol}^{-1}$ ,  $606.0 \text{ dm}^6 \text{ atm}^2 \text{ mol}^{-2}$   
 (3)  $606.0 \text{ dm}^6 \text{ atm}^2 \text{ mol}^{-2}$ ,  $1.65 \times 10^{-3} \text{ dm}^3 \text{ atm}^{-2} \text{ mol}^{-1}$   
 (4) 1,  $24.62 \text{ dm}^3 \text{ atm mol}^{-1}$ ,  $1.65 \times 10^{-3} \text{ dm}^{-6} \text{ atm}^{-2} \text{ mol}^2$

25. Consider the following reversible chemical reactions :

[JEE-MAINS(online)-19]



The relation between  $K_1$  and  $K_2$  is :

- (1)  $K_2 = K_1^3$       (2)  $K_2 = K_1^{-3}$       (3)  $K_1 K_2 = 3$       (4)  $K_1 K_2 = \frac{1}{3}$

26. 5.1g  $NH_4SH$  is introduced in 3.0 L evacuated flask at  $327^\circ C$ . 30% of the solid  $NH_4SH$  decomposed to  $NH_3$  and  $H_2S$  as gases. The  $K_p$  of the reaction at  $327^\circ C$  is ( $R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$ , Molar mass of S =  $32 \text{ g mol}^{-1}$ , molar mass of N =  $14 \text{ g mol}^{-1}$ ) [JEE-MAINS(online)-19]

- (1)  $1 \times 10^{-4} \text{ atm}^2$       (2)  $4.9 \times 10^{-3} \text{ atm}^2$       (3)  $0.242 \text{ atm}^2$       (4)  $0.242 \times 10^{-4} \text{ atm}^2$

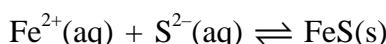
**EXERCISE (JA)**

1. The thermal dissociation equilibrium of  $\text{CaCO}_3(\text{s})$  is studied under different conditions.

**[JEE 2013]**

For this equilibrium, the correct statement(s) is(are)

- (A)  $\Delta H$  is dependent on T
- (B) K is independent of the initial amount of  $\text{CaCO}_3$
- (C) K is dependent on the pressure of  $\text{CO}_2$  at a given T
- (D)  $\Delta H$  is independent of the catalyst, if any
2. For the following reaction, the equilibrium constant  $K_c$  at 298 K is  $1.6 \times 10^{17}$ .



When equal volumes of 0.06 M  $\text{Fe}^{2+}(\text{aq})$  and 0.2 M  $\text{S}^{2-}(\text{aq})$  solutions are mixed, the equilibrium concentration of  $\text{Fe}^{2+}(\text{aq})$  is found to be  $Y \times 10^{-17}$  M. The value of Y is (upto two decimal places)

**[JEE 2019]**

## ANSWER KEY

### EXERCISE (S-1)

1. (a) incomplete (b) almost complete

2. (a)  $K_p = \frac{(P_{SO_3})}{(P_{SO_2})(P_{O_2})^{\frac{1}{2}}}$  ;  $K_c = \frac{[SO_3]^{\frac{1}{2}}}{[SO_2][O_2]^2}$

(b)  $K_c = [H_2O]$  [here  $H_2O(\ell)$  is a pure liquid so its concentration is 1.]

$$\begin{aligned} K_p &= P_{H_2O} \\ &= \text{vapour pressure} \\ &= \text{aqueous tension} \end{aligned}$$

(c)  $K_c = [NH_3]^2 [CO_2]$  ( $\because$  active mass of solid is 1)

$$K_p = (P_{NH_3})^2 P_{CO_2}$$

(d)  $K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$  [here  $H_2O$  is not in excess]

$K_p$  is not defined for liquid phase.

(e)  $K_c = \frac{[NH_4^+][OH^-]}{[NH_3]}$  [here  $H_2O(\ell)$  is in excess (solvent) so its concentration is 1]

(f)  $K_{PC} = \frac{P_{H_2} \times [Zn^{2+}]}{[H^+]^2}$  [ $\because$  active mass of solid is 1]

3. (a) Here,  $\Delta n_g = 1 + 1 - 1 = 1$

$$K_p = K_c (RT)^1 = K_c RT$$

(b) Here,  $\Delta n_g = 2 - (3+1) = -2$

$$K_p = K_c (RT)^{-2}$$

(c) Here,  $\Delta n_g = 2 - (1+1) = 0$

$$K_p = K_c (RT)^0 = K_c$$

(d) Here,  $\Delta n_g = 2 + 1 - 2 = 1$

$$K_p = K_c (RT)^1 = K_c RT$$

(e) Here,  $\Delta n_g = 2 - (2 + 1) = -1$

$$K_p = K_c (RT)^{-1} = K_c / RT$$

4.  $\therefore K_1 > K_2$   
 So the stability of  $XO < XO_2$   
 For reactants, stability increases when value of K decreases.

5.  $K_c > K_p$  so the reaction will proceed in the reverse direction.

6. (a)  $K_p = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$  [∴ Water is not a solvent here]  
 (b)  $K_p = \frac{(0.171) \times (0.171)}{(1 - 0.171) \times (0.180 - 0.171)} = 3.92$   
 (c)  $K_p = \frac{(0.214) \times (0.214)}{(0.786) \times (0.286)} = 0.204 \neq K_p$   
 $\therefore$  Equilibrium has not been reached.

7.  $2 \times 10^9$   
 8. 0.9  
 9.  $K_p = 100$   
 10.  $K_p = 0.2463$   
 11.  $64 \times 10^{-32}$   
 12.  $K_p = 0.44$   
 13.  $K_p = 1.2$  atm.  
 14.  $[HI] = \frac{1}{3} M$   
 $[I_2] = [H_2] = \frac{1}{30} M$   
 15. (a) 0.1 (b) 0.4  
 16.  $[A] = 5 M, [B] = 5 M, [C] = 1 M, [D] = 25 M$   
 17. new equilibrium       $PCl_5$        $PCl_3$        $Cl_2$   

Mole	4	4	2
Partial pressure	20 atm	20 atm	10 atm

  
 18.  $\alpha = \sqrt{\frac{K_p}{4P + K_p}}$   
 19. (A)  $\alpha = \frac{4}{5} = 0.8$  (B)  $K_p = 16$   
 20.  $K_p = 0.001$   
 21.  $[NO] = 2M, [N_2] = [O_2] = 0.5M$   
 22.  $P_{ClF} = P_{F_2} = 0.1 \text{ atm}, P_{ClF_3} = 0.5 \text{ atm}$  23.  $K_p = 0.4, a \sim 0.1$   
 24. 50% 25.  $K_p = 0.01 \text{ atm}$

26.  $K_p = 2.5 \text{ atm}$ ,  $P = 15 \text{ atm}$       27.  $K = 4$   
 28.  $P_{\text{CS}_2} = 1.8 \text{ atm}$ ,  $P_{\text{S}_2} = 0.2 \text{ atm}$       29. 22.4 mg  
 30.  $P_{\text{H}_2\text{O}} = 5 \times 10^{-15} \text{ atm}$       31. 0.821 atm  
 32. (a)  $K = [\text{CH}_3\text{OH}] / [\text{H}_2]^2[\text{CO}]$ ,  
 (b) 1.  $[\text{H}_2]$  increase,  $[\text{CO}]$  decrease,  $[\text{CH}_3\text{OH}]$  increase ;  
 2.  $[\text{H}_2]$  increase,  $[\text{CO}]$  decrease,  $[\text{CH}_3\text{OH}]$  decrease ;  
 3.  $[\text{H}_2]$  increase,  $[\text{CO}]$  increase,  $[\text{CH}_3\text{OH}]$  increase ;  
 4.  $[\text{H}_2]$  increase,  $[\text{CO}]$  increase,  $[\text{CH}_3\text{OH}]$  increase ;  
 5.  $[\text{H}_2]$  increase,  $[\text{CO}]$  increase,  $[\text{CH}_3\text{OH}]$  decrease ;  
 6. no change  
 33. 2  
 34. 250  
 35.  $k_r$  increase more than  $k_f$ , this means that  $E_a$  (reverse) is greater than  $E_a$  (forward). Hence exothermic reaction.

### EXERCISE (O-1)

- |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|
| 1. (D)  | 2. (C)  | 3. (D)  | 4. (B)  | 5. (C)  | 6. (C)  |
| 7. (A)  | 8. (C)  | 9. (A)  | 10. (A) | 11. (A) | 12. (C) |
| 13. (C) | 14. (A) | 15. (B) | 16. (B) | 17. (A) | 18. (D) |
| 19. (B) | 20. (D) | 21. (C) | 22. (B) | 23. (B) | 24. (A) |
| 25. (C) | 26. (C) | 27. (C) | 28. (B) | 29. (C) | 30. (D) |
| 31. (A) | 32. (A) | 33. (C) | 34. (A) | 35. (D) |         |

### EXERCISE (O-2)

- |            |            |          |              |          |
|------------|------------|----------|--------------|----------|
| 1. (B)     | 2. (C,D)   | 3. (C,D) | 4. (A,B,C,D) | 5. (C,D) |
| 6. (A,C,D) | 7. (A,B,C) | 8. (C,D) | 9. (A,C)     | 10. (A)  |
| 11. (D)    | 12. (A)    | 13. (A)  | 14. (B)      | 15. (C)  |
| 16. (B)    | 17. (A)    | 18. (D)  | 19. (A)      | 20. (A)  |

**Match the column :**

21. (A) - P,R,S (B) - P,Q,R,S (C) - P, Q, R, S ; (D) - Q  
 22. (A) - (s), (B) - (p,q,s), (C) - (p,q,r), (D) - (r)  
 23. (D) 24. (C) 25. (A)

### EXERCISE (JM)

- |              |              |              |              |
|--------------|--------------|--------------|--------------|
| 1. Ans. (3)  | 2. Ans. (1)  | 3. Ans. (3)  | 4. Ans. (1)  |
| 5. Ans. (4)  | 6. Ans. (2)  | 7. Ans. (2)  | 8. Ans. (1)  |
| 9. Ans. (3)  | 10. Ans. (4) | 11. Ans. (4) | 12. Ans. (2) |
| 13. Ans. (4) | 14. Ans. (1) | 15. Ans. (4) | 16. Ans. (2) |
| 17. Ans. (4) | 18. Ans. (3) | 19. Ans. (1) | 20. Ans. (4) |
| 21. Ans. (3) | 22. Ans. (2) | 23. Ans. (2) | 24. Ans. (4) |
| 25. Ans. (2) | 26. Ans. (3) |              |              |

### EXERCISE (JA)

1. Ans.(A,B,D)      2. Ans.(8.92 or 8.93)

## CHAPTER 5

## IONIC EQUILIBRIUM

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## IMPORTANT NOTES

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## CHAPTER 5

# IONIC EQUILIBRIUM

## 1. INTRODUCTION

Ionic equilibrium deals with the equilibrium of any substance with its ions in solution. The substance producing ions are called electrolytes.

According to conductivity, substances are of two types :

**(i) Non-Conductor :**

Those substances which do not show the flow of current or electricity.

**Ex.** Non - metals, plastic rubber, wood, etc.

Exception – Graphite is a non-metal but shows conductivity due to motion of free electrons.

**(ii) Conductors :**

Those substances which show conductivity or flow of current are called conductors. These are of 2 types :

**(a) Metallic or electronic conductors :**

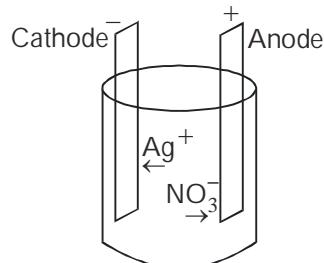
Those conductor which show conductivity due to motion of free electrons. Resistance increases with temperature.

**Ex.** All metals, Graphite

**(b) Ionic or electrolytic conductors :**

Those conductors which show conductivity due to movement of free ions. Ions are in free state in the solutions of ionic compounds. On passing electric current through the solution, ions move towards oppositely charged electrodes, i.e., the cation moves towards cathode (negative electrode) and the anion moves towards anode (positive electrode).

The current flows through the solution due to the movement of the ions. Resistance decrease with temperature.



According to strength, ionic conductors are of two types :

**(i) Strong electrolyte :** Those ionic conductors which are completely ionized in aqueous solution are called as strong electrolyte.

For strong electrolyte the value of degree of dissociation is 100%.

**i.e. :  $\alpha = 1$**

- Ex.**
- (a) Strong acid  $\rightarrow \text{H}_2\text{SO}_4, \text{HCl}, \text{HNO}_3, \text{HClO}_4, \text{H}_2\text{SO}_5, \text{HBr}, \text{HI}, \text{HBrO}_4, \text{HIO}_4, \text{RSO}_3\text{H}$
  - (b) Strong base  $\rightarrow \text{KOH}, \text{NaOH}, \text{Ba(OH)}_2, \text{CsOH}, \text{RbOH}$
  - (c) All soluble salts  $\rightarrow \text{NaCl}, \text{KCl}, \text{CuSO}_4, \dots$

- (ii) **Weak electrolytes :** Those electrolytes which are partially ionized in aqueous solution are called as weak electrolytes. For weak electrolytes the value of  $\alpha$  is less than one.

- Ex.** (a) **Weak acid :** HCN, CH<sub>3</sub>COOH, HCOOH, H<sub>2</sub>CO<sub>3</sub>, H<sub>3</sub>PO<sub>3</sub>, H<sub>3</sub>PO<sub>2</sub>, etc.  
 (b) **Weak base :** NH<sub>4</sub>OH, Cu(OH)<sub>2</sub>, Zn(OH)<sub>2</sub>, Fe(OH)<sub>3</sub>, Al(OH)<sub>3</sub>, etc.

## 1.2 DEGREE OF DISSOCIATION / IONISATION

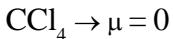
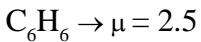
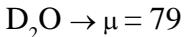
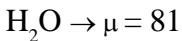
- When an electrolyte is dissolved in a solvent (H<sub>2</sub>O), it spontaneously dissociates into ions.
- It may dissociate partially ( $\alpha < 1$ ) or sometimes completely ( $\alpha \approx 1$ )
- The degree of dissociation ( $\alpha$ ) of an electrolyte is the fraction of mole of the electrolyte that has dissociated under the given conditions.

$$\alpha = \frac{\text{No. of moles dissociated}}{\text{No. of moles taken initially}}$$

## 1.3 FACTORS AFFECTING THE VALUE OF DEGREE OF DISSOCIATION:

- (i) **Dilution :**  $\alpha \propto \sqrt{V}$ . So on dilution,  $\alpha$  increases
- (ii) **Temperature :** On increasing temperature, ionization increases so,  $\alpha$  increases
- (iii) **Nature of electrolyte :**
- |                        |                      |
|------------------------|----------------------|
| (a) Strong electrolyte | (b) Weak electrolyte |
| $\alpha = 100\%$       | $\alpha \ll 100\%$   |
- (iv) **Nature of solvent :**

If dielectric constant,  $\mu$ , of solvent increases, then the value of  $\alpha$  increases.



**Ex.1** Which one has greater  $\alpha_1$  or  $\alpha_2$  for the following equation :

- (i) NH<sub>4</sub>OH + H<sub>2</sub>O  $\rightarrow \alpha_1$   
 (ii) NH<sub>4</sub>OH + D<sub>2</sub>O  $\rightarrow \alpha_2$

**Sol.** Dielectric constant of H<sub>2</sub>O is more than that of D<sub>2</sub>O, so  $\alpha_1 > \alpha_2$

(v) **Mixing of Ions :**

Common ion Effect	Opposite ion Effect
$\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ On mixing NH <sub>4</sub> Cl $\text{NH}_4\text{Cl} \rightarrow \text{NH}_4^+ + \text{Cl}^-$ Due to mixing of common ion, concentration of ammonium ion will increase therefore equilibrium will shift in backward direction means $\alpha$ decreases.	$\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ On mixing HCl $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$ Due to reaction of OH <sup>-</sup> ions with H <sup>+</sup> ion, concentration of OH <sup>-</sup> will decrease ∴ Equilibrium will shift in forward direction means $\alpha$ increases.

## 1.4 OSTWALD'S DILUTION LAW (FOR WEAK ELECTROLYTE)

- For a weak electrolyte  $A^+B^-$  dissolved in water, if  $\alpha$  is the degree of dissociation then

AB	$\rightleftharpoons$	$A^+$	$+ B^-$
initial conc.		C M	0      0
conc-at eq.		$C(1-\alpha)M$	$C\alpha M$ $C\alpha M$

Then according to law of mass action,

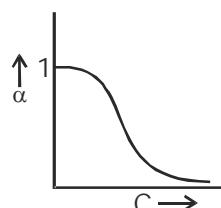
$$K_{\text{diss}} = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} = \text{dissociation constant of the weak electrolyte.}$$

$\left[ C = \frac{1}{V} \text{, then } V = 1/C \text{ (volume of solution in which 1 mole is present) is called dilution,}\right.$   
 $\text{so } K_{\text{diss}} = \frac{\alpha^2}{(1-\alpha)V} \left. \right]$

If  $\alpha$  is negligible in comparison to unity,  $1 - \alpha \approx 1$ . so  $K_{\text{diss}} = \alpha^2 C \Rightarrow \alpha = \sqrt{\frac{K_{\text{diss}}}{C}} = \sqrt{K_{\text{diss}} V}$

$$\alpha \propto \frac{1}{\sqrt{\text{concentration}}}$$

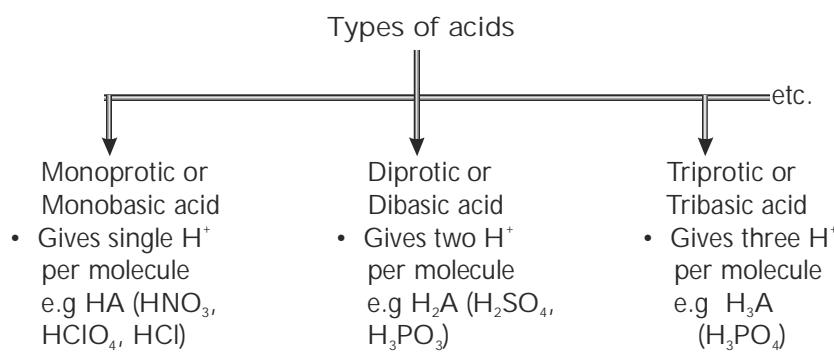
- As concentration increases  $\Rightarrow \alpha$  decreases
- At infinite dilution  $\alpha$  reaches its maximum value, unity.



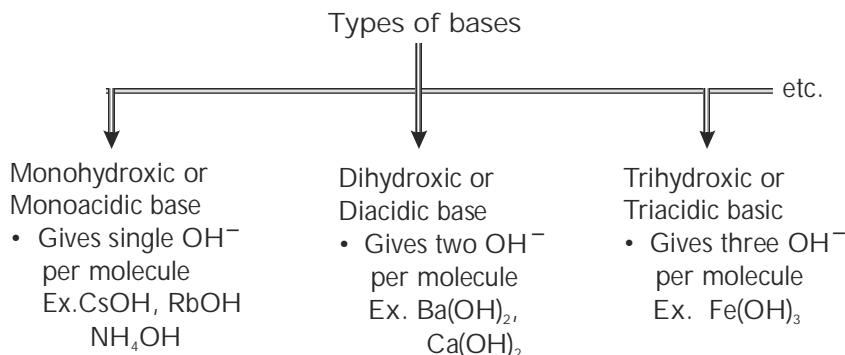
## 2. ACIDS BASES AND SALTS

### 2.1 Arrhenius concept :

- Arrhenius Acid :** Substance which gives  $H^+$  ion on dissolving in water ( $H^+$  donor)  
**Ex.**  $HNO_3$ ,  $HClO_4$ ,  $HCl$ ,  $HI$ ,  $HBr$ ,  $H_2SO_4$ ,  $H_3PO_4$  etc.

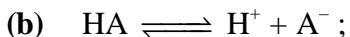


- (ii) **Arrhenius base :** Any substance which releases  $\text{OH}^-$  (hydroxyl) ion in water ( $\text{OH}^-$  ion donor)



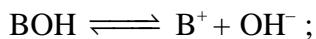
- (iii) **Strength of Acid or Base :**

(a) Strength of acids or bases depends on the extent of its ionisation. Hence equilibrium constant  $K_a$  or  $K_b$  respectively of the following equilibria give a quantitative measurement of the strength of the acid or base.



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \text{dissocation or ionisation constant of acid.}$$

(c) Similarly



$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} = \text{dissocation or ionisation constant of base}$$

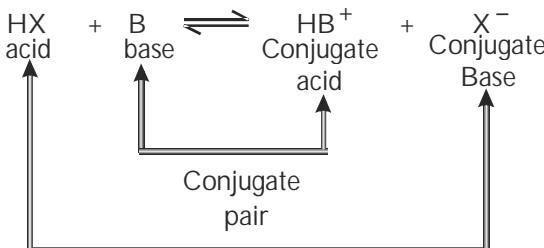
(d) Larger the value of  $K_a$  or  $K_b$ , stronger is the acid or base respectively.

## 2.2 Bronsted - Lowry concept : (Conjugate acid - base concept) (Protonic concept)

- (i) **Acid :** substances which donate  $\text{H}^+$  are Bronsted Lowry acids ( $\text{H}^+$  donor)

- (ii) **Base :** substances which accept  $\text{H}^+$  are Bronsted Lowry bases ( $\text{H}^+$  acceptor)

- (iii) **Conjugate acid - base pairs :** In a typical acid base reaction,  $\text{HX} + \text{B} \rightleftharpoons \text{X}^- + \text{HB}^+$

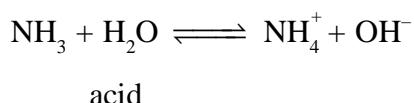
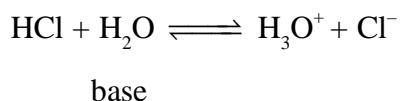


- Forward reaction - Here HX being a proton donor is an acid  
 $\text{B}$  being a proton acceptor is a base.
- Backward reaction - Here  $\text{HB}^+$  being a proton donor is an acid  
 $\text{X}^-$  being a proton acceptor is a base.

- | <b>Acid</b>   | <b>Base</b>          | <b>Conjugate Acid</b>  | <b>Conjugate Base</b>  |
|---|----------------------|--|--|
| • HCl   | + H <sub>2</sub> O   | $\rightleftharpoons$   | H <sub>3</sub> O <sup>+</sup> + Cl <sup>-</sup>              |
| • HSO <sub>4</sub> <sup>-</sup>   | + NH <sub>3</sub>    | $\rightleftharpoons$   | NH <sub>4</sub> <sup>+</sup> + SO <sub>4</sub> <sup>2-</sup> |
| • [Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> + H <sub>2</sub> O | $\rightleftharpoons$ | H <sub>3</sub> O <sup>+</sup> + [Fe(H <sub>2</sub> O) <sub>5</sub> (OH)] <sup>2+</sup> |  |
| • Conjugate acid - base pair differ by only one proton.                 |                      |  |  |
| • Strong acid will have weak conjugate base and vice versa.             |                      |  |  |

<b>Acid</b>	<b>Conjugate base</b>	<b>Base</b>	<b>Conjugate acid</b>
HCl	Cl <sup>-</sup>	NH <sub>3</sub>	NH <sub>4</sub> <sup>+</sup>
H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>
HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	RNH <sub>2</sub>	RNH <sub>3</sub> <sup>+</sup>
H <sub>2</sub> O	OH <sup>-</sup>		

(iv) **Amphoteric (amphiprotic)** : Substances which can act as acid as well as base are known as amphoteric



(v) **Classification of Bronsted - Lowery Acids and Bases :**

Bronsted - Lowery acids and bases can be

- (i) Molecular      (ii) Cationic and      (iii) Anionic

**Table - 1**

<b>Type</b>	<b>Acid</b>	<b>Base</b>
Molecular	HCl, HNO <sub>3</sub> , HClO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , H <sub>3</sub> PO <sub>4</sub> , H <sub>2</sub> O etc.	NH <sub>3</sub> , N <sub>2</sub> H <sub>4</sub> , Amines, H <sub>2</sub> O, Alcohol, Ethers, etc.
Cationic	NH <sub>4</sub> <sup>+</sup> , N <sub>2</sub> H <sub>5</sub> <sup>+</sup> , PH <sub>4</sub> <sup>+</sup> , [Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> , [Al(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> etc.	[Fe(H <sub>2</sub> O) <sub>5</sub> OH] <sup>2+</sup> [Al(H <sub>2</sub> O) <sub>5</sub> OH] <sup>2+</sup> etc.
Anionic	HS <sup>-</sup> , HSO <sub>3</sub> <sup>-</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , HSO <sub>4</sub> <sup>-</sup> HCO <sub>3</sub> <sup>-</sup> , HPO <sub>4</sub> <sup>2-</sup> , etc. all amphiprotic anions	Cl <sup>-</sup> , Br <sup>-</sup> , OH <sup>-</sup> , HSO <sub>4</sub> <sup>-</sup> , CN <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> , SO <sub>4</sub> <sup>2-</sup> , NH <sub>2</sub> <sup>-</sup> , CH <sub>3</sub> COO <sup>-</sup> , etc. all amphiprotic anions

### 2.3 Lewis concept (electronic concept) :

(i) **Acid** : An acid is a molecule/ion which can accept an electron pair with the formation of a coordinate bond.

**Ex.** Electron deficient molecules :  $\text{BF}_3$ ,  $\text{AlCl}_3$ , etc.

Cations :  $\text{H}^+$ ,  $\text{Fe}^{2+}$ ,  $\text{Na}^+$ , etc.

Molecules with vacant orbitals :  $\text{SF}_4$ ,  $\text{PF}_3$

(ii) **Base** : A base is any molecule/ion which has a pair of electrons which can be donated.

**Ex.** Molecules with lone pairs :  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$

Anions :  $\text{OH}^-$ ,  $\text{H}^-$ ,  $\text{NH}_2^-$ , etc.

## 3. PROPERTIES OF WATER

### (i) Molar concentration / Molarity of water :

$$\text{Molarity} = \text{No. of moles/litre} = \frac{1000 \text{ g/litre}}{18 \text{ g/mole}} = 55.55 \text{ mole/litre} = 55.55 \text{ M} \text{ (density} = 1 \text{ g/cc)}$$

### (ii) Ionic product of water :

According to arrhenius concept,  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$

So, ionic product of water,  $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$  at  $25^\circ$  (experimental)

Dissociation of water is endothermic, so on increasing temperature  $K_w$  increases.

### (iii) Degree of dissociation of water :

$$\begin{aligned} \text{H}_2\text{O} &\rightleftharpoons \text{H}^+ + \text{OH}^- \Rightarrow \alpha = \frac{\text{decrease in concentration}}{\text{initially concentration}} \\ &= \frac{10^{-7}}{55.55} = 18 \times 10^{-10} \text{ or } 1.8 \times 10^{-7} \% \quad [\text{at } 25^\circ\text{C}] \end{aligned}$$

### (iv) Dissociation or ionisation constant of water :

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad K_a = K_b = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \times 10^{-16}$$

$$\text{So, } \text{pK}_a = \text{pK}_b = -\log(1.8 \times 10^{-16}) = 16 - \log 1.8 = 15.74$$

**Ex.2.** At dissociation constant of heavy water is  $4 \times 10^{-15}$  at  $35^\circ\text{C}$ . If its density is  $1.04 \text{ g/mL}$ . Calculate its ionic product & degree of dissociation.

$$\text{Sol. } K_w = K_d[D_2\text{O}] = \left( 4 \times 10^{-15} \times \frac{1040}{20} \right) = 2.08 \times 10^{-13}$$

$$d = \sqrt{\frac{K_w}{C}} = \sqrt{\frac{2.08 \times 10^{-13}}{52}} = 12.64 \times 10^{-8}$$

***Ex.3 Calculate ionic product of H<sub>2</sub>O at 50°C.***

$$Sol. \quad \Delta H = 13.7 \times 10^3 \text{ cal}$$

$$\log \frac{K_2}{10^{-14}} = \frac{13.7 \times 10^3}{2} \left( \frac{1}{298} - \frac{1}{323} \right)$$

**Ex.4** The hydronium ion conc. in an aq.  $H_2CO_3$  solution is  $4 \times 10^{-4} M$  at  $25^\circ C$   $OH^-$  ion conc. in the solution is :

- $$(A) 0 \quad (B) 2.5 \times 10^{-10} \quad (C) 2.5 \times 10^3 \quad (D) 2.5 \times 10^{-11} M$$

*Answer : (D)*

**Ex.5** Select the correct option from the following ?

- (A)  $pK_w$  increases with increase of temperature
  - (B)  $pK_w$  decreases with increase of temperature
  - (C)  $pK_w = 14$  at all temperatures
  - (D)  $pK_w = pH$  at all temperatures

**Sol. (B)**

#### 4. ACIDITY AND pH SCALE :

- (i) Acidic strength means the tendency of an acid to give  $\text{H}_3\text{O}^+$  or  $\text{H}^+$  ions in water.  
So greater than tendency to give  $\text{H}^+$ , more will be the acidic strength of the substance.

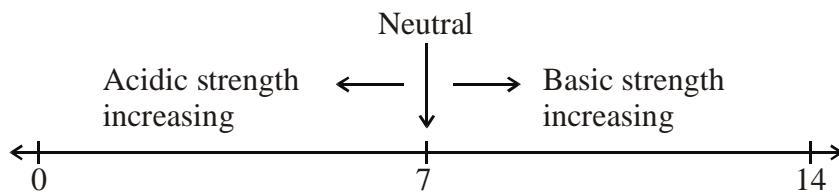
(ii) Basic strength means the tendency of a base to give  $\text{OH}^-$  ions in water.  
So greater the tendency to give  $\text{OH}^-$  ions, more will be basic strength of the substance.

(iii) The concentration of  $\text{H}^+$  ions is written in a simplified form introduced by **Sorenson** known as pH scale. pH is defined as negative logarithm of activity of  $\text{H}^+$  ions.  
 $\therefore \text{pH} = -\log a_{\text{H}^+}$  (where  $a_{\text{H}^+}$  is the activity of  $\text{H}^+$  ions)

(iv) Activity of  $\text{H}^+$  ions is the molar concentration of free  $\text{H}^+$  ions or  $\text{H}_3\text{O}^+$  ions in a dilute solution, but unitless.

(v) Now  $\text{pH} = -\log[\text{H}^+] = 7$  and  $\text{pOH} = -\log[\text{OH}^-] = 7$  for water at  $25^\circ\text{C}$  (experimental)

$$\left. \begin{array}{l} \text{pH} = 7 = \text{pOH} \Rightarrow \text{neutral} \\ \text{pH} < 7 \text{ or } \text{pOH} > 7 \Rightarrow \text{acidic} \\ \text{pH} > 7 \text{ or } \text{pOH} < 7 \Rightarrow \text{Basic} \end{array} \right\} \text{at } 25^\circ\text{C}$$



#### 4.1 pH Calculation of different Types of solutions :

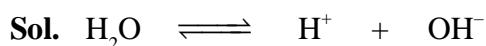
##### (a) Strong acid solution :

(i) If concentration of  $H^+$  ions is greater than  $10^{-6} M$ ,  $H^+$  ions coming from water can be neglected,

So  $[H^+] = \text{normality of strong acid solution}$

(ii) If concentration is less than  $10^{-6} M$ ,  $H^+$  ions coming from water cannot be neglected. So  $[H^+] = \text{normality of strong acid} + H^+ \text{ ions coming from water in presence of this strong acid}$

**Ex.6 Calculate pH of  $10^{-8} M HCl$  solution.**



$$10^{-8} + x \quad x$$

$$K_w = [H^+][OH^-]$$

$$10^{-14} = x(x + 10^{-8})$$

$$\Rightarrow x^2 + x \times 10^{-8} - 10^{-14} = 0$$

$$x = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4 \times 10^{-14}}}{2} = \frac{-10^{-8} + 10^{-7} \sqrt{4 + \frac{1}{100}}}{2} = \frac{(\sqrt{401} - 1)10^{-8}}{2} = 0.95 \times 10^{-7}$$

$$[H^+] = 10.5 \times 10^{-8} = 1.05 \times 10^{-7}$$

$$pH = -\log [H^+]$$

$$pH = 7 - \log 1.05 \approx 6.98$$

#### 4.2 Strong base solution :

Calculate the  $[OH^-]$  which will be equal to normality of the strong base solution and then use

$$K_w = [H^+] \times [OH^-] = 10^{-14}, \text{ to calculate } [H^+]$$

**Ex.7 Calculate pH of  $10^{-7} M$  of NaOH solution**

**Sol.**  $[OH^-]$  from NaOH =  $10^{-7}$

$[OH^-]$  from water =  $x < 10^{-7} M$  (due to common ion effect)



$$- \quad (x + 10^{-7}) \quad x$$

$$K_w = [H^+] [OH^-] = 10^{-14} = x(x + 10^{-7})$$

$$x^2 + 10^{-7}x - 10^{-14} = 0$$

$$\Rightarrow x = \frac{\sqrt{5}-1}{2} \times 10^{-7} = 0.618 \times 10^{-7} \quad (\sqrt{5} = 2.236)$$

$$[OH^-] = 10^{-7} + 0.618 \times 10^{-7} = 1.618 \times 10^{-7}$$

$$pOH = 7 - \log(1.618) = 6.79$$

$$pH = 14 - 6.79 = 7.21$$

**4.3 pH of mixture of two strong acids :** If  $V_1$  volume of a strong acid solution of normality  $N_1$  is mixed with  $V_2$  volume of another strong acid solution of normality  $N_2$ , then

$$\text{Number of } \text{H}^+ \text{ ions from I-solution} = N_1 V_1$$

$$\text{Number of } \text{H}^+ \text{ ions from II-solution} = N_2 V_2$$

If final normality is  $N$  and final volume is  $V$ , then

$$NV = N_1 V_1 + N_2 V_2$$

[dissociation equilibrium of none of these acids will be disturbed as both are strong acid]

$$[\text{H}^+] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$$

[where  $N = M \times n$   
 $n = \text{Basicity of acid}$ ]

**4.4 pH of mixture of two strong bases :**

Similar to above calculation

$$[\text{OH}^-] = N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2} \quad [\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]}$$

[where  $N = M \times n$   
 $n = \text{Acidity of base}$ ]

**Ex.8 Calculate pH of mixture of (400 mL,  $\frac{1}{200} M H_2SO_4$ ) + (400 mL,  $\frac{1}{100} M HCl$ ) + (200 mL of water)**

**Sol.**  $N_1 V_1 = \frac{1}{200} \times \frac{400}{1000} \times 2 = \frac{4}{1000}$ ,  $N_2 V_2 = \frac{4}{1000}$ ,  $\text{H}^+$  ions from water will be neglected

$$N_1 V_1 + N_2 V_2 = 8 \times 10^{-3} \quad [\text{H}^+] = \frac{8 \times 10^{-3}}{1} = 8 \times 10^{-3}$$

$$\text{pH} = 3 - \log 8 = 2.1$$

**Ex.9 500 mL of  $10^{-5} M NaOH$  is mixed with 500 mL of  $2.5 \times 10^{-5} M$  of  $Ba(OH)_2$ . To the resulting solution 99 L water is added. Calculate pH.**

$$\text{Sol. } [\text{OH}^-] = \frac{500 \times 10^{-5} + 500 \times 2 \times 2.5 \times 10^{-5}}{1000} = 3 \times 10^{-5} M$$

$$M_1 = 3 \times 10^{-5} M$$

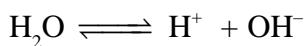
$$V_2 + V_1 = 1 L$$

$$V_F = 100 L$$

no. of moles of  $[\text{OH}^-]$  initially = no. of moles of  $[\text{OH}^-]$

$$3 \times 10^{-5} = M_2 \times 100$$

$$\therefore M_2 = 3 \times 10^{-7} < 10^{-6}$$



$$x \quad (x + 3 \times 10^{-7})$$

$$K_w = x(x + 3 \times 10^{-7}) = 10^{-14}$$

$$\therefore x = \left( \frac{\sqrt{13} - 3}{2} \right) \times 10^{-7}$$

$$x = 0.302 \times 10^{-7}$$

$$[\text{OH}^-]_{\text{Net}} = 3.302 \times 10^{-7}$$

#### 4.5 pH of mixture of a strong acid and a strong base :

- Acid Base neutralisation reaction will take place.
- The solution will be acidic or basic depending on which component has been taken in excess.
- If  $V_1$  volume of a strong acid solution of normality  $N_1$  is mixed with  $V_2$  volume of a strong base solution of normality  $N_2$ , then

$$\text{Number of H}^+ \text{ ions from I-solution} = N_1 V_1$$

$$\text{Number of OH}^- \text{ ions from II-solution} = N_2 V_2$$



$$\text{If } N_1 V_1 > N_2 V_2$$

$$\text{If } N_2 V_2 > N_1 V_1$$

$$[\text{H}^+] = N = \frac{N_1 V_1 - N_2 V_2}{V_1 + V_2}$$

$$[\text{OH}^-] = N = \frac{N_2 V_2 - N_1 V_1}{V_1 + V_2}$$

Solution will  
be acidic in nature

Solution will  
be basic in nature

$$[\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]}$$

#### Ex.10 Calculate pH of mixture of

$$(400 \text{ mL}, \frac{1}{200} M \text{ Ba(OH)}_2) + (400 \text{ mL}, \frac{1}{50} M \text{ HCl}) + (200 \text{ mL of water})$$

**Sol.**  $[\text{H}^+] = \frac{400 \times \frac{1}{50} - 400 \times \frac{1}{200} \times 2}{1000} = 4 \times 10^{-3}$ , so  $\text{pH} = 3 - 2 \log 2 = 2.4$

**Ex.11** What will be the resultant pH when 150 mL of an aqueous solution of HCl (pH = 2.0) is mixed with 350 mL of an aqueous solution of NaOH (pH = 12.0) ?

**Sol.** pH of HCl = 2

$$\therefore [\text{HCl}] = 10^{-2} \text{ M}$$

$$\text{pH of NaOH} = 12, \quad \text{pOH} = 2 \quad \therefore [\text{NaOH}] = 10^{-2} \text{ M}$$

	HCl	+	NaOH	→	NaCl	+	H <sub>2</sub> O
Meq. initial	$150 \times 10^{-2}$		$350 \times 10^{-2}$		0		0
	= 1.5		= 3.5				
Meq. final	0		2		1.5		1.5

$$\therefore [\text{OH}^-] \text{ from NaOH} = \frac{2}{500} = 4 \times 10^{-3} \text{ M}$$

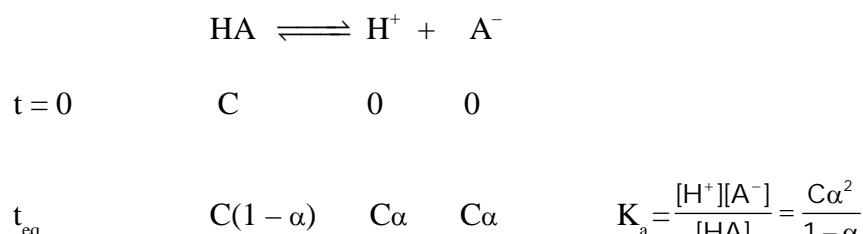
$$\text{pOH} = -\log[\text{OH}^-] = -\log(4 \times 10^{-3})$$

$$\therefore \text{pOH} = 2.3979$$

$$\therefore \text{pH} = 14 - \text{pOH} = 14 - 2.3979 = 11.6021$$

#### 4.6 pH of a weak acid or weak base (monoprotic) Solution :

- Weak acid does not dissociate 100 % therefore we have to calculate the percentage dissociation using K<sub>a</sub> dissociation constant of the acid.
- We have to use Ostwald's Dilution law (as have been derived earlier)



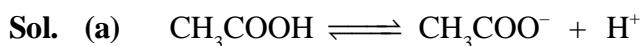
$$\text{If } \alpha \ll 1 \Rightarrow (1 - \alpha) \approx 1 \Rightarrow K_a \approx C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} \quad (\text{is valid if } \alpha < 0.1 \text{ or } 10\%)$$

$$[\text{H}^+] = \text{C}\alpha = \text{C} \sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C} \quad \text{So} \quad \text{pH} = \frac{1}{2}(\text{p}K_a - \log C)$$

On increasing the dilution  $\Rightarrow C \downarrow = \alpha \uparrow$  and  $[\text{H}^+] \downarrow \Rightarrow \text{pH} \uparrow$

**Ex.12 Calculate pH of : (a)  $10^{-1} M CH_3COOH$  (b)  $10^{-3} M CH_3COOH$  (c)  $10^{-6} M CH_3COOH$**

Take  $K_a = 2 \times 10^{-5}$



C	0	0
$C(1 - \alpha)$	$C\alpha$	$C\alpha$

$$K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-1}}} = \sqrt{2 \times 10^{-4}} \quad (\alpha \ll 0.1)$$

$$\text{So, } [H^+] = 10^{-1} \times \sqrt{2} \times 10^{-2} \Rightarrow \text{pH} = 3 - \frac{1}{2} \log 2 = 2.85$$

(b)  $\alpha = \sqrt{\frac{K_a}{C}} \Rightarrow \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-3}}} = \sqrt{2 \times 10^{-2}} \quad (\alpha > 0.1)$

So we have to do the exact calculations

$$K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow 2 \times 10^{-5} = \frac{10^{-3} \times \alpha^2}{1-\alpha} \Rightarrow \alpha = 13.14 \%$$

$$[H^+] = 10^{-3} \times 0.1314 = 1.314 \times 10^{-4} \Rightarrow \text{pH} = 4 - \log(1.314) \approx 3.8$$

(c) If approximation is used the,  $\alpha = \sqrt{\frac{2 \times 10^{-5}}{10^{-6}}} = \sqrt{20} > 1$ ,

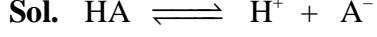
So we have to do the exact calculation,  $2 \times 10^{-5} = 10^{-6} \frac{\alpha^2}{1-\alpha} \Rightarrow \alpha \approx 0.95$  or 95%

$$[H^+] = 0.95 \times 10^{-6} = 9.5 \times 10^{-7} \Rightarrow \text{pH} = 7 - \log(9.5) = 6.022$$

- At very low concentration (at infinite dilution) weak electrolyte will be almost 100% dissociate, so behave as strong electrolyte.  
(pH) of  $10^{-6} M HCl \approx$  pH of  $10^{-6} M CH_3COOH \approx 6$ )

**Ex.13  $K_a$  for acid HA is  $2.5 \times 10^{-8}$  calculate for its decimolar solution at  $25^\circ C$ .**

- (i) % dissociation      (ii) pH      (iii)  $OH^-$  ion concentration



C	0	0
$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$K_a = \frac{[H^+][A^-]}{[HA]} \Rightarrow K_a = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \approx C\alpha^2$$

(i)  $\therefore \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2.5 \times 10^{-8}}{1/10}} \quad (C = 1/10 M)$   
 $= 5 \times 10^{-4} = 0.05\%$

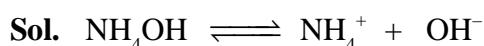
$$(ii) \quad [\text{H}^+] = C\alpha = \frac{1}{10} \times 5 \times 10^{-4} = 5 \times 10^{-5} \text{ mol/L}$$

$$\text{So } \text{pH} = 5 - \log 5 = 4.30$$

$$(iii) \quad [\text{H}^+] [\text{OH}^-] = 1 \times 10^{-14}$$

$$\therefore \quad [\text{OH}^-] = \frac{10^{-14}}{5 \times 10^{-5}} = 2 \times 10^{-10} \text{ mol/L}$$

**Ex.14** Determine the degree of dissociation of  $0.05 \text{ M } \text{NH}_4\text{OH}$  at  $25^\circ\text{C}$  in a solution of  $\text{pH} = 10$ .



$$\begin{array}{ccc} \text{C} & & 0 \\ & & 0 \end{array}$$

$$\text{Given, pH} = 10$$

$$[\text{H}^+] = 10^{-10}$$

$$[\text{H}^+] [\text{OH}^-] = 1 \times 10^{-14}$$

$$\therefore \quad [\text{OH}^-] = \frac{1 \times 10^{-14}}{10^{-10}} = 10^{-4} = C\alpha$$

$$\therefore \quad \alpha = \frac{[\text{OH}^-]}{C} = \frac{10^{-4}}{0.05} = 2 \times 10^{-3} \text{ or } 0.2 \%$$

**Ex.15** The concentration of  $[\text{H}^+]$  and  $[\text{OH}^-]$  of the  $10^{-1} \text{ M}$  aqueous solution of 2% ionised weak acid is :

(A)  $2 \times 10^{-3} \text{ M}$  and  $5 \times 10^{-12} \text{ M}$

(B)  $1 \times 10^{-3} \text{ M}$  and  $3 \times 10^{-11} \text{ M}$

(C)  $2 \times 10^{-4} \text{ M}$  and  $5 \times 10^{-11} \text{ M}$

(D)  $3 \times 10^{-2} \text{ M}$  and  $4 \times 10^{-13} \text{ M}$

**Sol.** (A)

$$[\text{H}^+] = C\alpha = 2 \times 10^{-3} \text{ M} \text{ or } [\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]} = 5 \times 10^{-12} \text{ M}$$

**Ex.16** When a  $0.1 \text{ N}$  solution of an acid at  $25^\circ\text{C}$  has a degree of ionisation of 4%, the concentration of  $\text{OH}^-$  present is :

(A)  $2.5 \times 10^{-3}$

(B)  $2.5 \times 10^{-11}$

(C)  $2.5 \times 10^{-12}$

(D)  $2.5 \times 10^{-13}$

**Sol.** (C)

$$[\text{H}^+] = C\alpha = 0.1 \times 4 \times 10^{-2} = 4 \times 10^{-3} \text{ M} \text{ or } [\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]} = 2.5 \times 10^{-12} \text{ N}$$

**Ex.17** The degree of dissociation of acetic acid in a 0.1 M solution is  $1.32 \times 10^{-2}$ . Calculate dissociation constant of acid and its  $pK_a$  value :



Initially	0.1	0	0
at equilibrium	$0.1(1 - 0.0132)$	$0.1 \times 0.0132$	$0.1 \times 0.0132$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{0.1 \times 0.0132 \times 0.1 \times 0.0132}{0.1(1 - 0.0132)} = 1.76 \times 10^{-5}$$

$$pK_a = -\log K_a = -\log (1.76 \times 10^{-5}) = 4.75$$

#### 4.7 pH of a mixture of weak acid (monoprotic) and a strong acid solution :

- Weak acid and Strong acid both will contribute  $\text{H}^+$  ion.
- For the first approximation we can neglect the  $\text{H}^+$  ions coming from the weak acid solution and calculate the pH of the solution from the concentration of the strong acid only.
- To calculate exact pH, we have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.
- If  $[\text{SA}] = C_1$  and  $[\text{WA}] = C_2$ , then  $[\text{H}^+]$  from  $\text{SA} = C_1$  the weak acid will dissociate as follows.



$C_2$	0	0
-------	---	---

$$C_2(1 - \alpha) \quad C_2\alpha + C_1 \quad C_2\alpha \quad K_a = \frac{(C_2\alpha + C_1)C_2\alpha}{C_2(1 - \alpha)} \quad (\alpha \ll 1)$$

(The weak acids dissociation will be further suppressed because of presence of strong acid, common ion effect)

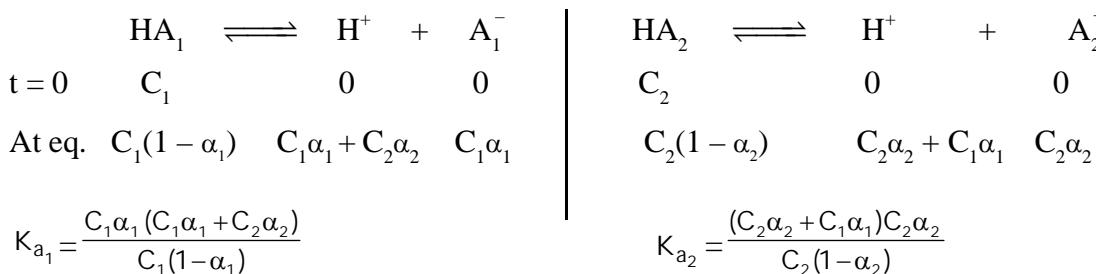
$$K_a = (C_2\alpha + C_1)\alpha$$

$$\text{Total H}^+ \text{ ion concentration} = C_1 + C_2\alpha$$

- If the total  $[\text{H}^+]$  from the acid is more than  $10^{-6} \text{ M}$ , then contribution from the water can be neglected, if not then we have to take  $[\text{H}^+]$  from the water also.

#### **4.8 pH of a mixture of two weak acid (both monoprotic) solution :**

- Both acids will dissociate partially.
  - Let the acid are  $\text{HA}_1$  &  $\text{HA}_2$  and their final concentrations are  $C_1$  &  $C_2$  respectively, then



(Since  $\alpha_1$ ,  $\alpha_2$  both are small in comparision to unity)

$$K_{a_1} = (C_1 \alpha_1 + C_2 \alpha_2) \alpha_1 ; \quad K_{a_2} = (C_1 \alpha_1 + C_2 \alpha_2) \alpha_2 \quad \Rightarrow \quad \frac{K_{a_1}}{K_{a_2}} = \frac{\alpha_1}{\alpha_2}$$

$$[\text{H}^+] = C_1 \alpha_1 + C_2 \alpha_2 = \frac{C_1 K_{a_1}}{\sqrt{C_1 K_{a_1} + C_2 K_{a_2}}} + \frac{C_2 K_{a_2}}{\sqrt{C_1 K_{a_1} + C_2 K_{a_2}}} \Rightarrow [\text{H}^+] = \sqrt{C_1 K_{a_1} + C_2 K_{a_2}}$$

- If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected.

$$\text{So, } [\text{H}^+] = C_1\alpha_1 + C_2\alpha_2 \approx C_1\alpha_1$$

**Ex.18** Calculate pH of solution obtained by mixing equal vol. of 0.02 M HOCl & 0.2 M CH<sub>3</sub>COOH solution given that K<sub>a<sub>1</sub></sub> (HOCl) = 2 × 10<sup>-4</sup>, K<sub>a<sub>1</sub></sub> (CH<sub>3</sub>COOH) = 2 × 10<sup>-5</sup>

*Also calculate OH<sup>-</sup>, OCl<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>*

**Sol.** Final solution volume become double

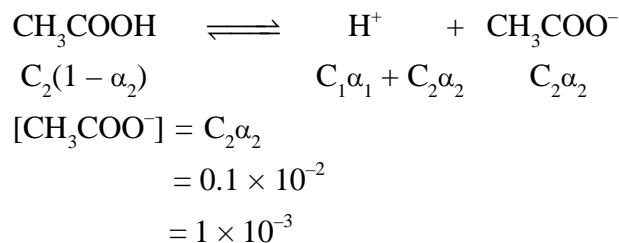
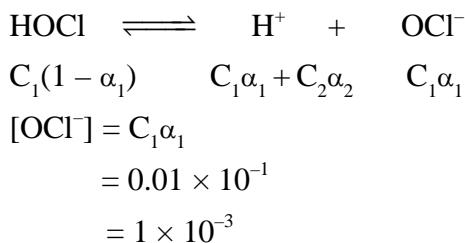
$$C_1 = 0.01, \quad C_2 = 0.1$$

$$[\text{H}^+] = \sqrt{K_{a_1} C_1 + K_{a_2} C_2} = \sqrt{2 \times 10^{-4} \times 0.01 + 2 \times 10^{-5} \times 0.1}$$

$$= \sqrt{2 \times 10^{-6} + 2 \times 10^{-6}} = 2 \times 10^{-3}$$

$$\text{pH} = 3 - \log 2 = 3 - 0.3010 = 2.69$$

$$\alpha_1 = \frac{2 \times 10^{-4}}{2 \times 10^{-3}} = 10^{-1} \quad \alpha_2 = \frac{2 \times 10^{-5}}{2 \times 10^{-3}} = 10^{-2}$$



$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{10^{-14}}{2 \times 10^{-3}} = 0.5 \times 10^{-11} = 5 \times 10^{-12} \text{ M}$$

$$[\text{HOCl}] = 10^{-2}(1 - 0.1) = 9 \times 10^{-3} \text{ M}$$

$$[\text{CH}_3\text{COOH}] = 10^{-1}(1 - 0.01) \approx 10^{-1}$$

#### 4.9 pH of a solution of a polyprotic weak acid :

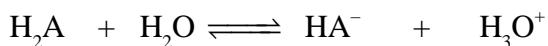
- Diprotic acid is the one, which is capable of giving 2 protons per molecule in water. Let us take a weak diprotic acid ( $\text{H}_2\text{A}$ ) in water whose concentration is  $c$  M.
- In an aqueous solution, following equilibria exist.

If

$$\alpha_1 = \text{degree of ionization of } \text{H}_2\text{A} \text{ in presence of } \text{HA}^- \quad K_{a_1} = \text{first ionisation constant of } \text{H}_2\text{A}$$

$$\alpha_2 = \text{degree of ionisation of } \text{HA}^- \text{ in presence of } \text{H}_2\text{A} \quad K_{a_2} = \text{second ionisation constant of } \text{H}_2\text{A}$$

##### I step



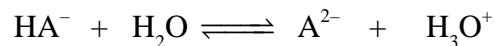
$$\text{at eq. } c(1 - \alpha_1) \quad c\alpha_1(1 - \alpha_2) \quad (c\alpha_1 + c\alpha_1\alpha_2)$$

$$(K_{eq})_1 [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} = K_{a_1}$$

$$\therefore K_{a_1} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1(1 - \alpha_2)]}{c(1 - \alpha_1)}$$

$$= \frac{[c\alpha_1(1 + \alpha_2)][c\alpha_1(1 - \alpha_2)]}{1 - \alpha_1} \quad \dots\dots \text{(i)}$$

##### II step



$$\text{at eq. } c\alpha_1(1 - \alpha_2) \quad c\alpha_1\alpha_2 \quad (c\alpha_1 + c\alpha_1\alpha_2)$$

$$(K_{eq})_2 [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^{2-}]}{[\text{HA}^-]} = K_{a_2}$$

$$K_{a_2} = \frac{(c\alpha_1 + c\alpha_1\alpha_2)[c\alpha_1\alpha_2]}{c\alpha_1(1 - \alpha_2)}$$

$$= \frac{[c\alpha_1(1 + \alpha_2)][c\alpha_1\alpha_2]}{1 - \alpha_2} \quad \dots\dots \text{(ii)}$$

Knowing the values of  $K_{a_1}$ ,  $K_{a_2}$  and  $c$ , the values of  $\alpha_1$  and  $\alpha_2$  can be calculated using equations

(i) and (ii) After getting the values of  $\alpha_1$  and  $\alpha_2$ ,  $[\text{H}_3\text{O}^+]$  can be calculated as

$$[\text{H}_3\text{O}^+]_T = c\alpha_1 + c\alpha_1\alpha_2$$

Finally, for calculation of pH

- If the total  $[\text{H}_3\text{O}^+] < 10^{-6}$  M, the contribution of  $\text{H}_3\text{O}^+$  from water should be added.
- If the total  $[\text{H}_3\text{O}^+] > 10^{-6}$  M, then  $[\text{H}_3\text{O}^+]$  contribution from water can be ignored.

Using this  $[\text{H}_3\text{O}^+]$ , pH of the solution can be calculated.

❖ **Approximation :**

For diprotic acids,  $K_{a_2} \ll K_{a_1}$  and  $\alpha_2$  would be even smaller than  $\alpha_1$

$$\therefore 1 - \alpha_2 \approx 1 \text{ and } 1 + \alpha_2 \approx 1$$

Thus, equation (i) can be reduced to  $K_{a_1} = \frac{C\alpha_1 \times \alpha_1}{1 - \alpha_1}$

This is expression similar to the expression for a weak monoprotic acid.

- Hence, for a diprotic acid (or a polyprotic acid) the  $[H_3O^+]$  can be calculated from its first equilibrium constant expression alone provided  $K_{a_2} \ll K_{a_1}$ .

**Ex.19 Calculate pH of  $[HS^-]$ ,  $[S^{2-}]$ ,  $[Cl^-]$  in a solution which is 0.1 M HCl & 0.1 M  $H_2S$  given that**

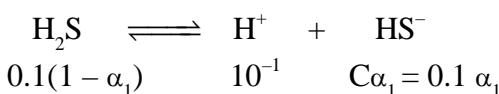
$$K_{a_1}(H_2S) = 10^{-7}, K_{a_2}(H_2S) = 10^{-14} \text{ also calculate } \alpha_1 \text{ & } \alpha_2.$$

**Sol.** HCl +  $H_2S$

$$0.1 \quad 0.1$$

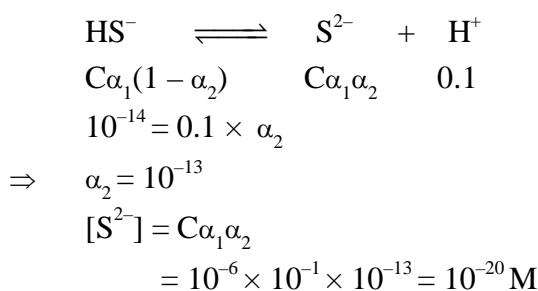
$$C_1 = C_2 = 0.1$$

$$\therefore pH = 1 \quad (\text{most of } [H^+] \text{ comes from HCl})$$



$$K_{a_1} = \frac{C\alpha_1 \times 10^{-1}}{C(1 - \alpha_1)} = \frac{10^{-7}}{10^{-1}} = \alpha_1 \quad (\because 1 - \alpha_1 = 1)$$

$$\Rightarrow \alpha_1 = 10^{-6}$$



#### 4.10 ISOHYDRIC SOLUTIONS

- Solutions of electrolytes are said to be isohydric if the concentration of the common ion present in them is the same and on mixing such solutions, there occurs no change in the degree of dissociation of either of the electrolyte.
- Let the isohydric solution is made by  $HA_1$  and  $HA_2$  acids, then  $[H^+]$  of both acids should be equal i.e.

$$\sqrt{K_{a_1} C_1} = \sqrt{K_{a_2} C_2}$$

or

$$\frac{K_{a_1}}{K_{a_2}} = \frac{C_2}{C_1}$$

## 4.11 RELATIVE STRENGTH OF WEAK ACIDS AND BASES

For two acids of equimolar concentrations.

$$\frac{\text{Strength of acid (I)}}{\text{Strength of acid (II)}} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

$$\text{Similarly for bases, } \frac{\text{Strength of base (I)}}{\text{Strength of base (II)}} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

The modern method is to convert  $K_a$  as a power of 10 and express acid strength by power of 10 with sign changed and call this new unit  $pK_a$ . Thus, if  $K_a$  for acid is equal to  $10^{-4}$ ,  $pK_a = 4$ . So higher  $pK_a$  value means lower acid strength, that is,  $pK_a = -\log K_a$

Also,  $pK_b = -\log K_b$

## 5. SALTS

- (i) Salts are the ionic compounds formed when its positive part (Cation) come from a base and its negative part (Anion) come from an acid.
- (ii) Salts may taste salty, bitter or sweet or tasteless.
- (iii) Solution of salts may be acidic, basic or neutral.
- (iv) Fused salts and their aqueous solutions conduct electricity and undergo electrolysis.
- (v) The salts are generally crystalline solids.

### 5.1 Classification of salts :

The salts may be classified into four categories.

#### (a) Normal salt :

- (i) The salt formed by the loss of all possible protons (replaceable  $H^+$  ions)

**Ex.**  $\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{Na}_3\text{BO}_3$ ,  $\text{Na}_2\text{HPO}_3$ ,  $\text{NaH}_2\text{PO}_2$  etc.

#### (b) Acid salts :

- (i) Salts formed by incomplete neutralisation of polybasic acids. Such salts contain one or more replaceable H atom.

**Ex.**  $\text{NaHCO}_3$ ,  $\text{NaHSO}_4$ ,  $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$  etc.

- (ii) Above salts when neutralized by base form normal salts.

#### (c) Basic salts :

- (i) Salts formed by incomplete neutralisation of poly acidic bases are called basic salts. These salt contain one or more hydroxyl groups.

**Ex.**  $\text{Zn(OH)Cl}$ ,  $\text{Mg(OH)Cl}$ ,  $\text{Fe(OH)}_2\text{Cl}$ ,  $\text{Bi(OH)}_2\text{Cl}$  etc.

- (ii) Above salts when neutralised by acids form normal salts.

## 5.2 HYDROLYSIS OF SALTS

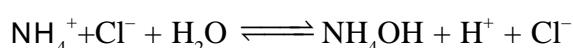
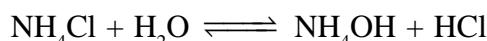
Salt hydrolysis is defined as the process in which water reacts with cation or anion or both of a salt to change the concentration of  $H^+$  and  $OH^-$  ions of water.

Salt hydrolysis is reverse process of neutralization.

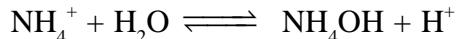


### 5.2.1 Hydrolysis of strong acid - weak base [SA - WB] type salt –

**Ex.**  $\text{CaSO}_4$ ,  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{ZnCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{CaCl}_2$



- (i) In this type of salt hydrolysis, cation reacts with  $\text{H}_2\text{O}$ , therefore called as **cationic hydrolysis**.
- (ii) Solution is acidic in nature (SAWB) as  $[\text{H}^+]$  is increased.
- (iii) pH of the solution is less than 7.
- (iv) **Relation between  $K_h$ ,  $K_w$  &  $K_b$**



$$\text{Hydrolysis constant } K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \quad \dots\dots(i)$$



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \quad \dots\dots(ii)$$



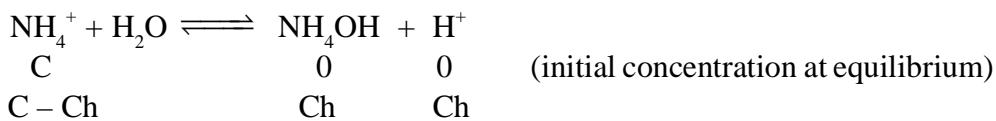
$$K_w = [\text{OH}^-][\text{H}^+] \quad \dots\dots(iii)$$

Now multiplying Eq. (1) & (2) = Eq. (3)

$$\frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} = [\text{H}^+][\text{OH}^-]$$

$$\text{i.e. } K_h \times K_b = K_w$$

$$K_h = \frac{K_w}{K_b}$$

(v) **Degree of hydrolysis – (Represented by h)**

$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} = \frac{\text{Ch}^2}{(1-h)}$$

Since  $h \ll 1$

then  $(1-h) \approx 1$

$$\therefore K_h = \text{Ch}^2$$

$$\Rightarrow h = \sqrt{\frac{K_h}{C}}$$

$$\therefore \Rightarrow h = \sqrt{\frac{\frac{K_w}{K_b}}{C}} \Rightarrow h = \boxed{\sqrt{\frac{K_w}{K_b \times C}}}$$

(vi) **pH of the solution :**

$$\text{pH} = -\log [\text{H}^+]$$

$$\Rightarrow [\text{H}^+] = \sqrt{\frac{K_w \times C}{K_b}}$$

On taking  $-\log$  on both sides

$$\text{pH} = -\log \left( \frac{K_w \times C}{K_b} \right)^{\frac{1}{2}}$$

$$\text{pH} = -\frac{1}{2} \log K_w - \frac{1}{2} \log C - \frac{1}{2} (-\log K_b)$$

$$\text{pH} = 7 - \frac{1}{2} \text{p}K_b - \frac{1}{2} \log C$$

**Ex.20** Find out the  $K_h$  of centi normal  $[10^{-2} \text{ N}]$  solution of  $\text{NH}_4\text{Cl}$  (SA - WB) if dissociation constant of  $\text{NH}_4\text{OH}$  is  $10^{-6}$  and  $K_w = 10^{-14}$ . Find out degree of hydrolysis and also find  $[\text{H}^+]$  and pH of solution?

(Given :  $K_w = 10^{-14}$ ;  $K_b = 10^{-6}$ )

**Sol.** (1)  $K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$

(2)  $h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-8}}{10^{-2}}} = \sqrt{10^{-6}} = 10^{-3}$

(3)  $[\text{H}^+] = \text{Ch}$   
 $= 10^{-2} \times 10^{-3} = 10^{-5}$

(4)  $\text{pH} = -\log [\text{H}^+] = -\log [10^{-5}] = +5 \log 10 = +5 \times 1 = 5$

**Ex.21 How many grams of  $\text{NH}_4\text{Cl}$  should be dissolved per litre of solution to have a pH of 5.13 ?**

$K_b$  for  $\text{NH}_3$  is  $1.8 \times 10^{-5}$ .

**Sol.**  $\text{NH}_4\text{Cl}$  is a salt of strong acid and weak base for solutions of such salts.

$$\text{pH} = \frac{1}{2} [\text{pK}_W - \log C - \text{pK}_b]$$

$$\Rightarrow 10.26 = 14 - \log C - 4.74$$

$$\Rightarrow \log C = 9.26 - 10.26 = -1.0$$

$$\therefore C = 10^{-1} \text{ M}$$

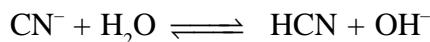
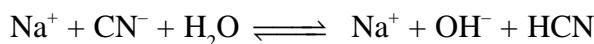
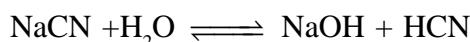
$$[\text{NH}_4^+ \text{Cl}] = 10^{-1} \text{ M}$$

$$W_{\text{NH}_4\text{NO}_3} = 10^{-1} \times 53.5 \text{ g L}^{-1}$$

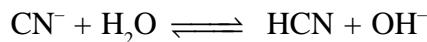
$$= 5.35 \text{ g L}^{-1}$$

### 5.2.2 Hydrolysis of [WA – SB] type salt :

**Ex.** KCN, NaCN,  $\text{K}_2\text{CO}_3$ ,  $\text{BaCO}_3$ ,  $\text{K}_3\text{PO}_4$



- (i) In this type of salt hydrolysis anion reacts with water therefore called as anionic hydrolysis.
- (ii) Solution is basic in nature as  $[\text{OH}^-]$  increases.
- (iii) pH of the solution is greater than 7.
- (iv) **Relation between  $K_h$ ,  $K_w$ ,  $K_a$**

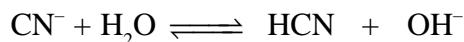


$$K_h = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} \quad \dots\dots \text{(i)}$$

$$\frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} \times \frac{[\text{CN}^-][\text{H}^+]}{[\text{HCN}]} = [\text{H}^+][\text{OH}^-]$$

$$K_h = \frac{K_w}{K_a}$$

### (v) Degree of hydrolysis :



C	0	0	Initial concentration at equilibrium
C – Ch	Ch	Ch	

$$K_h = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

$$K_h = \frac{\text{Ch}^2}{(1-h)}$$

Since  $h \ll 1$ , therefore  $(1 - h) \approx 1$

$$\therefore K_h = Ch^2$$

$$h^2 = \frac{K_h}{C} \Rightarrow h = \sqrt{\frac{K_h}{C}}$$

$$h = \sqrt{\frac{K_w}{K_a \times C}}$$

#### (vi) pH of the solution

$$[\text{OH}^-] = Ch$$

$$[\text{OH}^-] = \sqrt{\frac{K_w \times C}{K_a}}$$

$$[\text{H}^+] = \frac{K_w}{\sqrt{\frac{K_w \times C}{K_a}}} \Rightarrow [\text{H}^+] = \sqrt{\frac{K_w \times K_a}{C}}$$

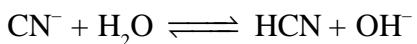
On taking  $-\log$  on both sides

$$\text{pH} = -\frac{1}{2} [\log K_w + \log K_a - \log C]$$

$$\text{pH} = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

**Ex.22 Calculate the pH and degree of hydrolysis of 0.01 M solution of NaCN,  $K_a$  for HCN is  $6.2 \times 10^{-12}$ .**

**Sol.** NaCN is a salt of strong base NaOH and weak acid HCN.  $\text{Na}^+$  does not react with water whereas  $\text{CN}^-$  reacts with water as here under



$$K_h = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = \frac{K_w}{K_a} = \frac{10^{-14}}{6.2 \times 10^{-12}} = 1.6 \times 10^{-3}$$

Let,  $x$  moles of salt undergo hydrolysis then concentrations of various species would be

$$[\text{CN}^-] = (0.01 - x) \approx 0.01, [\text{HCN}] = x$$

$$[\text{OH}^-] = x$$

$$\therefore K_h = \frac{x \cdot x}{0.01} = 1.6 \times 10^{-3}$$

$$\therefore x^2 = 1.6 \times 10^{-5}$$

$$\therefore x = 4 \times 10^{-3}$$

$$[\text{OH}^-] = x = 4 \times 10^{-3} \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{4 \times 10^{-3}} = 0.25 \times 10^{-11}$$

$$\text{pH} = -\log(0.25 \times 10^{-11}) = 11.6020$$

$$\text{Degree of hydrolysis} = \frac{x}{0.01} = \frac{4 \times 10^{-3}}{0.01} = 4 \times 10^{-1}$$

**Ex.23.** Calculate for 0.01 N solution of sodium acetate -

(i) **Hydrolysis constant**

(ii) **Degree of hydrolysis**

(iii) **pH**

Given  $K_a$  of  $\text{CH}_3\text{COOH} = 1.9 \times 10^{-5}$ .

**Sol.** For  $\text{CH}_3\text{COONa} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{NaOH}$

Initial	C	0	0
---------	---	---	---

After	C(1-h)	Ch	Ch
-------	--------	----	----

$$(i) K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.9 \times 10^{-5}} = 5.26 \times 10^{-10}$$

$$(ii) h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{5.26 \times 10^{-10}}{0.01}} = 2.29 \times 10^{-4} \text{ M}$$

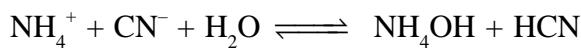
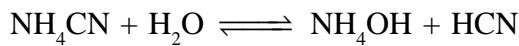
$$(iii) [\text{OH}^-] \text{ from NaOH, a strong base} = Ch = 0.01 \times 2.29 \times 10^{-4} = 2.29 \times 10^{-6} \text{ M}$$

$$\text{pOH} = 5.64$$

$$\therefore \text{pH} = 14 - 5.64 = 8.36$$

### 5.2.3 Hydrolysis of (WA - WB) type salt :

**Ex.**  $\text{NH}_4\text{CN}$ ,  $\text{CaCO}_3$ ,  $(\text{NH}_4)_2\text{CO}_3$ ,  $\text{ZnHPO}_3$

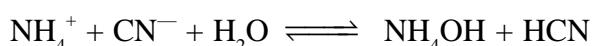


Solution is almost neutral but it may be acidic or basic depending upon the nature of acid & base & pH of the solution is near to 7.

For WA - WB types of salt :

	$K_a > K_b$	$K_b > K_a$	$K_a = K_b$
1. Hydrolysis	Cationic-anionic	Anionic-cationic	Neutral hydrolysis
2. Nature	Acidic	Basic	Neutral
3. pH	$pH < 7$	$pH > 7$	$pH = 7$

(i) Relation between  $K_h$ ,  $K_w$ ,  $K_a$  &  $K_b$



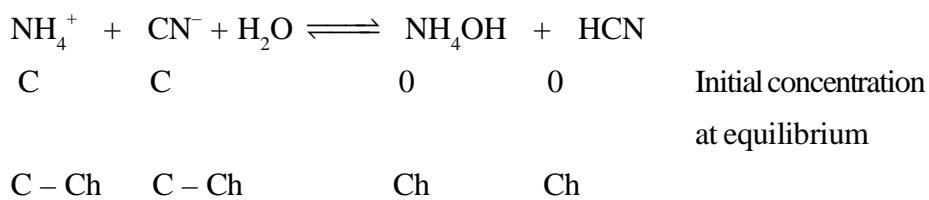
$$K_h = \frac{[\text{NH}_4\text{OH}][\text{HCN}]}{[\text{NH}_4^+][\text{CN}^-]} \quad \dots\dots (\text{i})$$

$$\frac{[\text{NH}_4\text{OH}][\text{HCN}]}{[\text{NH}_4^+][\text{CN}^-]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \times \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = [\text{H}^+] [\text{OH}^-]$$

$$K_h \times K_b \times K_a = K_w$$

$$K_h = \frac{K_w}{K_a \times K_b}$$

(ii) Degree of Hydrolysis :



$$K_h = \frac{[\text{NH}_4\text{OH}][\text{HCN}]}{[\text{NH}_4^+][\text{CN}^-]}$$

Since  $h \llll 1$

Then  $(1 - h) \approx 1$

$$\therefore K_h = h^2 \quad \text{or} \quad h^2 = \frac{K_w}{K_a \times K_b}$$

$$h = \sqrt{\frac{K_w}{K_a \times K_b}} \quad \dots\dots (\text{v})$$

### (iii) pH of the solution

From eq. (iii)

$$K_a = \frac{[H^+][CN^-]}{[HCN]}$$

$$[H^+] = \frac{K_a \times [HCN]}{[CN^-]}$$

$$[H^+] = \frac{K_a \times Ch}{C - Ch} = \frac{K_a \times h}{1 - h}$$

Since  $h \ll 1, (1 - h) \approx 1$

$$[H^+] = K_a \times h \quad [\text{Now put the value of } h \text{ from eq. (5)}]$$

$$= K_a \times \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$\boxed{[H^+] = \sqrt{\frac{K_w \times K_a}{K_b}}}$$

On taking  $-\log$  on both sides

$$-\log [H^+] = -\log \left( \frac{K_w \times K_a}{K_b} \right)^{\frac{1}{2}}$$

$$pH = -\frac{1}{2} [\log K_w + \log K_a - \log K_b]$$

$$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

**Note :** Degree of hydrolysis of [WA – WB] type salt does not depend on the concentration of salt.

#### Ex.24 Salt of weak acid and weak base

(i) Calculate pH of the mixture (25 mL of 0.1 M  $NH_4OH$  + 25 mL of 0.1 M  $CH_3COOH$ ).

Given that  $K_a : 1.8 \times 10^{-5}$ , and  $K_b = 1.8 \times 10^{-5}$

Sol.	$NH_4OH$	+	$CH_3COOH$	$\rightarrow$	$CH_3COONH_4$	+	$H_2O$
Initial milli moles	$25 \times 0.1$		$25 \times 0.1$		0		0
	= 2.5			= 2.5		-	
Final milli moles	0		0		2.5		2.5

As salt is formed (salt of weak acid and weak base) and pH will be decided by salt hydrolysis

$$pH = \frac{pK_w + pK_a - pK_b}{2} = \frac{1}{2} (-\log 10^{-14} - \log 1.8 \times 10^{-5} + \log 1.8 \times 10^{-5}) = 7$$

**Ex.25** In the following which one has highest / maximum degree of hydrolysis.

- (1)  $0.01\text{ M} - \text{NH}_4\text{Cl}$       (2)  $0.1\text{ M} - \text{NH}_4\text{Cl}$   
 (3)  $0.001\text{ M} - \text{NH}_4\text{Cl}$       (4) Same

**Sol.** [3]

$$\left( h = \sqrt{\frac{K_w}{C}} \text{ if } C \text{ decreases, } h \text{ increases} \right)$$

**Ex.26** In the following which one has lowest value of degree of hydrolysis.

- (1)  $0.01\text{ M} - \text{CH}_3\text{COONH}_4$       (2)  $0.1\text{ M} - \text{CH}_3\text{COONH}_4$   
 (3)  $0.001\text{ M} - \text{CH}_3\text{COONH}_4$       (4) Same

**Sol.** [4]

**Ex.27** Find out the concentration of  $[\text{H}^+]$  in  $0.1\text{M}$   $\text{CH}_3\text{COONa}$  solution ( $K_a = 10^{-5}$ )

**Sol.** Salt is  $[\text{WA} - \text{SB}]$  type

$$\therefore [\text{H}^+] = \sqrt{\frac{K_w \times K_a}{C}} = \sqrt{\frac{10^{-14} \times 10^{-5}}{10^{-1}}} = \sqrt{10^{-19} \times 10^{+1}} = \sqrt{10^{-18}} = 10^{-9}$$

**Ex.28** Calculate the degree of hydrolysis of a mixture containing  $0.1\text{N}$   $\text{NH}_4\text{OH}$  and  $0.1\text{N}$   $\text{HCN}$

$$K_a = 10^{-5} \quad \& \quad K_b = 10^{-5}$$

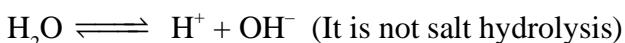
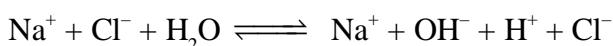
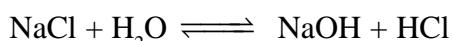
**Sol.** Salt is  $[\text{WA} - \text{WB}]$

$$h = \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{10^{-14}}{10^{-5} \times 10^{-5}}}$$

$$= \sqrt{10^{-14} \times 10^{+10}} = \sqrt{10^{-4}} = 10^{-2}$$

#### 5.2.4 Hydrolysis of $[\text{SA} - \text{SB}]$ type salt :

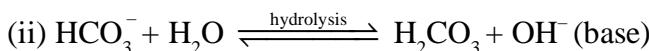
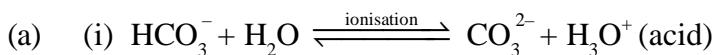
**Ex.**  $\text{NaCl}$ ,  $\text{BaCl}_2$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{KClO}_4$  etc.



- (1) Hydrolysis of salt of  $[\text{SA} - \text{SB}]$  is not possible
- (2) Solution is neutral in nature ( $\text{pH} = \text{pOH} = 7$ )
- (3)  $\text{pH}$  of the solution is 7

### 5.2.5 Hydrolysis of Amphiprotic Anion :

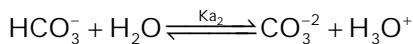
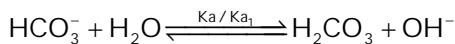
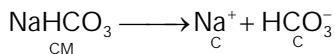
$\text{NaHCO}_3$ ,  $\text{NaHS}$ , etc., can undergo ionisation to form  $\text{H}^+$  ion and can undergo hydrolysis to form  $\text{OH}^-$  ( $\text{Na}^+$  ion is not hydrolysed)



$$\text{pH}(\text{HCO}_3^-) = \left( \frac{\text{pK}_{a_1} + \text{pK}_{a_2}}{2} \right)$$

(b) Similarly for  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  amphiprotic anions.

$$\text{pH}_{(\text{H}_2\text{PO}_4^-)} = \left( \frac{\text{pK}_{a_1} + \text{pK}_{a_2}}{2} \right) \quad \text{and} \quad \text{pH}_{(\text{HPO}_4^{2-})} = \left( \frac{\text{pK}_{a_2} + \text{pK}_{a_3}}{2} \right)$$



$\therefore \text{H}^+$  and  $\text{OH}^-$  also react

$\therefore$  We can safely assume that both reactions have nearly same degree of dissociation

$$\therefore [\text{H}_2\text{CO}_3] \approx [\text{CO}_3^{2-}] \quad \dots(1)$$

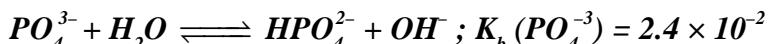
$$\frac{\text{K}_w}{\text{Ka}_1} = \frac{[\text{H}_2\text{CO}_3][\text{OH}^-]}{[\text{HCO}_3^-]} \Rightarrow \frac{1}{\text{Ka}_1} = \frac{[\text{H}_2\text{CO}_3]}{[\text{H}^+][\text{HCO}_3^-]} \quad \dots(2)$$

$$\frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} = \text{Ka}_2 \quad \dots(3)$$

Divide (2) by (3)

$$[\text{H}^+] = \sqrt{\text{Ka}_1 \text{Ka}_2} \Rightarrow \text{pH} = \frac{\text{pKa}_1 + \text{pKa}_2}{2}$$

**Ex.29 Calculate the pH of 0.5 M  $\text{Na}_3\text{PO}_4$  in aqueous solution ?**



**Sol.**  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$  are conjugate acid and base so  $K_a \times K_b = 10^{-14}$

$$K_a(\text{HPO}_4^{2-}) = \frac{10^{-14}}{2.4 \times 10^{-2}} = 4.17 \times 10^{-13}$$

$$\text{pK}_a = -\log K_a = 12.38$$

$$\text{or} \quad \text{pH} = 7 + \frac{1}{2} \text{pK}_a + \frac{1}{2} \log C$$

$$\text{pH} = 13.04$$

## 6. BUFFER SOLUTIONS

A solution that resists change in pH value upon addition of small amount of strong acid or base or when solution is diluted is called buffer solution.

The capacity of a solution to resist alteration in its pH value is known as buffer capacity and the mechanism of buffer solution is called buffer action.

## 6.1 Types of buffer solutions

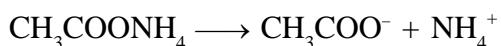


## 6.2 SIMPLE BUFFER SOLUTION :

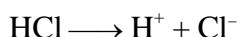
A salt of weak acid and weak base in water e.g.  $\text{CH}_3\text{COONH}_4$ ,  $\text{HCOONH}_4$ ,  $\text{AgCN}$ ,  $\text{NH}_4\text{CN}$ .

## **Buffer action of simple buffer solution**

Consider a simple buffer solution of  $\text{CH}_3\text{COONH}_4$ , since it is a salt will dissociate completely.



If a strong acid such as HCl is added then



The  $\text{H}^+$  ions from the added acid ( $\text{HCl}$ ) combine with  $\text{CH}_3\text{COO}^-$  ions to form  $\text{CH}_3\text{COOH}$ , which is a weak acid so will not further ionized.

Thus there is no rise in  $H^+$  ion concentration and the pH remains constant.



- If a strong base is added as NaOH



Thus change in  $\text{OH}^-$  ion concentration is resisted by  $\text{NH}_4^+$  ions by forming  $\text{NH}_4\text{OH}$  which is a weak base. So it will not further ionized and pH remains constant.

pH of a simple buffer solution :-

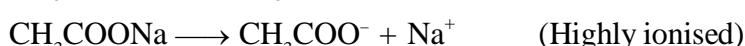
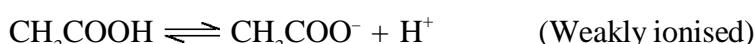
$$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

### 6.3 MIXED BUFFER SOLUTIONS :

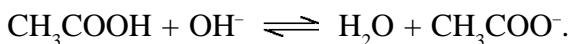
### 6.3.1 Acidic buffer solution :

An acidic buffer solution consists of solution of a weak acid and its salt with strong base. The best known example is a mixture of solution of acetic acid and its salt with strong base ( $\text{CH}_3\text{COONa}$ ).

Other example:



When a few drops of an acid (HCl) are added to it, the H<sup>+</sup> ions from the added acid (HCl) combine with the CH<sub>3</sub>COO<sup>-</sup> ions to form CH<sub>3</sub>COOH. Thus there is no rise in H<sup>+</sup> ion concentration and the pH of solution remains constant. On the other hand, when a few drops of base(NaOH) are added, the OH<sup>-</sup> of the added base reacts with acetic acid to form unionise water and acetate ions.



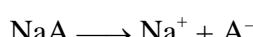
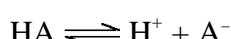
Thus there is no increase in OH<sup>-</sup> ion concentration and hence the pH of the solution remains constant.

### pH of a acidic buffer solution (Henderson equation) :

Consider a buffer mixture (acidic buffer)



where A = CH<sub>3</sub>COO, A<sup>-</sup> = CH<sub>3</sub>COO<sup>-</sup>



Applying law of mass action to dissociation equilibrium of HA

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} ; \text{ so } [\text{H}^+] = \frac{K_a[\text{HA}]}{[\text{A}^-]}$$

taking log,  $\log [\text{H}^+] = \log K_a + \log \frac{[\text{HA}]}{[\text{A}^-]}$

$$-\log [\text{H}^+] = -\log K_a - \log \frac{[\text{HA}]}{[\text{A}^-]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

[A<sup>-</sup>] = Initial concentration of salt as it is mainly comes from salt.

[HA] = Initial concentration of the acid.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \text{ (it is known as Henderson-Hasselbalch equation.)}$$

**Note :** A solution can act as buffer only if ratio of concentration of salt to acid is between 0.1 to 10.

CH <sub>3</sub> COOH	:	CH <sub>3</sub> COONa
1		10
10		1

pH = pK<sub>a</sub> + 1  
pH = pK<sub>a</sub> - 1

Thus pH range of an acidic buffer solution is (pK<sub>a</sub> + 1) to (pK<sub>a</sub> - 1)

$$\text{pH range} = \text{p}K_a \pm 1$$

Maximum buffer action will be only when ratio of concentration of acid and salt is 1. So for maximum buffer action, pH = pK<sub>a</sub>

**Ex.30 How much volume of 0.2 M solution of acetic acid should be added to 100 mL of 0.2 M solution of sodium acetate to prepare a buffer solution of pH = 6.00 ? (pK<sub>a</sub> for acetic acid is 4.74)**

**Sol.** pH = pK<sub>a</sub> + log  $\frac{[\text{Salt}]}{[\text{Acid}]}$

$$\log \frac{[\text{Salt}]}{[\text{Acid}]} = \text{pH} - \text{pK}_a = 6.00 - 4.74 = 1.26 \quad \therefore \quad \frac{[\text{Salt}]}{[\text{Acid}]} = 18.2$$

$$\text{Moles of CH}_3\text{COONa in solution} = \frac{100 \times 0.2}{1000} = 0.02$$

Let, volume of 0.2 acetic acid added = V mL

$$\therefore \text{Moles of acetic acid} = \frac{V \times 0.2}{1000}$$

$$\therefore \frac{0.02}{V \times \frac{0.2}{1000}} = 18.2$$

$$\therefore V = 5.49 \text{ mL}$$

**Ex.31 Calculate the pH after the addition of 80 mL and 100 mL respectively of 0.1 N NaOH to 100 mL, 0.1 N CH<sub>3</sub>COOH. (Given pK<sub>a</sub> for CH<sub>3</sub>COOH = 4.74)**

**Sol.** If 80 mL of 0.1 N NaOH is added to 100 mL of 0.1 N CH<sub>3</sub>COOH, acidic buffer will form as

H <sub>3</sub> CCOOH	+	NaOH	→	H <sub>3</sub> CCOONa	+ H <sub>2</sub> O
Initial	0.01 eq.	0.008 eq.		0	0
Final	0.002 eq.	0		0.008 eq.	

$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 4.74 + \log \frac{0.008}{0.002} = 5.342$$

If 100 mL of 0.1 N NaOH is added to 100 mL of 0.1 N CH<sub>3</sub>COOH, complete neutralization takes place and the concentration of H<sub>3</sub>CCOONa =  $\frac{0.1}{2} \text{ M} = 0.05 \text{ M}$

$$\text{Now, pH} = 7 + \frac{1}{2} \text{pK}_a + \frac{1}{2} \log C = 8.72$$

**Ex.32 Calculate the pH of a solution when 0.20 moles of HCl is added to one litre solution containing-**

(a) 1 M each of acetic acid and acetate ion ?

(b) 0.1 M each of acetic acid and acetate ion ?

Given K<sub>a</sub> for acetic acid is  $1.8 \times 10^{-5}$ .

**Sol.** (a) Initially [Acetic acid] = 1 M

$$[\text{Acetate}] = 1 \text{ M}$$

Now 0.2 moles of HCl are added to it.

	HCl	+	CH <sub>3</sub> COO <sup>-</sup>	→	CH <sub>3</sub> COOH	+	Cl <sup>-</sup>
Mole before reaction	0.2		1		1		0
Mole after reaction	0		0.8		1.2		0.2

$$\therefore \text{New } [CH_3COOH] = 1.2 ; [CH_3COO^-] = 0.8$$

$$\therefore pH = pK_a + \log \frac{[\text{conjugate}]}{[\text{acid}]}$$

$$\therefore pH = -\log 1.8 \times 10^{-5} + \log \frac{0.8}{1.2} = 4.5686$$

(b) In II case initially [Acetic acid] = 0.1 M

[Acetate] = 0.1 M

Now 0.2 mole of HCl are added to it

	HCl	+	$CH_3COO^-$	$\rightarrow$	$CH_3COOH$	+	$Cl^-$
Mole before reaction	0.2		0.1		0.1		0
Mole after reaction		0.1		0	0.2		0.1
$\therefore$	[H <sup>+</sup> ] from free HCl = 0.1 M						
$\therefore$	pH = 1						

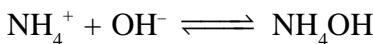
**Note:**  $CH_3COOH$  no doubt gives H<sup>+</sup> but being weak acid as well as in presence of HCl does not dissociate appreciably and thus, H<sup>+</sup> from  $CH_3COOH$  may be neglected.

### 6.3.2 Basic buffer solution :

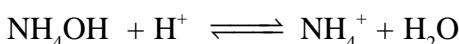
A basic buffer solution consists of a mixture of a weak base and its salt with strong acid. The best known example is a mixture of NH<sub>4</sub>OH and NH<sub>4</sub>Cl.



When a few drops of a base (NaOH) are added, the OH<sup>-</sup> ions from NaOH combine with NH<sub>4</sub><sup>+</sup> ions to form feebly ionised NH<sub>4</sub>OH thus there is no rise in the concentration of OH<sup>-</sup> ions and hence the pH value remains constant.

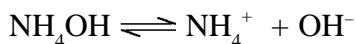


If a few drops of a acid (HCl) are added the H<sup>+</sup> from acid combine with NH<sub>4</sub>OH to form H<sub>2</sub>O and NH<sub>4</sub><sup>+</sup> ions.



Thus the addition of acid does not increase the H<sup>+</sup> ion concentration and hence pH remains unchanged.

- pH of basic buffer solution :**



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

$$[\text{OH}^-] = \frac{K_b [\text{NH}_4\text{OH}]}{[\text{NH}_4^+]} = \frac{K_b [\text{Base}]}{[\text{Salt}]}$$

( $\text{NH}_4^+$  mainly comes from salt)

taking  $-\log$  on both side

$$-\log \text{OH}^- = -\log \frac{K_b [\text{Base}]}{[\text{Salt}]} \Rightarrow \text{pOH} = -\log K_b - \log \frac{[\text{Base}]}{[\text{Salt}]}$$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \Rightarrow \text{pH} = 14 - \text{pOH}$$

- pOH range :**

A solution can act as buffer solution only if ratio of concentration of salt to base is from 0.1 to 10.

$\text{NH}_4\text{OH}$	:	$\text{NH}_4\text{Cl}$
1		10 $\text{pOH} = \text{p}K_b + 1$
10		1 $\text{pOH} = \text{p}K_b - 1$

So pOH range is  $\text{p}K_b \pm 1$

- Condition for maximum buffer action :**

$$[\text{NH}_4\text{OH}] : [\text{NH}_4\text{Cl}]$$

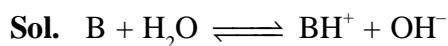
$$1 \qquad \qquad \qquad 1$$

$$\text{pOH} = \text{p}K_b + \log \frac{1}{1}$$

$$\text{pOH} = \text{p}K_b \quad \text{and} \quad \text{pH} = 14 - \text{p}K_b$$

Maximum buffer action because pH remains constant.

**Ex.33** An organic base B has  $K_b$  value equal to  $1 \times 10^{-8}$ . In what amounts should 0.01 M HCl and 0.01 M solution of B be mixed to prepare 1 L of a buffer solution having pH = 7.0 ?



$$K_b = \frac{[BH^+][OH^-]}{[B]} = 1 \times 10^{-8}$$

$$pOH = pK_b + \log \frac{[BH^+]}{[B]}$$

$$\Rightarrow 7 = -\log(10^{-8}) + \log \frac{[BH^+]}{[B]} \Rightarrow 7 = 8 + \log \frac{[BH^+]}{[B]}$$

$$\log \frac{[BH^+]}{[B]} = -1$$

$$\therefore \frac{[BH^+]}{[B]} = 10^{-1} = 0.1$$

Let, volume of HCl taken = xL

$\therefore$  Volume of base taken =  $(1 - x)$  L

After the reaction, millimole of  $BH^+$  formed =  $0.01 \times (x)$

Millimoles of base left =  $0.01 (1 - 2x)$

$$\therefore \frac{[BH^+]}{[B]} = \frac{x}{[1 - 2x]} = 0.1$$

$\therefore x = 0.083$  L = Volume of HCl

$\therefore$  Volume of base = 0.917 L

**Ex.34** Which of the following buffers containing  $NH_4OH$  and  $NH_4Cl$  show the lowest pH value?

<i>conc. of</i>	<i>conc. of</i>
$NH_4OH (mol L^{-1})$	$NH_4Cl (mol L^{-1})$
(A) 0.50	0.50
(B) 0.10	0.50
(C) 0.50	1.50
(D) 0.50	0.10

Sol. (B)  $pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$  for  $NH_4Cl = 0.5$  and  $NH_4OH = 0.1$

pOH will be maximum and so pH will be minimum.

**Ex.35** A solution of weak base BOH was titrated with 0.1 N HCl. The pH of the solution was found to be 10.04 and 9.14 after the addition of 5 mL and 20 mL of the acid respectively. Find the dissociation constant of the base.

**Sol.** **Case I :**

BOH	+	HCl	→	BCl	+	H <sub>2</sub> O
Millimole before reac.	a	0.1 × 5 = 0.5		0		0
Millimole after reac.	(a - 0.5)		0		0.5	0.5

$$\therefore \text{pOH} = -\log K_b + \log \frac{[\text{BCl}]}{[\text{BOH}]} \dots\dots\dots(\text{i})$$

$$\because \text{pH} = 10.04 \quad \text{so} \quad \text{pOH} = 3.96$$

$$\therefore 3.96 = -\log K_b + \log \frac{0.5}{(a - 0.5)} \dots\dots\dots(\text{ii})$$

**Case II :**

BOH	+	HCl	→	BCl	+	H <sub>2</sub> O
Millimole before reac.	a	0.1 × 20 = 2		0		0
Millimole after reac.	(a - 2)		0		2	2

$$\therefore \text{pOH} = -\log K_b + \log \frac{[\text{BCl}]}{[\text{BOH}]} \dots\dots\dots(\text{iii})$$

$$\because \text{pH} = 9.14 \quad \therefore \quad \text{pOH} = 4.86$$

$$\therefore 4.86 = -\log K_b + \log \frac{2}{(a - 2)} \dots\dots\dots(\text{iv})$$

Solving Eqs. (ii) and (iv),  $K_b = 1.81 \times 10^{-5}$

## 7. INDICATORS

The stage of titration when complete reaction occur between the solution is called **equivalent point**. The stage of titration when sudden change in colour of solution is observed is called **end point**. A perfect indicator response sudden colour change exactly on completion of reaction. An **indicator** is a substance which response sudden change in colour of solution at the end point or neutral point of the acid-base titration. At **end point**  $N_1 V_1 = N_2 V_2$

- (i) The indicators in acid-base titration changes colour on changing the pH of solution.
- (ii) All the acid-base indicators are either weak organic acid or base and having different colour for unionized and ionised form.

- (iii) A mixture of two colour is recognized in a single colour if the conc. of one is 10 times or more than that of others. (This 10 time is flexible)



colour X                      colour Y

$$\text{Diss. const. or (Ionisation const)} = K_a = K_{in} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$\text{pH} = \text{pK}_{in} + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

- (a) The solution will appear only of colour Y, if  $\frac{[\text{A}^-]}{[\text{HA}]} \geq 10 \Rightarrow \text{pH} \geq (\text{pK} + 1)$

- (b) The solution will appear only of colour X, if  $\frac{[\text{A}^-]}{[\text{HA}]} \leq \frac{1}{10} \Rightarrow \text{pH} \leq (\text{pK} - 1)$

pH of solution below and above which solution appears in a single colour is called pH range of indicator.

Indicator	pH range	Colour change	pK <sub>a</sub>
Methyl orange	3.2 – 4.5	Pink to yellow	3.7
Methyl red	4.4 – 6.5	Red to yellow	5.1
Litmus	5.5 – 7.5	Red to blue	7.0
Phenol red	6.8 – 8.4	Yellow to red	7.8
Phenolphthalein	8.3 – 10.5	Colourless to pink	9.6

**Ex.36** The disso. const. of a basic indicator is  $2 \times 10^{-7}$ . Calculate its pH range.

$$\text{Sol. } 5.7 - 7.7 = \text{pOH} \quad \therefore \quad \text{pH} = 6.3 - 8.3$$

**Ex.37** The pH range of an acidic indicator HIn is 4.0 - 5.2 . Calculate dissociation constant.

Also calculate  $\frac{\text{In}^-}{\text{HIn}}$  for the appearance of solution in single colour.

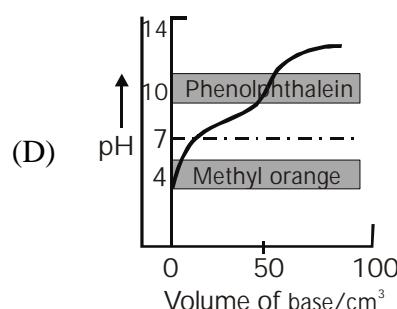
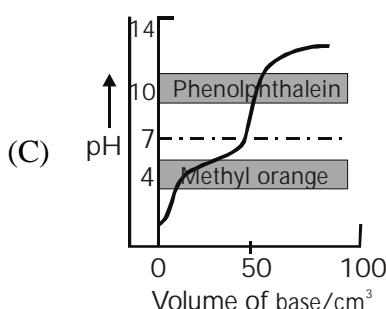
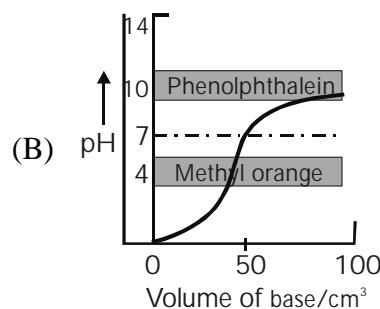
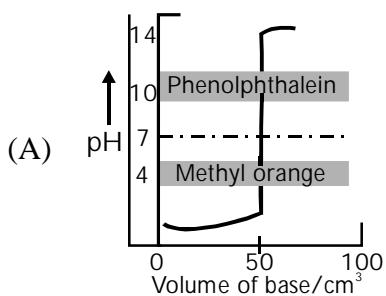
$$\text{Sol. Diss. constant} = 2.5 \times 10^{-5}, 4$$

## 7.1 TITRATION OF STRONG ACID AGAINST STRONG ALKALI :

The graph (A) shows how pH changes during the titration of  $50 \text{ cm}^3$  of 0.1 M HCl with 0.1 M NaOH.



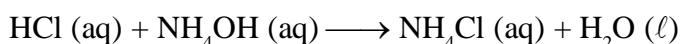
The pH of 0.1 M solution of HCl in the beginning would be 1. As alkali is added, the pH changes slowly in the beginning. However, at the equivalence point pH changes rapidly from about 3.5 to 10. It can be shown by simple calculations that pH of the solution is 3.7 when  $49.8 \text{ cm}^3$  of 0.1 M NaOH solution have been added. The pH suddenly changes to 10 after addition of  $50.1 \text{ cm}^3$  of the NaOH solution. Thus, any indicator having pH range between 3.5 to 10 will identify the equivalence point. This means that any one of phenolphthalein, methyl orange or bromothymol blue could be used as an indicator.



**Titration curves :** (A) strong base with strong acid ; (B) weak base with strong acid ; (C) strong base with weak acid ; (D) weak base with weak acid.

## 7.2 TITRATION OF STRONG ACID AGAINST WEAK ALKALI :

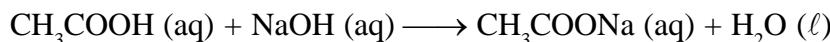
The graph (B) shows how pH changes during titration of  $50 \text{ cm}^3$  of 0.1 M HCl with 0.1 M  $\text{NH}_3$ .



In this case, the pH changes rapidly from 3.5 to 7.0 at the equivalence point. Methyl orange, methyl red and bromocresol green are suitable indicators for this type of titration. Phenolphthalein is unsuitable because its pH range lies outside the vertical portion of the curve.

### 7.3 TITRATION OF WEAK ACID AGAINST STRONG BASE :

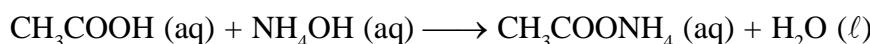
The graph (C) shows how pH changes during titration of 50 cm<sup>3</sup> of 0.1 M CH<sub>3</sub>COOH with 0.1 M NaOH.



The vertical portion of this titration curve lies between pH range 7 to 10.6. Phenolphthalein is suitable indicator for this titration. Methyl orange is not suitable for this titration because its pH range lies on the flat portion of the curve.

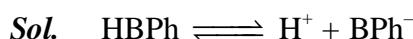
### 7.4 TITRATION OF WEAK ACID AGAINST WEAK BASE :

The graph (D) represents the titration curve obtained for titration of 50 cm<sup>3</sup> of 0.1 M CH<sub>3</sub>COOH with 0.1 M NH<sub>3</sub>.



For this type of titration there is no sharp increase in pH at the equivalence point. No indicator is suitable for this type of titration.

**Ex.38** *Bromophenol blue is an indicator with a value of K<sub>a</sub> = 6.84 × 10<sup>-6</sup>. At what pH it will work as an indicator? Also report the % of this indicator in its basic form at a pH of 5.84.*



$$K_a = \frac{[\text{H}^+][\text{BPh}^-]}{[\text{HBPh}]}, \text{ when } \text{BPh}^- = \text{HBPh}, \text{ indicator will work. Thus}$$

$$[\text{H}^+] = 6.84 \times 10^{-6}$$

$$\therefore \text{pH} = 5.165$$

Also if pH = 5.84

$$\text{or } [\text{H}^+] = 1.44 \times 10^{-6}, \text{ then}$$

$$K_a = \frac{[\text{H}^+][\text{BPh}^-]}{[\text{HBPh}]} \quad \text{or} \quad 6.84 \times 10^{-6} = \frac{1.44 \times 10^{-6} \cdot C\alpha}{C(1-\alpha)} \quad \text{or} \quad \alpha = 0.83 \text{ or } 83 \%$$



## 8. SOLUBILITY (s) & SOLUBILITY PRODUCT ( $K_{sp}$ )

### 8.1 SOLUBILITY :

At constant temperature, the maximum number of moles of solute which can be dissolved in a solvent to obtain 1 litre of saturated solution is called solubility.

Solubility depends on the following –

- (i) Temperature
- (ii) Presence of common ion
- (iii) Nature of solvent

### 8.2 SOLUBILITY PRODUCT( $K_{sp}$ ) :

When a sparingly soluble salt such as AgCl is put into water, a very small amount of AgCl dissolves in water and most of the salt remains undissolved in its saturated solution.

- A solution which remains in contact with undissolved solute is said to be saturated.
- The salt AgCl is an electrolyte, its dissociation occurs in solution. Hence, the quantity of AgCl that dissolves in water dissociates into  $\text{Ag}^+$  and  $\text{Cl}^-$  ions. Thus, in the saturated solution of AgCl an equilibrium exists between undissolved solid AgCl and its ions,  $\text{Ag}^+$  and  $\text{Cl}^-$  ions.



according to law of mass action

$$K = \frac{[\text{Ag}^+] \cdot [\text{Cl}^-]}{[\text{AgCl}]}$$

Since, the concentration of undissolved solid AgCl is constant. Thus, the product  $K \cdot [\text{AgCl}]$  gives another constant which is designated as  $K_{sp}$

$$\text{So, } K \cdot [\text{AgCl}] = [\text{Ag}^+] \cdot [\text{Cl}^-]$$

$$\therefore K_{sp} = [\text{Ag}^+] \cdot [\text{Cl}^-]$$

- **$K_{sp}$  for  $\text{CaCl}_2$**        $\text{CaCl}_2(s) \rightleftharpoons \text{Ca}^{+2}(\text{aq}) + 2\text{Cl}^-(\text{aq})$

$$\text{Solubility product in terms of concentration of ions } K_{sp} = [\text{Ca}^{+2}] [\text{Cl}^-]^2$$

- **$K_{sp}$  for  $\text{AlCl}_3$**        $\text{AlCl}_3(s) \rightleftharpoons \text{Al}^{+3}(\text{aq}) + 3\text{Cl}^-(\text{aq})$

$$\text{Solubility product in terms of concentration of ions } K_{sp} = [\text{Al}^{+3}] [\text{Cl}^-]^3$$

- **General form**       $\text{A}_x \text{B}_y(s) \rightleftharpoons x\text{A}^{+y}(\text{aq}) + y\text{B}^{-x}(\text{aq})$

$$K_{sp} = [\text{A}^{+y}]^x [\text{B}^{-x}]^y$$

**Thus, solubility product is defined as the product of concentrations of the ions raised to a power equal to the number of ions given by the dissociation of electrolyte at a given temperature when the solution is saturated.**

### 8.3 APPLICATION OF SOLUBILITY PRODUCT ( $K_{sp}$ ) :

#### 8.3.1 To find out the solubility (S) :

(i)  $K_{sp}$  of AB (Mono-mono, di-di, tri-tri valency) type salt –

**Ex.** NaCl, BaSO<sub>4</sub>, CH<sub>3</sub>COONa, CaCO<sub>3</sub>, NaCN, KCN, NH<sub>4</sub>CN, NH<sub>4</sub>Cl etc.



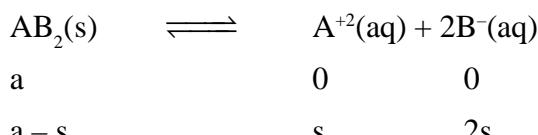
a	0	0
(a-s)	s	s

$$K_{sp} = [A^+] [B^-]$$

$$K_{sp} = s^2 \quad \text{or} \quad s = \sqrt{K_{sp}}$$

(ii)  $K_{sp}$  of AB<sub>2</sub> or A<sub>2</sub>B (Mono-di or di-mono valency) type salt –

**Ex.** CaCl<sub>2</sub>, CaBr<sub>2</sub>, K<sub>2</sub>S, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub> etc.



$$K_{sp} = [A^{+2}] [B^-]^2$$

$$K_{sp} = s \times (2s)^2 = s \times 4s^2 = 4s^3$$

$$s = \left( \frac{K_{sp}}{4} \right)^{\frac{1}{3}}$$

(iii) General form :



a	0	0
a - s	xs	ys

$$K_{sp} = [A^{+y}]^x \cdot [B^{-x}]^y$$

$$K_{sp} = (xs)^x \cdot (ys)^y$$

$$K_{sp} = x^x \cdot y^y \cdot s^{(x+y)}$$

#### 8.4 COMMON ION EFFECT ON SOLUBILITY :

Solubility of substances always decreases in the presence of common ion. According to Le-Chatelier's principle, on increasing common ion concentration equilibrium shifts in backward direction until the equilibrium is reestablished so, the solubility of substances decreases.

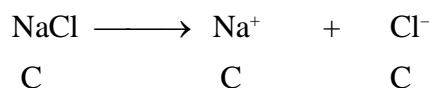
**Ex.** Find out the solubility of AgCl in water and in the presence of CM – NaCl solution?



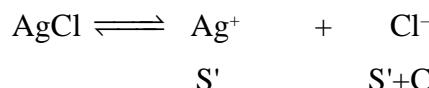
$$K_{sp} = [\text{Ag}^+] [\text{Cl}^-]$$

$$K_{sp} = S^2$$

In NaCl solution



Let solubility of AgCl in the presence of NaCl solution is  $S' \text{ mol L}^{-1}$



$$K_{sp} = [\text{Ag}^+]' [\text{Cl}^-]'$$

$$K_{sp} = S' (S' + C) = S'^2 + S'C \quad (\text{Neglecting the higher power terms of } S')$$

$$K_{sp} = S' C$$

$$S' = \frac{K_{sp}}{C}$$

#### 8.5 SIMULTANEOUS SOLUBILITY :

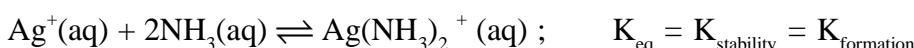
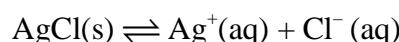
When two sparingly soluble salts are added in water simultaneously, there will be two simultaneous equilibria in the solution.

#### 8.6 SOLUBILITY IN APPROPRIATE BUFFER SOLUTIONS :

Appropriate buffer means that the components of buffer should not interfere with the salt or only  $\text{H}^+$  or  $\text{OH}^-$  ions should be interacting with the ions of the salt.

#### 8.7 EFFECT ON SOLUBILITY BECAUSE OF COMPLEX FORMATION :

Solubility of AgCl in aqueous  $\text{NH}_3$  is roughly 10,000 times as its solubility in water, due to complex formation.



$$\text{and } \frac{1}{K_{\text{stability}}} = K_{\text{dissociation}} = K_{\text{instability}}$$

### 8.8 CONDITION OF PRECIPITATION /IONIC PRODUCT (IP OR Q<sub>sp</sub>) :

- Ionic product (IP) of an electrolyte is defined in the same way as K<sub>sp</sub>. The only difference is that ionic product expression contains the initial concentration of ions or the concentration at any time whereas the expression of K<sub>sp</sub> contains only equilibrium concentration. Thus, for AgCl.

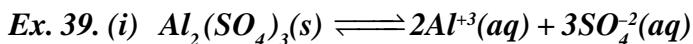
$$IP = [Ag^+]_i [Cl^-]_i \text{ and } K_{sp} = [Ag^+]_{eq} \cdot [Cl^-]_{eq}$$

- Ionic product changes with concentration but K<sub>sp</sub> does not.
- To decide whether an ionic compound will precipitate, its K<sub>sp</sub> is compared with the value of ionic product. The following three cases arise :
  - IP < K<sub>sp</sub> : The solution is unsaturated and precipitation will not occur.
  - IP = K<sub>sp</sub> : The solution is saturated and solubility equilibrium exists.
  - IP > K<sub>sp</sub> : The solution is supersaturated and hence precipitation of the compound will occur.

Thus, a salt is precipitated when its ionic product exceeds the solubility product of the salt.

### 8.9 SELECTIVE PRECIPITATION :

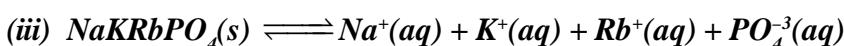
When the k<sub>sp</sub> values differ then one of the salt can be selectively precipitated.



$$K_{sp} = 2^2 \times 3^3 \times (S)^{2+3} = 4 \times 27 \times S^5 = 108 S^5$$



$$K_{sp} = 2^2 \times 1^1 \times 1^1 (S)^{2+1+1} = 4S^4$$



$$K_{sp} = 1^1 \times 1^1 \times 1^1 \times 1^1 (S)^{1+1+1+1} = S^4$$

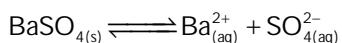
*Ex. 40.* If solubility product of the base M(OH)<sub>3</sub> is  $2.7 \times 10^{-11}$ , the concentration of OH<sup>-</sup> will be

- (1)  $3 \times 10^{-3}$       (2)  $3 \times 10^{-4}$       (3)  $10^{-3}$       (4)  $10^{-11}$

Answer : (3)

*Ex. 41.* The solubility of BaSO<sub>4</sub> in water is  $1.07 \times 10^{-5}$  mol dm<sup>-3</sup>. Estimate its solubility product.

*Sol.* Solubility equilibrium for BaSO<sub>4</sub> is

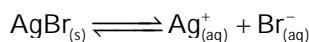


$$\text{Now, } S = 1.07 \times 10^{-5} M$$

$$\text{Hence, } K_{sp} = (1.07 \times 10^{-5})^2 = 1.145 \times 10^{-10}$$

**Ex.42.** The solubility product of  $\text{AgBr}$  is  $5.2 \times 10^{-13}$ . Calculate its solubility in  $\text{mol dm}^{-3}$  and  $\text{g dm}^{-3}$ . (Molar mass of  $\text{AgBr}$  =  $187.8 \text{ g mol}^{-1}$ )

**Sol.** The solubility equilibrium of  $\text{AgBr}$  is



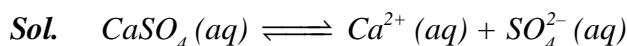
The molar solubility  $S$  of  $\text{AgBr}$  is given by

$$S = \sqrt{K_{\text{sp}}} = \sqrt{5.2 \times 10^{-13}} = 7.2 \times 10^{-7} \text{ mol dm}^{-3}$$

$$\begin{aligned} \text{The solubility in } \text{g dm}^{-3} &= \text{molar solubility } (\text{mol dm}^{-3}) \times \text{molar mass } (\text{g mol}^{-1}) \\ &= 7.2 \times 10^{-7} \times 187.8 = 1.35 \times 10^{-4} \text{ g dm}^{-3} \end{aligned}$$

**Ex.43.** What is the maximum volume of water required to dissolve 1 g of calcium sulphate at  $25^\circ\text{C}$ .

For calcium sulphate,  $K_{\text{sp}} = 9.0 \times 10^{-6}$ .



If  $S$  is the solubility of  $\text{CaSO}_4$  in moles  $\text{L}^{-1}$

$$K_{\text{sp}} = [\text{Ca}^{2+}] \times [\text{SO}_4^{2-}] = S^2$$

$$\therefore S = \sqrt{K_{\text{sp}}} = \sqrt{9.0 \times 10^{-6}}$$

$$\begin{aligned} &= 3 \times 10^{-3} \text{ mol L}^{-1} \\ &= 3 \times 10^{-3} \times 136 \text{ g L}^{-1} = 0.408 \text{ g L}^{-1} \end{aligned}$$

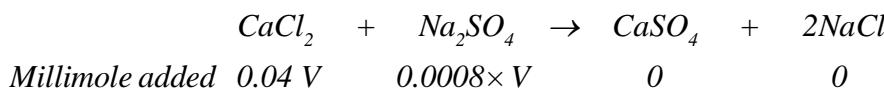
For dissolving 0.408 g of  $\text{CaSO}_4$  water required = 1 L

$$\therefore \text{For dissolving 1 g CaSO}_4 \text{ water required} = \frac{1}{0.408} \text{ L} = 2.45 \text{ L}$$

**Ex.44.** Equal volumes of 0.04 M  $\text{CaCl}_2$  and 0.0008 M  $\text{Na}_2\text{SO}_4$  are mixed. Will a precipitate form?

$K_{\text{sp}}$  for  $\text{CaSO}_4 = 2.4 \times 10^{-5}$

**Sol.**



Suppose  $V \text{ mL}$  of both are mixed

$$\therefore [\text{Ca}^{2+}] = \frac{0.04 \text{ V}}{2V}$$

$$[\text{SO}_4^{2-}] = \frac{0.0008 \text{ V}}{2V}$$

$$\therefore [\text{Ca}^{2+}] [\text{SO}_4^{2-}] = \frac{0.04 \text{ V}}{2V} \times \frac{0.0008 \text{ V}}{2V} = 8 \times 10^{-6}$$

Thus,  $[Ca^{2+}][SO_4^{2-}]$  in solution  $< K_{sp}$

$$8 \times 10^{-6} < 2.4 \times 10^{-5}$$

$\therefore CaSO_4$  will not precipitate.

**Ex. 45.** Calculate simultaneous solubility of silver thiocyanate and silver bromide in water given that  $k_{sp}$  of silver thiocyanate =  $10^{-12}$  and  $k_{sp}$  of silver bromide =  $5 \times 10^{-13}$  respectively.

**Sol.** Let the solubility of  $AgSCN$  be  $x$  and that of  $AgBr$  is  $y$ , then



$$x + y \quad x \quad x + y \quad y$$

$$10^{-12} = x(x + y) \quad \dots\dots (i)$$

$$5 \times 10^{-13} = y(x + y) \quad \dots\dots (ii)$$

On solving we get,  $x = 2y$

$$So \quad y = 4.08 \times 10^{-7} \quad and \quad x = 8.16 \times 10^{-7}$$

**Ex. 46.** What  $[H^+]$  must be maintained in saturated  $H_2S(0.1\text{ M})$  to precipitate  $CdS$  but not  $ZnS$ , if  $[Cd^{2+}] = [Zn^{2+}] = 0.1$  initially?

$$K_{sp} = (CdS) = 8 \times 10^{-27}$$

$$K_{sp} = (ZnS) = 1 \times 10^{-21}$$

$$K_a = (H_2S) = 1.1 \times 10^{-21}$$

**Sol.** In order to prevent precipitation of  $ZnS$

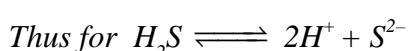
$$[Zn^{2+}][S^{2-}] < K_{sp}(ZnS) = 1 \times 10^{-21}$$

(ionic product)

$$or \quad (0.1)[S^{2-}] < 1 \times 10^{-21}$$

$$or \quad [S^{2-}] < 1 \times 10^{-20}$$

This is the maximum value of  $[S^{2-}]$  before  $ZnS$  will precipitate. Let  $[H^+]$  to maintain this  $[S^{2-}]$  be  $x$ .



$$K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{x^2(1 \times 10^{-20})}{0.1} = 1.1 \times 10^{-21}$$

$$or \quad x = [H^+] = 0.1\text{ M}$$

$\therefore$  No  $ZnS$  will precipitate at a concentration of  $H^+$  greater than  $0.1\text{ M}$

**Ex. 47.** What must be the concentration of aq.  $NH_3$  (eq.) which must be added to a solution containing  $4 \times 10^{-3} M Ag^+$  and  $0.001 M NaCl$ , to prevent the precipitation of  $AgCl$ .

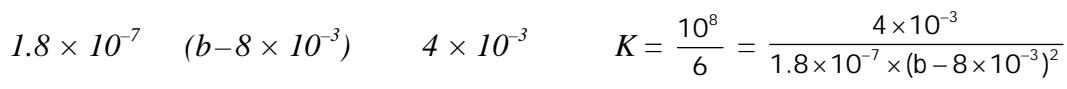
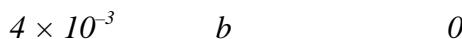
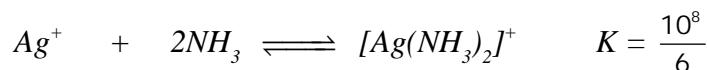
Given that  $K_{sp}(AgCl) = 1.8 \times 10^{-10}$  and the formation constant of  $[Ag(NH_3)_2]^+$  is  $K_{formation} = \frac{10^8}{6}$ .

**Sol.** Calculate silver ion concentration which can be allowed to remain in the solution,

$$1.8 \times 10^{-10} = [Ag^+][Cl^-]$$

$$[Ag^+] = \frac{1.8 \times 10^{-10}}{0.001} = 1.8 \times 10^{-7} M,$$

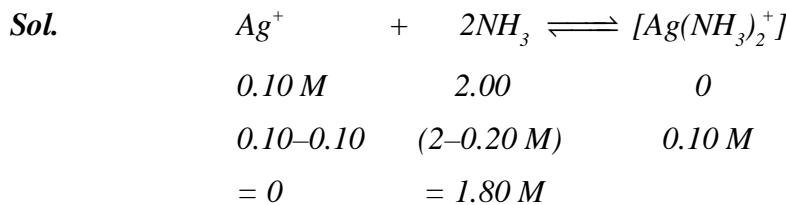
This quantity is so small that almost all the  $Ag^+$  ion will be consumed.



$$\Rightarrow b = 0.0445$$

**Ex. 48.** 0.10 mol sample of  $AgNO_3$  is dissolved in one litre of  $2.00 M NH_3$ . Is it possible to form  $AgCl(s)$  in the solution by adding 0.010 mol of  $NaCl$ ?

$$(K_{sp(AgCl)} = 1.8 \times 10^{-10}, K_{f[Ag(NH_3)_2]^+} = 1.6 \times 10^7)$$



It is assumed that all  $Ag^+$  ions have been complexed and only  $x$  amount is left

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} \Rightarrow 1.6 \times 10^7 = \frac{0.10}{x(1.80)^2}$$

$$\therefore x = 1.93 \times 10^{-9} M = [Ag^+] undisolved$$

$$[Cl^-] = 1.0 \times 10^{-2} M$$

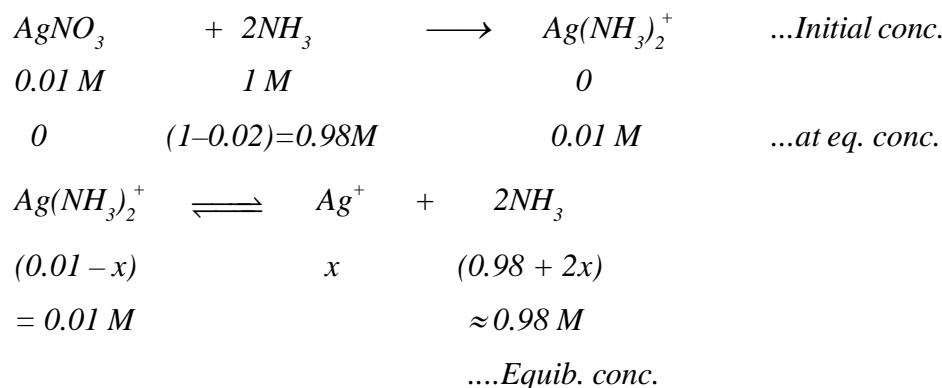
$$\therefore [Ag^+][Cl^-] = 1.93 \times 10^{-9} \times 1.0 \times 10^{-2} = 1.93 \times 10^{-11} < 1.8 \times 10^{-10} [K_{sp(AgCl)}]$$

Hence,  $AgCl(s)$  will not precipitate.

**Ex. 49.** What is the concentration of  $\text{Ag}^+$  ions in  $0.01 \text{ M } \text{AgNO}_3$  that is also  $1.0 \text{ M } \text{NH}_3$ ? Will  $\text{AgCl}$  precipitate from a solution that is  $0.01 \text{ M } \text{AgNO}_3$ ,  $0.01 \text{ M } \text{NaCl}$  and  $1 \text{ M } \text{NH}_3$ ?

$$K_d(\text{Ag}[\text{NH}_3]_2^+) = 5.88 \times 10^{-8}; K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}.$$

**Sol.** Let us first assume that  $0.01 \text{ M } \text{AgNO}_3$  shall combine with  $0.02 \text{ M } \text{NH}_3$  to form  $0.01 \text{ M } \text{Ag}(\text{NH}_3)_2^+$  and then consider its dissociation.



Since  $x \lll 1$

$$K_d = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = 5.88 \times 10^{-8}$$

$$\therefore [\text{Ag}^+] = \frac{5.88 \times 10^{-8} \times 0.01}{(0.98)^2} = 6.12 \times 10^{-10} \text{ M}$$

Further, ionic product of  $\text{AgCl} = [\text{Ag}^+][\text{Cl}^-] = (6.12 \times 10^{-10})(0.01) = 6.12 \times 10^{-12}$

Because the ionic product is smaller than  $K_{sp} = 1.8 \times 10^{-10}$ , no precipitate should form.

## EXERCISE (S-1)

## IONIZATION CONSTANTS AND pH

1. Calculate the number of  $H^+$  present in one ml of solution whose pH is 13.
2. (i)  $K_w$  for  $H_2O$  is  $9 \times 10^{-14}$  at  $60^\circ C$ . What is pH of water at  $60^\circ C$ . ( $\log 3 = 0.47$ )  
(ii) What is the nature of solution at  $60^\circ C$  whose  
(a)  $pH = 6.7$       (b)  $pH = 6.35$
3. The value of  $K_w$  at the physiological temperature ( $37^\circ C$ ) is  $2.56 \times 10^{-14}$ . What is the pH at the neutral point of water at this temperature? ( $\log 2 = 0.3$ )
4. Calculate pH of following solutions :  
(a) 0.1 M HCl  
(b) 0.1 M  $CH_3COOH$  ( $K_a = 1.8 \times 10^{-5}$ ) ( $\log \sqrt{1.8} = 0.13$ )  
(c) 0.1 M  $NH_4OH$  ( $K_b = 1.8 \times 10^{-5}$ )  
(d)  $10^{-8}$  M HCl [ $\sqrt{401} = (20.02)$ ] [ $\log 1.051 = 0.03$ ]  
(e)  $10^{-10}$  M NaOH  
(f)  $10^{-6}$  M  $CH_3COOH$  ( $K_a = 1.8 \times 10^{-5}$ )  
(g)  $10^{-8}$  M  $CH_3COOH$  ( $K_a = 1.8 \times 10^{-5}$ ) [ $\sqrt{401} = (20.02)$ ] [ $\log 1.051 = 0.03$ ]  
(h) Decimolar solution of Baryta ( $Ba(OH)_2$ ), diluted 100 times. ( $\log 2 = 0.3$ )  
(i)  $10^{-3}$  mole of KOH dissolved in 100 L of water.  
(j) Equal volume of HCl solution ( $pH = 4$ ) + 0.0019 N HCl solution
5. Calculate :  
(a)  $K_a$  for a monobasic acid whose 0.10 M solution has pH of 4.50.  
(b)  $K_b$  for a monoacidic base whose 0.10 M solution has a pH of 10.50.
6. Calculate the ratio of degree of dissociation ( $\alpha_2/\alpha_1$ ) when an acetic acid solution is diluted 100 times. Assume  $\alpha << 1$ , even on dilution. [Given  $K_a = 10^{-5}$  M]
7. Calculate the ratio of degree of dissociation of acetic acid and hydrocyanic acid (HCN) in 1 M their respective solution of acids.[Given  $K_{a(CH_3COOH)} = 1.8 \times 10^{-5}$ ;  $K_{a(HCN)} = 6 \times 10^{-10}$ ]
8. How many moles of HCl must be removed from 1 litre of aqueous HCl solution to change its pH from 2 to 3 ?
9. pH of a dilute solution of HCl is 6.95. Calculate molarity of HCl solution.

$$\begin{aligned} 10^{-6.95} &= 11.22 \times 10^{-8} \\ 10^{-7.05} &= 8.90 \times 10^{-8} \end{aligned}$$

10. The pH of aqueous solution of ammonia is 10. Find molarity of solution.  $K_b(NH_4OH) = 10^{-5}$ .
11. The solution of weak monoprotic acid which is 0.01 M, has pH = 3. Calculate  $K_a$  of weak acid.
12. Boric acid is a weak monobasic acid. It ionizes in water as



Calculate pH of 0.5 M boric acid.

### MIXTURE OF TWO OR MORE ACIDS / BASES

13. The pH of the solution produced when an aqueous solution of strong acid pH 5 is mixed with equal volume of an aqueous solution of strong acid of pH 3 is :-
14. Calculate pH of following solutions : [log 0.3 = - 0.522]
  - (a) 0.1 M  $H_2SO_4$  (50 ml) + 0.4 M HCl 50 (ml)
  - (b) 0.1 M HA + 0.1 M HB [  $K_a(HA) = 5 \times 10^{-5}$  ;  $K_a(HB) = 4 \times 10^{-5}$  ]
15. Calculate pH of a solution containing 0.1M HA ( $K_a = 10^{-5}$ ) & 0.1 M HCl.
16. Calculate  $[H^+]$  and  $[CHCl_2COO^-]$  in a solution that is 0.01 M in HCl and 0.01 M in  $CHCl_2COOH$ .  
Take ( $K_a = 3 \times 10^{-2}$ ) ( $\sqrt{28} = 5.3$ )
17. Calculate  $[H^+]$ ,  $[CH_3COO^-]$  and  $[C_7H_5O_2^-]$  in a solution that is 0.2 M in acetic acid and 0.1M in benzoic acid.  $K_a(\text{acetic}) = 1.8 \times 10^{-5}$  ,  $K_a(\text{benzoic}) = 5.4 \times 10^{-5}$ .

### POLYPROTIC ACIDS & BASES

18. What are the concentration of  $H^+$ ,  $H_2C_2O_4$ ,  $HC_2O_4^-$  and  $C_2O_4^{2-}$  in a 0.1 M solution of oxalic acid ?

$$[K_1 = 10^{-2} \text{ M and } K_2 = 10^{-5} \text{ M}] \left[ \sqrt{41} = 6.4 \right]$$

19. Calculate  $[H^+]$ ,  $[H_2PO_4^-]$ ,  $[HPO_4^{2-}]$  and  $[PO_4^{3-}]$  in a 0.01M solution of  $H_3PO_4$ .

$$\text{Take } K_1 = 10^{-3}, K_2 = 10^{-8}, K_3 = 10^{-13}, \sqrt{41} = 6.4$$

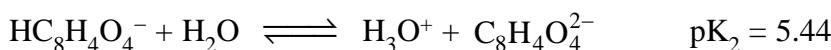
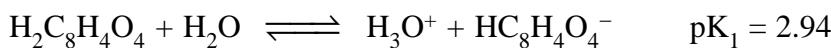
20. Calculate pH of 0.2 M –  $B(OH)_2$  solution.

$$(K_{b1} = 2 \times 10^{-5}; K_{b2} = 4 \times 10^{-11}, \log 2 = 0.3)$$

### HYDROLYSIS

21. What is the  $OH^-$  concentration of a 0.18 M solution of  $CH_3COONa$ . [ $K_a(CH_3COOH) = 1.8 \times 10^{-5}$ ]
22. Calculate the pH of a 2.0 M solution of  $NH_4Cl$ . [ $K_b(NH_3) = 2 \times 10^{-5}$ ]
23. 0.25 M solution of pyridinium chloride  $C_5H_6N^+Cl^-$  was found to have a pH of 2.699. What is  $K_b$  for pyridine,  $C_5H_5N$  ? ( $\log 2 = 0.3010$ )

24. Calculate the extent of hydrolysis & the pH of 0.02 M  $\text{CH}_3\text{COONH}_4$ .  
 $[\text{K}_b(\text{NH}_3) = 1.8 \times 10^{-5}, \text{K}_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}]$
25. Calculate the percent hydrolysis in a 0.06 M solution of KCN.  $[\text{K}_a(\text{HCN}) = 6 \times 10^{-10}]$
26. Calculate the extent of hydrolysis of 0.005 M  $\text{K}_2\text{CrO}_4$ .  $[\text{K}_2 = 3.2 \times 10^{-7}$  for  $\text{H}_2\text{CrO}_4]$   
 (It is essentially strong for first ionization).
27. A 0.010 M solution of  $\text{PuO}_2(\text{NO}_3)_2$  was found to have a pH of 4.0. What is the hydrolysis constant,  $\text{K}_h$ , for  $\text{PuO}_2^{2+}$ , and what is  $\text{K}_b$  for  $\text{PuO}_2\text{OH}^+$ ?
28. What is the pH of 0.1M  $\text{NaHCO}_3$ ?  $\text{K}_1 = 5 \times 10^{-7}, \text{K}_2 = 5 \times 10^{-11}$  for carbonic acids.
29. Calculate pH of 0.05M potassium hydrogen phthalate,  $\text{KHC}_8\text{H}_4\text{O}_4$ .



30. The acid ionization (hydrolysis) constant of  $\text{Zn}^{2+}$  is  $1.0 \times 10^{-9}$
- Calculate the pH of a 0.001 M solution of  $\text{ZnCl}_2$
  - What is the basic dissociation constant of  $\text{Zn}(\text{OH})^+$ ?

### BUFFER SOLUTION

31. Calculate the pH of solution containing 0.1M - HCN and 0.1M - NaCN.  $\text{K}_a$  of HCN =  $10^{-9}$
32. Calculate the pH of solution containing 0.2 M -  $\text{NH}_4\text{OH}$  and 0.1 M –  $\text{NH}_4\text{Cl}$ .  $\text{K}_b$  of  $\text{NH}_4\text{OH} = 1.8 \times 10^{-5}$ . ( $\log 2 = 0.3, \log 1.8 = 0.26$ )
33. 0.4 mole  $\text{CH}_3\text{COONa}$  is added in 500 ml 0.4 M –  $\text{CH}_3\text{COOH}$  solutions. What is the pH of final solution ?  $\text{K}_a$  of  $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$ . ( $\log 2 = 0.3, \log 1.8 = 0.26$ ).
34. A buffer of pH 9.26 is made by dissolving x moles of ammonium sulphate and 0.1 mole of ammonia into 100 mL solution. If  $\text{pK}_b$  of ammonia is 4.74, calculate value of x.
35. Determine  $[\text{OH}^-]$  of a 0.050 M solution of ammonia to which sufficient  $\text{NH}_4\text{Cl}$  has been added to make the total  $[\text{NH}_4^+]$  equal to 0.100.  $[\text{K}_b(\text{NH}_3) = 1.8 \times 10^{-5}, \text{pK}_b = 4.74]$
36. Calculate the pH of a solution containing 0.2 M  $\text{HCO}_3^-$  and 0.1 M  $\text{CO}_3^{2-}$   
 $[\text{K}_1(\text{H}_2\text{CO}_3) = 4 \times 10^{-7}; \text{K}_2(\text{HCO}_3^-) = 4 \times 10^{-11}]$
37. Calculate the pH of a solution prepared by mixing 50.0 mL of 0.200 M  $\text{HC}_2\text{H}_3\text{O}_2$  and 50.0 mL of 0.100 M NaOH.  $[\text{K}_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}, \text{pK}_a = 4.74]$
38. 50 mL of 0.1 M NaOH is added to 75 mL of 0.1 M  $\text{NH}_4\text{Cl}$  to make a basic buffer. If  $\text{pK}_a$  of  $\text{NH}_4^+$  is 9.26, calculate pH.

39. Calculate the pH of a solution which results from the mixing of 50.0 ml of 0.3 M HCl with 50.0 ml of 0.4 M  $\text{NH}_3$ .  $[K_b(\text{NH}_3) = 1.8 \times 10^{-5}$ ,  $pK_b = 4.74]$
40. In 100 ml buffer solution of 0.1M  $\text{CH}_3\text{COOH}$  & 0.1M  $\text{CH}_3\text{COONa}$ , how many millimoles of NaOH should be added to increase its pH by 0.3.

Given ( $\log 2 = 0.3$ )

### ACID BASE REACTIONS & TITRATIONS

41. Calculate  $\text{OH}^-$  concentration at the equivalent point when a solution of 0.2 M acetic acid is titrated with a solution of 0.2 M NaOH.  $K_a$  for the acid =  $10^{-5}$ .
42. Calculate the hydronium ion concentration and pH at the equivalence point in the reaction of 22.0 mL of 0.10M acetic acid,  $\text{CH}_3\text{COOH}$ , with 22.0 mL of 0.10 M NaOH.  $[K_a = 2 \times 10^{-5}]$
43. Calculate the hydronium ion concentration and the pH at the equivalence point in a titration of 50.0 mL of 0.40 M  $\text{NH}_3$  with 0.40M HCl.  $[K_b = 2 \times 10^{-5}]$
44.  $\text{CH}_3\text{COOH}$  (50 ml, 0.1 M) is titrated against 0.1 M NaOH solution. Calculate the pH at the addition of 0 ml, 10 ml 20 ml, 25 ml, 40 ml, 50 ml of NaOH.  $K_a$  of  $\text{CH}_3\text{COOH}$  is  $2 \times 10^{-5}$ .  
 $[\log 2 = 0.3010, \log 3 = 0.4771]$

### INDICATORS

45. For the acid indicator thymol blue, pH is 3 when half the indicator is in unionised form. Find the % of indicator in unionised form in the solution with  $[\text{H}^+] = 4 \times 10^{-3}$  M.
46. Bromophenol blue is an acid indicator with a  $K_a$  value of  $6 \times 10^{-5}$ . What % of this indicator is in its basic form at a pH of 5 ?
47. At what pH does an indicator change colour if the indicator is a weak acid with  $K_{\text{ind}} = 4 \times 10^{-4}$ . For which one(s) of the following neutralizations would the indicator be useful ? Explain.  
 (a)  $\text{NaOH} + \text{CH}_3\text{COOH}$       (b)  $\text{HCl} + \text{NH}_3$       (c)  $\text{HCl} + \text{NaOH}$
48. An acid indicator has a  $K_a$  of  $3 \times 10^{-5}$ . The acid form of the indicator is red & the basic form is blue. By how much must the pH change in order to change the indicator form 75% red to 75 % blue ?  $[\log 3 = 0.4771]$

### SOLUBILITY & SOLUBILITY PRODUCT

49. The values of  $K_{\text{sp}}$  for the slightly soluble salts MX and  $\text{QX}_2$  are each equal to  $4.0 \times 10^{-18}$ . Which salt is more soluble? Explain your answer fully.
50. The solubility of  $\text{PbSO}_4$  in water is 0.0608 g/L. Calculate the solubility product constant of  $\text{PbSO}_4$ .  
 Molar mass  $\text{PbSO}_4 = 304$  g/mole
51. How many mole  $\text{CuI}$  ( $K_{\text{sp}} = 5 \times 10^{-12}$ ) will dissolve in 1.0 L of 0.10 M NaI solution ?
52. A solution of saturated  $\text{CaF}_2$  is found to contain  $4 \times 10^{-4}$  M fluoride ion. Calculate the  $K_{\text{sp}}$  of  $\text{CaF}_2$ . Neglect hydrolysis.

53. The solubility of  $\text{ML}_2$  (formula weight = 60 g/mol) in water is  $2.4 \times 10^{-5}$  g/100 mL solution. Calculate the solubility product constant for  $\text{ML}_2$ .

54. Calculate the solubility of  $\text{A}_2\text{X}_3$  in pure water, assuming that neither kind of ion reacts with water. For  $\text{A}_2\text{X}_3$ ,  $K_{\text{sp}} = 1.08 \times 10^{-23}$

55. Determine the solubility of  $\text{AgCl}$  in 0.1 M  $\text{BaCl}_2$ . [ $K_{\text{sp}}$  for  $\text{AgCl} = 1 \times 10^{-10}$ ]

56. Calculate solubility of  $\text{Ca}_3(\text{PO}_4)_2$  ( $K_{\text{sp}} = 10^{-15}$ ) in presence of 0.1 M  $\text{CaCl}_2$  solution.

## SIMULTANEOUS SOLUBILITY

- 57.** Calculate the Simultaneous solubility of AgSCN and AgBr.  $K_{sp}$  (AgSCN) =  $3.2 \times 10^{-12}$ ,  $K_{sp}$ (AgBr) =  $8 \times 10^{-13}$ .

**58.** Calculate  $F^-$  in a solution saturated with respect of both  $MgF_2$  and  $SrF_2$ .  $K_{sp}(MgF_2)$ =  $9.5 \times 10^{-9}$ ,  $K_{sp}(SrF_2)$  =  $4 \times 10^{-9}$ .

## COMPLEX FORMATION

- 59.** Calculate the solubility of AgCl in 0.2 M - NH<sub>3</sub> solution.  
Given : K<sub>sp</sub> of AgCl =  $2 \times 10^{-10}$ , K<sub>f</sub> of Ag(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> =  $8 \times 10^6$ .

**60.** Calculate the solubility of AgCN in 0.4 M - KCN solution  
(i) neglecting complex formation  
(ii) considering complex formation. Given : K<sub>sp</sub> of AgCN =  $8 \times 10^{-10}$ , K<sub>d</sub> of Ag(CN)<sub>2</sub><sup>-</sup> =  $4 \times 10^{-8}$ .

## SOLUBILITY (CONSIDERING HYDROLYSIS)

- 61.** Calculating the solubility of MX in water. Also calculate pH of solution.  
Given :  $K_{sp}$  of MX =  $4 \times 10^{-8}$  ;  $K_a$  of HX =  $2 \times 10^{-6}$  and MOH is strong base.

**62.** Calculate the solubility of AgCN in a buffer solution at pH = 3.0..  
Given :  $K_{sp}$  of AgCN =  $8 \times 10^{-10}$  ,  $K_a$  of HCN =  $5 \times 10^{-10}$ .

## PRECIPITATION

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 EXERCISE (O-1)
 

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## Single correct

1. The conjugate acid of  $\text{NH}_2^-$  is
 

(A) $\text{NH}_3$	(B) $\text{NH}_2\text{OH}$	(C) $\text{NH}_4^+$	(D) $\text{N}_2\text{H}_4$
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2. Which of the following is not a Bronsted acid:-
 

(A) $\text{CH}_3\text{NH}_4^+$	(B) $\text{CH}_3\text{COO}^-$	(C) $\text{H}_2\text{O}$	(D) $\text{HSO}_4^-$
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3. In the reaction
 
$$\text{HNO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_3^-$$
 the conjugate base of  $\text{HNO}_3$  is :-  

(A) $\text{H}_2\text{O}$	(B) $\text{H}_3\text{O}^+$	(C) $\text{NO}_3^-$	(D) $\text{H}_3\text{O}^+$ and $\text{NO}_3^-$
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4. Out of the following, amphiprotic species in aqueous medium are
 

I. $\text{HPO}_3^{2-}$	II. $\text{OH}^-$	III. $\text{H}_2\text{PO}_4^-$	IV. $\text{HCO}_3^-$
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(A) I, III, IV      (B) I and III      (C) III and IV      (D) All
5. When ammonia is added to water, it decreases the concentration of which of the following ion
 

(A) $\text{OH}^-$	(B) $\text{H}_3\text{O}^+$	(C) $\text{NH}_4^+$	(D) $\text{NH}_4^+$ & $\text{OH}^-$
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6. Which of the following pair is Lewis acid & Lewis base & Product of these is also Lewis base
 

(A) $\text{BF}_3$ , $\text{NH}_3$	(B) $\text{SiCl}_4$ , $2\text{Cl}^-$	(C) $\text{CH}_3^+$ , $\text{OC}_2\text{H}_5^-$	(D) All of these
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7. Ionic product of water will increase, if :-
 

(A) Pressure is decreased	(B) $\text{H}^+$ is added
(C) $\text{OH}^-$ is increased	(D) Temperature is increased
8. At  $60^\circ\text{C}$ , pure water has  $[\text{H}_3\text{O}^+] = 10^{-6.7}$  mol/lit. what is the value of  $K_w$  at  $60^\circ\text{C}$  :-
 

(A) $10^{-6}$	(B) $10^{-12}$	(C) $10^{-67}$	(D) $10^{-13.4}$
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9. Liquid  $\text{NH}_3$  ionises to a slight extent. At a certain temperature its self ionization constant  $K_{\text{SIC}(\text{NH}_3)} = 10^{-30}$ . The number of  $\text{NH}_4^+$  ions present per  $100 \text{ cm}^3$  of pure liquid are
 

(A) $10^{-15}$	(B) $6.022 \times 10^8$	(C) $6.022 \times 10^7$	(D) None
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10. The pH of solution is increased from 3 to 6. Its  $\text{H}^+$  ion conc. will be :-
 

(A) Reduced to half	(B) Doubled
(C) Reduced by 1000 times	(D) Increased by 1000 times
11. pOH of [1/200] mol/m<sup>3</sup>  $\text{H}_2\text{SO}_4$  (aq.) solution at  $25^\circ\text{C}$  is-
 

(A) 2	(B) 5	(C) 9	(D) 12
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12. Degree of dissociation of 0.1 N  $\text{CH}_3\text{COOH}$  is :-(Dissociation constant =  $1 \times 10^{-5}$ )
 

(A) $10^{-5}$	(B) $10^{-4}$	(C) $10^{-3}$	(D) $10^{-2}$
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13. The pH of a 0.02 M ammonia solution which is 5% ionised will be :-
 

(A) 2	(B) 11	(C) 5	(D) 7
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- 14.** The pH of an aqueous solution of 1.0 M solution of a weak monoprotic acid which is 1% ionised is  
(A) 1 (B) 2 (C) 3 (D) 11

**15.** The concentration of  $[H^+]$  and concentration of  $[OH^-]$  of a 0.1 M aqueous solution of 2% ionised weak acid is [ionic product of water =  $1 \times 10^{-14}$ ]  
(A)  $0.02 \times 10^{-3}$  M and  $5 \times 10^{-11}$  M (B)  $1 \times 10^{-3}$  M and  $3 \times 10^{-11}$  M  
(C)  $2 \times 10^{-3}$  M and  $5 \times 10^{-12}$  M (D)  $3 \times 10^{-2}$  M and  $4 \times 10^{-13}$  M

**16.** What is the quantity of NaOH present in 250 cc of the solution, so that it gives a pH = 13 :-  
(A)  $10^{-13}$  g (B)  $10^{-1}$  g (C) 1.0 g (D) 4.0 g

**17.** An aqueous solution of HCl is  $10^{-9}$  M HCl. The pH of the solution should be:-  
(A) 9 (B) Between 6 and 7  
(C) 7 (D) Unpredictable

**18.** The moles of  $H^+$  from  $H_2O$  in a 1l,  $\sqrt{5} \times 10^{-7}$  M HCl solution at  $25^\circ C$ , is ( $\sqrt{5} = 2.23$ )  
(A)  $10^{-7}$  (B)  $6.85 \times 10^{-8}$  (C)  $3.85 \times 10^{-8}$  (D)  $10^{-8}$

**19.** Which one of the following has highest pH:-  
(A) Distilled water (B) 1 M  $NH_3$   
(C) 1 M NaOH (D) Water saturated with chlorine

**20.** 8 gm NaOH and 4.9 gm  $H_2SO_4$  are present in one litre of the solution. What is its pH  
(A) 1 (B) 13 (C) 12 (D) 2

**21.** 10 ml of  $\frac{M}{200} H_2SO_4$  is mixed with 40 ml of  $\frac{M}{200} H_2SO_4$ . The pH of the resulting solution is  
(A) 1 (B) 2 (C) 2.3 (D) none of these

**22.** Which of the following solution will have pH close to 1.0?  
(A) 100 ml of M/100 HCl + 100 ml of M/10 NaOH  
(B) 55 ml of M/10 HCl + 45 ml of M/10 NaOH  
(C) 10 ml of M/10 HCl + 90 ml of M/10 NaOH  
(D) 75 ml of M/5 HCl + 25 ml of M/5 NaOH

**23.** A solution with pH 2.0 is more acidic than the one with pH 6.0 by a factor of:  
(A) 3 (B) 4 (C) 3000 (D) 10000

**24.** The first and second dissociation constants of an acid  $H_2A$  are  $1.0 \times 10^{-5}$  and  $5.0 \times 10^{-10}$  respectively. The overall dissociation constant of the acid will be :  
(A)  $5.0 \times 10^{-5}$  (B)  $5.0 \times 10^{15}$  (C)  $5.0 \times 10^{-15}$  (D)  $0.2 \times 10^5$

**25.** If  $pK_b$  for fluoride ion at  $25^\circ C$  is 10.4, the ionisation constant of hydrofluoric acid in water at this temperature is :  
(A)  $4 \times 10^{-11}$  (B)  $3 \times 10^{-3}$  (C)  $2.5 \times 10^{-4}$  (D)  $2 \times 10^{-2}$

**26.** pH of an aqueous solution of NaCl at  $85^\circ C$  should be  
(A) 7 (B)  $> 7$  (C)  $< 7$  (D) 0





- 48.** In a buffer solution the ratio of concentration of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  is 1 : 1. When it changes in 2 : 1, what will be the value of pH of buffer ?
- (A) Increase      (B) Decrease      (C) No effect      (D) None
- 49.** The buffer solution play an important role in :-
- (A) Increasing the pH value      (B) Decreasing the pH value  
 (C) Keeping the pH constant      (D) Solution will be neutral
- 50.** The total number of different kind of acidic buffers obtained during the titration of  $\text{H}_3\text{PO}_4$  with  $\text{NaOH}$  are :
- (A) 3      (B) 1      (C) 2      (D) 0
- 51.** Which of the following solutions does not act as buffer :
- (A)  $\text{H}_3\text{PO}_4 + \text{NaH}_2\text{PO}_4$       (B)  $\text{NaHCO}_3 + \text{H}_2\text{CO}_3$   
 (C)  $\text{NH}_4\text{Cl} + \text{HCl}$       (D)  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
- 52.** Half of the formic acid solution is neutralised on addition of a KOH solution to it. If  $K_a(\text{HCOOH}) = 2 \times 10^{-4}$  then pH of the solution is : - ( $\log 2 = 0.3010$ )
- (A) 3.6990      (B) 10.3010      (C) 3.85      (D) 4.3010
- 53.** When 0.02 moles of NaOH are added to a litre of buffer solution, its pH changes from 5.75 to 5.80. What is its buffer capacity :-
- (A) 0.4      (B) 0.05      (C) - 0.05      (D) 2.5
- 54.** Calculate pH when 100 ml of 0.2M NaOH is reacted with 100 ml of 0.2 M  $\text{CH}_3\text{COOH}$  ( $K_a = 10^{-5}$ )
- (A) 9      (B) 7      (C) 5      (D) 2
- 55.** At  $90^\circ\text{C}$ , pure water has  $[\text{H}^+] = 10^{-6} \text{ M}$ , if 100 ml of 0.2 M  $\text{HNO}_3$  is added to 20 ml of 1 M NaOH at  $90^\circ\text{C}$  then pH of the resulting solution will be
- (A) 5      (B) 6      (C) 7      (D) None of these
- 56.** When 20 ml of  $\frac{\text{M}}{20}$  NaOH are added to 10 ml of  $\frac{\text{M}}{10}$  HCl, the resulting solution will:-
- (A) Turn blue litmus red  
 (B) Turn phenolphthalein solution pink colour  
 (C) Turn methyl orange red  
 (D) Will have no effect on either red or blue litmus

- 57.** The rapid change of pH near the stoichiometric point of an acid–base titration is the basis of indicator detection. pH of the solution is related to ratio of the concentrations of the conjugate acid ( $\text{HIn}$ ) and base ( $\text{In}^-$ ) forms of the indicator by the expression :-
- (A)  $\log \frac{[\text{HIn}]}{[\text{In}^-]} = \text{pK}_{\text{In}} - \text{pH}$       (B)  $\log \frac{[\text{HIn}]}{[\text{In}^-]} = \text{pH} - \text{pK}_{\text{In}}$
- (C)  $\log \frac{[\text{In}^-]}{[\text{HIn}]} = \text{pH} + \text{pK}_{\text{In}}$       (D)  $\log \frac{[\text{In}^-]}{[\text{HIn}]} = \text{pK}_{\text{In}} - \text{pH}$
- 58.** Calculate the pH range in which an acid indicator with  $K_{\text{acid}}$  (indicator) =  $1.0 \times 10^{-5}$  changes colour when the concentration of the indicator is  $1 \times 10^{-3}\text{M}$ .
- (A)  $5 \pm 1$       (B)  $11 \pm 1$       (C)  $3 \pm 1$       (D)  $8 \pm 1$
- 59.** In what pH range will a  $1 \times 10^{-4}\text{ M}$  solution of an indicator with  $K_b$  (indicator) =  $1 \times 10^{-11}$  change colour?
- (A)  $7.0 \pm 1$       (B)  $3.0 \pm 1$       (C)  $5.5 \pm 1$       (D)  $11.0 \pm 1$
- 60.** Indicator which is used in the titration of  $\text{CH}_3\text{COOH}$  &  $\text{NaOH}$  :-
- (A) Methyl orange      (B) Methyl red      (C) Phenolphthalein      (D) Litmus
- 61.** Phenolphthalein is a :-
- (A) Strong acid      (B) Strong base      (C) Weak base      (D) Weak acid
- 62.** pH-range of Methyl red indicator is :-
- (A)  $4.2\text{--}6.2$       (B)  $6.8\text{--}10.8$       (C)  $8\text{--}9.6$       (D)  $6.8\text{--}8.2$
- 63.** In the volumetric estimation of  $\text{HCl}$ , if we make use of phenolphthalein as an indicator, which base is unsuitable for the titration :-
- (A)  $\text{NaOH}$       (B)  $\text{RbOH}$       (C)  $\text{KOH}$       (D)  $\text{NH}_4\text{OH}$
- 64.** Phenolphthalein does not act as an indicator for the titration between :-
- (A)  $\text{KOH}$  and  $\text{H}_2\text{SO}_4$       (B)  $\text{NaOH}$  and  $\text{CH}_3\text{COOH}$   
 (C) Oxalic acid and  $\text{KMnO}_4$       (D)  $\text{Ba}(\text{OH})_2$  and  $\text{HCl}$
- 65.** For weak acid and strong base titration, the indicator used is :-
- (A) Potassium di-chromate      (B) Methyl orange  
 (C) Litmus      (D) Phenolphthalein
- 66.** The solubility of  $\text{A}_2\text{X}_3$  is  $y \text{ mol dm}^{-3}$ . Its solubility product is
- (A)  $6 y^2$       (B)  $64 y^4$       (C)  $36 y^5$       (D)  $108 y^5$

67. If  $K_{sp}$  for  $\text{HgSO}_4$  is  $6.4 \times 10^{-5}$ , then solubility of this substance in mole per  $\text{m}^3$  is  
 (A)  $8 \times 10^{-3}$       (B)  $6.4 \times 10^{-5}$       (C)  $8 \times 10^{-6}$       (D) 8
68. If the solubility of  $\text{AgCl}$  (formula mass=143) in water at  $25^\circ\text{C}$  is  $1.43 \times 10^{-4}$  gm/100 ml of solution then the value of  $K_{sp}$  will be :-  
 (A)  $1 \times 10^{-5}$       (B)  $2 \times 10^{-5}$       (C)  $1 \times 10^{-10}$       (D)  $2 \times 10^{-10}$
69. One litre of saturated solution of  $\text{CaCO}_3$  is evaporated to dryness, 7.0 g of residue is left. The solubility product for  $\text{CaCO}_3$  is:-  
 (A)  $4.9 \times 10^{-3}$       (B)  $4.9 \times 10^{-5}$       (C)  $4.9 \times 10^{-9}$       (D)  $4.9 \times 10^{-7}$
70.  $\text{A}_3\text{B}_2$  is a sparingly soluble salt of molar mass M ( $\text{g mol}^{-1}$ ) and solubility  $x \text{ g lit}^{-1}$ . The ratio of the molar concentration of  $\text{B}^{3-}$  to the solubility product of the salt is  
 (A)  $108 \frac{x^5}{M^5}$       (B)  $\frac{1}{108} \frac{M^4}{x^4}$       (C)  $\frac{1}{54} \frac{M^4}{x^4}$       (D) None
71. Solubility of  $\text{Ag}_2\text{CrO}_4$  ( $K_{sp} = 4 \times 10^{-13}$ ) in 0.1 M  $\text{K}_2\text{CrO}_4$  solution will be :-  
 (A)  $10^{-3}$  M      (B)  $10^{-6}$  M      (C)  $4 \times 10^{-6}$  M      (D)  $5 \times 10^{-7}$  M
72. How many times solubility of  $\text{CaF}_2$  is decreased in  $4 \times 10^{-3}$  M KF (aq.) solution as compare to pure water at  $25^\circ\text{C}$ . Given  $K_{sp}(\text{CaF}_2) = 3.2 \times 10^{-11}$   
 (A) 50      (B) 100      (C) 500      (D) 1000
73. At  $30^\circ\text{C}$ , In which of the one litre solution, the solubility of  $\text{Ag}_2\text{CO}_3$  (solubility product =  $8 \times 10^{-12}$ ) will be maximum :-  
 (A) 0.05 M  $\text{Na}_2\text{CO}_3$       (B) Pure water  
 (C) 0.05 M  $\text{AgNO}_3$       (D) 0.05 M  $\text{NH}_3$
74. What will happen if the pH of the solution of 0.001 M  $\text{Mg}(\text{NO}_3)_2$  solution is adjusted to pH = 9 ( $K_{sp}$  of  $\text{Mg}(\text{OH})_2 = 8.9 \times 10^{-12}$ )  
 (A) ppt will take place      (B) ppt will not take place  
 (C) Solution will be saturated      (D) None of these
75.  $\text{Na}_3\text{PO}_4$  which should be added in 10 L of  $1.0 \times 10^{-5}$  M -  $\text{BaCl}_2$  solution without any precipitation of  $\text{Ba}_3(\text{PO}_4)_2$  is [ $K_{sp}$  of  $\text{Ba}_3(\text{PO}_4)_2$ ] =  $4 \times 10^{-23}$   
 (A)  $2 \times 10^{-4}$  gm      (B) 0.328 gm      (C) 0.164 gm      (D) 0.82 gm

## EXERCISE (O-2)

### Single correct :

- 1.** The pH of the solution produced when an aqueous solution of strong acid pH 5 is mixed with equal volume of an aqueous solution of strong acid of pH 3 is :-  
(A) 3.3                   (B) 3.5                   (C) 4.5                   (D) 4.0

**2.** How many moles of HCl must be removed from 1 litre of aqueous HCl solution to change its pH from 2 to 3 :-  
(A) 1                   (B) 0.02                   (C) 0.009                   (D) 0.01

**3.** Which of the following is most soluble in water?  
(A) MnS ( $K_{sp} = 8 \times 10^{-37}$ )                   (B) ZnS ( $K_{sp} = 7 \times 10^{-16}$ )  
(C) Bi<sub>2</sub>S<sub>3</sub> ( $K_{sp} = 1 \times 10^{-72}$ )                   (D) Ag<sub>3</sub>(PO<sub>4</sub>) ( $K_{sp} = 1.8 \times 10^{-18}$ )

**4.** Solubility of AgBr will be minimum in :-  
(A) Pure water           (B) 0.1 M CaBr<sub>2</sub>           (C) 0.1 M NaBr           (D) 0.1 M AgNO<sub>3</sub>

**5.** pH of solution at first 1/4<sup>th</sup> equivalence point of Na<sub>2</sub>CO<sub>3</sub> when titrated with HCl will be  
(for H<sub>2</sub>CO<sub>3</sub>  $K_{a_1} = 10^{-7}$ ;  $K_{a_2} = 10^{-11}$ )  
(A) 7 + log 3           (B) 7 - log 3           (C) 11 + log 3           (D) 11 - log 3

**6.** An acid-base indicator has a  $K_a = 1.0 \times 10^{-5}$ . The acid form of the indicator is red and the basic form is blue. Calculate the pH change required to change the colour of the indicator from 80% red to 80% blue.  
(A) 1.20                   (B) 0.80                   (C) 0.20                   (D) 1.40

### **Assertion /Reason :**

7. **Statement-1** pH of  $10^{-7}$  M NaOH solution is exist between 7 to 7.3 at 25°C.  
**Statement-2** Due to common ion effect ionization of water is reduced.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.

8. **Statement-1** In general phenolphthalein is used as an indicator for the titration of weak acid (HA) against strong base (NaOH)  
**Statement-2** At equivalent point solution is basic.  
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
(C) Statement-1 is true, statement-2 is false.  
(D) Statement-1 is false, statement-2 is true.

9. **Statement-1 :** Moles of  $\text{Sr}^{2+}$  furnished by sparingly soluble substance  $\text{Sr}(\text{OH})_2$  decreases due to dilution.  
**Statement-2 :** Solubility product constant of  $\text{Sr}(\text{OH})_2$  is not affected by dilution.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
10. **Statement-1 :** On dilution of a concentrated solution of  $\text{CH}_3\text{COOH}$ , the concentration of  $[\text{H}^+]$  decreases.  
**Statement-2 :** Increase in volume is more than the increase in degree of ionisation.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
- Multiple correct :**
11. Which of the following is correct for 0.1 M BOH solution ( $K_b = 10^{-5}$ )  
 (A) pH of solution is 11  
 (B)  $\text{OH}^-$  concentration is  $10^{-3}$  mol/L  
 (C) it's salt with HCl (i.e. BCl) form the acidic solution in water  
 (D) Phenolphthalein indicator can be used during the titration of BOH with HCl
12. For weak monobasic acid, HA, the dissociation constant is  $2 \times 10^{-6}$ , at 25°C. Which of the following is/are correct regarding this acid? [log2= 0.3]  
 (A)  $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$ ;  $K_{eq} = 5 \times 10^{-9}$   
 (B) The equilibrium constant for the reaction of HA with aq. NaOH is  $2 \times 10^8$   
 (C) The pH of 0.1 M, HA solution is 3.35  
 (D) solution of  $\text{A}^-$  is basic
13. Select correct statement for 50ml 0.1M  $\text{H}_2\text{A}$ (aq.) solution ;  $K_{a_1} = 10^{-5}$  ;  $K_{a_2} = 10^{-8}$   
 (A)  $[\text{H}^+] = 2[\text{A}^{2-}]$   
 (B) pH of 0.1M  $\text{H}_2\text{A}$  solution is 3  
 (C) In above  $\text{H}_2\text{A}$  solution when 5 milimoles of NaHA are added then pH increases by 2 units  
 (D) 50 ml of 0.1M NaOH required to neutralised completely 50 ml of 0.1M  $\text{H}_2\text{A}$  solution

- 14.** A solution containing 0.01M each of  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$  &  $\text{Cr}^{3+}$  ion. If solid  $\text{Na}_2\text{S}$  is added slowly to the solution then correct statement is based on given data -

**Precipitate**     $\text{PbS}$      $\text{Ag}_2\text{S}$      $\text{ZnS}$      $\text{Cr}_2\text{S}_3$

**Ksp**                 $10^{-11}$      $10^{-12}$      $10^{-8}$      $10^{-10}$

- (A)  $\text{Pb}^{2+}$  will start precipitating first
- (B)  $\text{Cr}^{3+}$  will start precipitating last
- (C)  $\text{Zn}^{2+}$  will start precipitating before  $\text{Ag}^+$
- (D) When  $\text{Zn}^{2+}$  just starts precipitating then  $\text{Pb}^{2+}$  ion gets 99.9% precipitated

- 15.** If  $K_1$  &  $K_2$  be first and second ionisation constant of  $\text{H}_3\text{PO}_4$  and  $K_1 \gg K_2$  which is/are incorrect.

(A)  $[\text{H}^+] = [\text{H}_2\text{PO}_4^-]$

(B)  $[\text{H}^+] = \sqrt{K_1[\text{H}_3\text{PO}_4]}$

(C)  $K_2 = [\text{HPO}_4^{2-}]$

(D)  $[\text{H}^+] = 3[\text{PO}_4^{3-}]$

- 16.** 10 ml. of a solution contains 0.1 M  $\text{NH}_4\text{Cl}$  + 0.01M  $\text{NH}_4\text{OH}$ . Which addition would not change the pH of solution :-

- (A) Adding 1 ml. water
- (B) Adding 5 ml. of 0.1 M  $\text{NH}_4\text{Cl}$
- (C) Adding 5 ml. of 0.1 M  $\text{NH}_4\text{OH}$
- (D) Adding 10 ml. of 0.1 M  $\text{NH}_4\text{Cl}$

- 17.** When equal volumes of the following solutions are mixed, precipitation of

$\text{AgCl}$  ( $K_{\text{sp}} = 1.8 \times 10^{-10}$ ) will occur only with:

- (A)  $10^{-4}$  M ( $\text{Ag}^+$ ) and  $10^{-4}$  M ( $\text{Cl}^-$ )
- (B)  $10^{-5}$  M ( $\text{Ag}^+$ ) and  $10^{-5}$  M ( $\text{Cl}^-$ )
- (C)  $10^{-6}$  M ( $\text{Ag}^+$ ) and  $10^{-6}$  M ( $\text{Cl}^-$ )
- (D)  $10^{-10}$  M ( $\text{Ag}^+$ ) and  $10^{-10}$  M ( $\text{Cl}^-$ )

#### Paragraph for Q.18 to Q.20

8 gm weak acid HX (molecular mass = 80) is dissolved in 100 ml water. ( $K_a = 10^{-4}$ )

- 18.** Find pH of solution-

- (A) 3.3
- (B) 2
- (C) 2.3
- (D) 3

- 19.** If it is titrated with 0.25 M NaOH find pH at equivalence point ( $\log 5 = 0.7$ )

- (A) 9.15
- (B) 8.65
- (C) 4.65
- (D) 4.85

- 20.** Find  $[\text{H}^+]$  if  $10^{-3}$  mol HCl is added to 100 ml original solution ( $\sqrt{41} = 6.4$  ;  $\sqrt{5} = 2.24$ )

- (A)  $0.62 \times 10^{-2}$
- (B)  $1.62 \times 10^{-2}$
- (C)  $2.7 \times 10^{-2}$
- (D)  $0.27 \times 10^{-2}$

## **Paragraph for Question 21 & 22**

A solution contains one mole each of HA & HB (both are weak acids) in one litre solution. Now one mole of NaOH is added to this solution so that both the acids are partially neutralised. Heat of neutralisation of HA & HB are  $-11.8$  and  $-12.4$  kcal per mole respectively and heat produced during partial neutralisation of HA & HB is  $-12.25$  kcal.

- 21.** Mole ratio of neutralisation of HA & HB is -  
(A) 1 : 4                    (B) 1 : 2                    (C) 1 : 3                    (D) 1 : 5

**22.** pH of solution containing mixture of 1 mol of HA & 1 mole of HB in 1 litre solution is  
 $K_a(\text{HA}) = 1 \times 10^{-5}$ ,  $K_a(\text{HB}) = 9 \times 10^{-5}$   
(A) 2                    (B) 3                    (C) 4                    (D) 5

### **MATCH THE COLUMN :**

- 23.** Match the effect of addition of 1 M NaOH to 100 mL 1 M  $\text{CH}_3\text{COOH}$  (in Column I) with pH (in Column II):

<b>Column-I</b>	<b>Column-II</b>
(A) 25 mL of NaOH	(P) $pK_a$
(B) 50 mL of NaOH	(Q) $pK_a + \log 3$
(C) 75 mL of NaOH	(R) $pK_a - \log 3$
(D) 100 mL of NaOH	(S) $\frac{1}{2} [pK_w + pK_a - \log 2]$

**24. Column-I**

<b>PH</b>	<b>Solution</b>
(A) 3	(P) When equal volumes of 0.2M $\text{NH}_4\text{OH}$ ( $K_b = 10^{-5}$ ) & 0.2M HCl are mixed
(B) 5	(Q) When equal volumes of 0.2M $\text{CH}_3\text{COONa}$ & 0.2M HCl are mixed ( $K_{a(\text{CH}_3\text{COOH})} = 10^{-5}$ )
(C) 8	(R) 0.1M $\text{Na}_2\text{HPO}_4$ (for $\text{H}_3\text{PO}_4$ ; $K_{a_1} = 10^{-4}$ ; $K_{a_2} = 10^{-6}$ ; $K_{a_3} = 10^{-10}$ )
(D) 9	(S) At 1 <sup>st</sup> half equivalence point of $\text{H}_2\text{CO}_3$ when titrated against 0.1M NaOH, $K_{a_1} = 10^{-5}$ , $K_{a_2} = 10^{-9}$
	(T) $\text{Mg(OH)}_2$ ; $K_{sp} = 5 \times 10^{-16}$

**TABLE TYPE QUESTION :**

<b>Column-I</b>	<b>Column-II</b>	<b>Column-III</b>
<b>(solution)</b>	<b>(pH of solution)</b>	<b>(Introduction about solution)</b>
(A) $\text{CH}_3\text{COOH}(0.2\text{M}, 1\text{L}) + \text{NaOH}(0.1\text{M}, 1\text{L})$	(P) 1.3	(1) pH is determined by strong acid
(B) $\text{CH}_3\text{COOH}(0.1\text{M}, 1\text{L}) + \text{HCl}(0.1\text{M}, 1\text{L})$	(Q) 7	(2) Buffer solution at its maximum buffer capacity
(C) $\text{CH}_3\text{COOH}(0.1\text{M}, 1\text{L}) + \text{NH}_4\text{OH}(0.1\text{M}, 1\text{L})$	(R) 9	(3) pH is determined by salt hydrolysis.
(D) $\text{NH}_4\text{Cl}(200\text{ ml}, 0.1\text{M}) + \text{NaOH}(100\text{ ml}, 0.1\text{M})$	(S) 5	(4) pH is determined by buffer solution

**(Given :  $(K_a)_{\text{CH}_3\text{COOH}} = 10^{-5}$ ,  $(K_b)_{\text{NH}_4\text{OH}} = 10^{-5}$ )**

25. Which of the following is incorrectly matched
- |               |               |               |               |
|---------------|---------------|---------------|---------------|
| (A) A - S - 4 | (B) B - P - 1 | (C) D - R - 2 | (D) C - Q - 1 |
|---------------|---------------|---------------|---------------|
26. If 0.15 mole NaOH is added in solution (B) of column-I then which of the following is correct
- |           |           |           |           |
|-----------|-----------|-----------|-----------|
| (A) S - 3 | (B) S - 4 | (C) R - 1 | (D) P - 3 |
|-----------|-----------|-----------|-----------|
27. If 0.1mole HCl is added in solution (A) of column-I then pH of the resulting solution will be
- |       |        |         |       |
|-------|--------|---------|-------|
| (A) 7 | (B) 13 | (C) 3.0 | (D) 1 |
|-------|--------|---------|-------|

## EXERCISE (JM)

1. The solubility in water of a sparingly soluble salt  $\text{AB}_2$  is  $1.0 \times 10^{-5}$  mol L $^{-1}$ . Its solubility product will be [AIEEE-2003]  
 (1)  $1 \times 10^{-15}$       (2)  $1 \times 10^{-10}$       (3)  $4 \times 10^{-15}$       (4)  $4 \times 10^{-10}$
2. The solubility of  $\text{Mg}(\text{OH})_2$  is  $x$  mole/lit. then its solubility product is- [AIEEE-2002]  
 (1)  $x^3$       (2)  $5x^3$       (3)  $4x^3$       (4)  $2x^2$
3. The molar solubility in mol L $^{-1}$  of a sparingly soluble salt  $\text{MX}_4$  is ' $s$ '. The corresponding solubility product is  $K_{\text{SP}}$ . ' $s$ ' is given in terms of  $K_{\text{SP}}$  by relation : [AIEEE-2004]  
 (1)  $s = (\text{K}_{\text{SP}} / 128)^{1/4}$       (2)  $s = (128\text{K}_{\text{SP}})^{1/4}$   
 (3)  $s = (256\text{K}_{\text{SP}})^{1/5}$       (4)  $s = (\text{K}_{\text{SP}}/256)^{1/5}$
4. The solubility product of a salt having general formula  $\text{MX}_2$ , in water is :  $4 \times 10^{-12}$ . The concentration of  $\text{M}^{2+}$  ions in the aqueous solution of the salt is - [AIEEE-2005]  
 (1)  $1.0 \times 10^{-4}$  M      (2)  $2.0 \times 10^{-6}$  M      (3)  $4.0 \times 10^{-10}$  M      (4)  $1.6 \times 10^{-4}$  M
5. Hydrogen ion concentration in mol/L in a solution of  $\text{pH} = 5.4$  will be - [AIEEE-2005]  
 (1)  $3.88 \times 10^6$       (2)  $3.98 \times 10^8$       (3)  $3.98 \times 10^{-6}$       (4)  $3.68 \times 10^{-6}$
6. In a saturated solution of the sparingly soluble strong electrolyte  $\text{AgIO}_3$  (molecular mass = 283) the equilibrium which sets in is - [AIEEE-2007]
- $$\text{AgIO}_3 \rightleftharpoons \text{Ag}_{(\text{aq})}^+ + \text{IO}_{3(\text{aq})}^-$$
- If the solubility product constant  $K_{\text{sp}}$  of  $\text{AgIO}_3$  at a given temperature is  $1.0 \times 10^{-8}$ , what is the mass of  $\text{AgIO}_3$  contained in 100 ml of its saturated solution ?  
 (1)  $28.3 \times 10^{-2}$  g      (2)  $2.83 \times 10^{-3}$  g      (3)  $1.0 \times 10^{-7}$  g      (4)  $1.0 \times 10^{-4}$  g
7. The  $\text{pK}_a$  of a weak acid,  $\text{HA}$ , is 4.80. The  $\text{pK}_b$  of a weak base,  $\text{BOH}$ , is 4.78. The pH of an aqueous solution of the corresponding salt.  $\text{BA}$ , will be - [AIEEE-2008]  
 (1) 9.58      (2) 4.79      (3) 7.01      (4) 9.22
8. Solid  $\text{Ba}(\text{NO}_3)_2$  is gradually dissolved in a  $1.0 \times 10^{-4}$  M  $\text{Na}_2\text{CO}_3$  solution. At what concentration of  $\text{Ba}^{2+}$  will a precipitate begin to form?  
 $(\text{K}_{\text{SP}}$  for  $\text{Ba CO}_3 = 5.1 \times 10^{-9})$  [AIEEE-2009]  
 (1)  $8.1 \times 10^{-8}$  M      (2)  $8.1 \times 10^{-7}$  M      (3)  $4.1 \times 10^{-5}$  M      (4)  $5.1 \times 10^{-5}$  M

- 9.** Solubility product of silver bromide is  $5.0 \times 10^{-13}$ . The quantity of potassium bromide (molar mass taken as  $120 \text{ g mol}^{-1}$ ) to be added to 1 litre of  $0.05 \text{ M}$  solution of silver nitrate to start the precipitation of  $\text{AgBr}$  is :- [AIEEE–2010]
- (1)  $5.0 \times 10^{-8} \text{ g}$       (2)  $1.2 \times 10^{-10} \text{ g}$       (3)  $1.2 \times 10^{-9} \text{ g}$       (4)  $6.2 \times 10^{-5} \text{ g}$
- 10.** In aqueous solution the ionization constants for carbonic acid are  
 $K_1 = 4.2 \times 10^{-7}$  and  $K_2 = 4.8 \times 10^{-11}$  [AIEEE–2010]  
 Select the correct statement for a saturated  $0.034 \text{ M}$  solution of the carbonic acid :-
- (1) The concentration of  $\text{H}^+$  is double that of  $\text{CO}_3^{2-}$   
 (2) The concentration of  $\text{CO}_3^{2-}$  is  $0.034 \text{ M}$   
 (3) The concentration of  $\text{CO}_3^{2-}$  is greater than that of  $\text{HCO}_3^-$   
 (4) The concentrations of  $\text{H}^+$  and  $\text{HCO}_3^-$  are approximately equal
- 11.** At  $25^\circ \text{ C}$ , the solubility product of  $\text{Mg(OH)}_2$  is  $1.0 \times 10^{-11}$ . At which pH, will  $\text{Mg}^{2+}$  ions start precipitating in the form of  $\text{Mg(OH)}_2$  from a solution of  $0.001 \text{ M}$   $\text{Mg}^{2+}$  ions ? [AIEEE–2010]
- (1) 8      (2) 9      (3) 10      (4) 11
- 12.** The  $K_{\text{sp}}$  for  $\text{Cr(OH)}_3$  is  $1.6 \times 10^{-30}$ . The molar solubility of this compound in water is :- [AIEEE–2011]
- (1)  $\sqrt[2]{1.6 \times 10^{-30}}$       (2)  $\sqrt[4]{1.6 \times 10^{-30}}$       (3)  $\sqrt[4]{1.6 \times 10^{-30}/27}$       (4)  $1.6 \times 10^{-30}/27$
- 13.** An acid HA ionises as  
 $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$   
 The pH of  $1.0 \text{ M}$  solution is 5. Its dissociation constant would be :- [AIEEE–2011]
- (1)  $1 \times 10^{-10}$       (2) 5      (3)  $5 \times 10^{-8}$       (4)  $1 \times 10^{-5}$
- 14.** If  $K_{\text{sp}}$  of  $\text{CaF}_2$  at  $25^\circ \text{ C}$  is  $1.7 \times 10^{-10}$ , the combination amongst the following which gives a precipitate of  $\text{CaF}_2$  is :- [JEE-MAIN(online)–2012]
- (1)  $1 \times 10^{-2} \text{ M}$   $\text{Ca}^{2+}$  and  $1 \times 10^{-5} \text{ M}$   $\text{F}^-$       (2)  $1 \times 10^{-4} \text{ M}$   $\text{Ca}^{2+}$  and  $1 \times 10^{-4} \text{ M}$   $\text{F}^-$   
 (3)  $1 \times 10^{-3} \text{ M}$   $\text{Ca}^{2+}$  and  $1 \times 10^{-5} \text{ M}$   $\text{F}^-$       (4)  $1 \times 10^{-2} \text{ M}$   $\text{Ca}^{2+}$  and  $1 \times 10^{-3} \text{ M}$   $\text{F}^-$
- 15.** The pH of a  $0.1$  molar solution of the acid HQ is 3. The value of the ionization constant,  $K_a$  of this acid is :- [AIEEE–2012]
- (1)  $1 \times 10^{-7}$       (2)  $3 \times 10^{-7}$       (3)  $1 \times 10^{-3}$       (4)  $1 \times 10^{-5}$



22. Zirconium phosphate  $[Zr_3(PO_4)_4]$  dissociates into three zirconium cations of charge +4 and four phosphate anions of charge -3. If molar solubility of zirconium phosphate is denoted by S and its solubility product by  $K_{sp}$  then which of the following relationship between S and  $K_{sp}$  is correct ?

[JEE-MAIN(Online)-2014]

- (1)  $S = \{K_{sp}/144\}^{1/7}$       (2)  $S = \{K_{sp}/(6912)\}^{1/7}$   
 (3)  $S = (K_{sp}/6912)^{1/7}$       (4)  $S = \{K_{sp}/6912\}^7$

23.  $pK_a$  of a weak acid (HA) and  $pK_b$  of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is

[JEE-MAIN(Offline)-2017]

- (1) 7.2      (2) 6.9      (3) 7.0      (4) 1.0

24. Addition of sodium hydroxide solution to a weak acid (HA) results in a buffer of pH 6. If ionisation constant of HA is  $10^{-5}$ , the ratio of salt to acid concentration in the buffer solution will be :

[JEE-MAIN(Online)-2017]

- (1) 4 : 5      (2) 1 : 10      (3) 10 : 1      (4) 5 : 4

25. 50 mL of 0.2 M ammonia solution is treated with 25 mL of 0.2 M HCl. If  $pK_b$  of ammonia solution is 4.75, the pH of the mixture will be:-

[JEE-MAIN(Online)-2017]

- (1) 8.25      (2) 4.75      (3) 9.25      (4) 3.75

26. Which of the following salts is the most basic in aqueous solution ? [JEE-MAIN(Offline)-2018]

- (1)  $CH_3COOK$       (2)  $FeCl_3$       (3)  $Pb(CH_3COO)_2$       (4)  $Al(CN)_3$

27. An alkali is titrated against an acid with methyl orange as indicator, which of the following is a correct combination ?

[JEE-MAIN(Offline)-2018]

Base	Acid	End point
(1) Strong	Strong	Pinkish red to yellow
(2) Weak	Strong	Yellow to pinkish red
(3) Strong	Strong	Pink to colourless
(4) Weak	Strong	Colourless to pink

28. An aqueous solution contains 0.10 M  $H_2S$  and 0.20 M HCl. If the equilibrium constants for the formation of  $HS^-$  from  $H_2S$  is  $1.0 \times 10^{-7}$  and that of  $S^{2-}$  from  $HS^-$  ions is  $1.2 \times 10^{-13}$  then the concentration of  $S^{2-}$  ions in aqueous solution is :

[JEE-MAIN(Offline)-2018]

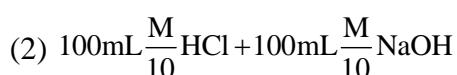
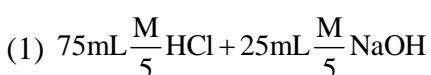
- (1)  $3 \times 10^{-20}$       (2)  $6 \times 10^{-21}$       (3)  $5 \times 10^{-19}$       (4)  $5 \times 10^{-8}$

29. A aqueous solution contains an unknown concentration of  $\text{Ba}^{2+}$ . When 50 mL of a 1 M solution of  $\text{Na}_2\text{SO}_4$  is added,  $\text{BaSO}_4$  just begins to precipitate. The final volume is 500 mL. The solubility product of  $\text{BaSO}_4$  is  $1 \times 10^{-10}$ . What is the original concentration of  $\text{Ba}^{2+}$ ?

[JEE-MAIN(Offline)-2018]

- (1)  $2 \times 10^{-9}$  M      (2)  $1.1 \times 10^{-9}$  M      (3)  $1.0 \times 10^{-10}$  M      (4)  $5 \times 10^{-9}$  M

30. Following four solutions are prepared by mixing different volumes of NaOH and HCl of different concentrations, pH of which one of them will be equal to 1 ? [JEE-MAIN(Online)-2018]



31. The minimum volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution ( $K_{\text{sp}}$  of  $\text{PbCl}_2 = 3.2 \times 10^{-8}$ ; atomic mass of Pb = 207 u) is : [JEE-MAIN(Online)-2018]

- (1) 0.36 L      (2) 0.18 L      (3) 17.98 L      (4) 1.798 L

32. If  $K_{\text{sp}}$  of  $\text{Ag}_2\text{CO}_3$  is  $8 \times 10^{-12}$ , the molar solubility of  $\text{Ag}_2\text{CO}_3$  in 0.1M  $\text{AgNO}_3$  is :

[JEE-MAIN(Online)-2019]

- (1)  $8 \times 10^{-12}$  M      (2)  $8 \times 10^{-10}$  M      (3)  $8 \times 10^{-11}$  M      (4)  $8 \times 10^{-13}$  M

33. 25 ml of the given HCl solution requires 30 mL of 0.1 M sodium carbonate solution. What is the volume of this HCl solution required to titrate 30 mL of 0.2 M aqueous NaOH solution?

[JEE-MAIN(Online)-2019]

- (1) 25 mL      (2) 50 mL      (3) 12.5 mL      (4) 75 mL

34. A mixture of 100 m mol of  $\text{Ca}(\text{OH})_2$  and 2g of sodium sulphate was dissolved in water and the volume was made up to 100 mL. The mass of calcium sulphate formed and the concentration of  $\text{OH}^-$  in resulting solution, respectively, are : (Molar mass of  $\text{Ca}(\text{OH})_2$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{CaSO}_4$  are 74, 143 and 136 g mol<sup>-1</sup>, respectively;  $K_{\text{sp}}$  of  $\text{Ca}(\text{OH})_2$  is  $5.5 \times 10^{-6}$ ) [JEE-MAIN(Online)-2019]

- (1) 1.9 g, 0.14 mol L<sup>-1</sup>      (2) 13.6 g, 0.14 mol L<sup>-1</sup>  
 (3) 1.9 g, 0.28 mol L<sup>-1</sup>      (4) 13.6 g, 0.28 mol L<sup>-1</sup>

35. The pH of rain water, is approximately :

[JEE-MAIN(Online)-2019]

- (1) 6.5      (2) 7.5      (3) 5.6      (4) 7.0

- 36.** 20 mL of 0.1 M  $\text{H}_2\text{SO}_4$  solution is added to 30 mL of 0.2 M  $\text{NH}_4\text{OH}$  solution. The pH of the resultant mixture is : [ $\text{pK}_b$  of  $\text{NH}_4\text{OH} = 4.7]$ . [JEE-MAIN(Online)-2019]

37. If solubility product of  $\text{Zr}_3(\text{PO}_4)_4$  is denoted by  $K_{\text{sp}}$  and its molar solubility is denoted by  $S$ , then which of the following relation between  $S$  and  $K_{\text{sp}}$  is correct [JEE-MAIN(Online)-2019]

$$(1) \quad S = \left( \frac{K_{sp}}{929} \right)^{1/9}$$

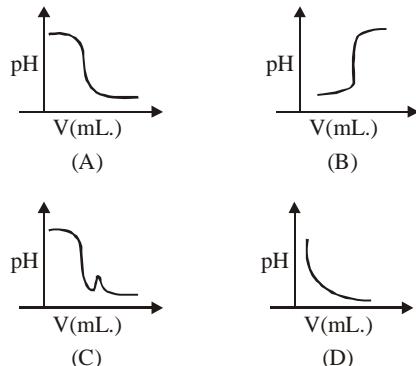
$$(2) S = \left( \frac{K_{sp}}{216} \right)^{1/7}$$

$$(3) S = \left( \frac{K_{sp}}{144} \right)^{1/6}$$

$$(4) S = \left( \frac{K_{sp}}{6912} \right)^{1/7}$$

- 38.** In an acid-base titration, 0.1 M HCl solution was added to the NaOH solution of unknown strength. Which of the following correctly shows the change of pH of the titration mixture in this experiment?

[JEE-MAIN(Online)-2019]



(1) (A)

(2) (C)

(3) (D)

(4) (B)

39. The pH of a 0.02M  $\text{NH}_4\text{Cl}$  solution will be [JEE-MAIN(Online)-2019]

[given  $K_b(\text{NH}_4\text{OH})=10^{-5}$  and  $\log 2=0.301$ ]

(1) 4.65

(2) 5.35

(3) 4.35

(4) 2.65

40. The molar solubility of  $\text{Cd}(\text{OH})_2$  is  $1.84 \times 10^{-5}$  M in water. The expected solubility of  $\text{Cd}(\text{OH})_2$  in a buffer solution of  $\text{pH} = 12$  is : [JEE-MAIN(Online)-2019]

(1)  $6.23 \times 10^{-11} \text{ M}$     (2)  $1.84 \times 10^{-9} \text{ M}$     (3)  $\frac{2.49}{1.84} \times 10^{-9} \text{ M}$     (4)  $2.49 \times 10^{-10} \text{ M}$

41. Two solutions A and B, each of 100 L was made by dissolving 4g of NaOH and 9.8 g of  $\text{H}_2\text{SO}_4$  in water, respectively. The pH of the resultant solution obtained from mixing 40 L of solution A and 10 L of solution B is\_\_\_\_\_. [JEE-MAIN(Online)-2020]

42. 3g of acetic acid is added to 250 mL of 0.1 M HCl and the solution made up to 500 mL.

To 20 mL of this solution  $\frac{1}{2}$  mL of 5 M NaOH is added. The pH of the solution is

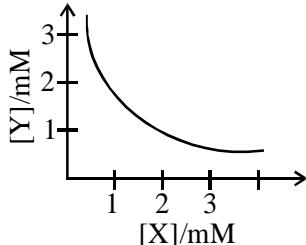
[Given :  $pK_a$  of acetic acid = 4.75, molar mass of acetic acid = 60 g/mol,  $\log 3 = 0.4771$ ]

Neglect any changes in volume

[JEE-MAIN(Online)-2020]

43. The stoichiometry and solubility product of a salt with the solubility curve given below is, respectively :

[JEE-MAIN(Online)-2020]



- (1)  $X_2Y$ ,  $2 \times 10^{-9} M^3$     (2)  $XY_2$ ,  $1 \times 10^{-9} M^3$     (3)  $XY_2$ ,  $4 \times 10^{-9} M^3$     (4)  $XY$ ,  $2 \times 10^{-6} M^3$

44. For the following Assertion and Reason, the correct option is : [JEE-MAIN(Online)-2020]

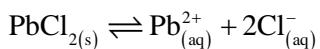
Assertion : The pH of water increases with increase in temperature.

Reason : The dissociation of water into  $H^+$  and  $OH^-$  is an exothermic reaction.

- (1) Both assertion and reason are true, but the reason is not the correct explanation for the assertion.
- (2) Both assertion and reason are false.
- (3) Assertion is not true, but reason is true.
- (4) Both assertion and reason are true, and the reason is the correct explanation for the assertion.

45. The  $K_{sp}$  for the following dissociation is  $1.6 \times 10^{-5}$

[JEE-MAIN(Online)-2020]



Which of the following choices is correct for a mixture of 300 mL 0.134 M  $Pb(NO_3)_2$  and 100 mL 0.4 M NaCl ?

- (1)  $Q < K_{sp}$
- (2)  $Q > K_{sp}$
- (3)  $Q = K_{sp}$
- (4) Not enough data provided

46. The solubility product of  $Cr(OH)_3$  at 298 K is  $6.0 \times 10^{-31}$ . The concentration of hydroxide ions in a saturated solution of  $Cr(OH)_3$  will be : [JEE-MAIN(Online)-2020]

- (1)  $(18 \times 10^{-31})^{1/4}$
- (2)  $(2.22 \times 10^{-31})^{1/4}$
- (3)  $(4.86 \times 10^{-29})^{1/4}$
- (4)  $(18 \times 10^{-31})^{1/2}$

## EXERCISE (JA)

1. What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH = 2.0) is mixed with 300 ml of an aqueous solution of NaOH (pH = 12.0) ? [JEE '1998]
2. The pH of 0.1 M solution of the following salts increases in the order [JEE 1999]

(A)  $\text{NaCl} < \text{NH}_4\text{Cl} < \text{NaCN} < \text{HCl}$       (B)  $\text{HCl} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{NaCN}$   
 (C)  $\text{NaCN} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{HCl}$       (D)  $\text{HCl} < \text{NaCl} < \text{NaCN} < \text{NH}_4\text{Cl}$
3. A buffer solution can be prepared from a mixture of [JEE 1999]

(A) sodium acetate and acetic acid in water  
 (B) sodium acetate and hydrochloric acid in water  
 (C) ammonia and ammonium chloride in water  
 (D) ammonia and sodium hydroxide in water.
4. The solubility of  $\text{Pb}(\text{OH})_2$  in water is  $6.7 \times 10^{-6}\text{M}$ . Calculate the solubility of  $\text{Pb}(\text{OH})_2$  in a buffer solution of pH = 8. [JEE '1999]
5. The average concentration of  $\text{SO}_2$  in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of  $\text{SO}_2$  in water at 298 K is 1.3653 moles litre<sup>-1</sup> and the  $\text{pK}_a$  of  $\text{H}_2\text{SO}_3$  is 1.92, estimate the pH of rain on that day. [JEE 2000]  

[Given :  $10^{-1.92} = 1.2 \times 10^{-2}$ ,  $\sqrt{5.5678} = 2.5627$ ,  $\log(1.2213) = 0.0868$ ]
6. For sparingly soluble salt ApBq, the relationship of its solubility product ( $L_s$ ) with its solubility (S) is - [JEE 2001]

(A)  $L_s = S^{p+q} \cdot p^p \cdot q^q$     (B)  $L_s = S^{p+q} \cdot p^p \cdot q^p$     (C)  $L_s = S^{pq} \cdot p^p \cdot q^q$     (D)  $L_s = S^{pq} \cdot (p \cdot q)^{p+q}$
7. 500 ml of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.  
 (a) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.  
 (b) If 6 g of NaOH is added to the above solution, determine final pH. Assume there is no change in volume on mixing.  $K_a$  of acetic acid is  $1.75 \times 10^{-5}$  M. [JEE 2002]
8. A solution which is  $10^{-3}$  M each in  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$  is treated with  $10^{-16}\text{M}$  sulphide ion. If  $K_{sp}$ ,  $\text{MnS}$ ,  $\text{FeS}$ ,  $\text{ZnS}$  and  $\text{HgS}$  are  $10^{-15}$ ,  $10^{-23}$ ,  $10^{-20}$  and  $10^{-54}$  respectively, which one will precipitate first ? [JEE 2003]

(A) FeS      (B) MnS      (C) HgS      (D) ZnS
9. Will the pH of water be same at 4°C and 25°C ? Explain. [JEE 2003]
10. 0.1 M of HA is titrated with 0.1 M NaOH, calculate the pH at end point.  
 Given  $K_a(\text{HA}) = 5 \times 10^{-6}$  and  $\alpha \ll 1$ . [JEE 2004]



20. The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (HA, 1M) is  $1/100^{\text{th}}$  of that of a strong acid (HX, 1M), at  $25^{\circ}\text{C}$ . The  $K_a$  of HA is [JEE 2013]  
 (A)  $1 \times 10^{-4}$       (B)  $1 \times 10^{-5}$       (C)  $1 \times 10^{-6}$       (D)  $1 \times 10^{-3}$
21. The  $K_{\text{sp}}$  of  $\text{Ag}_2\text{CrO}_4$  is  $1.1 \times 10^{-12}$  at  $298\text{ K}$ . The solubility (in mol/L) of  $\text{Ag}_2\text{CrO}_4$  in a  $0.1\text{ M}$   $\text{AgNO}_3$  solution is [JEE 2013]  
 (A)  $1.1 \times 10^{-11}$       (B)  $1.1 \times 10^{-10}$       (C)  $1.1 \times 10^{-12}$       (D)  $1.1 \times 10^{-9}$

**Paragraph For Questions 22 and 23**

When  $100\text{ mL}$  of  $1.0\text{ M}$  HCl was mixed with  $100\text{ mL}$  of  $1.0\text{ M}$  NaOH in an insulated beaker at constant pressure, a temperature increase of  $5.7\text{ }^{\circ}\text{C}$  was measured for the beaker and its contents.

(**Expt-1**). Because the enthalpy of neutralisation of a strong acid with a strong base is a constant ( $-57.0\text{ kJmol}^{-1}$ ), this experiment could be used to measure the calorimeter constant. In a second experiment (**Expt-2**),  $100\text{ mL}$  of  $2.0\text{ M}$  acetic acid ( $K_a = 2.0 \times 10^{-5}$ ) was mixed with  $100\text{ mL}$  of  $1.0\text{ M}$  NaOH (under identical conditions to (**Expt-1**)) where a temperature rise of  $5.6\text{ }^{\circ}\text{C}$  was measured.

(Consider heat capacity of all solutions as  $4.2\text{ Jg}^{-1}\text{K}^{-1}$  and density of all solutions as  $1.0\text{ g mL}^{-1}$ )

22. Enthalpy of dissociation (in  $\text{kJ mol}^{-1}$ ) of acetic acid obtained from the **Expt-2** is [JEE 2015]  
 (A) 1.0      (B) 10.0      (C) 24.5      (D) 51.4
23. The pH of the solution after **Expt-2**  
 (A) 2.8      (B) 4.7      (C) 5.0      (D) 7.0
24. The solubility of a salt of weak acid(AB) at pH 3 is  $Y \times 10^{-3}\text{ mol L}^{-1}$ . The value of Y is\_\_\_\_.  
 (Given that the value of solubility product of AB ( $K_{\text{sp}}$ ) =  $2 \times 10^{-10}$  and the value of ionization constant of HB( $K_a$ ) =  $1 \times 10^{-8}$ ) [JEE 2018]

## ANSWER KEY

### EXERCISE (S-1)

1. Ans.  $6.022 \times 10^7$
2. Ans. (i) 6.53 ; (ii) (a) Basic , (b) Acidic
3. Ans. 6.8
4. Ans. (a) 1, (b) 2.87, (c) 11.13 (d) 6.97, (e) 7, (f) 6 , (g) 6.97, (h) 11.30 (i) 9 , (j) 3
5. Ans. (a)  $K_a = 10^{-8}$ , (b)  $K_b = 10^{-6}$
6. Ans. 10
7. Ans. 173.2 : 1
8. Ans. 0.009
9. Ans.  $2.32 \times 10^{-8} M$
10. Ans.  $1.1 \times 10^{-3} M$
11. Ans.  $1.11 \times 10^{-4}$
12. Ans. 4.7
13. Ans. 3.3
14. Ans. (a) 0.522 , (b) 2.522
15. Ans. (1)
16. Ans.  $[H^+] = 1.65 \times 10^{-2} M$ ,  $[CHCl_2COO^-] = 6.5 \times 10^{-3} M$
17. Ans.  $[H^+] = 3 \times 10^{-3} M$ ,  $[CH_3COO^-] = 1.2 \times 10^{-3} M$ ,  $[C_7H_5O_2^-] = 1.8 \times 10^{-3} M$
18. Ans. 0.027 M, 0.073 M, 0.027 M,  $10^{-5} M$
19. Ans.  $[H^+] = [H_2PO_4^-] = 2.7 \times 10^{-3} M$ ,  $[HPO_4^{2-}] = 10^{-8} M$ ,  $[PO_4^{3-}] = 3.7 \times 10^{-19} M$
20. Ans. 11.3
21. Ans.  $10^{-5} M$
22. Ans. pH = 4.5
23. Ans.  $K_b = 6.25 \times 10^{-10}$
24. Ans. 0.56%, pH = 7
25. Ans. 1.667%
26. Ans. 0.25 %
27. Ans.  $10^{-6} ; 10^{-8}$
28. Ans. 8.3
29. Ans. 4.19
30. Ans. (a) 6, (b)  $1 \times 10^{-5}$
31. Ans. 9.0
32. Ans. 9.56
33. Ans. 5.04
34. Ans. 0.05 mol
35. Ans.  $[OH^-] = 9.0 \times 10^{-6} M$
36. Ans. (10.1)
37. Ans. 4.74
38. Ans. 9.56
39. Ans. 8.7782
40. Ans.(3.33)
41. Ans.  $10^{-5} M$
42. Ans. 8.7 ,  $[H_3O^+] = 2 \times 10^{-9} M$
43. Ans. 5 ,  $10^{-5} M$
44. Ans. (i) 2.85, (ii) 4.0969, (iii) 4.5229, (iv) 4.699, (v) 5.301, (vi) 8.699
45. Ans.  $[HI_n] = 80 \%$
46. Ans. 85.71%
47. Ans. (b), (c)
48. Ans.  $\Delta pH = 0.954$
49. Ans.  $QX_2$  is more soluble
50. Ans.  $4 \times 10^{-8}$
51. Ans.  $5 \times 10^{-11}$
52. Ans.  $3.2 \times 10^{-11}$
53. Ans.  $2.56 \times 10^{-16}$
54. Ans.  $1.0 \times 10^{-5} mol/lit$
55. Ans.  $5 \times 10^{-10} M$

56. Ans.  $\text{Ans. } 5 \times 10^{-7}$
57. Ans.  $4 \times 10^{-7} \text{ mol/L AgBr}, 1.6 \times 10^{-6} \text{ mol/L AgSCN}$
58. Ans.  $[\text{F}^-] = 3 \times 10^{-3} \text{ M}$
59. Ans.  $8 \times 10^{-3} \text{ M}$
60. Ans. (i)  $2 \times 10^{-9}$ , (ii)  $8 \times 10^{-3}$
61. Ans.  $S = 2 \times 10^{-4} \text{ M}, \text{pH} = 8.0$
62. Ans.  $4 \times 10^{-2} \text{ M}$
63. Ans. (a) no precipitation will occur, (b) a precipitate will form
64. Ans. No.
65. Ans. 0.284 gm

### EXERCISE (O-1)

- |             |             |             |             |             |
|-------------|-------------|-------------|-------------|-------------|
| 1. Ans.(A)  | 2. Ans.(B)  | 3. Ans.(C)  | 4. Ans.(C)  | 5. Ans.(B)  |
| 6. Ans.(C)  | 7. Ans.(D)  | 8. Ans.(D)  | 9. Ans.(C)  | 10. Ans.(C) |
| 11. Ans (C) | 12. Ans.(D) | 13. Ans.(B) | 14. Ans.(B) | 15. Ans.(C) |
| 16. Ans.(C) | 17. Ans.(B) | 18. Ans.(C) | 19. Ans.(C) | 20. Ans.(B) |
| 21. Ans.(B) | 22. Ans.(D) | 23. Ans.(D) | 24. Ans.(C) | 25. Ans.(C) |
| 26. Ans.(C) | 27. Ans.(B) | 28. Ans.(B) | 29. Ans.(A) | 30. Ans.(D) |
| 31. Ans.(B) | 32. Ans.(C) | 33. Ans.(C) | 34. Ans.(C) | 35. Ans.(B) |
| 36. Ans.(C) | 37. Ans.(D) | 38. Ans.(A) | 39. Ans.(C) | 40. Ans.(C) |
| 41. Ans.(C) | 42. Ans.(B) | 43. Ans.(C) | 44. Ans.(D) | 45. Ans.(A) |
| 46. Ans.(B) | 47. Ans.(D) | 48. Ans.(B) | 49. Ans.(C) | 50. Ans.(A) |
| 51. Ans.(C) | 52. Ans.(A) | 53. Ans.(A) | 54. Ans.(A) | 55. Ans.(B) |
| 56. Ans.(D) | 57. Ans.(A) | 58. Ans.(A) | 59. Ans.(B) | 60. Ans.(C) |
| 61. Ans.(D) | 62. Ans.(A) | 63. Ans.(D) | 64. Ans.(C) | 65. Ans.(D) |
| 66. Ans.(D) | 67. Ans.(D) | 68. Ans.(C) | 69. Ans.(A) | 70. Ans.(C) |
| 71. Ans.(B) | 72. Ans.(B) | 73. Ans.(D) | 74. Ans.(B) | 75. Ans.(B) |

### EXERCISE (O-2)

- |   |             |                   |              |               |
|---|-------------|-------------------|--------------|---------------|
| 1. Ans.(A)                                    | 2. Ans.(C)  | 3. Ans.(D)        | 4. Ans.(B)   | 5. Ans (C)    |
| 6. Ans.(A)                                    | 7. Ans.(A)  | 8. Ans.(B)        | 9. Ans.(D)   | 10. Ans.(A)   |
| 11. Ans. (A,B,C)                              |             | 12. Ans.(A,B,C,D) |              | 13. Ans.(B,C) |
| 14. Ans. (A, B, D)                            |             | 15. Ans. (D)      | 16. Ans.(A)  | 17. Ans. (A)  |
| 18. Ans (B)                                   | 19. Ans (B) | 20. Ans (B)       | 21. Ans. (C) | 22. Ans. (A)  |
| 23. Ans. A - (R), B - (P), C - (Q), D - (S)   |             |                   |              |               |
| 24. Ans (A) - Q; (B) - P, S; (C) - R; (D) - T |             |                   |              |               |
| 25. Ans.(D)                                   | 26. Ans.(B) | 27. Ans.(C)       |              |               |

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**EXERCISE (JM)**


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- |             |                 |                         |
|-------------|-----------------|-------------------------|
| 1. Ans.(3)  | 2. Ans.(3)      | 3. Ans.(4)              |
| 4. Ans.(1)  | 5. Ans.(3)      | 6. Ans.(2)              |
| 7. Ans.(3)  | 8. Ans.(4)      | 9. Ans.(3)              |
| 10. Ans.(4) | 11. Ans.(3)     | 12. Ans.(3)             |
| 13. Ans.(1) | 14. Ans.(4)     | 15. Ans.(4)             |
| 16. Ans.(4) | 17. Ans.(1)     | 18. Ans.(4)             |
| 19. Ans.(1) | 20. Ans.(1)     | 21. Ans.(4)             |
| 22. Ans.(3) | 23. Ans. (2)    | 24. Ans.(3)             |
| 25. Ans.(3) | 26. Ans.(1)     | 27. Ans.(2)             |
| 28. Ans.(1) | 29. Ans.(2)     | 30. Ans.(1)             |
| 31. Ans.(2) | 32. Ans.(2)     | 33. Ans.(1)             |
| 34. Ans.(3) | 35. Ans.(3)     | 36. Ans.(3)             |
| 37. Ans.(4) | 38. Ans.(1)     | 39. Ans.(2)             |
| 40. Ans.(4) | 41. Ans.(10.60) | 42. Ans. (5.22 to 5.24) |
| 43. Ans.(3) | 44. Ans(2)      | 45. Ans.(2)             |
| 46. Ans.(1) |                 |                         |

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**EXERCISE (JA)**


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- |                                     |                      |                  |
|-------------------------------------|----------------------|------------------|
| 1. Ans. pH = 11.3010                | 2. Ans.(B)           | 3. Ans.(A, B, C) |
| 4. Ans.s = $1.203 \times 10^{-3}$ M | 5. Ans. pH = 0.91325 | 6. Ans.(A)       |
| 7. Ans.(a) 0.0175% , (b) 4.757      | 8. Ans.(C)           |                  |
| 9. Ans.No, it will be > 7 at 0°C.   | 10. Ans.pH = 9       | 11. Ans.(A)      |
| 12. Ans.(B)                         | 13. Ans.(D)          | 14. Ans.(A)      |
| 15. Ans.(D)                         | 16. Ans.(D)          | 17. Ans.(8)      |
| 18. Ans.(C), (D)                    | 19. Ans.(7)          | 20. Ans.(A)      |
| 21. Ans.(B)                         | 22. Ans.(A)          | 23. Ans.(B)      |
| 24. Ans. (4.47)                     |                      |                  |