Fuel value per $cm^3 = \frac{200}{5077}$

= 3.94 kcal

40. (i) $CCl_4 \rightarrow CCl_4\,(g)$ $\Delta H^\circ = +30.5$ kj mol^{-1}

(ii) $C\,(s) + 2Cl_2(g) \rightarrow CCl_4\,(g)$

$\Delta H^\circ = -135.5$ kj mol^{-1}

(iii) $C(s) \rightarrow C(g)$ $\Delta H^\circ = +715$ kj mol^{-1}

(iv) $Cl_2(g) \rightarrow 2Cl(g)$ $\Delta H^\circ = +242$ kj mol^{-1}

Required equation

$CCl_4(g) \rightarrow C(g) + 4Cl(g)$ $\Delta H = ?$

Equation (iii) + 2 × Equation (iv) – Equation (ii) – Equation (i) gives the required equation

$\Delta H = 715 + 2(242) - 30.5 - (-135.5)$

= 1304 kj mol^{-1}

Bond enthalpy of (C-Cl) bond $= \frac{1304}{4}$

= 326 kj mol^{-1}

CHAPTER 5 A

Chemical Equilibrium

Chapter Contents

Law of mass action; Equilibrium constant, Le Chatelier's principle (effect of concentration, temperature and pressure); Significance of ΔG and ΔGo in chemical equilibrium; and Various levels of multiple-choice questions.

Type of Reactions

Chemical reactions are of two types:

Irreversible Reaction: Such reactions occur in one direction only and get completed.

Example, (i) When unreactive products or solid products are formed

$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

$2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$

(ii) All precipitate reactions are irreversible

Example,

$$\underset{\text{aq.}}{BaCl_2} + \underset{\text{aq.}}{H_2SO_4} \rightarrow \underset{\text{ppt.}}{BaSO_4} + \underset{\text{aq.}}{2HCl}$$

$$Pb(NO_3)_2 + 2KI \rightarrow PbI_2 + 2KNO_3$$

(iii) Neutralization reactions are also irreversible:

$$H_2SO_4 + 2KOH \rightarrow K_2SO_4 + 2H_2O$$

(iv) Redox reactions are also irreversible:

$$2FeCl_3 + SnCl_2 \rightarrow SnCl_4 + 2FeCl_2$$

(v) Combustion reactions are also irreversible:

$$2Mg + O_2 \rightarrow 2MgO$$

Reversible Reactions: Such reactions occur in both directions i.e., forward and backward direction however never complete as the products can give back the reactants under same or different conditions.

Example,

$$N_2 + O_2 \leftrightarrow 2NO$$

$$3Fe + 4H_2O \leftrightarrow Fe_3O_4 + 4H_2$$

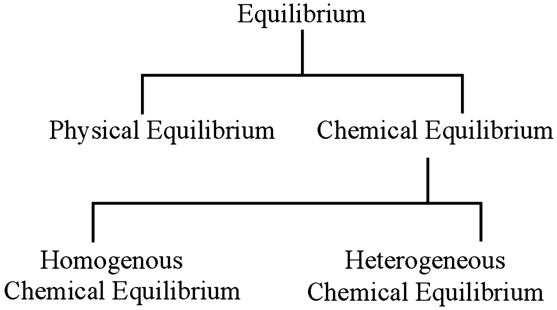
- Vapourization of water in open flask is irreversible reaction while in closed flask it is reversible
- Decomposition of $CaCO_3$ in open flask is irreversible reaction while in closed flask it is reversible.

Differences between Reversible and Irreversible Reactions:

Reversible Reaction	Irreversible Reaction
It takes place in forward as well as in backward directions.	It takes place only in forward direction.
It can never be completed.	It may be completed
Equilibrium state can be attained.	Equilibrium state is never attained.
The change in free energy (ΔG) is zero.	The change in free energy is negative i.e., $\Delta G < 0$.

EQUILIBRIUM

The word "equilibrium" in physical sense in explained as the "No change of state of the body". When the two opposing process (reaction) occur simultaneously with equal rates, the system is in the state of equilibrium. Equilibrium is classified as follows



When an equilibrium exists between same chemical species, it is called physical equilibrium.

Example,

$$\underset{\text{Ice}}{H_2O\,(s)} \xleftrightarrow[\text{1 atm}]{0^\circ C} \underset{\text{Water}}{H_2O\,(l)}$$

When an equilibrium exists between different chemical species, it is called chemical equilibrium.

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

If a chemical equilibrium has only one phase, it is called homogenous and if more than one phase it is called heterogeneous.

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

$$\text{R-COOH}\,(l) + \text{R-OH}(l) \rightleftharpoons \text{R-COOR}(l) + H_2O(l)$$

Phase = 1. Homogenous chemical equilibrium

$$2HgO\,(s) \rightleftharpoons 2Hg\,(l) + O_2\,(g)$$

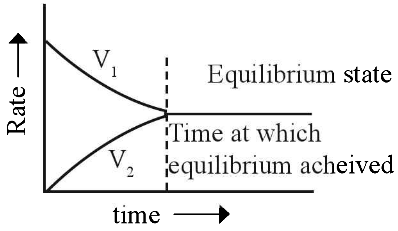
Phase = 3. Heterogeneous chemical equilibrium

CHEMICAL EQUILIBRIUM

It is defined as: "It is the stage of a reversible reaction at which the active masses of the reactants and the products become constant in mixture and do not change with time" and rate of forward reaction is equal to that of backward reaction.

Or

"It is the state of a reversible reaction at which measurable properties like colour, density, pressure concentration are nearly unchangeable."



Here V_1 and V_2 are rate of forward and backward reactions respectively.

i.e., Equilibrium is the state in a reversible reaction at which the rate of forward and backward reactions or two opposing reactions are same.

Features of Chemical Equilibrium

- It is obtained only when reversible reaction is carried out in a closed space.
- Here rate of forward reaction is equal to rate of backward reaction.
- Here both forward and backward reactions are taking place with same rate hence the relative amounts of the reactants and products present at equilibrium does not change with time.
- At constant temperature it is characterized by properties like colour, density, pressure etc.
- It is possible from both the sides.
- It is dynamic in nature. It means the reaction or process is not going to be ceased as reaction occurs in both directions with equal rates.
- A catalyst cannot alter the positive of equilibrium as it accelerates both the forward and backward

reactions to the same extant this means the same state of equilibrium is reaction i.e., a positive catalyst can set up equilibrium in less time but can not change it.

- At equilibrium ΔG is equal to zero i.e.,

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

  So

  $\Delta H = T\Delta S$

- Under the similar conditions of temperature concentration and pressure, the same state of equilibrium is reached.

Example,

When an equimolar mixture of H_2 and I_2 is heated to 713 K, 80% of this mixture changes into the product (HI) and if product is again heated as 713 K only 20 % of it changes into H_2 and I_2

Active Mass or Molar Concentration

It means the concentration of the reactant expressed in moles per litre or the pressure of a reacting gas in atmosphere. It is usually denoted by putting the symbol of the reactant in square bracket. E.g., [A].

$$C_A \text{ or } [A] = \frac{w}{m \times V\,(\text{lit})}\,.$$

$(A) = \gamma \times$ molarity

Here γ is the activity coefficient

In case of very dilute solution, γ is one. This means we can used molarity.

- Its unit is mol lit $^{-1}$.
- At constant temperature
  Partial pressure $\propto$ Active mass
- Active mass of a pure solid or a pure liquid is assumed to be one.
- Active mass of any gas at N.T.P. is 1/22.4.

Law of Mass Action

It was introduced by Guldberg and Waage. It states that "the rate at which a substance reacts is directly proportional to its active mass(effective molar concentration) and the rate at which substances react together is directly proportional to the product of their active masses" each raised to a power which is equal to the corresponding stoichiometric number the substance present in the chemical reaction.

$$A + B \underset{V_2}{\overset{V_1}{\longleftrightarrow}} C + D$$

If active masses of A, B, C and D are [A], [B], [C], [D] respectively then

Rate of reaction of A $\propto$ [A]

Rate of reaction of B $\propto$ [B]

$V_1 \propto [A]\,[B] = K_1\,[A]\,[B]$

$V_2 \propto [C]\,[D] = K_2\,[C]\,[D]$

Law of mass action is not applicable for solids as for them active mass is always one.

Example, $\underset{\text{Solid}}{KClO_3} \rightarrow 2KCl + 3O_2$

Reaction Quotient or Concentration Quotient (Q):

It is defined as the ratio of concentration of product upon the reacting species at any point of time other than the equilibrium stage. It can be determined as follows:

If we consider a reaction

$m_1A + m_2B \leftrightarrow n_1C + n_2D$ than

$$Q = \frac{[C]^{n1}\,[D]^{n2}}{[A]^{m1}\,[B]^{m2}}$$

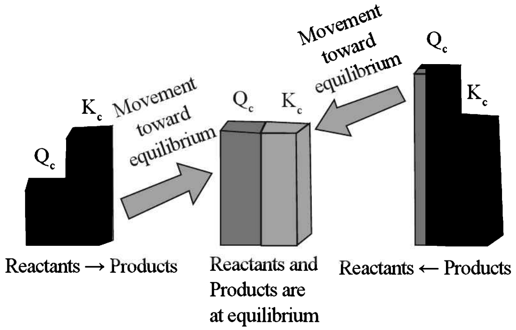
Q can be denoted as Q_C or Q_P if we use concentration in terms of mole per litre or partial pressure respectively.

- When $[C]^{n1}\,[D]^{n2} = [A]^{m1}\,[B]^{m2}$.

  Q = K (reaction is at equilibrium and rate of forward and backward reactions are equal).

- When Q > K here reaction will proceed or favour backward direction this means product changes into reactant to attain equilibrium.

- When Q < K (here reaction will proceed or favour forward direction i.e., reactant changes into product to attain equilibrium.



Equilibrium Constant

It is the ratio of rate of forward and backward reaction at a particular temperature or It is the ratio of active masses of the reactants to that of active masses of products at a particular temperature. It is denoted by Kc or Kp. The distinction between K_{eq} and K_c is that expression of K_{eq} involves all the species (whether they are pure solids, pure liquids, gases, solvents or solutions) while the expression K_c involves only those species whose concentration is a variable (gases and solution). It means Kc is a devoid of pure components (like pure solids and pure liquids) and solvents.

For a reaction

$$A + B \underset{V_2}{\overset{V_1}{\longleftrightarrow}} C + D$$

$$V_1 \propto [A]\,[B] \quad \text{or} = K_1\,[A]\,[B]$$

$$V_2 \propto [C]\,[D] \quad \text{or} = K_2\,[C]\,[D]$$

We know that at equilibrium $V_1 = V_2$

So $K_1\,[A]\,[B] = K_2\,[C]\,[D]$

$$\frac{K_1}{K_2} = \frac{[C]\,[D]}{[A]\,[B]}$$

$$Kc = \frac{[C]\,[D]}{[A]\,[B]} \text{ or } \frac{[\text{product}]}{[\text{reactant}]} \text{ at const temp.}$$

or

For a reaction given below equilibrium constant can be given as

$$m_1A + m_2B \leftrightarrow n_1C + n_2D$$

$$Kc = \frac{[C]^{n1}\ [D]^{n2}}{[A]^{m1}\ [B]^{m2}}$$

REMEMBER

Completion of reaction $\propto$ Kc

Stability of reaction $\propto$ 1/Kc

Stability of product $\propto$ Kc

Factors Effecting Equilibrium Constant

Kc does not depend upon:

- Initial concentration or pressure of reactants and products involved.
- The presence of a catalyst.
- The presence of an inert gas material.
- The direction from which equilibrium has been set up.

Kc depends upon: Equilibrium constant depends upon following factors.

1. Temperature

The variation of equilibrium constant with temperature is given by Van't Hoff equation as follows:

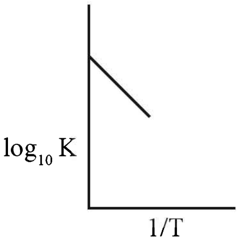
$$K = Ae^{-\Delta H^\circ/RT}$$

$$\log_{10}\frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303\,R}\ \frac{(T_2 - T_1)}{T_1 . T_2}$$

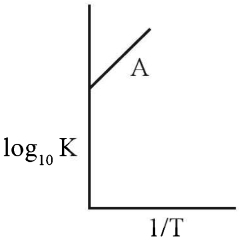
$$K \propto T \qquad (\Delta H = +ve)$$

$$K \propto 1/T \qquad (\Delta H = -ve)$$

When a graph is ploted between $\log_{10}K$ and 1/T a straight like will be formed and the slope is equal to $\frac{-\Delta H^\circ}{2.303R}$.



Endothermic



Exothermic

- In case of $\Delta H = 0$, equilibrium constant does not depend upon temperature.
- In case of ΔH = positive or endothermic reactions, equilibrium constant is more at higher temperature.
- In case of ΔH = negative or exothermic reactions, equilibrium constant is more at lower temperature.

2. Mode of Representation of Reaction

Let us consider a reaction

$$A + B \leftrightarrow C + D$$

$$Kc = \frac{[C]\,[D]}{[A]\,[B]}$$

Now if we write the above reaction as follows:

$$C + D \leftrightarrow A + B$$

$$Kc' = \frac{[A]\,[B]}{[C]\,[D]}$$

i.e., $Kc = 1/Kc'$

Example, $2SO_2 + O_2 \rightleftharpoons 2SO_3$

$$Kc = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

If the reaction is reversed $2SO_3 \rightleftharpoons 2SO_2 + O_2$

$$K'c = \frac{[SO_2]^2\,[O_2]}{[SO_3]^2} = \frac{1}{Kc}$$

3. Stoichiometric Representation of Chemical Equation

Let us consider a reaction

$$A + B \leftrightarrow C + D$$

$$Kc = \frac{[C]\,[D]}{[A]\,[B]}$$

If we write the above reaction as follows:

$m_1A + m_2B \leftrightarrow n_1C + n_2D$ then

$$Kc' = \frac{[C]^{n1}\,[D]^{n2}}{[A]^{m1}\,[B]^{m2}}$$

e.g.,– (1) $2NO_2 \leftrightarrow N_2 + 2O_2$

$$\text{Here } Kc = \frac{[NO_2]^2}{[N_2]\,[O_2]^2}$$

(2) $NO_2 \leftrightarrow \frac{1}{2} N_2 + O_2$

$$\text{Here } Kc = \frac{[NO]}{[N_2]^{1/2}\,[O]} = \sqrt{Kc}$$

(3) $N_2 + 3H_2 \leftrightarrow 2NH_3$ and

$NH_3 \leftrightarrow \frac{1}{2} N_2 + 3/2\, H_2$ then

$Kc' = 1/\sqrt{Kc}$

4. Nature of reactant or product

The value of equilibrium constant also depend on the nature of reactants as well as of the products it means the value of equilibrium constant changes by changing them .

Example,

$N_2 + O_2 \rightleftharpoons 2NO$

$N_2 + 2O_2 \rightleftharpoons 2NO_2$

For these reaction the value of equilibrium constant differs as product differs.

Equilibrium Constant in Terms of Partial Pressure:

If partial pressures of A, B, C, D are given as P_A, P_B P_C P_D respectively then for the reaction Kp is given as

$$m_1A + m_2B \leftrightarrow n_1C + n_2D$$

$$Kp = \frac{[Pc]^{n1}\,[P_D]^{n2}}{[P_A]^{m1}\,[P_B]^{m2}}$$

If we use total pressure, moles of reactant and products than Kp can be find out as follows

$$Kp = \frac{n_c^{\,n1} \times n_d^{\,n2}}{n_a^{\,m1} \times n_b^{\,m2}} \times \left(\frac{P}{\sum n}\right)^{\Delta n(g)}$$

Here $\Delta n_g = (n_1 + n_2) - (m_1 + m_2)$

It is interesting to know that Kp can exist only when equilibrium satisfies these two conditions.

(i) One of the reactant or the product must be in gaseous phase.

(ii) No component of the equilibrium must be present in solution phase.

Relation between Kp and Kc:

$$Kp = \frac{[Pc]^{n1}\,[P_D]^{n2}}{[P_A]^{m1}\,[P_B]^{m2}}$$

As $PV = nRT$

So $P = \frac{n}{V} RT$

As n/V = Concentration

So $P = CRT$

$$K_P = \frac{[C]^{n1}\,[RT]^{n1} \times [D]^{n2}\,[RT]^{n2}}{[A]^{m1}\,[RT]^{m1} \times [B]^{m2}\,[RT]^{m2}}$$

$$= \frac{[C]^{n1}\,[D]^{n2}}{[A]^{m1}\,[B]^{m2}}\,[RT]^{(n1 + n2) - (m1 + m2)}$$

$$Kp = Kc.(RT)^{(n1 + n2) - (m1 + m2)}$$

Δn = Sum of gaseous products – Sum of gaseous reactants

$$\Delta n = (n_1 + n_2) - (m_1 + m_2)$$

$$Kp = Kc.(RT)^{\Delta n}$$

Units of Equilibrium Constant (K):

$Kc = (mol/lit)^{\Delta n}$

$Kp = (atm)^{\Delta n}$

REMEMBER

- If Δn is zero Kp = Kc
  Here Kp and Kc have no units.
  e.g.,– $N + O_2 \leftrightarrow 2NO$
- If Δn is positive then Kp > Kc
  e.g.,– $PCl_5 \leftrightarrow PCl_3 + Cl_2$
  $2NH_3 \leftrightarrow N_2 + 3H_2$
- If Δn is negative then Kc > Kp
  e.g.,– $2SO_2 + O_2 \leftrightarrow 2SO_3$

Equilibrium Constant for a Multi step Reaction:
For a multistep reaction equilibrium constant is given as

$$K = K_1 . K_2 . K_3$$

It means if a equilibrium reaction can be expressed as the sum of two or more equilibrium reactions, then the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

e.g.,– $H_2O_2 + 2H^+ \rightarrow 2I^- \rightarrow I_2 + 2H_2O$

Steps: $H_2O_2 + I^- \rightarrow OH^- + HOI\ (K_1)$

$H^+ + OH^- \rightarrow H_2O\ (K_2)$

$HOI + H^+ + I^- \rightarrow H_2O + I_2\ (K_3)$

Here $K = K_1 . K_2 . K_3$

Expressions of K_c and K_p for Some Reactions

(i) Evaluation of KC and Kp for HI formation

	H_2 (g) +	I_2 (g) ⇌	2HI (g)
Initially	a mole	b mole	0 mole
At eq.	(a – X) mole	(b – X) mole	2X mole

Molar concentration or active mass of the various species at equilibrium will be

$$[H_2] = \frac{a - X}{V}\ m\,L^{-1}$$

$$[I_2] = b - \frac{X}{V}\ m\,L^{-1}$$

$$[HI] = \frac{2X}{V}\ m\,L^{-1}$$

According to law of mass action

$$K_C = \frac{[HI]^2}{[H_2]\,[I_2]}\ .$$

$$= \frac{4X^2}{(a - X)\,(b - X)}\ .$$

Evaluation of K_P:

	H_2 (g) +	I_2 (g) ⇌	2HI (g)
Initially	a mole	b mole	0 mole
At eq.	(a – X) mole	(b – X) mole	2X mole

Total number of moles = (a – X) + (b – X) + 2X
= a + b

Partial pressure of the three species can be calculated as:

$$P\,(H_2) = \frac{(a - X)\,P}{(a + b)}$$

$$P\,(I_2) = \frac{(b - X)\,P}{(a + b)}$$

$$P\,(HI) = \frac{(2X)\,P}{(a + b)}$$

On substituting the values in the law of mass action

$$K_P = \frac{(P_{HI})^2}{(P_{H2})\,(P_{I2})}\ .$$

$$= \frac{4X^2}{(a - X)\,(b - X)}\ .$$

(ii) In case of NO formation: Following the process used in HI formation, we get

$$Kc = \frac{4x^2}{(a–x)(b–x)}\ .$$

$$Kp = \frac{4x^2}{(a–x)(b–x)}\ .$$

(iii) In case of NH_3 formation:

$$Kc\quad \frac{4x^2\,v^2}{27(a - x)^4}\ .$$

or 1

$$Kp = \frac{16x^2\,(2 - x)^2}{27(1 - x)^4\,P^2}\ .$$

or 1

(iv) In case of PCl_5 dissociation:

$$Kc = \frac{x^2}{(a - x)V}\ .$$

$$Kp = \frac{P\,x^2}{(1 - x^2)}\ .$$

Illustrations

1. At 440°C the equilibrium constant (K) for the following reaction is 49.5.

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

If 0.2 mole of H_2 and 0.2 mole of I_2 are placed in a 10 L vessel and permitted to react at this temperature. What will be the concentration of each substance at equilibrium?

Solution $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

H_2	I_2	$2HI$	
0.2	0.2	0	Initially
0.2 – X	0.2 – X	2X	At eq.

$$K_C = \frac{[HI]^2}{[H_2][I_2]}\ .$$

$$= \frac{(2X)^2}{(0.2-X)(0.2-X)}\ .$$

$$49.5 = \frac{(2X)^2}{(0.2-X)^2}\ .$$

On solving

X = 0.16

[HI] = 2 × 0.16 2

= 0.32

$[H_2] = [I_2] = 0.2 - 0.16 = 0.04$

2. 0.5 mole of hydrogen and 0.5 mole of iodine react in a 10 litre evacuated vessel at 450°C hydrogen iodide is formed. The equilibrium constant K_C for the reaction is 50.

(i) Calculate the value of K_P.

(ii) Calculate the moles of iodine which are in excess.

Solution (i) $H_2 + I_2 \rightleftharpoons 2HI$

1 mole 1 mole 2 mole

As $K_P = K_C(RT)^{\Delta n} = 50(RT)^0$

So $K_P = 50$

(ii) $H_2 + I_2 \rightleftharpoons 2HI$

H_2	I_2	$2HI$	
0.5	0.5	0	Initially
0.5 – X	0.5 – X	2X	At. eq.

$$K_C = \frac{[HI]^2}{[H_2][I_2]}\ .$$

$$= \frac{(2X)^2}{(0.5-X)(0.5-X)}\ .$$

$$\frac{50}{4} = \frac{(X)^2}{(0.5-X)^2}\ .$$

$$\frac{X}{0.5-X} = 3.53$$

X = 0.39

Excess of iodine = 0.5 – 0.39 = 0.11 moles

3. One mole of H_2, two moles of I_2 and three moles of HI are injected in a one litre flask. What will be the concentration of H_2, I_2 and HI at equilibrium at 490°C? The equilibrium constant for the reaction at 490°C is 45.9.

Solution $[H]_2 = 1$, $[I_2] = 2$, $[HI] = 3$ mole L^{-1}

Suppose X mole of H_2 and X mole of I_2 reacted at equilibrium, then

H_2	I_2	$2HI$	
1 – X	2 – X	3 + 2X	At. eq.

$$K_C = \frac{[HI]^2}{[H_2][I_2]}\ .$$

$$45.9 = \frac{(3+2X)^2}{(1-X)(2-X)}\ .$$

On solving, we get

X = 0.684

At equilibrium

$[H_2] = 1 - X = 1 - 0.684 = 0.316$ mole L^{-1}

$[I_2] = 2 - X = 2 - 0.684 = 1.316$ mole L^{-1}

$[HI] = 3 + 2X = 3 + (2)(0.684) = 4.368$ mole L^{-1}

4. The concentration equilibrium constant, K_C for the reaction

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

At 400 K is 0.5. Find K_P.

($R = 0.082$ L atm K^{-1} mol^{-1})

Solution $K_P = K_C(RT)^{\Delta n}$

For the equilibrium

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

$K_C = 0.5$, T = 400 K

$\Delta n = 2 - (1 + 3) = -2$

$R = 0.082$ L atm K^{-1} mol^{-1}

$K_P = (0.5) \times (0.082 \times 400)^{-2}$

$= \dfrac{0.5}{(32.8)^2} = 4.65 \times 10^{-4}$ atm^{-2}

5. For the reaction,

$CO_2\,(g) + H_2\,(g) \rightleftharpoons CO\,(g) + H_2O\,(g)$

At 1100 K and 1.02×10^5 N m^{-2} pressure, the partial pressure of CO_2, H_2 and CO are 2.18×10^4, 2.58×10^4 and 2.72×10^4 N m^{-2} respectively. Find the K_P for the reaction.

Solution $CO_2\,(g) + H_2\,(g) \rightleftharpoons CO\,(g) + H_2O\,(g)$

$$K_P = \frac{p_{CO} \times p_{H2O}}{P_{CO2} \times p_{H2}}$$

Partial pressure of H_2O (g)

$= 1.02 \times 10^5 - (2.18 \times 10^4 + 2.58 \times 10^4 + 2.72 \times 10^4)$

$= 2.72 \times 10^4$

So

$$K_P = \frac{2.72 \times 10^4 \times 2.72 \times 10^4}{2.18 \times 10^4 \times 2.58 \times 10^4}$$

$= 1.3154$

6. For the reaction $H_2 + I_2 \leftrightarrow 2HI$. The equilibrium concentration of H_2, I_2 and HI are 8.0, 3.0 and 28.0 mo21 per litre respectively. Calculate the equilibrium constant of the reaction.

Solution $H_2\,(g) \quad + \quad I_2\,(g) \leftrightarrow 2HI\,(g)$

8.0 3.0 28.0 molar conc. at eq.

$$K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(28.0)^2}{8.0 \times 3.0}\,.$$

$= 32.66.$

7. Find the value of Kp for dissociation of

$2HI \leftrightarrow H_2 + I_2$

If the equilibrium concentration of HI, H_2 and I_2 are 3.53, 0.4789 and 0.4789 mole $litre^{-1}$ respectively.

Solution $2HI \leftrightarrow H_2 + I_2$

3.53 0.4789 0.4789 molar conc. at eq.

$$K_C = \frac{[H_2]\,[I_2]}{[HI]^2} = \frac{0.4789 \times 0.4789}{[3.53]^2}$$

$= 1.84 \times 10^{-2}$

$K_p = K_C\,(RT)^{\Delta n}$

Here $\Delta n = 0$

$Kp = K_C = 1.814 \times 10^{-2}$

8. A gaseous mixture contains 0.30 mol CO, 0.10 mol H_2 and 0.2 mol H_2O, plus an unknown amount of CH_4 in each litre. This mixture is in equilibrium at 1200 K.

$CO\,(g) + 3H_2\,(g) \leftrightarrow CH_4\,(g) + H_2O\,(g)$

What is the concentration of CH_4 in this mixture? The equilibrium constant, $K_C = 3.92$.

Solution $CO\,(g) + 3H_2\,(g) \leftrightarrow CH_4\,(g) + H_2O\,(g)$

0.30 0.10 X 0.2 eq. moles

$\dfrac{0.30}{1}$ $\dfrac{0.10}{1}$ $\dfrac{X}{1}$ $\dfrac{0.2}{1}$ eq. conc.

$$K_C = \frac{[CH_4]\,[H_2O]}{[CO]\,[H_2]^3}$$

$$3.92 = \frac{X \times 0.2}{0.30 \times (0.10)^3}\,.$$

$X = 5.88 \times 10^{-3}$ mol $litre^{-1}$

9. Iron filings and water were placed in a 5.0 liter tank and sealed. The tank was heated to 1000°C. Upon analysis the tank was found to contain 1.10 g of hydrogen and 42.50 g of water vapour. The following reaction occurred in the tank:

$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$

Calculate the equilibrium constant for the reaction.

Solution $K = \dfrac{[Fe_3O_4]\,[H_2]^4}{[Fe]^3\,[H_2O]^4}$

$$K = \frac{k\,[H_2]^4}{k_1\,[H_2O]^4}\,.$$

Here k and k_1 are the concentrations of $[Fe_3O_4]$ and [Fe] respectively.

Or $K \times \frac{k_1}{k} = K^1 = \frac{[H_2]^4}{[H_2O]^4}$.

$$[H_2] = \frac{1.10/2.02}{5.0} = 0.11 \text{ moles per litre}$$

$$[H_2O] = \frac{42.50/18.02}{5.0} = 0.47 \text{ mole per litre}$$

$$K^1 = \frac{(0.11)^4}{(0.47)^4} = 0.0030.$$

10. The K_P value for the reaction:

$H_2 + I_2 \rightleftharpoons 2HI$, at 460°C is 49. If the initial pressure of H_2 and I_2 is 0.5 atm respectively. Determine the partial pressure of each gas at equilibrium.

Solution

	H_2	+	I_2	$\rightleftharpoons$	2HI
Initial pr.	0.5		0.5		0
At. eq.	(0.5 – X)		(0.5 – X)		2X

$$K_P = \frac{(2X)^2}{(0.5-X)^2} = 49$$

$$\frac{2X}{0.5-X} = 7$$

$$2X = 3.5 - 7X$$

$$9X = 3.5$$

$$X = \frac{3.5}{9} = 0.389$$

At equilibrium:

$P'H_2 = 0.5 - 0.389 = 0.111$ atm

$P'I_2 = 0.5 - 0.389 = 0.111$ atm

$P'HI = 0.389 \times 2 = 0.778$ atm

11. K_C for $CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$ at 986°C is 0.63. A mixture of 1 mole H_2O (g) and 3 mole CO (g) is allowed to react to come to an equilibrium. The equilibrium pressure is 2.0 atm.

(i) How many moles of H_2 are present at equilibrium?

(ii) Calculate partial pressure of each gas at equilibrium.

Solution

(i)

	CO (g) +	H_2O (g) $\rightleftharpoons$	CO_2 (g) +	H_2 (g)
Initial mole	3	1	0	0
Mole at eq.	(3 – X)	(1 – X)	X	X

Total mole at equilibrium

$= 3 - X + 1 - X + X + X = 4$

$$K_C = \frac{X^2}{(3-X)(1-X)} \ .$$

$$0.63 = \frac{X^2}{3 + X^2 - 4X} \quad (\text{as } K_C = 0.63)$$

$X = 0.681$

Mole of H_2 formed = 0.681

(ii) Total pressure at equilibrium = 2 atm

Total mole at equilibrium = 4

$P'_g = P_M \times$ mole fraction of that gas

$$P'CO_2 = PH_2 = \frac{X \,.\, P}{4}$$

$$= \frac{0.681 \times 2}{4} = 0.34 \text{ atm}$$

$$P'CO = \frac{(2-X)\,P}{4} = 1.16 \text{ atm}$$

$$P'H_2O = \frac{(1-X)\,P}{4} = 0.16 \text{ atm}$$

12. An equilibrium mixture at 300 K contains N_2O_4 and NO_2 at 0.28 and 1.1 atmosphere respectively. If the volume of container is doubled, calculate the new equilibrium pressure of two gases.

Solution

	$_2O_4$	$\rightleftharpoons$	$2NO_2$
Pressure at eq.	0.28		1.1

$$K_P = \frac{(PNO_2)^2}{PN_2O_4} = \frac{(1.1)^2}{0.28} = 4.32 \text{ atm}$$

If volume of container is doubled i.e., pressure decreases and will become half, the reaction will proceed in the direction where the reaction shows an increase in mole i.e., decomposition of N_2O_4 is favoured.

	N_2O_4	$\rightleftharpoons$	$2NO_2$
New pressure at eq.	$\frac{(0.28-P)}{2}$		$\frac{(1.1}{2}+2P)$

Here reactant N_2O_4 equivalent to pressure P is used up in doing so.

$$K_P = \frac{[(1.1 \backslash 2) + 2P]^2}{[(0.28/2) - P]} = \frac{[0.55 + 2P]^2}{[0.14 - P]} = 4.32$$

$P = 0.045$

$PN_2O_4 = 0.14 - 0.045 = 0.095$ atm

PNO_2 at new equilibrium $= 0.55 + 2 \times 0.045$

$PNO_2 = 0.64$ atm.

13. At 25°C and 1 atmospheric pressure, the partial pressures in equilibrium mixture of gaseous N_2O_4 and NO_2 are 0.7 and 0.3 atm respectively. Calculate the partial pressures of these gases when they are in equilibrium at 25°C and a total pressure of 10 atm.

Solution

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Pressure at eq.	0.7		0.3

$$K_P = \frac{(PNO_2)^2}{PN_2O_4} = \frac{0.3 \times 0.3}{0.7} = 0.1286 \text{ atm}$$

Suppose decomposition at 10 atm pressure

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial mole	1		0
Mole at eq.	$(1 - X)$		$2X$

$$K_P = \frac{(n_{NO2})^2}{n_{N2\,O4}} \text{ x } (P/\sum n)^{\Delta n}$$

$$= \frac{(2X)^2}{(1 - X)} \times [10/(1 + X)]^1$$

$$1.286 = \frac{4X^2 \times 10}{(1 - X^2)}$$

$X = 0.0565$

$$P'NO_2 = \frac{2X}{(1 + X)} \text{ x } P = \frac{2 \times 0.0565 \times 10}{(1 + 0.0565)}$$

$= 1.07$ atm

$$P'N_2O_4 = \frac{(1 - 0.0565)}{1 + 0.0565} \times 10 = 8.93 \text{ atm}$$

14. At 540 K, 0.10 mole of PCl_5 are heated in a 8 litre flask. The pressure of the equilibrium mixture is found to be 1.0 atm. Calculate K_P and K_C for the reaction.

Solution

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl
Mole before diss.	0.1		0		0
Mole after diss.	$(0.1 - X)$		X		X

Given: Volume of container = 8 litre

$$K_C = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]} = \frac{(X/8)\,.\,(X/8)}{(0.1 - X)/8}$$

$$= \frac{X^2}{8\,(0.1 - X)} \qquad \text{...... (i)}$$

$PV = nRT$

$1 \times 8 = (0.1 + X) \times 0.082 \times 540$

$X = 0.08 \qquad$ .... (ii)

From Equation (i) and (ii)

$$K_C = \frac{0.08 \times 0.08}{8\,(0.1 - 0.08)} = 4 \times 10^{-2} \text{ mol litre}^{-1}$$

$K_P = K_C\,(RT)^{\Delta n}$

As $\Delta n = +1$

$= 4 \times 10^{-2} \times (0.082 \times 540)$

$= 1.77$ atm

15. At some temperature and under a pressure of 4 atm, PCl_5 is 10 % dissociated. Calculate the pressure at which PCl_5 will be 20 % dissociated, temperature remaining same.

Solution

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl
Mole before diss.	0.1		0		0
Mole after diss.	$(0.1 - \alpha)$		α		α

Given: $\alpha = 0.1$ at 4 atm pressure

$$K_P = \frac{n\,(PCl_3) \times n\,(Cl_2)}{n\,(PCl_5)} \times (P/\sum n)^{\Delta n}$$

$$= \frac{\alpha \times \alpha}{(1 - \alpha)}\,[P/(1 + \alpha)]^1$$

$$= \frac{P\alpha^2}{(1 - \alpha)} = \frac{4 \times (0.1)^2}{1 - (0.1)^2}$$

$K_P = 0.040$ atm

Again when α is needed at 0.2, K_P remains constant.

So $K_P = \dfrac{P\alpha^2}{1 - \alpha^2}$.

$$0.040 = \frac{P \times (0.2)^2}{1 - (0.2)^2}$$

$P = 0.96$ atm

Degree of Dissociation (α):

It is the ratio of number of molecules dissociated at equilibrium to initial number of molecules.
It is given as:

	X	$\rightleftharpoons$	nY
Initial no. of moles	1		0
No. of moles at eq.	$(1-\alpha)$		$n\alpha$

Total number of moles at eq. $= (1-\alpha) + n\alpha$
$= 1 + (n-1)\alpha$

Suppose the initial volume be V litre. Thus the volume at equilibrium

$= [1 + (n-1)\alpha]V.$

Suppose 'd' is the observed vapour density at a particular temperature when degree of dissociation is 'α' and D is the vapour density when there is no dissociation.

$$D \propto \frac{1}{V} \quad \ldots \text{(i)}$$

$$d \propto \frac{1}{[1+(n-1)\alpha]V} \quad \ldots \text{(ii)}$$

Dividing eq. (i) by (ii),

$$\frac{D}{d} = 1 + (n-1)\alpha$$

$$\frac{D}{d} - 1 = (n-1)\alpha$$

$$\frac{D}{d} - d = (n-1)\alpha$$

$$\alpha = \frac{D-d}{(n-1)\,d}\ .$$

Here $D = \frac{\text{Molecular weight}}{2}$

d = Vapour density

$$\alpha = M - \frac{m}{m(n-1)}\ .$$

Here M = Initial molecular mass

m = Molecular mass at equilibrium

e.g., In the dissociation of PCl_5, NH_4Cl and N_2O_4, the value of n = 2 so

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

$$N_2O_4 \rightleftharpoons 2NO_2$$

Illustrations

16. Calculate the per cent dissociation of H_2S (g) if 0.1 mole of H_2S is kept in 0.4 litre vessel at 1000 K. For the reaction

$2H_2S\,(g) \rightleftharpoons 2H_2\,(g) + S_2\,(g)$ the value of K_C is 1.0×10^{-6}.

Solution $2H_2S\,(g) \rightleftharpoons 2H_2\,(g) + S_2\,(g)$

$0.1 - X \qquad X \qquad X/2 \quad$ At eq.

V = 0.4 L

$$K_C = \frac{[H_2]^2\,[S_2]}{[H_2S]^2}$$

$$= \frac{[X/V]^2\,[X/2V]}{[(0.1-X)/V]^2}$$

As X is very-very small so $0.1 - X = 0.1$

$$K_C = \frac{X^3}{2V\,(0.1)^2} = 1.0 \times 10^{-6}$$

$$X^3 = 1.0 \times 10^{-6} \times 2 \times 0.4 \times 0.1 \times 0.1$$

$$= 8 \times 10^{-9}$$

$$X = 2 \times 10^{-3}$$

$$\%\ \text{dissociation} = \frac{2 \times 10^{-3} \times 100}{0.1}$$

$$= 2\ \%$$

17. The vapour density of N_2O_4 at a certain temperature is 30. Calculate, the percentage dissociation of N_2O_4 at this temperature.

Solution Normal molecular mass of N_2O_4 $= 28 + 64 = 92$

Normal vapour density (V.D. before dissociation)

$$(D) = \frac{\text{Normal molecular mass}}{2} = \frac{92}{2} = 46$$

Vapour density after dissociation (d) = 30.

$$N_2O_4(g) \leftrightarrow 2NO_2\,(g)$$

$$\text{Degree of dissociation (x)} = \frac{D-d}{d(n-1)}\ .$$

$$= \frac{46-30}{30\,(2-1)} = \frac{16}{30 \times 1} = 0.535$$

$$x\,\% = 53.5$$

18. What is the value of K_c for the reaction,

$I_2\,(g) \rightleftharpoons 2I\,(g)$

at 1473 K, when 1 mole of I_2 (g) introduced into an evacuated 1 litre flask such that only 5 % of it gets dissociated?

Solution For this reaction

$I_2\,(g) \rightleftharpoons$	$2I\,(g)$	
1	0	(Initially)
1 – X	2X	(at eq.)

$$Kc = \frac{[I]^2}{[I_2]} = \frac{(2X)^2}{1-X}\,.$$

As degree of dissociation is 5 %

$$X = 0.05$$

$$\text{So}\quad Kc = \frac{(2\times 0.05)^2}{1-0.05}$$

$$= \frac{0.01}{0.95} = 0.0105$$

19. The K_P for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is 640 mm at 775 K. Calculate the percentage dissociation of N_2O_4 at equilibrium pressure of 160 mm. At what pressure, the dissociation will be 50%?

Solution

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Mole before eq.	1		0
Mole at eq.	(1 – X)		2X

$$K_P = \frac{4X^2}{(1-X)} \times [P/\textstyle\sum_n]^{\Delta n}$$

$$640 = \frac{4X^2}{(1-X)} \text{ x } \frac{160}{(1+X)}\,.$$

$$4 = \frac{4X^2}{1-X^2}\,.$$

$$1 - X^2 = X^2$$

$$2X^2 = 1$$

$$X^2 = ½$$

$$X = 0.707 = 70.7\ \%$$

$$640 = \frac{2\times(0.5)^2}{0.5} \text{ x } \frac{P}{1.5}\,. \qquad \text{(as X = 0.5)}$$

$$P = 480 \text{ mm}$$

20. 0.1 mole of N_2O_4 (g) was sealed in a tube under atmospheric conditions at 25°C. Calculate the number of mole of NO_2 (g) present, if the equilibrium $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$, ($K_P$ = 0.14) is reached after some time.

Solution

N_2O_4	$\rightleftharpoons$	$2NO_2$
0.1		α
(0.1 – α)		2 α

As P ∝ 0.1

So 1 ∝ 0.1

If V and T are constant

$$P \propto 0.1 + \alpha$$

$$P = [(0.1 + \alpha)/0.1]$$

$$K_P = \frac{(2\alpha)^2}{(0.1-\alpha)} \times [P/(0.1+\alpha)]^1$$

$$K_P = \frac{40\,\alpha^2}{(0.1-\alpha\,)}\,.$$

$$\frac{40\,\alpha^2}{(0.1-\alpha)} = 0.14$$

$$\alpha = 0.017$$

$$NO_2 = 0.017 \times 2 = 0.034 \text{ mole.}$$

21. NH_3 is heated at 15 atm from 27°C to 347°C assuming volume constant. The new pressure becomes 50 atm at equilibrium of the reaction $2NH_3 \rightleftharpoons N_2 + 3H_2$. Calculate per cent of mole of NH_3 actually decomposed.

Solution

	$2NH_3$	$\rightleftharpoons$	N_2	+	$3H_2$
Initial mole	α		0		0
Mole at eq.	(α – 2X)		X		3X

Initial pressure of NH_3 of α mole

= 15 atm at 27°C

The pressure of α mole of NH_3

= P atm at 347°C

$$\frac{15}{300} = \frac{P}{620}\,.$$

$$P = 31 \text{ atm}$$

At constant volume and at 347°C

Mole ∝ Pressure

Before eq. $\alpha \propto 31$

After eq . $\alpha + 2X \propto 50$

$$\frac{\alpha + 2X}{\alpha} = \frac{50}{31}\ .$$

$$X = \frac{19}{62}\ \alpha$$

% of NH_3 decomposed $= \frac{2X}{\alpha} \times 100$

$$= \frac{2 \times 19\alpha}{62 \times \alpha} \times 100$$

$= 61.3\ \%$

22. (i) Find the vapour density of nitrogen tetroxide which dissociates according to this equation.

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

at 373 K given the degree of dissociation of N_2O_4 is 0.8

(ii) Also find the total pressure of the mixture at equilibrium (Given Kc = 0.2616 mole litre^{-1})

Solution

(i) The relationship between th degree of dissociation and the densities is given as

$$\alpha = \frac{D - D'}{D}$$

Here D = calculate vapour density

D' = observed vapour density at equilibrium

$$D \text{ of } N_2O_4 = \frac{\text{molecular weight}}{2} = \frac{92}{2} = 46$$

As α is given as equal to 0.8,

$$0.8 = \frac{46 - D'}{D'}$$

$D' = 25.56$

(ii) As $K_P = K_C (RT)^{\Delta n}$

$$N_2O_4 \rightleftharpoons 2NO_2$$

$\Delta n = 2 - 1 = 1$

So $K_P = K_C\ (RT)^2$

$= 0.2616 \times 0.082 \times 373 = 8$ atm

Suppose the initial concentration of N_2O_4 is 1 mole.

Initial concentration of $NO_2 = 0$

As the degree of dissociation is 0.8 equilibrium concentrations of N_2O_4 and NO_2 are $(1 - 0.8 = 0.2)$ and $(2 \times 0.8 = 1.6)$ respectively.

So the total number of moles at equilibrium

$= 0.2 + 1.6 = 1.8$ mole.

If P is the total pressure at equilibrium, we get

$$P_{NO2} = \frac{2 \times 0.8}{1.8} \times P$$

$$PN_2O_4 = \frac{0.2}{1.8} \times P$$

$$K_P = \frac{P^2\ NO_2}{PN_2O_4}\ .$$

$$8 \text{ atm} = \frac{(2 \times 0.8/1.8)^2\ P^2}{0.2\ P/1.8}$$

On solving, we get

Total pressure (P) = 1.125 atm

Relation between Standard Gibb's Free Energy and Equilibrium Constant:

Or

Van't Hoff Reaction Isotherm:

It shows the free energy change of a reaction at any given temperature, pressure and composition of the reacting system as follows:

$$\Delta G = \Delta G^\circ + RT \text{ In } J$$

As at equilibrium ΔG is 0 so $\Delta G^\circ = -RT \text{ In } J_{eq}$

Here J stands for reaction quotient of partial pressures of products and reactants.

$$\frac{\text{Concentration terms of products}}{\text{Concentration terms of reactants}}$$

J_{eq} means the partial pressure of the products and the reactants at the equilibrium i.e., J_{eq} can be replaced by Kp.

So $\Delta G^\circ = -RT \text{ In } Kp$

$\Delta G^\circ = -2.303\ RT \log_{10} K$

If $\Delta G^\circ > 0$ (+ve), $K < 1$

Backward reaction is feasible

If $\Delta G^\circ < 0$ (–ve), $K > 1$

Forward reaction is feasible

If $\Delta G^\circ = 0$, $K = 0$

Equilibrium state is obtained.

Illustrations

23. Calculate the value of log K_P for the reaction,

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

at 25°C. The standard enthalpy of formation of NH_3 (g) is –46 kJ and standard entropies of N_2 (g), H_2 (g), and NH_3 (g) are 191, 130, 192 JK^{-1} mol^{-1} respectively. ($R = 8.3\ JK^{-1}\ mol^{-1}$)

Solution $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

At equilibrium

$-\Delta G^\circ = 2.303\ RT \log_{10} K_P$ …… (i)

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

Given: ΔH° for $NH_3 = -46$ kJ

$\Delta S^\circ\text{reaction} = 2 \times S^\circ NH_3 - S^\circ N_2 - 3 \times S^\circ H_2$

$= 2 \times 192 - 191 - 3 \times 130$

$= -197$ J

$T = 273 + 25 = 298$ K

$\Delta G^\circ = -92 \times 10^3 - 298 \times (-197)$

(ΔH° for reaction $= -46 \times 2$ kJ)

$= -92000 + 58706$

$\Delta G^\circ = -33294$ J

From equation (i)

$+33294 = 2.303 \times 298 \times 8.3 \log_{10} K_P$

$\log_{10} K_P = 5.845.$

24. Given values of ΔG°_t at 25°C for liquid ethanol (–174 kJ/mol) and gaseous ethanol (–168.6 kJ/mol), Calculate the vapour pressure of ethanol at 25°C?

Solution $C_2H_5OH\,(l) \rightleftharpoons C_2H_5OH\,(g)$

$\Delta G^\circ = [\Delta G^\circ_f (C_2H_5OH)\,(g) - \Delta G^\circ_f (C_2H_5OH)\,(g)]$

$\Delta G^\circ = (1)(-168.6) - (1)(-174.9)$

$= +6.3$ kJ

$\Delta G^\circ = -RT \text{ In } K$

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

$$\frac{-(6.3\ \text{kJ/mol})}{[8.314 \times 10^{-3}\ \text{kJ/(K.mol)}]\ (298\ \text{K})} = -2.54$$

$K = e^{-2.54} = 0.079$

$K = K_P = PC_2H_5OH = 0.079$ atm

LE CHATELIERS PRINCIPLE

It describes the effect of change in concentration, pressure and temperature on the reversible system.

According to it, "If the system at equilibrium is subjected to a change of concentration or temperature or pressure, the system adjusts itself in such a way as to annual the effect of that change i.e., the effect of these changes can be neglected or minimized."

Effect of Concentration

- An increases in concentration of any substance favours the reaction in which it is used up i.e., in opposite direction.
- An increase of concentration of reactant favours formation of more product i.e., forward reaction.
- Increase in concentration of product favours backward reaction. i.e., its continuous removal is essential for more formation of it.

Effect of Pressure

- High pressure is favorable for the reaction in which there is a decrease in volume or nr > np.
- Low pressure is favorable for the reaction in which there is an increase in volume or nr < np.
- Pressure is kept constant when volume is constant or nr = np.

  Here nr = moles of gaseous reactant

  np = moles gaseous product

Effect of Temperature

- Increase in temperature favours the forward reaction in the endothermic reaction ($\Delta H = +ve$)
- Decrease in temperature favours the forward reaction in the exothermic reaction ($\Delta H = -ve$).

Applications of Le Chatelier's Principle

1. On Physical Equilibrium

(i) **Ice-Water System (Melting of Ice)**:

Ice ↔ water – heat ($\Delta H = +ve$)

As it is an endothermic process and there is a decrease in volume so, the favourable conditions for melting of ice are high temperature and high pressure

(ii) **Water-Steam System (Evaporation of Water):**

Water ↔ steam – heat ($\Delta H = +ve$)

(As it is an endothermic process and there is a) increase in volume so, the favourable conditions for evaporation of water are high temperature and low pressure.

(iii) **Solubility of Gases in Liquids:** When a gas dissolves in a liquid, there is a decrease in its volume so an increase in pressure will favour the dissolution of a gas in liquid i.e., solubility of a gas is directly proportional to partial pressure of the gas (Henry's law)

On opening carbonated water bottle, CO_2 comes out as its pressure decreases.

(iv) **Effect of Temperature on Solubility:** Exothermic substances like CaO, $Ca(OH)_2$, KOH are more soluble in cold water than in hot water i.e., low temperature favours their solubility.

Endothermic substances like sugar, urea are more soluble in hot water than in cold water i.e., high temperature favours their solubility.

(v) **Effect of Pressure on Boiling Point:** On increasing pressure boiling point increases as vapour pressure decreases.

(vi) **Effect of Pressure on Melting Point**:

$$\text{Solid } (V_1) \rightleftharpoons \text{Liquid } (V_2)$$

If $V_1 > V_2$ melting is favoured by increase of pressure so melting point decreases for such solids.

If $V_1 < V_2$ melting is favoured by lower pressure so melting point increases for such solids.

REMEMBER

- Conversion of a solid into liquid, liquid into gas is favoured by high temperature in most of the cases.
- Melting of solids is accompanied by increase of volume so low pressure favours their melting while high pressure favours solidification.

2. On Chemical Equilibrium

(i) **Formation of Nitric Oxide**:

$$N_2\,(g) + O_2\,(g) \leftrightarrow 2NO\,(g) - 43200 \text{ calorie}$$

Here favourable conditions for formation of NO are more concentration of N_2, O_2, constant pressure (as np = nr) and high temperature (as it is endothermic).

(ii) **Formation of Ammonia**:

$$N_2\,(g) + 3H_2\,(g) \leftrightarrow 2NH_3\,(g) + 22400 \text{ cal.}$$

Favourable conditions for NH_3 formation are more concentration of N_2, H_2, high pressure (as np < nr) and low temperature (as it is exothermic).

Effect of Adding Inert Gas on Equilibrium

- When np is equal to nr there is no effect of adding an inert gas either at constant volume or pressure.
- When np ≠ nr there is no effect of adding an inert gas at constant volume.
- When np ≠ nr at constant pressure on adding inert gas equilibrium will shift towards more volume side. e.g., Dissociation of ammonia will be more at constant pressure by adding inert gas like argon (Ar).

Solved Problems from the IITs

1. For the reaction,

$$CO\,(g) + 2H_2\,(g) \rightleftharpoons CH_3OH\,(g)$$

hydrogen gas is introduced into a five litre flask at 327°C, containing 0.2 mole of CO (g) and a catalyst, until the pressure is 4.92 atmosphere. At this point 0.1 mole of CH_3OH (g) is formed. Calculate the equilibrium constants K_P and K_C.

[IIT 1990]

Solution Let the number of moles of hydrogen introduced be 'm' moles.

Total moles of CO and hydrogen = 0.2 + m

As PV = nRT

P = 4.92 atm,

V = 5 litre

R = 0.082

T = (273 + 327) = 600 K

$4.92 \times 5 = 0.082 \times 600 \times (0.2 + m)$

$$0.2 + m = \frac{4.92 \times 5}{0.082 \times 600}.$$

m = 0.3 mole

$$CO\,(g) + 2H_2\,(g) \rightleftharpoons CH_3OH\,(g)$$

At eq.	$0.2 - X$	$0.3 - 2X$	X
	$0.2 - 0.1$	$0.3 - 0.2$	0.1
	$= 0.1$	$= 0.1$	
Active Masses	$\frac{0.1}{5}$	$\frac{0.1}{5}$	$\frac{0.1}{5}$

According to law of mass action

$$K_C = \frac{[CH_3OH]}{[CO]\,[H_2]^2}.$$

$$= \frac{(0.1/5)}{(0.1/5) \times (0.1/5)^2}.$$

$= 2500\ mol^{-2}\ L^2$

$K_P = K_C\,(RT)^{\Delta n}$

As $\Delta n = -2$

$K_P = 2500 \times (0.082 \times 600)^{-2}$

$$K_P = \frac{2500}{49.2 \times 49.2}.$$

$= 1.0327\ atm^{-2}$.

2. 0.15 mole of CO taken in a 2.5 litre flask is maintained at 705 K along with a catalyst so that the following reaction can take place:

$$CO\,(g) + 2H_2\,(g) \rightleftharpoons CH_3OH\,(g)$$

Hydrogen is introduced until the total pressure of the system is 8.5 atm at equilibrium and 0.08 mole of methanol is formed. Calculate (i) K_P and K_C (ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place.

[IIT 1993]

Solution Let the total number of moles of gases be n at equilibrium.

As PV = nRT

Given P = 8.5 atm, V = 2.5 L

$R = 0.0821\ atm\ L\ mol^{-1}\ K^{-1}$

T = 705 K

$$n = \frac{8.5 \times 2.5}{0.0821 \times 705} = 0.367\ mol$$

$$CO\,(g) + 2H_2\,(g) \rightleftharpoons CH_3OH\,(g)$$

Initial mole	0.15	$(nH_2)_0$	0
At eq.	$0.15 - X$	$[(nH_2)_0 - 2X]$	$X = 0.08$

Number of moles of CO at equilibrium

= 0.15 – 0.08 = 0.07 mole

Number of moles of H_2 at equilibrium

= total moles – moles of CO – moles of CH_3OH

= (0.367 – 0.07 – 0.08)

= 0.217 mole

According to law of mass action

$$K_C = \frac{[CH_3OH]}{[CO]\,[H_2]^2}.$$

$$= \frac{(0.08/25)}{(0.07/2.5) \times (0.217 \times 2.5)^2}.$$

$= 151.6\ mol^{-2}\ L^2$

$K_P = K_C\,(RT)^{\Delta n}$

$= 151.6 \times (0.0821 \times 705)^{-2}$

$= 0.045\ atm^2$

As $[(n_{H2})_0 - 2X] = 0.217$

$(n_{H2})_0 = 0.217 + 2 \times 0.08$

= 0.377 mole

$(n_{CO})_0 = 0.15$

Total moles (n_0) = 0.377 + 0.15 = 0.527

$$\text{So}\ \ p_0 = \frac{n_0 RT}{V}$$

$$= \frac{0.527 \times 0.0821 \times 705}{2.5}$$

= 12.20 atm.

3. At temperature T, the compound AB_2 (g) dissociates according to the reaction,

$$2AB_2\,(g) \rightleftharpoons 2AB\,(g) + B_2\,(g)$$

with a degree of dissociation, X, which is small compared with unity. Deduce the expression or X in terms of the equilibrium constant, K_P and the total pressure P.

[IIT 1994]

Solution $2AB_2\,(g) \rightleftharpoons 2AB\,(g) + B_2\,(g)$

	$2AB_2\,(g)$	$2AB\,(g)$	$B_2\,(g)$
At. eq.	$(1 - X)$	X	$\frac{X}{2}$

Total moles at equilibrium = $1 - X + X + \frac{X}{2}$

$$= \frac{2 + X}{2}$$

$$p\,(AB_2) = \frac{2(1 - X)}{(2 + X)}\,.\,P$$

$$p\,(AB) = \frac{2X}{(2 + X)}\,.\,P$$

$$p\,(B_2) = \frac{X}{(2 + X)}\,.\,P$$

$$K_P = \frac{(p_{AB})^2\,(p_{B2})}{(p_{AB2})^2}$$

$$= \frac{[\{2X/(2 + X)\}.\,P]^2\,(X/2 + X)\,.P}{[2\,(1 - X)/(2 + X)\,.\,P]^2}$$

$$= \frac{X^3\,P}{(2 + X)\,(1 - X)^2}\,.$$

As X is very small, $(2 + X) = 2$ and $(1 - X) = 1$

$$\text{So } K_P = \frac{X^3\,P}{2}$$

$$X^3 = \frac{2\,K_P}{P}$$

$$X = (2K_P/P)^{1/3}$$

4. A sample of air consisting of N_2 and O_2 was heated to 2500 K until the equilibrium N_2 (g) + O_2 (g) $\rightleftharpoons$ 2NO (g)

was established with an equilibrium constant $Kc = 2.1 \times 10^{-3}$. At equilibrium, the mole % of NO was 1.8. Estimate the initial composition of air in mole fraction of N_2 and O_2

[IIT 1997]

Solution $N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)$

Let the total number of moles of N_2 and O_2 at initially = 100

Number of moles of N_2 at initially = a

Let the number of moles of NO present at equilibrium = X

	$N_2\,(g)$ +	$O_2\,(g)$	$\rightleftharpoons$ $2NO\,(g)$
Initially	a	100 – a	0
At eq.	(1 – X)	(100 – a – X)	2X

$$\frac{2X}{100} = \frac{1.8}{100}\,.$$

$$X = 0.9$$

$$\text{As } K_C = \frac{[NO]^2}{[N_2]\,[O_2]}\,.$$

$$\text{So } \frac{2.1 \times 10^{-3} = (2X)^2}{(a - X)\,(100 - a - X)}\,.$$

$$2.1 \times 10^{-3} = \frac{(2 \times 0.9)^2}{(a - 0.9)\,(100 - a - 0.9)}\,.$$

$$a = 79$$

% if N_2 in air = 79 %

% of O_2 in air = 100 – 79 = 21 %

5. When 3.06 g of solid NH_4HS is introduced into a two-litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.

(i) Calculate K_C and K_P for the reaction at 27°C.

(ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask?

[IIT 1999]

Solution (i) $NH_4HS\,(s) \rightleftharpoons NH_3\,(g) + H_2S\,(g)$

	$NH_4HS\,(s)$	$NH_3\,(g)$	$H_2S\,(g)$
Initial moles	$\frac{3.06}{51} = 0.06$	0	0
Eq. moles	(0.06 – 0.018)	0.018	0.018
Molar conc.	1	$\frac{0.018}{2}$	$\frac{0.018}{2}$

$$\alpha = \frac{0.06 \times 30}{100} = 0.018$$

$$K_C = \frac{[NH_3]\,[H_2S]}{[NH_4HS]}$$

$$= \frac{(0.018/2)^2}{1}$$

$= 8.1 \times 10^{-5}$ mol L^{-1}

$K_P = K_C \times (RT)^{\Delta n}$

$K_P = 8.1 \times 10^{-5} \times (0.082 \times 300)^2$

$= 0.079$ atm^2

(ii) Addition of NH_4HS will not effect the equilibrium position.

6. In the following equilibrium,

$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

When 5 moles of each is taken and the temperature is kept at 298 K, the total pressure was found to be 20 bar.

Given: $\Delta G^\circ_f\,(N_2O_4) = 100$ kJ

$\Delta G^\circ_f\,(NO_2) = 50$ kJ

(a) Find ΔG of the reaction at 298 K.

(b) Find the direction of the reaction.

[IIT 2004]

Solution Reaction quotient $= \dfrac{[P\,(NO_2)\,]^2}{P\,(N_2O_4)}$

$= \dfrac{100}{10} = 10$

$\Delta G^\circ_{\text{Reaction}} = 2\,\Delta G^\circ_f\,(NO_2) - \Delta G^\circ_f\,(N_2O_4)$

$= 2 \times 50 - 100 = 0$

Here negative value of ΔG shows that reaction will be in forward direction.

7. The equilibrium constant of the reaction,

$A_2\,(g) + B_2\,(g) \rightleftharpoons 2AB\,(g)$

at 100°C is 50. If a one litre flask containing one mole of flask containing one mole of A_2 is connected to a two litre flask containing two moles of B_2, how many moles of AB will be formed at 373 K?

[IIT 1985]

Solution

$A_2\,(g) + B_2\,(g) \rightleftharpoons 2AB\,(g)$

Initially $1 \quad 2 \quad 0$

at eq. $(1 - X) \quad (2 - X) \quad 2X$

(total volume = 3 lit)

Active masses $\dfrac{(1 - X)}{3} \quad \dfrac{(2 - X)}{3} \quad \dfrac{2X}{3}$

According to law of mass action,

$$K_C = \frac{[AB]^2}{[A_2]\,[B_2]} = \frac{(2x/3)^2}{\frac{(1 - X)}{3}\,\frac{(2 - X)}{3}}.$$

$$= \frac{4X^2}{(1 - X)\,(2 - X)}.$$

$$\frac{4X^2}{(1 - X)\,(2 - X)} = 50$$

$4X^2 = (2 - 3X + X^2) \times 50$

$2X^2 = (2 - 3X + X^2) \times 25$

$23X^2 - 75X + 50 = 0$

$$X = \frac{75 \pm \sqrt{\{(75)^2 - 4 \times 23 \times 50\}}}{2 \times 23}$$

$X = 2.317$ or 0.934

The value of X cannot be more than one that is, greater than the number of moles of A_2 so

$X = 0.943$

Number of moles of AB = 2X

$= (2 \times 0.934)$

$= 1.868$

8. At a certain temperature, equilibrium constant (K_C) is 16 for the reaction:

$SO_2\,(g) + NO_2\,(g) \rightleftharpoons SO_3\,(g) + NO\,(g)$

If we take one mole of each of the four gases in one litre container, what would be the equilibrium concentration of NO and NO_2?

[IIT 1987]

Solution $SO_2\,(g) + NO_2\,(g) \rightleftharpoons SO_3\,(g) + NO\,(g)$

Initial conc. $1 \quad 1 \quad 1 \quad 1$

Eq. conc. $(1 - X) \quad (1 - X) \quad 1 + X \quad 1 + X$

According to law of mass action

$$K_C = \frac{[SO_3]\,[NO]}{[SO_2]\,[NO_2]}\,.$$

$$= \frac{(1 + X)\,(1 + X)}{(1 - X)\,(1 - X)} = 16$$

$$\frac{1 + X}{1 - X} = 4$$

$$1 + X = 4 - 4X$$

$$5X = 3$$

$$X = 3/5 = 0.6$$

Concentration of NO_2 at equilibrium = (1 – 0.6)

= 0.4 mole

Concentration of NO at equilibrium = (1 + 0.6)

= 1.6 mole

9. N_2O_4 is 25% dissociated at 37°C and one atmospheric pressure. Calculate (i) K_P and (ii) the percentage dissociation at 0.1 atmospheric and 37°C.

[IIT 1988]

Solution $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

$$\begin{array}{lcc} \text{Initial} & 1 & 0 \\ \text{At eq.} & (1 - X) & 2X \end{array}$$

Total moles = (1 – X) + 2X = (1 + X)

$$p\,(N_2O_4) = \frac{(1 - X)}{(1 + X)}\,.\,P$$

$$p\,(NO_2) = \frac{2X}{(1 + X)}\,.\,P$$

Given X = 0.25 and P = 1 atm

$$p\,(N_2O_4) = \frac{(1 - 0.25)}{(1 + 0.25)} \times 1 = 0.6 \text{ atm}$$

$$p\,(NO_2) = \frac{(2 \times 0.25)}{(1 + 0.25)} \times 1 = 0.4 \text{ atm}$$

$$K_P = \frac{(p_{NO2})^2}{p\,N_2O_4} = \frac{0.4 \times 0.4}{0.6} = 0.267 \text{ atm}$$

Let the degree of dissociation of N_2O_4 at 0.1 atm be ‘a’ then,

$$p\,(N_2O_4) = \frac{(1 - a)}{(1 + a)} \times 0.1$$

$$p\,(NO_2) = \frac{2a}{(1 + a)} \times 0.1$$

$$K_P = \frac{(2a/1 + a)^2 \times (0.1)^2}{\dfrac{(1 - a)}{(1 + a)} \times 0.1}$$

$$= \frac{4a^2 \times 0.1}{(1 - a)\,(1 + a)} = \frac{0.4\,a^2}{(1 - a^2)}$$

$$0.267 = \frac{0.4\,a^2}{(1 - a^2)}$$

$$0.267 = 0.667\,a^2$$

$$a = 0.632$$

So dissociation of N_2O_4 = 63.2 %.

10. One mole of nitrogen and three moles of hydrogen are mixed in a 4 litre container. If 0.25 % of nitrogen is converted into ammonia by the following reaction:

$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$,

Find the equilibrium constant (K_C) in concentration units. What will be the value of K for the following equilibrium?

$½\,N_2\,(g) + 3/2\,H_2\,(g) \rightleftharpoons NH_3\,(g)$.

[IIT 1989]

Solution $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

$$\begin{array}{lccc} \text{At eq.} & (1 - X) & (3 - 3X) & 2X \\ \text{Active masses} & \dfrac{(1 - 0.0025)}{4} & \dfrac{(3 - 0.0075)}{4} & \dfrac{(0.0050)}{4} \end{array}$$

According to law of mass action

$$K_C = \frac{[NH_3]^2}{[N_2]\,[H_2]_3}\,.$$

$$= \frac{(0.0050/4)^2}{(0.9975/4)\,(2.9925/4)^3}\,.$$

$= 1.49 \times 10^{-5}$ lit^{2}mol^{-2}

K for the reaction,

$½\,N_2\,(g) + 3/2\,H_2\,(g) \rightleftharpoons NH_3\,(g)$

is equal to $\sqrt{K_C}$.

$K = \sqrt{K_C} = \sqrt{(1.49 \times 10^{-5})}$

$= 3.86 \times 10^{-3}$ lit mol^{-1}

11. The equilibrium constant K_P for the reaction,

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$$

is 900 atm^{-1} at 800 K. A mixture containing SO_3 and O_2 having initial partial pressure of 1 and 2 atm respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K.

[IIT 1989]

Solution The system in the initial stage does not have SO_2. SO_3 decomposes to form SO_2 and O_2 until equilibrium is reached. The partial pressure of SO_3 decreases.

Suppose the decrease in partial pressure is 2X.

$$\begin{array}{llll} & 2SO_2\,(g) + & O_2\,(g) \rightleftharpoons & 2SO_3\,(g) \\ \text{At eq.} & 2X & 2 + X & 1 - 2X \end{array}$$

According to law of mass action

$$K_P = \frac{(1-2X)^2}{(2X)^2\,(2+X)}.$$

[As (2 + X) = 2]

$$900 = \frac{(1-2X)^2}{8X^2}$$

$$\frac{1-2X}{X} = 84.45$$

On solving

$X = 0.0115$ atm

So the partial pressures at equilibrium are:

$p\,(SO_2) = 2 \times 0.0115 = 0.023$ atm

$p\,(O_2) = 2 + 0.0115 = 2.0115$ atm

$p\,(SO_3) = 1 - 2 \times 0.0115 = 0.977$ atm

12. For the reaction,

$$CO\,(g) + 2H_2\,(g) \rightleftharpoons CH_3OH\,(g)$$

hydrogen gas is introduced into a five litre flask at 327°C, containing 0.2 mole of CO (g) and a catalyst, until the pressure is 4.92 atmosphere. At this point 0.1 mole of CH_3OH (g) is formed. Calculate the equilibrium constants K_P and K_C.

[IIT 1990]

Solution Let the number of moles of hydrogen introduced be 'm' moles.

Total moles of CO and hydrogen = 0.2 + m

As PV = nRT

P = 4.92 atm,

V = 5 litre

R = 0.082

T = (273 + 327) = 600 K

$4.92 \times 5 = 0.082 \times 600 \times (0.2 + m)$

$$0.2 + m = \frac{4.92 \times 5}{0.082 \times 600}.$$

m = 0.3 mole

$$\begin{array}{llll} & CO\,(g) + & 2H_2\,(g) \rightleftharpoons & CH_3OH\,(g) \\ \text{At eq.} & 0.2 - X & 0.3 - 2X & X \\ & 0.2 - 0.1 & 0.3 - 0.2 & 0.1 \\ & = 0.1 & = 0.1 & \\ \text{Active Masses} & \frac{0.1}{5} & \frac{0.1}{5} & \frac{0.1}{5} \end{array}$$

According to law of mass action,

$$K_C = \frac{[CH_3OH]}{[CO]\,[H_2]^2}.$$

$$= \frac{(0.1/5)}{(0.1/5) \times (0.1/5)^2}.$$

$= 2500\ mol^{-2}\,L^2$

$K_P = K_C\,(RT)^{\Delta n}$

As $\Delta n = -2$

$K_P = 2500 \times (0.082 \times 600)^{-2}$

$$K_P = \frac{2500}{49.2 \times 49.2}.$$

$= 1.0327\ atm^{-2}$.

13. 0.15 mole of CO taken in a 2.5 litre flask is maintained at 705 K along with a catalyst so that the following reaction can take place:

$$CO\,(g) + 2H_2\,(g) \rightleftharpoons CH_3OH\,(g)$$

Hydrogen is introduced until the total pressure of the system is 8.5 atm at equilibrium and 0.08 mole of methanol is formed. Calculate (i) K_P

and K_C (ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place.

[IIT 1993]

Solution Let the total number of moles of gases be n at equilibrium.

As PV = nRT

Given P = 8.5 atm, V = 2.5 L

$R = 0.0821$ atm L mol^{-1} K^{-1}

T = 705 K

$$n = \frac{8.5 \times 2.5}{0.0821 \times 705} = 0.367 \text{ mol}$$

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Initial mole 0.15 $(nH_2)_0$ 0

At eq. $0.15 - X$ $[(nH_2)_0 - 2X]$ $X = 0.08$

Number of moles of CO at equilibrium

= 0.15 – 0.08 = 0.07 mole

Number of moles of H_2 at equilibrium

= total moles – moles of CO – moles of CH_3OH

= (0.367 – 0.07 – 0.08)

= 0.217 mole

According to law of mass action

$$K_C = \frac{[CH_3OH]}{[CO]\,[H_2]^2}\,.$$

$$= \frac{(0.08/25)}{(0.07/2.5) \times (0.217 \times 2.5)^2}\,.$$

$= 151.6\ mol^{-2}\ L^2$

$K_P = K_C(RT)^{\Delta n}$

$= 151.6 \times (0.0821 \times 705)^{-2}$

$= 0.045\ atm^2$

As $[(n_{H2})_0 - 2X] = 0.217$

$(n_{H2})_0 = 0.217 + 2 \times 0.08$

= 0.377 mole

$(n_{CO})_0 = 0.15$

Total moles $(n_0) = 0.377 + 0.15 = 0.527$

$$\text{So } p_0 = \frac{n_0 RT}{V}$$

$$= \frac{0.527 \times 0.0821 \times 705}{2.5}$$

= 12.20 atm.

14. At temperature T, the compound AB_2 (g) dissociates according to the reaction,

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

with a degree of dissociation, X, which is small compared with unity. Deduce the expression for X in terms of the equilibrium constant, K_P and the total pressure P.

[IIT 1994]

Solution $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$

At. eq. $(1 - X)$ X $\frac{X}{2}$

Total moles at equilibrium $= 1 - X + X + \frac{X}{2}$

$$= \frac{2 + X}{2}$$

$$p(AB_2) = \frac{2(1 - X)}{(2 + X)}\,.\,P$$

$$p(AB) = \frac{2X}{(2 + X)}\,.\,P$$

$$p(B_2) = \frac{X}{(2 + X)}\,.\,P$$

$$K_P = \frac{(p_{AB})^2\,(p_{B2})}{(p_{AB2})^2}$$

$$= \frac{[\{2X/(2 + X)\}.\,P]^2\,(X/2 + X)\,.P}{[2\,(1 - X)/(2 + X)\,.\,P]^2}$$

$$= \frac{X^3\,P}{(2 + X)\,(1 - X)^2}\,.$$

As X is very small, (2 + X) = 2 and (1 – X) = 1

$$\text{So } K_P = \frac{X^3\,P}{2}$$

$$X^3 = \frac{2\,K_P}{P}$$

$X = (2K_P/P)^{1/3}$

15. A sample of air consisting of N_2 and O_2 was heated to 2500 K until the equilibrium $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

was established with an equilibrium constant $Kc = 2.1 \times 10^{-3}$. At equilibrium, the mole % of

NO was 1.8. Estimate the initial composition of air in mole fraction of N_2 and O_2

[IIT. 1997]

Solution $N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)$

Let the total number of moles of N_2 and O_2 at initially = 100

Number of moles of N_2 at initially = a

Let the number of moles of NO present at equilibrium = X

	$N_2\,(g)$ +	$O_2\,(g)$	$\rightleftharpoons$ $2NO\,(g)$
Initially	a	100 – a	0
At eq.	(1 – X)	(100 – a – X)	2X

$$\frac{2X}{100} = \frac{1.8}{100}.$$

X = 0.9

$$\text{As } K_C = \frac{[NO]^2}{[N_2]\,[O_2]}.$$

$$\text{So } 2.1 \times 10^{-3} = \frac{(2X)^2}{(a - X)\,(100 - a - X)}.$$

$$2.1 \times 10^{-3} = \frac{(2 \times 0.9)^2}{(a - 0.9)\,(100 - a - 0.9)}.$$

a = 79

% if N_2 in air = 79 %

% of O_2 in air = 100 – 79 = 21 %

16. When 3.06 g of solid NH_4HS is introduced into a two–litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.

(i) Calculate K_C and K_P for the reaction at 27°**C.**

(ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask?

[IIT 1999]

Solution (i) $NH_4HS\,(s) \rightleftharpoons NH_3\,(g) + H_2S\,(g)$

	$NH_4HS\,(s)$	$NH_3\,(g)$	$H_2S\,(g)$
Initial moles	$\frac{3.06 = 0.06}{51}$	0	0
Eq. moles	(0.06 – 0.018)	0.018	0.018
Molar conc.	1	$\frac{0.018}{2}$	$\frac{0.018}{2}$

$$\alpha = \frac{0.06 \times 30}{100} = 0.018$$

$$K_C = \frac{[NH_3]\,[H_2S]}{[NH_4HS]}$$

$$= \frac{(0.018/2)^2}{1}$$

$= 8.1 \times 10^{-5}$ mol L^{-1}

$K_P = K_C \times (RT)^{\Delta n}$

$K_P = 8.1 \times 10^{-5} \times (0.082 \times 300)^2$

$= 0.079$ atm^2

(ii) Addition of NH_4HS will not effect the equilibrium position.

17. In the following equilibrium,

$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

When 5 moles of each is taken and the temperature is kept at 298 K, the total pressure was found to be 20 bar.

Given: $\Delta G^\circ_f(N_2O_4) = 100$ kJ

$\Delta G^\circ_f\,(NO_2) = 50$ kJ

(a) Find ΔG of the reaction at 298 K.

(b) Find the direction of the reaction.

[IIT 2004]

Solution $\text{Reaction quotient} = \frac{[P\,(NO_2)\,]^2}{P\,(N_2O_4)}$

$$= \frac{100}{10} = 10$$

$\Delta G^\circ_{\text{Reaction}} = 2\,\Delta G^\circ_f\,(NO_2) - \Delta G^\circ_f\,(N_2O_4)$

$= 2 \times 50 - 100 = 0$

As $\Delta G = \Delta G^\circ - 2.303\,RT \log_{10} Q_P$

$= 0 - 2.303 \times 8.314 \times 298 \log_{10} 10$

= –57.05.8 J

= –5.705 kJ

Here negative value of ΔG shows that reaction will be in forward direction.

MULTIPLE-CHOICE QUESTIONS

Straight Objective Type Questions (Single Choice only)

1. In a reaction $A_2\ (g) + 4B_2\ (g) \leftrightarrow 2AB_4\ (g);\ \Delta H < 0$. The formation of AB_4 (g) will be favoured by

   a. low temperature and high pressure

   b. high temperature and high pressure

   c. low temperature and low pressure

   d. high temperature and low pressure

2. For which of the following reaction, $K_p = K_c$?

   a. $2NOCl\ (g) \leftrightarrow 2NO\ (g) + Cl_2\ (g)$

   b. $N_2\ (g) + 3H_2\ (g) \leftrightarrow 2NH_3\ (g)$

   C. $H_2\ (g) + Cl_2\ (g) \leftrightarrow 2HCl\ (g)$

   d. $PCl_3\ (g) + Cl_2\ (g) \leftrightarrow PCl_5\ (g)$

3. In what manner will increase of pressure affect the following equation?

   $C\ (s) + H_2O\ (g) \leftrightarrow CO\ (g) + H_2\ (g)$

   a. shift in the reverse direction

   b. shift in the forward direction

   C. increase in the yield of hydrogen

   d. no effect

4. Which one of the following statements does not describe the equilibrium state?

   a. The rate of forward reaction is equal to the rate of the reverse reaction.

   b. Equilibrium is dynamic and there is no net conversion to reactants and products.

   c. The concentration of the reactants is equal to the concentration of the products.

   d. The concentration of the reactants and products reach a constant level.

5. Which of the following statements is false regarding the equilibrium constant, Kc?

   a. When quoting K_C it is customary to omit units.

   b. The numerical value of K_C depends on the form of the balanced equation.

   c. K_C for a reaction at a particular temperature always has the same value.

   d. K_C for the reverse reaction is the negative of K_C for the forward reaction.

6. Which statement is true about equilibrium constant? The value of K_C

   a. remains same

   b. changes as product concentration changes

   c. changes as reactant concentration changes

   d. changes as temperature changes.

7. Write the equilibrium equation for the forward reaction:

   $2CH_4\ (g) + 3O_2\ (g) \rightleftharpoons 2CO\ (g) + 4H_2O\ (g)$

   a. $K_C = \dfrac{[CH_4]^2 + [O_2]^3}{[CO]^2 + [H_2O]^4}$.

   b. $K_C = \dfrac{[CO]^2\,[H_2O]^4}{[CH_4]^2\,[O_2]^3}$

   c. $K_C = \dfrac{2\,[CH_4] + 3\,[O_2]}{2\,[CO] + 4\,[H_2O]}$.

   d. $K_C = \dfrac{2\,[CO] + 4\,[H_2O]}{2\,[CH_4] + 3\,[O_2]}$

8. Nitric oxide reacts with oxygen to form nitrogen dioxide:

   $2NO\ (g) + O_2\ (g) \rightleftharpoons 2NO_2\ (g)$

   What is K_C' for the reverse reaction if the equilibrium concentration of NO is 0.300 M, O_2 is 0.200 M, and NO_2 is 0.530 M at 25°C?

   a. 0.1584 **b.** 6.24

   c. 0.0641 **d.** 1.641

9. If K_C is the equilibrium constant for a forward reaction what is $K_{C'}$ for the reverse reaction?

   a. $1/K_C$ **b.** $-K_C$

   c. K_C **d.** None of these

10. Given the reaction:

    $2HI \rightleftharpoons H_2 + I_2$. If K_C' for the reverse reaction is 1.85×10^{-2} at 425°C, what is K_C for the forward reaction at the same temperature?

    a. 58.1 **b.** 64.2

    c. 54.1 **d.** 5.41

11. For the reaction

    $N_2\ (g) + 2O_2\ (g) \rightleftharpoons 2NO_2\ (g)$,

$K_C = 8.3 \times 10^{-10}$ at 25°C. What is the concentration of N_2 gas at equilibrium when the concentration of NO_2 is twice the concentration of O_2 gas?

a. 2.4×10^{9} M **b.** 4.8×10^{9} M

c. 2.8×10^{9} M **d.** 2.8×10^{9} M

12. If $K_C = 7.04 \times 10^{-2}$ for the reaction:

$2HBr\ (g) \rightleftharpoons H_2\ (g) + Br_2\ (g)$

What is the value of K_C for the reaction:

$\frac{1}{2} H_2\ (g) + \frac{1}{2} Br_2\ (g) \rightleftharpoons HBr\ (g)$?

a. 2.68 **b.** 0.385

c. 37.7 **d.** 3.77

13. If K_C equals to 0.11 at 25°C for the reaction: $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$, what is K_C for the reaction: $NO_2\ (g) \rightleftharpoons \frac{1}{2} N_2O_4\ (g)$?

a. 1.5 **b.** 3.0

c. 6.0 **d.** 5.5

14. Which one of the following statements about the equilibrium constant (Kp) is false?

a. Total pressures are used in the equilibrium equation in place of molar concentrations.

b. The units for Kp are usually omitted.

c. Δn = the sum of the coefficients of the gaseous products – the sum of the coefficients of the gaseous reactants

d. The relationship between Kp and K_C is:

$Kp = K_C (RT)^{\Delta n}$

15. Given the reaction at a certain temperature

$2HI\ (g) \rightleftharpoons H_2\ (g) + I_2\ (g)$. At equilibrium, the partial pressure of HI is 1.8×10^{-3} atm and the partial pressures for H_2 and I_2 are 0.10 atm each. Find Kp at that temperature.

a. 3.1×10^{3} **b.** 3.1×10^{-3}

c. 4.8×10^{4} **d.** 2.8×10^{-2}

16. If $K_C = 2.0 \times 10^{33}$ at 25°C, for the following reaction:

$H_2\ (g) + Cl_2\ (g) \rightleftharpoons 2HCl\ (g)$, then find Kp at the same temperature.

a. 3.5×10^{32} **b.** 2.0×10^{33}

c. 1.8×10^{33} **d.** 4.0×10^{34}

17. Phosphorous pentachloride decomposes to phosphorous trichloride and chlorine gas at elevated temperatures by the following reaction:

$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$. If $K_C = 1.8$ at 250°C, what is the value of Kp at the same temperature.

a. 77 **b.** 67

c. 7.7×10^{-4} **d.** 6.7×10^{-2}

18. The decomposition of ammonia is:

$2NH_3\ (g) \rightleftharpoons N_2\ (g) + 3H_2\ (g)$. If Kp is 1.5×10^{3} at 400°C, what is the partial pressure of ammonia at equilibrium when N_2 is 0.10 atm and H_2 is 0.15 atm?

a. 4.1×10^{-6} atm

b. 1.5×10^{3} atm

c. 3.8×10^{-4} atm

d. 4.7×10^{-4} atm

19. The decomposition of ammonia is:

$2NH_3\,(g) \rightleftharpoons N_2(g) + 3H_2\,(g)$. If the partial pressure of ammonia is 1.6×10^{-3} atm and the partial pressures of N_2 and H_2 are each 0.25 atm at equilibrium, what is the value for K_C at 400°C for the forward reaction?

a. 0.20 **b.** 0.50

c. 2.8×10^{-3} **d.** 1.50

20. The decomposition of ammonia is:

$2NH_3\ (g) \rightleftharpoons N_2\ (g) + 3H_2\ (g)$. If the pressure of ammonia is 1.0×10^{-3} atm, and the pressures of N_2 and H_2 are each 0.20 atm, what is the value for Kp at 400°C for the reverse reaction?

a. 6.2×10^{-4} **b.** 2.6×10^{-4}

c. -6.2×10^{-4} **d.** 4.2×10^{-4}

21. A 1.50 L vessel contains an equilibrium mixture of 0.100 mol of NO, 0.150 mol of Br_2, and 0.250 mol of NOBr at 25°C. What is the value of Kp for the following reaction:

$2NO\ (g) + Br_2\ (g) \rightleftharpoons 2NOBr\ (g)$

a. 25.6 **b.** 12.8

c. 2.56 **d.** 5.26

22. As a rule, which of the following phases are not included in the equilibrium constant expression?

I. Pure liquids

II. Pure solids

III. Aqueous solutions

IV. Gases

a. I and III **b.** I and II

c. II and III **d.** I and IV

23. Which equilibrium below is homogeneous?

a. $2CO\ (g) + O_2\ (g) \rightleftharpoons 2CO_2\ (g)$

b. $NH_4NO_3\ (s) \rightleftharpoons N_2O\ (g) + 2H_2O\ (g)$

c. $BaSO_4\ (s) \rightleftharpoons Ba^{2+}\ (aq) + SO_4^{\ 2-}\ (aq)$

d. $2H_2O_2\ (l) \rightleftharpoons 2H_2O\ (l) + O\ (g)$

24. What is the equilibrium equation for the dissociation of formic acid in water?

$HCOOH\,(aq) + H_2O\,(l) \rightleftharpoons$

$H_3O^+\,(aq) + HCOO^-\,(aq)$

a. $K_C = \dfrac{[HCOOH]}{[H_3O^+]\,[HCOO^-]}$.

b. $K_C = \dfrac{[H_3O^+]\,[HCOO^-]}{[HCOOH]}$.

c. $K_C = \dfrac{[H_3O^+]\,[HCOO^-]}{[HCOOH]\,[H_2O]}$

d. $K_C = \dfrac{[HCOOH]\,[H_2O]}{[H_3O^+]\,[HCOO^-]}$.

25. What is the equilibrium equation for the following reaction?

$C_2H_4\,(g) + 3O_2\,(g) \rightleftharpoons 2CO_2\,(g) + 2H_2O\,(l)$

a. $Kp = \dfrac{[P_{CO_2}]^2}{[P_{C_2H_4}]\,[P_{O_2}]^3}$.

b. $Kp = \dfrac{[P_{C_2H_4}]\,[P_{O_2}]^3}{[P_{CO_2}]^2\,[P_{H_2O}]^2}$.

c. $Kp = \dfrac{[P_{C_2H_4}]\,[P_{O_2}]^3}{[P_{CO_2}]^2}$

d. $Kp = \dfrac{[P_{CO_2}]^2\,[P_{H_2O}]^2}{[P_{C_2H_4}]\,[P_{O_2}]^3}$

26. For which one of the following reactions will $K_C = Kp$?

a. $COCl_2\,(g) \rightleftharpoons CO\,(g) + Cl_2\,(g)$

b. $2O_3\,(g) \rightleftharpoons 3O_2\,(g)$

c. $ZnO\,(s) + CO\,(g) \rightleftharpoons Zn\,(s) + CO_2\,(g)$

d. $CO\,(g) + 2H_2\,(g) \rightleftharpoons CH_3OH\,(g)$

27. If $K_C = 0.900$ and $Kp = 538$ for a hypothetical reaction, which of the equations below could represent the reaction at 25°C?

a. $A\,(g) \rightleftharpoons 2C\,(s) + D\,(g)$

b. $B\,(g) \rightleftharpoons C\,(l) + D\,(l)$

c. $A\,(l) + 2B\,(g) \rightleftharpoons 2C\,(g)$

d. $A\,(g) + B\,(s) \rightleftharpoons 3C\,(g)$

28. Given the hypothetical reaction:

$2A\,(s) + nB(g) \rightleftharpoons 3C\,(g)$, $Kp = 0.0105$ and $K_C = 0.45$ at 250°C. What is the value of the coefficient 'n'?

a. 2 **b.** 3

c. 4 **d.** 5

29. For the reaction,

$A\,(g) + 2B\,(g) \rightleftharpoons 2C\,(g)$, $K_C = 1 \times 10^{-10}$ at 25°C. Which of the following statements is true?

a. The reaction is favoured in the reverse direction

b. The value of Kp will be larger than the value for K_C.

c. $\Delta n = +1$

d. The concentration of the products is greater than the concentration of the reactants.

30. Which statement is true for a reaction with K_C equal to 2.43×10^{-12}?

a. The reaction proceeds nearly all the way to completion

b. The reaction proceeds hardly at all towards completion

c. Increasing the temperature will not change the value of K_C

d. There are appreciable concentrations of both reactants and products

31. For the reaction:

$4HCl\,(g) + O_2\,(g) \rightleftharpoons 2Cl_2\,(g) + 2H_2O\,(l)$, the equilibrium constant is 0.063 at 400 K. If the reaction quotient is 0.100, which of the following statement is not correct?

a. $[O_2]$ will increase

b. $[Cl_2]$ will decrease

c. $[H_2O]$ will increase

d. $[HCl]$ will increase

32. The equilibrium constant is equal to 5.00 at 1300 K for the reaction:

$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$

If initial concentrations are $[SO_2] = 1.20$ M, $[O_2] = 0.45$ M and $[SO_3] = 1.80$ M, the system is

a. Not at equilibrium and will remain in an unequilibrated state.

b. At equilibrium

c. Not at equilibrium and will shift to the right to achieve an equilibrium state.

d. Not at equilibrium and will shift to the left to achieve an equilibrium state.

33. The equilibrium constant (Kp) equals to 3.40 at 25°C for the isomerisation reaction:

Cis-2-butene $\rightleftharpoons$ trans-2-butene

If a flask initially contains 1.00 atm of each gas, in what direction will the system shift to reach equilibrium?

a. The system is already at equilibrium

b. The system is not at equilibrium and will remain in an unequilibrated state.

c. It will shift left.

d. It will shift right.

34. At a certain temperature, bromine and nitric oxide react to form nitrosyl bromide:

Br_2 (g) + 2NO (g) $\rightleftharpoons$ 2NOBr (g)

When initial amounts of Br_2, NO and NOBr are mixed, the concentration of NOBr increases. Which of the statements is true?

a. $K_C = Q$

b. $K_C < Q$

c. $K_C > Q$

d. More information is needed to make a statement about K_C.

35. At a certain temperature, bromine and nitric oxide react to form nitrosyl bromide.

Br_2 (g) + 2NO (g) $\rightleftharpoons$ 2NOBr (g). When 0.010 mol Br_2 is mixed with 0.025 mol NO and 0.015 mol NOBr in a 2.50 litre flask, the concentration of NOBr decreases. Which of the statements is true?

a. $K_C < 90$ **b.** $K_C > 90$

c. $K_C < 45$ **d.** $K_C > 36$

36. At a certain temperature, K_C equals 1.4×10^2 for the reaction:

2CO (g) + O_2 (g) $\rightleftharpoons$ 2CO_2 (g)

If a 2.50 litre flask contains 0.400 mol of CO_2 and 0.100 mol of O_2 at equilibrium, how many moles of CO are also present in the flask?

a. 0.169 mol **b.** 0.238 mol

c. 1.69 mol **d.** 0.0894 mol

37. For the isomerisation reaction:

Butane $\rightleftharpoons$ Isobutane

Kp equals 25 at 500°C. If the initial pressures of butane and isobutane are 10. atm and 0.0 atm respectively, what are the pressures of the two gases at equilibrium?

a. P (butane) = 10 atm and
P (isobutane) = 0.40 atm

b. P (butane) = 9.8 atm and
P (isobutane) = 0.38 atm

c. P (butane) = 0.46 atm and
P (isobutane) = 10 atm

d. P (butane) = 0.38 atm and
P (isobutane) = 9.6 atm

38. At a certain temperature the equilibrium constant (K_C) equal 0.11 for the reaction

2 ICl (g) $\rightleftharpoons$ I_2 (g) + Cl_2 (g)

What is the equilibrium concentration of ICl if 0.75 mol of I_2 and 0.75 mol of Cl_2 are initially mixed in a 2.0 litre flask?

a. 0.45 M **b.** 1.45 M

c. 0.14 M **d.** 0.90 M

39. The esterification of acetic acid and ethanol is given by the reaction below:

C_2H_5OH (aq) + CH_3COOH (aq) $\rightleftharpoons$

$CH_3COOC_2H_5$ (aq) + H_2O (l)

When 1.00 mol of ethanol was mixed with 2.00 mol of acid in a 1.00 litre flask, 0.86 mol of ester was formed at room temperature. What is the value of the equilibrium constant (Kc)?

a. 2.8 **b.** 5.4

c. 6.4 **d.** 10.8

40. Kp is equal to 48.70 at 731 K for the reaction: H_2 (g) + I_2 (g) $\rightleftharpoons$ 2HI (g). Initially the mixture contains 0.08592 atm each of H_2 and I_2 and 1.0000 atm of HI. What is the pressure of HI at equilibrium?

a. 0.9108 atm **b.** 0.8796 atm

c. 0.1908 **d.** 0.02859

41. When baking soda is heated it decomposes according to the following reaction:

2$NaHCO_3$ (s) $\rightleftharpoons$

Na_2CO_3 (s) + H_2O (g) + CO_2 (g)

If sufficient baking soda is placed in a container and heated to 90°C, the total pressure of the gases is 0.5451 atm. What is the value of Kp at the temperature?

a. 0.05428 **b.** 0.18754

c. 0.4728 **d.** 0.07428

42. Ammonium carbamate can dissociate into gases at 25°C according to the reaction:

NH_2COONH_4 (s) $\rightleftharpoons$ 2NH_3 (g) + CO_2 (g)

If sufficient ammonium carbamate is sealed in a flask, the total pressure will be 0.117 atm at equilibrium. What is the value of Kp at 25°C?

a. 1.47×10^{-3} **b.** 2.37×10^{-4}
c. 4.77×10^{-3} **d.** 3.58×10^{-4}

43. Gaseous hydrogen bromide decomposes at elevated temperatures according to the following equation:

$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$

At a certain temperature a 2.00 litre flask is initially filled only with 0.600 mol of HBr. What is the value of K_C at that temperature if the flask contains 0.104 mol of H_2 at equilibrium?

a. 3.04×10^{-2} **b.** 6.40×10^{-3}
c. 7.04×10^{-2} **d.** 2.24×10^{-2}

44. K_C is 1.67×10^{20} at 25°C for the formation of iron(III) oxalate complex ion:

$Fe^{3+}(aq) + 3C_2O_4^{2-}(aq) \rightleftharpoons [Fe(C_2O_4)_3]^{3-}(aq)$

If 0.0100 M Fe^{3+} is initially mixed with 1.00 M oxalate ion, what is the concentration of Fe^{3+} ion at equilibrium?

a. 2.48×10^{-23} M
b. 6.56×10^{-23} M
c. 1.67×10^{20} M
d. 5.68×10^{23} M

45. Acids donate protons to water according to the general equation:

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

Consider the following acids and their equilibrium constants for reaction with water at 25°C. If all the acids have same initial concentration, which is the strongest acid (that is, which donates the most protons to water)?

a. HNO_3, $K_C = 5.4 \times 10^{-4}$
b. HIO_3, $K_C = 1.7 \times 10^{-1}$
c. $HBrO$, $K_C = 3.7 \times 10^{-3}$
d. HF, $K_C = 2.2 \times 10^{-3}$

46. The solubility of 1:1 salts is measured by the equilibrium constant for the general reaction: MX (s) = $M^{n+}(aq) + X^{n-}(aq)$. Given the following salts and their equilibrium constants for the reaction above at 25°C, which salt is the least soluble?

a. $BaCO_3$, $K_C = 3.6 \times 10^{-9}$
b. $SrCO_3$, $K_C = 5.6 \times 10^{-10}$
c. $MgCO_3$, $K_C = 6.4 \times 10^{-7}$
d. $CaCO_3$, $K_C = 4.5 \times 10^{-6}$

47. Which of the following changes in reaction conditions will after the composition of an equilibrium mixture of gases?

a. Increasing the temperature
b. Decreasing the pressure or volume
c. Addition of reactants or products
d. All of the above will alter the equilibrium concentrations

48. Which of the following changes in reactions conditions will not alter the equilibrium concentrations?

a. Increasing the temperature
b. Decreasing the pressure or volume
c. Addition of an inert gas to the reaction mixture
d. Addition of reactants or products

49. "If a stress is applied to a reaction mixture at equilibrium, the reaction occurs in the direction that will relieve the stress". This statement is called

a. Law of mass action
b. Le Chatelier's principle
c. First law of thermodynamics
d. Law of combining volumes

50. The pink and blue species below form a violet coloured mixture at equilibrium:

$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons$
(Pink)

$[CoCl_4]^{2-}(aq) + 6H_2O(l)$
(Blue)

As the concentration of $[Co(H_2O)_6]^{2+}$ is increased, what happens to the solution?

a. No colour change is observed
b. The solution becomes colourless
c. The concentration of $[CoCl_4]^{2-}$ decreases
d. The concentration of $[CoCl_4]^{2-}$ increases

51. The overall reaction for photosynthesis can be represented by the following equation

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

The enthalpy change for this reaction is 2802 kJ. Which of the following changes in condition will shift the equilibrium to the right?

a. Increase the temperature
b. Remove one-half of $C_6H_{12}O_6(s)$
c. Increase the pressure of O_2
d. Remove CO_2 by reaction with CaO (s).

52. The dissolution of calcium hydroxide is exothermic.

$Ca(OH)_2\ (s) \rightleftharpoons Ca^{2+}\ (aq) + 2OH^-\ (aq)$

What happens when the solution of $Ca(OH)_2$ is heated?

a. The $Ca(OH)_2$ (s) completely dissolves.

b. The amount of $Ca(OH)_2$ (s) decreases.

c. The amount of $Ca(OH)_2$ (s) increases.

d. The amount of $Ca(OH)_2$ (s) remains unchanged.

53. Which change in the system will drive equilibrium to the left in the following reaction?

$N_2O_5\ (g) \rightleftharpoons NO_2\ (g) + NO_3\ (g)$

a. Increase the volume

b. Increase the pressure

c. Decrease the amount of NO_3

d. Increase the amount of N_2O_5

54. Iron oxide ores are reduced to iron metal by exothermic reaction with carbon monoxide.

$FeO\ (s) + CO\ (g) \rightleftharpoons Fe\ (s) + CO_2\ (g)$

Which of the following changes in condition will cause the equilibrium to shift to the right?

a. Add CO_2

b. Add FeO

c. Add CO

d. Raise the temperature

55. Ammonium bromide is a crystalline solid that decomposes endothermically when heated: $NH_4Br\ (s) \rightleftharpoons NH_3\ (g) + HBr\ (g)$. When solid NH_4Br is added to an evacuated flask at 300°C, which change in reaction conditions below will cause the equilibrium to shift to the right?

a. Decrease the temperature

b. Double the volume of the container

c. Add more NH_3

d. Add more NH_4Br

56. A crude type of disappearing ink is based on the following endothermic equilibrium:

$[Co(H_2O)_6]Cl_2\ (aq) \rightleftharpoons$
(Colourless)

$[CoCl_2(H_2O)_4]\ (aq) + 2H_2O\ (g)$
(Blue)

If the reactant solution is used to write on a piece of paper and the paper is allowed to partially dry, what can be done to bring out the coloured handwriting.

a. Put the paper in the oven

b. Add water

c. Put the paper in the freezer

d. Decrease the volume

57. The enthalpy for the following reaction is 136 kJ. If the reaction takes place in a closed container, which one of the following reaction conditions will not decrease the concentration of water vapour?

$2NaHCO_3\ (s) \rightleftharpoons$
$Na_2CO_3\ (s) + CO_2\ (g) + H_2O\ (g)$

a. Cool the container

b. Add CO_2

c. Remove some $NaHCO_3$

d. Decrease the volume of the container

58. Calcium carbonate is relatively insoluble and the dissolution reaction is endothermic.

$CaCO_3\ (s) \rightleftharpoons Ca^{2+}\ (aq) + CO_3^{2-}\ (aq)$

Which change in reaction condition bellow will shift the equilibrium to the right?

a. Increase the temperature

b. Add an anion with which Ca^{2+} is even more soluble than calcium carbonate

c. Add an acid to react with CO_3^{2-} ion

d. All of the above will shift reaction to the right.

59. The decomposition of nitrosyl bromide is exothermic:

$2NOBr\ (g) \rightleftharpoons 2NO\ (g) + Br_2\ (g)$. Which of the following changes in reaction condition will shift the reaction to the left?

a. Decrease the temperature

b. Increase the container volume

c. Add more NOBr

d. None of these

60. Which of the following changes in reaction conditions will not alter the composition of a homogeneous equilibrium mixture of gases?

a. Increasing the pressure or volume

b. Decrease the temperature

c. Addition of reactants or products

d. Addition of a catalyst

61. Which of the following statements about a catalyst is true?

a. A catalyst provides a lower energy pathway for a reaction.

b. A catalyst changes the position of the equilibrium in a reaction

c. A catalyst increases the temperature of a reaction

d. A catalyst is consumed in a chemical reaction.

62. A catalyst increases the rate of a chemical reaction by providing a lower energy mechanism for the reaction. When this occurs, which one of the following is not affected?

a. Activation energy for the reverse reaction

b. Equilibrium constant

c. Activation energy for the forward reaction

d. Rate of the reverse reaction.

63. A reaction reaches dynamic equilibrium at a given temperature when

a. Opposing reactions cease and the system is static.

b. The amount of products exceeds the amount of reactants

c. The relative amounts of reactants and products are constant and rate (forward) = rate (reverse)

d. k (forward) = k (reverse)

64. At 25°C, a certain first order reaction has a rate constant equal to $1.00 \times 10^{-3}\ s^{-1}$ and an equilibrium constant (K_C) equal to 4.18. What is the rate constant for the reverse reaction?

a. $1.48 \times 10^{-3}\ s^{-1}$

b. $2.39 \times 10^{-4}\ s^{-1}$

c. $4.29 \times 10^{-3}\ s^{-1}$

d. $3.39 \times 10^{-4}\ s^{-1}$

65. Nickel metal can be prepared by the reduction of nickel oxide:

$$NiO\ (s) + CO\ (g) \rightleftharpoons CO_2\ (g) + Ni\ (s)$$

At 936 K, Kp = 4.54×10^3 and at 1125 K, Kp = 1.58×10^3. Which statement is true?

a. The reaction is exothermic

b. The activation energy decreases with increasing temperature.

c. The reaction is endothermic

d. The activation energy increases with increasing temperature.

66. The reaction below virtually goes to completion because cyanide ion forms very stable complexes with Ni^{2+} ion:

$$[Ni(H_2O)_6]^{2+}\ (aq) + 4\ CN^-\ (aq) \rightarrow [Ni(CN)_4]^{2-}\ (aq) + 6H_2O\ (l)$$

At the same time, incorporation of ^{14}C labeled cyanide ($^{14}CN^-$) is very rapid:

Which statement below is correct with regard to stability and rate of reaction?

a. Unstable species react rapidly

b. Equilibrium is static

c. Stable species can react rapidly

d. Stable species do not react rapidly

Brainteasers Objective Type Questions (Single choice only)

67. When reaction (1) and (2) below are added together, the result is reaction (3).

I. $H_2O\ (l) + HNO_2\ (aq) \rightleftharpoons H_3O^+\ (aq) + NO_2^-\ (aq)$

II. $H_3O^+\ (aq) + OH^-\ (aq) \rightleftharpoons 2H_2O\ (l)$

III. $HNO_2\ (aq) + OH^-\ (aq) \rightleftharpoons NO_2^-\ (aq) + H_2O\ (l)$

If $K_1 = 4.50 \times 10^{-4}$, and $K_2 = 1.00 \times 10^{14}$, find the equilibrium constant K_3.

a. 2.50×10^{12} **b.** 0.50×10^{10}

c. 4.50×10^{10} **d.** 3.56×10^{8}

68. Find the equilibrium constant for the reaction: A (g) + B (g) ⇌ 2C (g) at 25°C when k equals $1.4 \times 10^{-12}\ M^{-1}\ s^{-1}$ for the reaction A (g) + B (g) → 2C (g) at 25°C and k equals $2.7 \times 10^{-13}\ M^{-1}\ s^{-1}$ for the reaction:

2C (g) → A (g) + B (g) at 25°C.

a. 5.2 **b.** 6.4

c. 3.6 **d.** 7.1

69. For the reaction:

$PCl_5\ (g) \leftrightarrow PCl_3\ (g) + Cl_2\ (g)$

the forward reaction at constant temperature is favoured by

I. introducing an inert gas at constant volume

II. introducing chlorine gas at constant volume

III. introducing an inert gas at constant pressure

IV. increasing the volume of the container

V. introducing PCl_5 at constant volume.

a. I, II ,III **b.** IV, V

c. II, III, V **d.** III, IV, V

70. An equilibrium mixture of CO, O_2 and CO_2 at a certain temperature contains 0.0010 M CO_2 and 0.0015 M O_2. At this temperature (K_C) equals 1.4×10^2 for the reaction:

$2CO\,(g) + O_2\,(g) \rightleftharpoons 2CO_2\,(g)$

What is the equilibrium concentration of CO?

a. 1.1×10^{-3} M

b. 2.2×10^{-3} M

c. 4.8×10^{-2} M

d. 6.6×10^{-6} M

71. The equilibrium constant (Kp) equals 3.40 for the isomerization reaction:

cis-2-butene $\rightleftharpoons$ trans-2-butene

If a flask initially contains 0.250 atm of cis-2-butene and 0.125 atm of trans-2-butene, what is the equilibrium pressure of each gas?

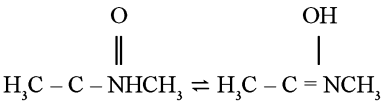
a. P (cis-2-butene) = 0.085 atm,
P (trans-2-butene) = 0.290 atm

b. P (cis-2-butene) = 0.058 atm,
P (trans-2-butene) = 0.230 atm

c. P (cis-2-butene) = 0.028 atm,
P (trans-2-butene) = 0.156 atm

d. P (cis-2-butene) = 0.034 atm,
P (trans-2-butene) = 0.128 atm

72. The following two isomers of C_3H_7NO exist in equilibrium with each other in solution:



$$H_3C-\overset{\overset{\large O}{\|}}{C}-NHCH_3 \rightleftharpoons H_3C-\overset{\overset{\large OH}{|}}{C}=NCH_3$$

If $K_C = 0.57$ at 25°C and the initial concentration of the reactant is 0.50 M and the product is 0.70 M, what are the concentrations at equilibrium?

a. [Reactant] = 0.46 M and
[Product] = 0.28 M

b. [Reactant] = 0.69 M and
[Product] = 0.48 M

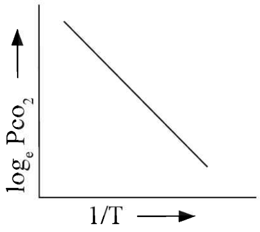
c. [Reactant] = 0.96 M and
[Product] = 0.47 M

d. [Reactant] = 0.76 M and
[Product] = 0.44 M

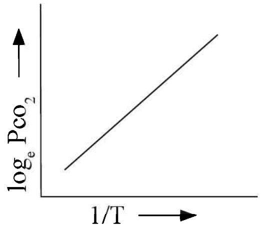
73. For the chemical equilibrium,

$CaCO_3\,(s) \rightleftharpoons CaO(s) + CO_2(g)$

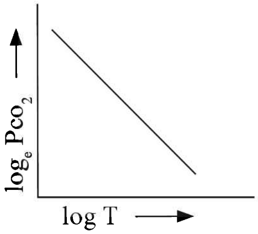
ΔH_f° can be determined from which one of the following plots?



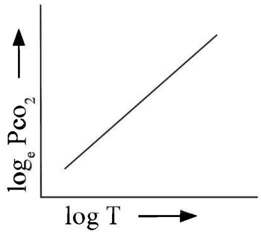
a.



b.



c.



d.

74. Phosphorous pentachloride decomposes to phosphorous trichloride at high temperatures according to the reaction:

$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$

At 250°C, 0.250 M PCl_5 is added to a flask. If $K_C = 1.80$, What are the equilibrium concentrations of each gas?

a. $[PCl_5] = 2.26$ M, $[PCl_3] = 2.04$ M,
$[Cl_2] = 20.4$ M

b. $[PCl_5] = 0.0280$ M, $[PCl_3] = 0.222$ M,
$[Cl_2] = 0.222$ M

c. $[PCl_5] = 1.28$ M, $[PCl_3] = 1.028$ M,
$[Cl_2] = 1.028$ M

d. $[PCl_5] = 3.82$ M, $[PCl_3] = 0.879$ M,
$[Cl_2] = 20.4$ M

75. Cyclohexane (C_6H_{12}) undergoes a molecular rearrangement in the presence of $AlCl_3$ to form methylcyclopentane (MCP) according to the equation:

$C_6H_{12} \rightleftharpoons MCP$

If $K_C = 0.143$ at 25°C for this reaction, predict the direction the reaction will shift, if the initial concentrations of C_6H_{12} and MCP are 0.200 M and 0.100 M, respectively. The system

a. is already at equilibrium
b. will shift right
c. will shift left
d. is not at equilibrium and will remain in an unequilibrated state.

76. Oxalic acid can donate two protons to water in successive reactions:

I. $H_2C_2O_4\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+(aq) + HC_2O_4^-\,(aq)$

II. $HC_2O_4^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + C_2O_4^{2-}\,(aq)$

If $K_{C_1} = 5.9 \times 10^{-2}$ and $K_{C_2} = 6.4 \times 10^{-5}$ at 25°C, what is the value of K_C for reaction (3)?

III. $H_2C_2O_4\,(aq) + 2H_2O\,(l) \rightleftharpoons 2H_3O^+\,(aq) + C_2O_4^{2-}\,(aq)$

a. 7.6×10^{-4} **b.** 5.8×10^{-3}
c. 6.4×10^{-5} **d.** 3.8×10^{-6}

77. The equilibrium constant for gaseous reaction:

$A + B \rightleftharpoons C + D$

is 100 at 25°C. Consider the following statements in this regard. If the initial concentration of all the four species were 1.0 M each, then the equilibrium concentration of

I. A would be 0.182 mol/L
II. C would be 0.818 mol/L
III. D would be 1.818 mol/L

Of these statements:

a. I and III are correct
b. I and II are correct
c. II and III are correct
d. I, II and III are correct

78. What is the equilibrium constant (K_C) for the reaction:

$2Hg\,(l) + O_2\,(g) \rightleftharpoons 2HgO\,(s)$ if the amounts of reactants and products at equilibrium are 1.00 g of HgO (s), 2.00 ml of Hg (l), and 1.60 M O_2 (s)? (The molar mass and density of HgO (s) is 217 g/mol and 1.10 g/cm³. The molar mass and density of Hg (l) is 201 g/mol and 13.6 g/ml).

a. 0.625 **b.** 1.625
c. 6.25×10^{-3} **d.** 1.28×10^3

79. An equilibrium mixture for the reaction

$2H_2S\,(g) \leftrightarrow 2H_2\,(g) + S_2\,(g)$

had 1 mole of H_2S, 0.2 mole of H_2 and 0.8 mole of S_2 in a 2 litre flask. The value of Kc in mol L^{-1} is

a. 0.08 **b.** 0.016
c. 0.004 **d.** 0.160

80. Cyclohexane (C_6H_{12}) undergoes a molecular rearrangement in the presence of $AlCl_3$ to form methylcyclopentane ($CH_3C_5H_9$), according to the equation

$C_6H_{12} \rightleftharpoons CH_3C_5H_9$

If $K_C = 0.143$ at 25°C for this reaction, find the equilibrium concentrations of C_6H_{12} and $CH_3C_5H_9$ if the initial concentrations are 0.200 M and 0.100 M respectively

a. $[C_6H_{12}] = 0.286$ and
$[CH_3C_5H_9] = 0.016$ M

b. $[C_6H_{12}] = 0.262$ and
$[CH_3C_5H_9] = 0.038$ M

c. $[C_6H_{12}] = 0.186$ and
$[CH_3C_5H_9] = 0.162$ M

d. $[C_6H_{12}] = 0.164$ and
$[CH_3C_5H_9] = 0.621$ M

81. What is the correct sequence of active masses in increasing order in gaseous mixture containing one gram per litre of each of the following?

I. NH_3 **II.** N_2
III. H_2 **IV.** O_2

Select the correct answer using the codes given below:

a. III, I, IV, II **b.** III, IV, II, I
c. II, I, IV, III **d.** IV, II, I, III

82. The equilibrium

$SO_2Cl_2\,(g) \leftrightarrow SO_2\,(g) + Cl_2\,(g)$

is attained at 25°C in a closed container and inert gas helium is introduced. Which of the following statement(s) is/are correct?

I. concentrations of SO_2, Cl_2 and SO_2Cl_2 change
II. more chlorine is formed

III. concentration of SO_2 is reduced

IV. more SO_2Cl_2 is formed

a. I, II, III **b.** II, III, IV

c. III, IV **d.** none

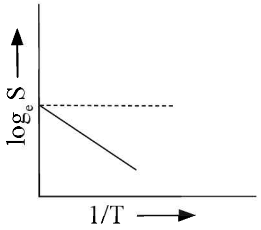
83. One mole of N_2O_4 (g) at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of N_2O_4 (g) decomposes to NO_2 (g). The resultant pressure is

a. 1.2 atm **b.** 2.4 atm

c. 2.0 atm **d.** 1.0 atm

84. The solubility of a solute in water varies with temperature and given as $S = Ae^{-\Delta H/RT}$

Here ΔH is enthalpy of the solution. For the given solute, variation of $\log_e S$ with temperature can be shown by the figure given below



This solute may be

a. $CaSO_4$ **b.** $CuSO_4$

c. $CuSO_4.5H_2O$ **d.** ZnO

85. A mixture of carbon monoxide, hydrogen and methanol is at equilibrium. The balanced chemical equation is

$CO\ (g) + 2H_2\ (g) \rightleftharpoons CH_3OH\ (g).$

At 250°C, the mixture contains 0.0960 M CO, 0.191 M H_2, and 0.150 M CH_3OH. What is the value for K_C?

a. 4.52 **b.** 42.8

c. 52.9 **d.** 0.581

86. The oxidation of sulphur dioxide by oxygen to sulphur trioxide has been implicated as an important step in the formation of acid rain:

$2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g).$

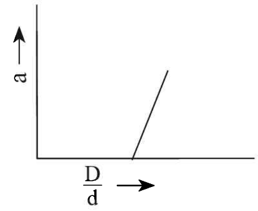
If the equilibrium partial pressures of SO_2, O_2 and SO_3 are 0.564 atm, 0.102 atm, and 0.333 atm respectively at 1000 K, what is the Kp at that temperature?

a. 2.24 **b.** 4.68

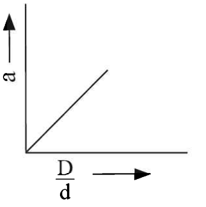
c. 3.42 **d.** 13.42

87. For the dissociation of PCl_5 into PCl_3 and Cl_2 in gaseous phase reaction, if d is the observed vapour density and D the theoretical vapour density with 'a' as degree of dissociation. Variation of D/d with 'a' is given by which graph?

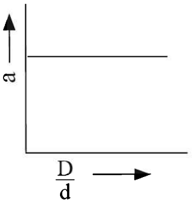
a.



b.



c.



d. None of these

88. What is the value for K_{eq} for the following reaction:

$PbCl_2\ (s) \rightleftharpoons Pb^{2+}\ (aq) + 2Cl^-\ (aq)$, if $PbCl_2$ (s) = 1.50 g, $[Pb^{2+}] = 1.6 \times 10^{-2}$ M and $[Cl^-] = 3.2 \times 10^{-2}$ M at equilibrium? (The molar mass of $PbCl_2$ (s) is 278 g/mol and its density is 5.85 g/cm³).

a. 2.6×10^{-6} **b.** 0.8×10^{-6}

c. 1.6×10^{-5} **d.** 6.4×10^{-4}

89. The hexaammine cobalt (III) ion is very unstable in acidic aqueous solution:

$[Co(NH_3)_6]^{3+}\ (aq) + 6H_3O^+\ (aq) \rightarrow$

$[Co(H_2O)_6]^{4+}\ (aq) + 6NH_4^+\ (aq)$

However, solutions of hexaammine cobalt(III) can be stored in acidic solution for months without noticeable decomposition. Which statement below about the equilibrium constant and the activation energy for the reaction is true?

a. Keq > 10^3 and Ea is very large

b. Keq < 10^3 and Ea is very small

c. Keq < 10^3 and Ea is very large

d. Keq > 10^3 and Ea is very small

90. For the decomposition of PCl_5 (g) in a closed vessel, the degree of dissociation is α at total pressure (P).

$PCl_5 (g) \rightleftharpoons PCl_3 (g) + Cl_2 (g); K_P$

Which among the following relations is correct?

a. $\alpha = \sqrt{[(K_P + P)/K_P]}$

b. $\alpha = \sqrt{[K_P/(K_P + P)]}$

c. $\alpha = 1/\sqrt{(K_P + P)}$

d. $\alpha = \sqrt{(K_P + P)}$

91. The equilibrium constant Kc for the reaction $N_2 (g) + 2O_2 (g) \leftrightarrow 2NO_2 (g)$ at a particular temperature is 6.0×10^{-5}. The ratio of the concentration of NO_2 to O_2 at equilibrium is 0.0152. The equilibrium concentration of N_2 is

a. 0.253 mol/litre

b. 3.85×10^2 mol/litre

c. 3.85 mol/litre

d. 2.53×10^2 mol/litre

92. NiO is to be reduced to nickel metal in an industrial process by use of the reaction.

$NiO(s) + CO(g) \rightleftharpoons Ni(s) + CO_2(g)$

At 1600 K the equilibrium constant for the reaction is $K_p = 6.0 \times 10^2$. If a CO pressure of 150 torr is to be employed in the furnace and total pressure never exceeds 760 torr, will reduction occur?

a. No

b. Yes

c. Cannot be said

d. May or maynot

93. For the reaction

$N_2 (g) + 3H_2 (g) \leftrightarrow 2NH_3 (g)$, $\Delta H = -93.6$ kJ mol^{-1}, the concentration of H_2 at equilibrium can be increased by

I. lowering the temperature

II. increasing the volume of the system

III. adding N_2 at constant volume

IV. adding H_2 at constant volume

a. II, IV

b. only II is correct

c. I, II and III are correct

d. III and IV are correct

e. only IV is correct

94. Which of the following reactions, initially at equilibrium, will shift to the left when the temperature is decreased at constant pressure?

I. $2C_2H_2(g) + 5O_2 (g) \rightleftharpoons 4CO_2(g) + 2H_2O(l)$ $\Delta H = -1297$ kJ

II. $CO_2(g) \rightleftharpoons O_2(g) + C(s)$
$\Delta H = 393$kJ

III. $4Fe(s) + 3O_2 (g) \rightleftharpoons 2Fe_2O_3(s)$
$\Delta H = -1644$kJ

a. (i) **b.** (ii)

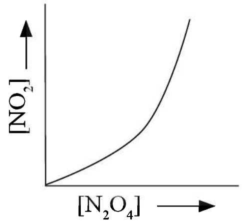
c. (iii) **d.** all of them

95. The graph which represents all the equilibrium concentrations for the reaction

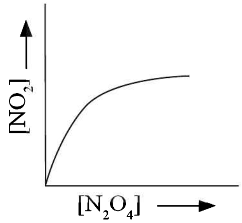
$N_2O_4(g) \rightleftharpoons 2NO_2$

(the concentrations of N_2O_4 (g) and of NO_2 (g) for which the following reation will be at equilibrium will lie on which of the following graph)

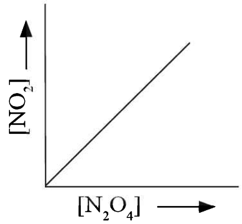
a.



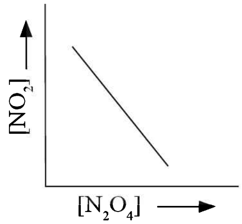
b.



c.



d.



96. $K_c = 0.0112$ at 25°C for the reaction $N_2(g) + O_2 \rightleftharpoons 2NO(g)$

What the change in the state of the reaction occurs (if any) if $[N_2]_0 = 2.00M$, $[O_2]_0 = 0.500M$?

- **a.** Reaction produces more NO, $Q < K_c$.
- **b.** No change occurs in concentrations, $Q = K_c$.
- **c.** Temperature increases.
- **d.** Reaction produces more reactants, $Q > K_c$

Multiple Correct Answer Type Questions

97. $N_2O_2 \rightleftharpoons 2NO, K_1$

$\frac{1}{2} N_2 + \frac{1}{2} O_2 \rightleftharpoons NO, K_2$

$2NO \rightleftharpoons N_2 + O_2, K_3$

$NO \rightleftharpoons \frac{1}{2} N_2 + \frac{1}{2} O_2, K_4$

Correct relation between K_1, K_2, K_3 and K_4 is/are

- **a.** $\sqrt{(K_1 \times K_4)} = 1$
- **b.** $K_1 \times K_3 = 1$
- **c.** $\sqrt{(K_1 \times K_2)} = 1$
- **d.** $\sqrt{K_3} \times K_2 = 1$

98. The following reaction attains equilibrium at high temperature

$N_2 (g) + 2H_2O (g) + \text{heat} \rightleftharpoons$
$2NO (g) + 2H_2 (g)$

The amount of NO is affected by

- **a.** Addition of catalyst
- **b.** Compressing the reaction mixture
- **c.** Increasing the nitrogen concentration
- **d.** Decreasing the hydrogen concentration

99. The equilibrium constant for the reaction

$CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (g)$ can be given as

- **a.** $K_C = ([CaO][CO_2])/[CaCO_3]$
- **b.** $K_C = [CO_2]$
- **c.** $K_P = P_{CO_2}$
- **d.** $K_C = [CaCO_3]/([CaO][CO_2])$

100. Which of the following does not affect the value of equilibrium constant of a reaction?

- **a.** Change in temperature
- **b.** Addition of a catalyst
- **c.** Change in the concentration of the reactants
- **d.** Change in pressure

101. Which of the following statement is/are incorrect here?

- **a.** Equilibrium constant of an exothermic reaction decreases with the increase of temperature
- **b.** K_P is always greater than K_C
- **c.** At equilibrium, concentrations of reactants and products become constant as the reaction stops
- **d.** Addition of a catalyst speeds up the forward reaction more than he backward reaction

102. For the reaction

$PCl_5 (g) \rightleftharpoons PCl_3 (g) + Cl_2 (g)$

the forward reaction at constant temperature is favoured by

- **a.** Increasing the volume of the container
- **b.** Introducing PCl_5 at constant volume
- **c.** Introducing an inert gas at constant volume
- **d.** Introducing Cl_2 (g) at constant volume

103. When $NaNO_3$ is heated in a closed vessel oxygen is liberated and $NaNO_2$ is left behind. At equilibrium, which are not correct?

- **a.** Increase of pressure favours reverse reaction
- **b.** Increase of temperature favours forward reaction
- **c.** Addition of $NaNO_2$ favours reverse reaction
- **d.** Addition of $NaNO_3$ favours forward reaction

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

- **a.** A plot of P vs 1/V is linear at constant temperature
- **b.** A plot of $\log_{10} K_P$ vs 1/T is linear
- **c.** A plot of log [X] vs time is linear for a first order reaction, $X \rightarrow P$
- **d.** A plot of $\log_{10} P$ vs 1/T is linear at constant volume

105. Which of the following have $K_P = K_C$ here?

- **a.** $2NO (g) + Cl_2 (g) \rightleftharpoons 2NOCl (g)$
- **b.** $N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH (g)$
- **c.** $H_2 (g) + X_2 (g) \rightleftharpoons 2HX (g)$
- **d.** $N_2 (g) + O_2 (g) \rightleftharpoons 2NO (g)$

106. Which of the following statement is/are correct about the equilibrium?

- **a.** $\Delta G = 0$
- **b.** Catalyst has no effect on equilibrium
- **c.** K_{eq} changes with temperature
- **d.** Value of K_{eq} changes by increasing concentration of equilibrium

107. Which of the following reaction can have same units of K_P?

a. $NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$

b. $2SO_3\ (g) \rightleftharpoons 2SO_2\ (g) + O_2\ (g)$

c. $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl\ (g)$

d. $XX_2\ (g) \rightleftharpoons XY\ (g) + Y\ (g)$

108. The degree of dissociation (α)

$$\alpha = \frac{D - d}{(n - 1)d}.$$

Incorrect match for the equilibrium

a. $P \rightleftharpoons \frac{4n}{5} Q + \frac{n}{2} R$

b. $P \rightleftharpoons \frac{n}{3} Q + \frac{2n}{3} R$

c. $P \rightleftharpoons \frac{5n}{6} Q + \frac{n}{6} R$

d. $P \rightleftharpoons \frac{n}{2} Q + \frac{n}{2} R$

109. Which of the following statement is/are correct for a reversible reaction?

a. At a given temperature both Q and K vary with the progress of the reaction.

b. When Q > K, the reaction proceeds in backward direction before coming to stand still.

c. Reaction quotient (Q) is the ratio of the product or arbitrary molar concentrations of the products to those of the reactants.

d. Q may be < > = K.

110. Which of the following factors will not disturb the equilibrium state of this reaction?

$N_2\ (g) + O_2\ (g) \rightleftharpoons 2NO\ (g)$

a. Change in temperature

b. Change in pressure

c. Addition of N_2

d. Addition of a catalyst

111. For the gas phase reaction,

$C_2H_4 + H_2 \rightleftharpoons C_2H_6$ ($\Delta H = -32.7$ kcal), carried out in a closed vessel, the equilibrium concentration of C_2H_4 can be increased by

a. Decreasing the pressure

b. Adding some C_2H_6

c. Increasing the temperature

d. Removing some H_2

112. If the volume of the reaction flask is reduced to half of its initial value and temperature is kept constant then in which of the following cases the position of the equilibrium will shift?

a. $CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$

b. $I_2\ (g) \rightleftharpoons 2I\ (g)$

c. $NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (s)$

d. $2NOCl\ (g) \rightleftharpoons 2NO\ (g) + Cl_2\ (g)$

113. For the reaction,

$2X\ (g) + Y\ (g) \rightleftharpoons 2Z\ (g)$, $\Delta H = +15.6$ kJ

Which of the following will increase the extent of the reaction at equilibrium?

a. Addition of catalyst

b. Increasing concentration of Z

c. Increasing the temperature

d. Increasing the pressure

114. In this three step endothermic reaction

$$A_2\ (g) + B_2\ (g) \xrightarrow{\text{Step I}} 4C\ (g) \xrightarrow{\text{Step II}}$$
$$3D\ (g) \xrightarrow{\text{Step III}} 2E\ (g)$$

Which of the following statement is/are correct?

a. Step III is favoured by low temperature and high pressure

b. Step I is favoured by high temperature and low pressure

c. Step II is favoured by high temperature and high pressure

d. Step III is favoured by high temperature and low pressure

115. For which of the following reactions, $K_P/K_C = RT$?

a. $2HX\ (g) \rightleftharpoons H_2\ (g) + X_2\ (g)$

b. $N_2\ (g) + O_2\ (g) \rightleftharpoons 2NO\ (g)$

c. $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$

d. $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

116. Which of the following are homogeneous equilibria?

a. $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

b. $H_2\ (g) + X_2\ (g) \rightleftharpoons 2HX\ (g)$

c. $H_2O\ (l) \rightleftharpoons H_2O\ (g)$

d. $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$

117. Consider the following reversible reaction:

$CO\ (g) + 2H_2\ (g) \rightleftharpoons CH_3OH\ (g)$

$\Delta H = -92.5$ kJ

Which factor(s) will increase the yield of methanol at equilibrium?

a. Addition of inert gas at constant volume

b. Increased pressure on the system

c. Increased temperature

d. Increased partial pressure of hydrogen

118. The variation of equilibrium constant K with temperature is represented by

a. $\log_e K_2 - \log_e K_1 = -\frac{\Delta H}{R}\int_{T1}^{T2} d(1/T)$

b. $[(d \log_e K)/dT]_P = -\frac{\Delta H}{RT}$

c. $\log_e K = \text{constant} - \frac{RT}{\Delta H}$

d. $\log_e K = \text{constant} - \frac{\Delta H}{RT}$

119. The reactions in which the yield of the products can not be increased by the applications of high pressure is/are

a. $2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3(g)$

b. $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

c. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

d. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.

120. An inert gas is added to the reaction

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

at constant volume. Which of the following is/are incorrect?

a. Backward reaction is favoured

b. The reaction remains unaffected

c. The reaction ceases to proceed

d. Forward reaction is favoured

121. Which of the following is/are correct?

a. The equilibrium constant does not depend upon pressure

b. When pressure is applied on ice ⇌ water equilibrium more water will be formed

c. The equilibrium constant increases when a catalyst is introduced

d. Changes with temperature

Linked-Comprehension Type Questions

Comprehension 1

The decomposition of NH_4HS (s) takes place as follows:

$NH_4HS\,(s) \rightleftharpoons NH_3\,(g) + H_2S\,(g)$

If we take 3.06 gm of solid NH_4HS into a two litre evacuated vessel at 300 K. It undergoes 30% decomposition.

122. For this decomposition the value of K_C is?

a. 16.2×10^{-5} mol² lit⁻²

b. 8.1×10^{-5} mol² lit⁻²

c. 4.05×10^{-5} mol² lit⁻²

d. 1.62×10^{-3} mol² lit⁻¹

123. The value of K_P is

a. 0.0245 atm² **b.** 0.049 atm²

c. 8.1×10^{-5} atm² **d.** 0.081 atm²

124. What will be the effect of adding more amount of NH_4HS on equilibrium?

a. Equilibrium will shift in forward direction

b. Equilibrium will shift in backward direction

c. Equilibrium remains unaffected

d. Equilibrium first shifts in forward direction and then becomes constant

125. Which relation is correct here?

a. $K_P = K_C$

b. $K_P < K_C$

c. $K_P = K_C$

d. Can't be predicted here

Comprehension 2

The dynamic nature of chemical equilibrium can be easily demonstrated by in the synthesis of ammonia by Haber's method.

$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) + Q$ kcal

Haber took definite amount of N_2 and H_2 at suitable conditions of temperature and pressure. He was able to find amount of NH_3 and unreacted amount of H_2, N_2 at various time intervals.

126. Which of the following condition is not favourable for formation of more ammonia in this process

I. Higher temperature

II. More pressure

III. More concentration of NH_3

IV. More concentration of N_2 and H_2

a. I, II, III **b.** I, III

c. II, III, IV **d.** I, III, IV

127. If the value of K_P for this reaction at 673 K is found to be 16.4×10^{-3} then the value of ΔG° is

a. 11.733 kcal

b. 11.733 cal

c. 931.6 kcal

d. 9.316 cal

128. If at a temperature the value of K_C for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 1.49×10^{-5} mol^{-2} lit^2. What will be the value of K_C' for

$\frac{1}{2} N_2 + 3/2\ H_2 \rightleftharpoons 2NH_3$?

a. 1.49×10^{-5} lit/mole

b. 3.86×10^{-3} lit mol^{-1}

c. 3.86×10^{-3} lit^2 mol^{-2}

d. $1/\sqrt{(1.49 \times 10^{-5})}$ lit^{-2} mol^2

129. If the initial molar concentrations of N_2H_2 and NH_3 at 400°C are 0.142 M and 0.0265 M and 0.0384 M respectively predict which statements are correct here?

I. Here $Q > K_C$

II. The reactants are favoured

III. Here $Q < K_C$

IV. Product is favoured

a. I and III **b.** II and III

c. I and II **d.** III and IV

Comprehension 3

PCl_5 when heated in a sealed tube at 523 K undergoes decomposition as follows:

$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g) - \text{Heat}$

$(\Delta H = +ve)$

At this temperature its vapour density is found to be 57.92.

130. For the decomposition of PCl_5 (g) in a closed vessel which is the correct relation between total pressure (P), equilibrium constant (K_P) and degree of dissociation (α)

a. $\alpha = \sqrt{(K_P + P)}$

b. $\alpha = \sqrt{[1/(K_P + P)]}$

c. $\alpha = \sqrt{[K_P/(K_P + P)]}$

d. $\alpha = \sqrt{[(K_P + P)/K_P]}$

131. At this temperature when vapour density is 57.92. Find the degree of dissociation of PCl_5.

a. 72% **b.** 80%

c. 88% **d.** 40%

132. Find the volume percent of Cl_2 at equilibrium in PCl_5 under a total pressure of 1.5 atmosphere. [$K_P = 0.202$]

a. 12.8% **b.** 37.2%

c. 25.6% **d.** 1.28 %

133. The dissociation of PCl_5 is favoured by

I. Increase of pressure

II. Decrease of pressure

III. Increase of temperature

IV. More concentration of PCl_5

a. I, III, IV **b.** II, III, IV

c. I, IV **d.** III and IV

Comprehension 4

At 700K the equilibrium constant for the reaction

$CCl_4 \rightleftharpoons C(s) + 2Cl_2(g)$

is $K_p = 0.76$. A flask is charged with 2.00 atm of CCl_4, which then reaches equilibrium at 700 K.6

134. What is the value of K_c for this reaction at 700 K?

a. 1.30 **b.** 0.013

c. 0.026 **d.** 2.6

135. What fraction of the CCl_4 is converted into C and Cl_2?

a. 62% **b.** 25%

c. 26% **d.** 60%

136. What are the partial pressures of CCl_4 and Cl_2 at equilibrium?

a. 1.47 **b.** 14.7

c. 0.147 **d.** 147.0

Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given. Mark

- **a.** If A and R both are correct and R is the correct explanation of A;
- **b.** If A and R both are correct but R is not the correct explanation of A;
- **c.** A is true but R is false;
- **d.** A is false but R is true,

137. **(A):** For a reaction at equilibrium, the free energy for the reaction is minimum.

(R): The free energy for both reactants and products decreases and become equal.

138. **(A):** The endothermic reactions are favoured at lower temperature and the exothermic reactions are favoured at higher temperature.

(R): When a system in equilibrium is disturbed by changing the temperature, it will tend to adjust itself so as to overcome the effect of change.

139. **(A):** The reaction

$2NO\,(g) + O_2\,(g) \leftrightarrow 2NO_2$

is favoured in the forward direction with increase of pressure .

(R): The reaction is exothermic

140. **(A):** Concentration of the reactant and product does not change with time at equilibrium for a chemical reaction.

(R): The rate of a reaction is zero at equilibrium.

141. **(A):** In the Haber process,

$N_2 + 3H_2 \leftrightarrow 2NH_3$

Pressure is about 200 atm in presence of catalyst and temperature is kept 500°C even the reaction is exothermic.

(R): Energy needed for this reaction is easily obtained at this temperature.

142. **(A):** When $CaCO_3$ (s) is heated, the loss of CO_2 (g) from the system causes the reaction to go almost to completion to leave a residue of CaO (s).

(R): Heating causes gas particles to move with more energy.

143. **(A):** When the following equilibrium is studied in a vessel of twice the volume of the earlier one,

$A\,(g) \leftrightarrow B\,(g) + C\,(g)$

equilibrium constant is decreased.

(R): Equilibrium constant

$$Kc = \frac{x^2}{(1 - X)\,V}$$

144. **(A):** For the reaction $A + B \leftrightarrow C$, Kc = 2. If we start with 1 mol each of A, B, and C in 5 L flask, then at equilibrium, molar concentration of A and B decreases and that of C increases.

(R): Reaction quotient Q > Kc with given quantity of A, B, and C hence reaction is reversed.

145. **(A):** The equilibrium constant for a reaction having positive ΔH° increases with increase of temperature.

(R): The temperature dependence of the equilibrium constant is related to ΔH° and not ΔH° for the reaction.

146. **(A):** The value of K gives us a relative idea about the extent to which a reaction proceeds.

(R): The value of K is independent of the stoichiometry of reactants and products at the point of equilibrium.

147. **(A):** On opening a sealed soda bottle dissolved carbon dioxide gas escapes.

(R): Gas escapes to each the new equilibrium condition of lower pressure.

148. **(A):** The equilibrium constant is fixed and a characteristic for any given chemical reaction at a specified temperature.

(R): The composition of the final equilibrium mixture at a particular temperature depends upon the starting amount of reactants.

149. **(A):** Ice melts slowly at higher altitudes.

(R): The melting of ice is favoured at high pressure because ice $\longrightarrow$ water shows decrease in volume.

150. **(A):** When $Q = K_c$, reaction is at equilibrium

(R) At equilibrium ΔG is 0.

151. **(A):** Dissociation of PCl_5 decreases in presence of Cl_2

(R) An increase in concentration of Cl_2 favours backward reaction to decrease dissociation of PCl_5

152. **(A):** Water boils at high temperature in pressure cooker

(R) Inside the pressure cooker pressure is less than 1 atm.

153. **(A):** Some hydrated salts like blue vitriol dissolve in water with absorption of heat

(R) Le Chatelliers principle is not valid for solid – solid heterogeneous systems.

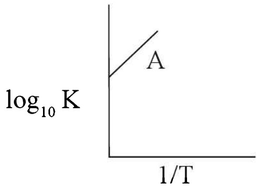
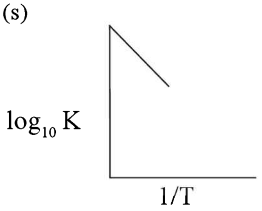
154. **(A):** For every chemical reaction at equilibrium standard Gibbs energy of reaction is zero.

(R): At constant temperature and pressure, chemical reactions are spontaneous in the direction of deceasing Gibbs energy.

[IIT 2008]

Matrix-Match Type Questions

155. Match the following:

Column I	**Column II**
A. N_2 (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g)	(p) Increase of pressure favours forward reaction
B. N_2 (g) + O_2 (g) $\rightarrow$ 2NO (g)	(q) Constant pressure favours forward reaction
C. NH_2COONH_4 (s) $\rightleftharpoons$ $2NH_3$(g) + CO_2(g)	(r) 
D. $CaCO_3$(s) $\rightleftharpoons$ CaO(s) + CO_2(g)	(s) 
	(t) Decrease in pressure favours forward reaction

156. Match the following:

Column I	**Column II**
(A) $2SO_2 + O_2 \rightarrow 2SO_3$ g g g	(p) No effect of catalyst on K_{eq}
(B) $N_2 + O_2 \rightarrow 2NO$ g g g	(q) No effect of pressure
(C) $P + Q \rightarrow 2R + S$ ΔH = Positive	(r) K_{eq} increases with rise in temperature
(D) $PCl_5 \rightarrow PCl_3 + Cl_2$	(s) K_{eq} decreases with rise in temperature

157. Match the following:

Column I	**Column II**
A. N_2 (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g)	(p) $K_P < K_C$
B. PCl_5 (g) $\rightleftharpoons$ PCl_3 (g) + Cl_2 (g)	(q) K_P does defined
C. $2SO_3 \rightleftharpoons 2SO_2 + O_2$	(r) $\Delta n > 0$
D. $CH_3COOC_2H_5$ (l) + H_2O (l) $\rightleftharpoons$ CH_3COOH (l) + C_2H_5OH (l)	(s) $K_P > K_C$
	(t) $P_{initial} > P_{eq}$

158. Match the following:

Column I	**Column II**
A. Law of mass action	(p) Guldberg wage
B. Active mass of $CaCO_3$ (s)	(q) Kp = Kc (RT)
C. $2SO_2 + O_2 \rightarrow 2SO_3$	(r) 1
D. $PCl_5 \leftrightarrow PCl_3 + Cl_2$	(s) zero
	(t) $Kp = Kc\,(RT)^{-1}$

159. Match the following:

Column I	**Column II**
A. N_2 (g) + $3H_2$ (g) $\leftrightarrow$ $2NH_3$ (l)	(p) heterogeneous reversible reaction
B. $CaCO_3$ (s) $\leftrightarrow$ CaO (s) + CO_2 (g)	(q) $2HI \rightarrow H_2$ (g) + I_2 (g)
C. Kp = Kc	(r) equilibrium state
D. rate of forward reaction = rate of backward	(s) homogeneous reversible reaction

160. Match the following:

Column I (Process)	**Column II (Favourable conditions)**
A. Melting of ice	(p) High pressure
B. Vaporization of water	(q) High temperature

C. Formation of nitric oxide	(r) More concentration of N_2
D. Formation of NH_3 by Haber's method	(s) Presence of inert gases
	(t) No change in pressure

161. Match the following:

Column I	**Column II**
A. N_2 (g) + O_2 (g) $\rightleftharpoons$ 2NO (g)	(p) $K_P > K_C$
B. $2SO_2$ (g) + O_2 (g) $\rightleftharpoons$ $2SO_3$ (g)	(q) $K_P = K_C$
C. PCl_5 (g) $\rightleftharpoons$ PCl_3 (g) + Cl_2 (g)	(r) $K_P < K_C$
D. $2KClO_3$ $2KCl + 3O_2$	(s) High temperature
	(t) Irreversible reaction

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162. For the reaction

$CO (g) + H_2O (g) \leftrightarrow CO_2 (g) + H_2 (g)$

at a given temperature, the equilibrium amount of CO_2 (g) can be increased by

a. adding a suitable catalyst
b. adding an inert gas
c. decreasing the volume of the container
d. increasing the amount of CO (g)

[IIT 1998]

163. For the chemical reaction

$3X (g) + Y (g) \leftrightarrow X_3Y (g)$, the amount of X_3Y at equilibrium is affected by

a. temperature and pressure
b. temperature only
c. pressure only
d. temperature, pressure and catalyst

[IIT 1999]

164. When two reactants A and B are mixed to give products C and D, the reaction quotient, Q, at the initial stages of the reaction

a. is zero
b. decreases with time
c. is independent of time
d. increases with time.

[IIT 2000]

165. For the reversible reaction,

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

At 500°C, the value of Kp is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of Kc, with concentration in mole $litre^{-1}$, is

a. $1.44 \times 10^{-5}/(0.082 \times 500)^{-2}$
b. $1.44 \times 10^{-5}/(8.314 \times 773)^{-2}$
c. $1.44 \times 10^{-5}/(0.082 \times 773)^{2}$
d. $1.44 \times 10^{-5}/(0.082 \times 773)^{-2}$

[IIT 2000]

166. At constant temperature, the equilibrium constant (Kp) for the decomposition reaction $N_2O_4 \leftrightarrow 2NO_2$ is expressed by

$Kp = (4x^2P)/(1 - x^2)$, where P = pressure, $\times$ = extent of decomposition. Which one of the following statements is true?

a. Kp increases with increase of P
b. Kp increases with increase of x
c. Kp increases with decrease of x
d. Kp remains constant with change in P and x.

[IIT 2001]

167. Consider the following equilibrium in a closed container: N_2O_4 (g) $\leftrightarrow$ $2NO_2$ (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 (Kp) and degree of dissociation (α)?

a. neither Kp nor α changes
b. both Kp and α change
c. Kp changes but α does not change
d. Kp does not change but α changes.

[IIT 2002]

168. $N_2 + 3H_2 \leftrightarrow 2NH_3$

Which is correct statement if N_2 is added at equilibrium condition?

a. The equilibrium will shift to forward direction because according to 2nd law of thermodynamics the entropy must increases in the direction of spontaneous reaction

b. The condition for equilibrium is $GN_2 + 3GH_2 = 2GNH_3$, where G is Gibbs free energy per mole of the gaseous species measured at the partial pressure. The condition of equilibrium in unaffected by the use of catalyst, which increases the rate of both the forward and backward reactions to the same extent.

c. The catalyst will increase the rate of forward reaction by α and that of backward reaction by β.

d. Catalyst will not alter the rate of either of the reaction.

[IIT 2006]

169. If Ag^+ $NH_3 \rightleftharpoons [Ag(NH_3)]^+$; $K_1 = 3.5 \times 10^{-3}$ and $[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; $K_2 = 1.74 \times 10^{-3}$ the formation constant of $[Ag(NH_3)_2]^+$ is

[IIT 2006]

a. 6.08×10^{-6} **b.** 6.08×10^{-6}
c. 6.08×10^{-9} **d.** none of these

170. The valve of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is (given: $\Delta r\ H^\circ$ 298 K = –54.07 KJ mol^{-1}, $\Delta r\ S^\circ$ 298 K = 10 JK^{-1} mol^{-1} and R = 8.314 JK^{-1} mol^{-1}; $2.303 \times 8.314 \times 298 = 5705$)

a. 10 **b.** 100
c. 5 **d.** 95

[IIT 2007]

ANSWERS

Straight Objective Type Questions

1. a **2.** c **3.** a **4.** c **5.** d **6.** d **7.** b **8.** c **9.** a **10.** c **11.** a **12.** c
13. b **14.** d **15.** b **16.** a **17.** c **18.** d **19.** a **20.** b **21.** a **22.** d **23.** b **24.** a
25. c **26.** b **27.** a **28.** b **29.** a **30.** c **31.** d **32.** c **33.** a **34.** b **35.** c **36.** b
37. d **38.** c **39.** a **40.** a **41.** d **42.** a **43.** b **44.** a **45.** d **46.** b **47.** c **48.** b
49. b **50.** b **51.** d **52.** c **53.** b **54.** d **55.** a **56.** c **57.** b **58.** c **59.** b **60.** a
61. c **62.** d **63.** d **64.** d **65.** a **66.** b

Brainteasers Objective Type Questions

67. c **68.** a **69.** b **70.** b **71.** a **72.** d **73.** a **74.** b **75.** c **76.** **d** **77.** a **78.** a
79. b **80.** b **81.** d **82.** d **83.** b **84.** c **85.** b **86.** c **87.** a **88.** c **89.** a **90.** b
91. c **92.** b **93.** a **94.** b **95.** b **96.** d

Multiple Correct Answer Type Questions

97. b, d **98.** b, c, d **99.** b, c **100.** a, b, c **101.** b, c, d **102.** a, b **103.** a, c, d
104. a, b, c **105.** c, d **106.** a, b, c **107.** c, d **108.** a, b, c, d **109.** b, c, d **110.** b, d
111. a, b, c, d **112** b, c, d **113.** c, d **114.** b, c **115.** c, d **116.** a, b **117.** b, d
118. a, d **119.** b, c **120.** a c d **121.** a, b, d

Linked-Comprehension Type Questions

Comprehension 1

122. b **123.** b **124.** c **125.** c

Comprehension 2

126. b **127.** a **128.** b **129.** c

Comprehension 3

130. c **131.** b **132.** c **133.** b

Comprehension 4

134. b **135.** c **136.** a

Assertion Reason Type Questions

137. a **138.** d **139.** b **140.** c

141. b **142.** b **143.** d **144** a

145. c **146.** c **147.** a **148.** c

149. a **150.** b **151.** a **152** c

153. b **154.** d

Matrix-Match Type Questions

155. A–(p, r,) B–(q, s), C–(t, s), D–(s, t)

156. A–(p, s) , B–(p, q, r) ,C–(p, r), D–(p, r)

157. A–(p, s), B–(r, s), C–(r, s), D–(q)

158. A–(p), B–(r), C–(t), D–(q)

159. A–(s), B–(p), C–(q), D–(s)

160. A–(p, q), B–(q), C–(q, r, t), D–(p, r, s)

161. A–(q, s), B–(r), C–(p, s), D–(s, t)

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162. d **163.** a **164.** d **165.** d **166.** d **167.** d **168.** b **169.** a **170.** a

Hints and Explanations

Straight Objective Type Questions

1. As the reaction is exothermic, the formation of AB_4 is favoured by low temperature.

As the forward reaction is accompanied by decrease in the number of moles. So it is favoured by high pressure.

2. $Kp = Kc$ when $\Delta n = 0$

$\Delta n = 2 - 2 = 0$

So the correct option is

$H_2 (g) + Cl_2 (g) \leftrightarrow 2HCl (g)$

3. It is according to Le-Chatelier's principle.

As np > nr.

73. This is according to Le-Chatelier's principle.

81. Let X = change in concentration of A

	A	+ B	⇌ C	+ D
Initial conc.	1.0 M	1.0 M	1.0 M	1.0 M
Eq. conc.	1 – X	1 – X	1 + X	1 + X

$$K = \frac{(1 + X)(1 + X)}{(1 - X)(1 - X)} = 100$$

$$= \frac{1 + X}{1 - X} = 10$$

$= 1 + X = 10 - 10X$

$= 11 X = 9$

$X = 9/11 = 0.818$

So

$[A] = 1 - 0.818 = 0.182$ M

$[C] = 1 + 0.818 = 1.818$ M

$[D] = 1.818$ M.

83. $Kc = \frac{[H_2]^2\,[S_2]}{[H_2S]^2}$

$[H_2] = \frac{2 \times 0.2}{2} = 0.2$ mole/L

$[S_2] = 0.8/2 = 0.4$ mole/L

$[H_2S] = 1$ mole/L

$Kc = \frac{[0.2]^2\,[0.4]}{1} = 0.016$ mole/L

85. Active masses of

$NH_3 = \frac{1\text{ g}/17\text{ g mol}}{1\text{ L}} = \frac{1}{17}$ mol/L

$N_2 = \frac{1\text{ g}/28\text{ g mol}}{1\text{ L}} = \frac{1}{28}$ mol/L

$H_2 = \frac{1\text{ g } 2\text{ g mol}^{-1}}{1\text{ L}} = \frac{1}{2}$ mol/L

$O_2 = 1\text{ g}/32\text{ g mol} = \frac{1}{32}$ mol/L

Increasing order of active masses is:

$1/32 < 1/28 < 1/17 < 1/2$ mol/L

$O_2 < N_2 < NH_3 < H_2$ that is, $4 < 2 < 1 < 3$.

86. When inert gas is added at constant volume, there is no effect on equilibrium. Hence none is correct.

87. $N_2O_4 \leftrightarrow 2NO_2$

1 0

1 – 0.2 0.4

= 0.8

Number of moles at 300 K = 1

No. of moles at 600 K = 0.8 + 0.4 = 1.2

V is constant

$\frac{P_2}{P_1} = \frac{n_2T_2}{= n_1T_1}$

$\frac{P_2}{1} = \frac{1.2 \times 600}{1 \times 300} = 2.4$ atm

88. As the slope of the graph is negative so ΔH is negative as dissolution of hydrated salt is endothermic so the solute is $CuSO_4.5H_2O$

91. $(1 + a) = D/d$

When $a = 0$, $D/d = 1$

When a increases, $(1 + a)$ increases so D/d also increases

95. $K_C = \frac{[NO_2]^2}{[N_2]\,[O_2]^2}$.

$[N_2] = \left[\frac{[NO_2]^2}{[O_2]}\right]\frac{1}{K_C}$.

$= \frac{(0.0152)^2}{6.0 \times 10^{-5}} = 3.85$ mol/litre

96. $K_c = K_p = \frac{PCO_2}{PCO} = 6.0 \times 10^2$

If PCO is 150 torr, PCO_2 can never exceed $760 - 150 = 610$ torr. Then $Q = 610/150 = 401$ Since this is less than K, the reaction will shift in the direction of more product. Reduction will therefore occur.

Linked-Comprehension Type Questions

126. $NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$

Initially $\frac{3.06}{51}$ mole 0 0

= 0.06 mole 0 0

At eq. $0.06 \times \frac{70}{100}$ $0.06 \times \frac{30}{100}$ $0.06 \times \frac{30}{100}$

= 0.042 = 0.018 = 0.018

$K_C = [NH_3]\,[H_2S]$

(As NH_4HS is solid so it is taken)

$= \frac{0.018}{2} \times \frac{0.018}{2}$

$= 8.1 \times 10^{-5}$ mol² lit⁻²

127. $K_P = K_C\,(RT)^{\Delta n}$

$= 8.1 \times 10^{-5} \times (0.082 \times 300)^2$

$= 0.049$ atm²

128. Since NH_4HS (s) is a compound so its active mass is assumed as unity in any condition.

129. As $\Delta n_g = 2$

that is, $K = K_C$

131. As $\Delta G^\circ = -2.303\ RT \log_{10} KP$

$\Delta G^\circ = -2.303 \times 2 \times 673 \times \log_{10}(1.64 \times 10^{-4})$

On solving, we get

$\Delta G^\circ = 11.733$ kcal

132. As $Kc' = \sqrt{Kc} = \sqrt{(1.49 \times 10^{-5})}$

$= 3.86 \times 10^{-3}$ lit mol⁻¹

135. As $\alpha = \frac{D - d}{(n - 1)\,d}$.

(As D = M/2 = 208.5/2 = 104.25)

$$\alpha = \frac{104.25 - 57.92}{(2-1) \times 57.92}.$$

On solving, we get

$\alpha = 0.8\%$

$\alpha\% = 0.8 \times 100 = 80\%$

132. As $K_P = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{\alpha^2}{1-\alpha^2} \cdot P$

$$0.202 = \frac{\alpha^2}{1-\alpha^2} \times 1.5$$

On solving, we get

$\alpha = 0.344$

Volume percent of Cl_2 = Mole fraction × 100

$$= \frac{\alpha}{1+\alpha} \times 100$$

$$= \frac{0.344}{1 + 0.344} \times 100 = 25.6\%$$

134. $K_c = \frac{K_p}{(RT)^{\Delta n}}$;

$\Delta n = +1$, T = 700K

$$K_c = \frac{0.76}{(0.082)(700)^{+1}}$$

= 0.01323 = 0.013

Assertion-Reason Type Questions

135. $CCl_4(g) \rightleftharpoons C(s) + 2Cl_2(g)$

Initialy	2.00atm	0 atm
Change	–x atm	+2x atm
At equil	(2.00–x)atm	2x atm

$$K_p = 0.76 = \frac{P_2Cl_2}{PCCl_4} = \frac{(2x)^2}{(2.00-x)}$$

$1.52 - 0.76x = 4x^2$;

$4x^2 + 0.76x - 1.52 = 0$

Using the quadratic formula ,

a = 4, b = 0.76, c = –152

$$x = \frac{-0.76 \pm \sqrt{(0.76)^2 - 4(4)(-1.52)}}{2(4)}$$

$$= \frac{0.76 + 4.99}{8} = 0.5287$$

= 0.53 atm

fraction CCl_4 reacted $= \frac{x \text{ atm}}{2.00 \text{ atm}}$

= 0.53

2.00

= 0.264 = 26%

140. $PCl_2 = 2x = 2(0.5287) = 1.06$ atm

$PCCl_4 = 2.00 - x = 2.00 - 0.5287$

= 1.47 atm

143. $2NO\ (g) + O_2\ (g) \leftrightarrow 2NO_2$

When pressure is increased then equilibrium shift in those direction where volume that is, number of moles decreases.

144. The rate of a reaction is first order of equilibrium.

150. The temperature dependence of the equilibrium constant is related to $\Delta S°$ as well as $\Delta H°$ for the reaction.

154. At equilibrium its free energy change , ΔG which is zero for a spontaneous process, $\Delta G < 0$

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162. Catalyst has no effect on equilibrium. Decreasing the volume or pressure has no effect because nr = np. Therefore, the equilibrium shifts in the forward direction by increasing the conc. of reactants CO_2 (g).

163. Temperature and pressure both effect equilibrium but catalyst has no effect (Le – Chatelier's principle).

164. Concentration of products increase with time so Q increases.

$$Q = \frac{[C][D]}{[A][B]}$$

165. $\Delta ng = 2 - 4 = -2$

$Kp = Kc.(RT)^{\Delta n}$

$Kc = Kp/(RT)^{\Delta n}$

$$= \frac{1.44 \times 10^{-5}}{(0.0821 \times 773)^{-2}}$$

166. K_p (equilibrium constant) is independent of pressure and concentration

167. When volume is decreased, pressure increases and this will favour backward reaction. Thus, degree of dissociation decreases but K_p does not change since temperature is constant.

168. $K_1 = 3.5 \times 10^{-3} = \frac{[Ag(NH_3)_2]^+}{[Ag^+]\ [NH_3]}$

$$K_2 = 1.74 \times 10^{-3} = \frac{[Ag(NH_3)_2]^+}{[Ag(NH_3)]^+\,[NH_3]}$$

$$K_3 = K_1 \times K_2 = \frac{[Ag(NH_3)_2]^+}{[Ag^+]\,[NH_3]_2}$$

formation constant K_3 for

$Ag^+ + 2\,NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$

$K_3 = 3.5 \times 10^{-3} \times 1.74 \times 10^{-3}$

$= 6.08 \times 10^{-6}$

1. $\Delta G^\circ = -2.303\ R \log_{10} K$

$\Delta H^\circ = T\ \Delta S^\circ = -2.303\ RT \log_{10} K$

$[-54.07 \times 10^3 - 298 \times 10]$

$= -2.303 \times 8.314 \times 298 \log_{10} K$

$$\log_{10} K = \frac{57050}{5705} = 10$$

Numericals For Practice

1. Three moles of PCl_5, three moles of PCl_3 and two moles of Cl_2 are taken in a closed vessel. If at equilibrium the vessel has 1.5 moles of PCl_5, the number of moles of PCl_3, present in it is

a. 8 **b.** 4.5
c. 2.1 **d.** 10

2. An acid reacts with glycerine to form complex and equilibrium is established.

$NiO\ (s) + CO\ (g) \rightleftharpoons Ni\ (s) + CO_2\ (g)$,

If the heat of reaction at constant volume for above reaction is 1200 cal more than at constant pressure and the temperature is 300 K, then which of the following expression is true?

a. $K_P = K_C$ **b.** $K_P < K_C$
c. $K_C < K_P$ **d.** None of these

3. Equivalent amounts of H_2 and I_2 are heated in a closed vessel till equilibrium is obtained. If 80% of the hydrogen is converted to HI, the K_C at this temperature is

a. 14 **b.** 19
c. 64 **d.** 0.32

4. $I_2 + I^- \rightleftharpoons I_3^-$. This reaction is set up in aqueous medium. We start with one mole of I_2 and 0.5 mole of I^- in 1 litre flask. After equilibrium is reached, addition of excess of $AgNO_3$ gave 0.25 mole of yellow precipitate immediately. Equilibrium constant of the reaction is

a. 13.6 **b.** 1.33
c. 2.26 **d.** 3.54

5. For the Equilibrium

$2IBr \rightleftharpoons I_2 + Br_2$

$Kc = 8.5 \times 10^{-3}$ at 150° C. If 0.025 mol of IBr is placed in a 2.0 –L container, what is the concentration of this substance after equilibrium is reached?

a. 1.10M **b.** 0.011M
c. 0.022M **c.** 2.20M

6. 1.6 mol of $PCl_{5(g)}$ is placed in 4 dm³ closed vessel. When the temperature is raised to 500 K, it decomposed and at equilibrium 1.2 mol of $PCl_{5(g)}$ remains. What is the K_C value for the decomposition of $PCl_{5(g)}$ to $PCl_{3(g)}$ and $Cl_{2(g)}$ at 500 K?

a. 0.012 **b.** 0.098
c. 0.033 **d.** 0.056
e. 0.002

7. Two moles of an equimolar mixture of two alcohols. R_1 – OH and R_2 – OH are esterified with one mole of acetic acid. If 80% of the acid is consumed and the quantities of ester formed under equilibrium are in the ratio of 3:2, the value of the equilibrium constant for the esterification of R_1 – OH with acetic acid is

a. ~3.7 **b.** ~3.1
c. ~1.3 **d.** ~3.5

8. The value of K_c is 4.00 at 25°C for the following equilibrium

$CH_3CO_2H + C_2H_5OH \rightleftharpoons CH_3CO_2C_2O_5 + H_2O$. What is the concentration of $CH_3CO_2C_2O_5$ at equilibrium if the reactants are initially 0.200 M each?

a. 0.085 M **b.** 0.133M
c. 0.206M **d.** 0.046M

9. A mixture of N_2O_4 (g) and NO_2 (g) under equilibrium has an average molar mass of 76. The mole fraction of N_2O_4 at equilibrium and the percent N_2O_4 dissociated are

a. 0.7 and 50.0 **b.** 0.6 and 25.0
c. 0.8 and 45.0 **d.** 0.6 and 35.0

10. The value of equilibrium constant of the reaction

$HI(g) \rightleftharpoons ½ H_2(g) + ½ I_2$ is 8.0

The equilibrium constant of the reaction

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ will be

a. 16 **b.** 1/8
c. 1/16 **d.** 1/64

11. Ammonium carbonate (solid), $H_2N.COONH_4$ (s), dissociates to give $NH_3(g)$ and CO_2 (g). The equilibrium constant for the dissociative equilibrium is 2.8×10^5 torr^3 at a certain temperature. The total dissociation pressure of the solid is

a. 123.6 torr **b.** 41.2 torr
c. 132.6 torr **d.** 2.8×10^5 torr

12. What is K_c for the reaction $2HI \rightleftharpoons H_2 + I_2(g)$ if 22.3 % of the HI decomposes at 731 K?

a. 9.66×10^{-3} **b.** 8.24×10^{-3}
c. 2.06×10^{-2} **d.** 436×10^{-3}

13. The dissociation equilibrium of a gas AB_2 can be represented as:

$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$

The degree of dissociation is 'X' and is small compared to 1. The expression relating the degree of dissociation (X) with equilibrium constant K_P and total pressure P is:

a. $(2K_P/P)^{1/2}$ **b.** (K_P/P)
c. $(2K_P/P)$ **d.** $(2K_P/P)^{1/3}$

14. For the gaseous equilibrium,

$A_2(g) + B_2(g) \leftrightarrow 2AB(g)$, the equilibrium constant at a certain temperature is 49. If an equimolar mixture of A and B is heated in a closed container to this temperature, the mole fraction of B_2 in the equilibrium mixture is

a. 1/8 **b.** 3/8
c. 1/9 **d.** 2/9

15. When pure NH_3 is maintained at 480°C and pressure of 1 atm, it dissociates to give a gaseous mixture containing 20 % NH_3 by volume. The degree of dissociation of NH_3 is

a. 5/2 **b.** 2/5
c. 2/3 **d.** 3/2

	$2NH_3(g) \rightleftharpoons$	$N_2(g)$	$+ 3H_2(g)$
Initially	A	0	0
At eq.	A(1–α)	Aα/2	3Aα/2

% of NH_3 by volume

$$= \frac{A(1-\alpha)}{A(1-\alpha) + \frac{A\alpha}{2} + \frac{3A\alpha}{2}} \times 100$$

According to condition,

$$\frac{1-\alpha}{1+\alpha} \times 100 = 20$$

On solving, we get

$\alpha = 2/3$.

16. The equilibrium constants K_{P1} and K_{P2} for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$, respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressure at these equilibria is

a. 1 : 36 **b.** 1 : 1
c. 1 : 3 **d.** 1 : 9

17. At 1000 K, the equilibrium constants for the following equilibria are K_1 and K_2.

$COCl_2(g) \leftrightarrow CO(g) + Cl_2(g)$ $K_1 = 0.329$

$2CO(g) + O_2(g) \leftrightarrow 2CO_2(g)$

$K_2 = 2.24 \times 10^{22}$

For the equilibrium,

$2COCl_2(g) + O_2(g) \leftrightarrow 2CO_2(g) + 2Cl_2(g)$, the equilibrium constant K_3 is

a. 2.424×10^{20} **b.** 4.86×10^{20}
c. 2.424×10^{21} **d.** 2.244×10^{22}

18. The equilibrium constant for the reaction

$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

is 2×10^{-6} at 185°C. Then the equilibrium constant for the reaction,

$4NO(g) + 2O_2(g) \rightleftharpoons 4NO_2(g)$

at the same temperature would be

a. 2.5×10^{11} **b.** 2.5×10^{-5}
c. 0.5×10^{11} **d.** 2.0×10^{-6}

19. The equilibrium constant for mutarotation, α-D-glucose ↔ β-D-glucose is 1.8. The percentage of the α-form in the equilibrium mixture is

a. 64.5 **b.** 35.7
c. 53.7 **d.** 44.8

20. What is K_c for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ if at 9°C a one liter solution of chloroform contains 0.250 mol of N_2O_4 and 1.64×10^{-3} mol of NO_2?

a. 634×10^5 **b.** 6.54×10^{-4}
c. 1.07×10^{-5} **d.** 2.26×10^{-6}

21. The concentration of H_3O^+ ions in a mixture of 0.05 M acetic acid and 0.5 M sodium acetate is (Ka for acetic acid is 1.5×10^{-5})

a. 1.1×10^{-6} **b.** 1.5×10^{-4}
c. 1.5×10^{-6} **d.** 2.0×10^{-4}

22. The equilibrium constant for the reaction

$SO_3 (g) \leftrightarrow SO_2 (g) + \frac{1}{2} O_2 (g)$

is $Kc = 4.9 \times 10^{-2}$. the value of Kc for the reaction

$2SO_2 (g) + O_2 (g) \leftrightarrow 2SO_3 (g)$

will be

a. 416 **b.** 2.40×10^{-3}
c. 9.8×10^{-2} **d.** 4.9×10^{-2}

23. The vapour density of N_2O_4 at a certain temperature is 30. The percentage dissociation of N_2O_4 at this temperature is

a. 25 **b.** 50
c. 75 **d.** 100

24. Ammonium carbamate when heated to 200°C gives a mixture of NH_3 and CO_2 vapours with a density of 16.0. What is the degree of dissociation of ammonium carbamate?

a. 1/2 **b.** 3/2
c. 1 **d.** 2
e. 5/2

25. At a certain temperature, the vapour density of PCl_5 in equilibrium with PCl_3 and Cl_2 is 90. The degree of dissociation of PCl_5 (mol. wt. 208.5) is

a. 15.8 **b.** 81.5
c. 8.5 **d.** 31.5

26. (A At 27°C, NO and Cl_2 gases are introduced in a 10 litre flask such that their initial partial pressures are 20 and 16 atm respectively. The flask already contains 24 g of magnesium. After some time, the amount of magnesium left was 0.2 moles due to the establishment of following two equilibria

$2NO (g) + Cl_2 (g) \rightleftharpoons 2NOCl (g)$

$1_2 (g) + Mg (s) \rightleftharpoons MgCl_2 (s), Kp = 0.2 \text{ atm}^{-1}$

The final pressure of NOCl would be

a. 18.06 atm **b.** 81.06 atm
c. 28.18 atm **d.** 45.86 atm

27. Solid NH_4HS is introduced into an evacuated flask at 24°C. The following reaction concentration of PH_3?

$NH_4HS \rightleftharpoons NH_3 (g) + H_2S(g)$

At equilibrium the total pressure (for NH_3 and H_2S taken together) was 0.614 atm. What is K_p for this equilibrium at 24°C?

a. 9.43 **b.** 94.30
c. 0.0943 **d.** 0.943

28. If, for an equilibrium, the equilibrium constants at 27°C and 127°C are respectively K_1 and K_2 and if $\Delta H°$ for the forward reaction in the above temperature range is 4576 cal, $\log_{10} K_2/K_1$ is

a. 5/6 **b.** – 5/6
c. $\frac{4576}{300 \times 400}$ **d.** $\frac{4576}{300 \times 400}$.

29. The $CaCO_3$ is heated in a closed vessel of volume 1 litre at 600 K to form CaO and CO_2. The minimum weight of $CaCO_3$ required to establish the equilibrium

$CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (g)$ is ($K_p = 2.25$ atm)

a. 2.45 **b.** 10.57 g
c. 4.57 g **d.** 14.75 g

30. When 2.00 mol of SO_2Cl_2 is placed in a 2.00-L flask at 303 K, 56 percent of the SO_2Cl_2decomposes to SO_2 and Cl_2:

$SO_2Cl_2 (g) \rightleftharpoons SO_2(g) + Cl_2(g)$

calculate K_c for this reaction at this temperature.

a. 0.71 **b.** 0.355
c. 3.55 **d.** 0.623

31. For the reaction,

$NiO (s) + CO (g) \rightleftharpoons Ni (s) + CO_2 (g)$,

$\Delta G°_P (J\,mol^{-1}) = -20700 - 12T$. Nickel is exposed to a current of hot carbon dioxide. The product gases at equilibrium at 1 atm pressure contain 500 ppm of carbon monoxide, the temperature should be

a. 273 K **b.** 204 K
c. 474 K **d.** 404 K

32. mixture of NO_2 and N_2O_4 has a vapour density of 38.3 at 300 K. What is the number of moles of NO_2 in 100 g of the mixture?

a. 0.043 **b.** 3.43
c. 4.34 **d.** 0.436
e. 1.43

33. Steam at pressure of 2 atm is passed through a furnace at 2000 K where in the reaction

$H_2O (g) \rightleftharpoons H_2 (g) + \frac{1}{2} O_2 (g), K_P = 6.4 \times 10^{-5}$

occurs. The percentage of oxygen in the exit stream would be

a. 0.08 **b.** 0.16
c. 0.36 **d.** 0.004

34. A 6.00- L vessel contained 0.0222 mole of PCl3 0.0189 mole of PCl_5, and 0.01044 moleof Cl_2 at 230°C in an equilibrium mixture. Calculate the value of K_{eq} for the reaction

$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

a. 24.45 **b.** 48.9
c. 4.89 **d.** 52.6

35. What per cent of CO_2 in air is just sufficient to prevent loss in weight when $CaCO_3$ is heated at 100°C? Equilibrium constant K_P for

$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$ is 0.0095 atm at 100°C.

a. 1.85% **b.** 0.15 %
c. 0.05% **d.** 0.95 %

ANSWER KEYS

Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.
1.	b	2.	b	3.	c	4.	b	5.	b
6.	c	7.	a	8.	b	9.	b	10.	d
11.	a	12.	c	13.	d	14.	c	15.	c
16.	a	17.	c	18.	a	19.	b	20.	c
21.	c	22.	a	23.	b	24.	c	25.	a
26.	a	27.	c	28.	a	29	c	30.	a
31.	d	32.	d	33.	a	34.	b	35.	a

Hints and Explanations

1. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$
3 2 1 (Initially)
(3 – x) (3+ x) (2+x) (At equilibrium)
Given that , (3 – x) = 1.5

Therefore no of moles of $PCl_{3(g)}$ present is

= 3 + 1.5 = 4.5

2. As $\Delta E - \Delta H = 1200$ cal

$\Delta H = \Delta E + \Delta nRT$

$\Delta nRT = \Delta H - \Delta E = -1200$

So $\Delta n = -2$

$K_P = K_C\,(RT)^{\Delta n}$

$$\frac{K_P}{K_C} = 1.648 \times 10^{-3}$$

Therefore, $K_P < K_C$

3. $H_2 + I_2 \rightleftharpoons 2HI$
Initial a a mol
At eq. a – 0.8a a – 0.8a 2 × 0.8a
= 0.2a =0.2a = 1.6a

molar– $\dfrac{0.2\,a}{V}$ $\dfrac{0.2\,a}{V}$ $\dfrac{1.6\,a}{V}$
conc.

$$K_C = \frac{[HI]^2}{[H_2]\,[I_2]} = \frac{(1.6a/V)^2}{(0.2a/V)\,(0.2a/V)}$$

$$= \frac{(1.6)^2}{(0.2)^2} = \frac{2.56}{0.04} = 64$$

4. $I_2 + I^- \rightleftharpoons I_3^-$
Initial conc. 1 0.5 0
Eq. conc. (1–X) (0.5–X) X
0.5 – X = 0.25
X = 0.25

$$Keq = \frac{[I_3^-]}{[I_2]\,[I^-]} = \frac{0.25}{0.25 \times 0.75} = 1.33$$

6. 1.6 mol of PCl_3 is placed in 4 dm^3 closed vessel

$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

1.6 mol 0 0 (Initially)

$(1.6 - x) \times$ mol $\times$ mol (At equilibrium)

Given that $1.6 - x = 1.2$

As $x = 0.4$ mol

Therefore, $[P_{Cl_5}] = \frac{1.2}{4} = 0.3$, $[P_{Cl_3}] = \frac{0.4}{4} = 0.1$

and $[Cl_2] = \frac{0.4}{4} = 0.1$

$$\text{So, } K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]} = \frac{0.1 \times 0.1}{0.3} = 0.033$$

7. $R_1OH + CH_3COOH \rightleftharpoons CH_3COOR_1 + H_2O$

$(1 - X)\ (1 - X - Y)\ X\ (X+Y)$

$R_2OH + CH_3COOH \rightleftharpoons CH_3COOR_2 + H_2O$

$(1 - Y)\ (1 - X - Y)\ Y\ (X+Y)$

As in esterification process the amount of acid consumed = 80%

So $X + Y = 0.8$

$X/Y = 3/2$

$X = 0.48$ and $Y = 0.32$

For first esterification process,

$$\text{Equilibrium constant} = \frac{X(X+Y)}{(1-X)(1-X-Y)}$$

$$K_{C1} = \frac{0.48 \times 0.8}{0.52 \times 0.2}$$

$K_{C1} \approx 3.7$

9. Molar masses: $N_2O_4 = 96$

$NO_2 = 46$

$M = x \,.\, 96 + (1 - x)\, 46 = 76$

$96x + 46 - 46\,x = 76$

$x = 0.6 = [N_2O_4]$ eq.

$N_2O_4 \leftrightarrow 2NO_2$

Equilibrium mixture contains 0.6 moles of N_2O_4 and 0.4 moles NO_2.

Initial moles of $N_2O_4 = 0.6 + \frac{0.4}{2} = 0.8$moles

$$\text{Percentage of dissociation} = \frac{0.2 \times 100}{0.8}$$

$= 25$

10. $HI\,(g) \rightleftharpoons \tfrac{1}{2} H_2\,(g) + \tfrac{1}{2} I_2\,(g)$

$$K = \frac{[H_2]^1}{{}^2\,[I_2]^{1/2}/[HI]} = 8$$

$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$

$$K' = \frac{[HI]^2}{[H_2]\,[I_2]} = (1/8)^2$$

$K' = 1/64.$

11. $H_2N.COONH_4\,(s) \leftrightarrow 2NH_3\,(g) + CO_2\,(g)$

(2p) (p)

$K_P = p^2_{NH3}\,.\,p_{CO2} = (2p)^2p = 4p^3$

$= 2.8 \times 10^5$ $torr^3$.

$p^3 = 0.7 \times 10^5\ torr^3 = 70 \times 10^3\ torr^3$

$p = 41.2$ torr

Total dissociation pressure = 3p

= 123.6 torr

13. $2AB_2\,(g) \rightleftharpoons 2AB\,(g) + B_2\,(g)$

2 0 0 intially

$2(1 - X)$ $2X$ X at. eq.

Amount of moles at equilibrium

$= 2(1 - X) + 2X + X = 2 + X$

$$K_P = \frac{[P_{AB}]^2\,[P_{B2}]}{[P_{AB2}]^2}$$

$$K_P = \frac{[\frac{2X}{2+X} \times P]^2 \times [\frac{X}{2+X} \times P]}{[\frac{2(1-X)}{2+X} \times P]^2}$$

$$K_P = \frac{\frac{4X^3}{2+X} \times P}{4\,(1-X)^2}$$

$$K_p = \frac{4X^3 \times P}{2} \times \frac{1}{4}.$$

(As $1 - X \approx 1$ & $2 + X \approx 2$)

$X = (8K_p/4P)^{1/3} = (2K_p/P)^{1/3}$

14. $A_2\,(g) + B_2\,(g) \leftrightarrow 2AB\,(g).$

$(a - x)$ $(a - x)$ $(2x)$

(total number of moles = 2a)

$$\text{Equilibrium constant } (K_p \text{ or } K_c) = \frac{4x^2}{(a-x)^2} = 49$$

Total number of moles at equilibrium = 2a

$$\frac{2x}{a-x} = 7; \frac{a-x}{2x} = \frac{1}{7}$$

$$\frac{a}{2x} - \frac{1}{2} = \frac{1}{7}; \frac{a}{2x} = \frac{9}{14}.$$

$2x/a = 14/9$

$x/a = 7/9$

$a - x/2a = 1/9$.

15. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

Initially A O O

At. eg. $A(1-\alpha)$ $A\alpha/z$ $3A\alpha/2$

% of NH_3 by volume

$$= \frac{A(1-\alpha)}{A(1-\alpha) + \frac{A\alpha}{2} + \frac{3A\alpha}{2}}$$

According to conditions

$\frac{1-\alpha}{1-\alpha} \times 100 = 20$; on solving weget

$\alpha = 2/3$

16. $X \rightleftharpoons 2Y$

1 0

$(1-x)$ $2x$

$$K_{P1} = \frac{(2x)^2}{(1-x)}(P_1/1+x)^1$$

$Z \rightleftharpoons P + Q$

1 0 0

$(1-x)$ x x

$$K_{P2} = \frac{(x)^2}{(1-x)} \qquad (P_2/1+x)^1$$

$$\frac{4 \times P_1}{P_2} = \frac{1}{9}$$

On solving, we get

$P_1 : P_2 = 1 : 36$

17. The first equilibrium is multiplied by 2 and added to equilibrium (2) to get equilibrium (3).

$K_3 = (K_1)^2 \times K_2$

$K_3 = (0.329)^2 \times 2.24 \times 10^{22}$

$= 0.2424 \times 10^{22} = 2.424 \times 10^{21}$

18. $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

$K = 2 \times 10^{-6}$

For the reverse reaction,

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

$$K = \frac{1}{2 \times 10^{-6}}.$$

Multiplying with 2,

$4NO(g) + 2O_2(g) \rightleftharpoons 4NO_2(g)$

$K = (1/2 \times 10^{-6})^2$

$= 0.25 \times 10^{12} = 2.5 \times 10^{11}$

19. α-D-glucose ↔ β-D-glucose

$(1-x)$ mole x mole

$$K = \frac{x}{1-x} = 1.8$$

$x = 1.8 - 1.8x$

$2.8\,x = 1.8$

$x = 1.8/2.8 = 9/14 = 0.643$

$(1-x) = 0.357$

α-form in the equilibrium mixture = 35.7%

20. $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

Initially 0.05 M 0 0

At eq. (0.05-X) X X

$CH_3COONa \rightarrow CH_3COO^- + Na^+$

Initially 0.05 M 0 0

At eq. 0 0.5 0.5

$[CH_3COO^-] = 0.5 + X = 0.5$

$[CH_3COOH] = 0.05 - X = 0.05$

$$1.5 \times 10^{-5} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$$= \frac{0.5 \times [H_3O^+]}{0.05}$$

$$[H_3O^+] = \frac{1.5 \times 10^{-5} \times 0.05}{0.5} = 1.5 \times 10^{-6}\text{ M}$$

22. $K_{C1} = 4.9 \times 10^{-2} = \frac{[SO_2][O_2]^{1/2}}{[SO_3]}$

$$K_{C2} = \frac{[SO_3]^2}{[SO_2]^2[O_2]}.$$

$K_{C2} = (1/K_{C1})^2 = (1/4.9 \times 10^{-2})^2$

$= 416.5$

23. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Vapour density $= \frac{92}{2} = 46$

Density = 30

$$\alpha = \frac{D-d}{d} = \frac{46-30}{30} = 0.5$$

So degree of dissociation = 50%.

24. $NH_2COONH_4 \rightarrow 2NH_3 + CO_2$

Initial 1 mole

After diss. $1 - \alpha$ 2α α

Total = $2 + 1\ \alpha$

Theoretical density (d) $\alpha\ \frac{1}{V}$.

Observed density (d) $\alpha\ \frac{1}{(1 + 2\ \alpha)V}$.

$D/d = 1 + 2\alpha$

$$\alpha = \frac{1}{2}\frac{(D - d)}{d}$$

$$= \frac{1}{2}\frac{(48 - 16.0)}{16.0} = 1.0$$

25. Degree of dissociation

$$\alpha = \frac{(V.D)_t - (V.D)_0}{(n - 1)\ (V.D)_0}$$

$$(V.D)_t = \frac{208.5}{2} = 104.25$$

$$\alpha = \frac{104.25 - 90}{90} = 0.158$$

26. $K_P = 0.2 = \frac{1}{PCl_2}$.

(PCl_2 at equilibrium = 5 atm)

$2NO\ (g) + Cl_2\ (g) \rightleftharpoons 2NOCl\ (g)$

Initially 20 16 0

At eq. 20-2X 16-X-Y 2X

$Cl_2\ (g) + Mg\ (s) \rightleftharpoons MgCl_2\ (s)$

Initially 16 1 0

At eq. 16-X-Y 1-Y' Y'

= 0.2

Y' = 0.8

(As Y' in in moles while Y is pressure in atm)

$$Y = \frac{0.8 \times 0.082 \times 300}{10} = 1.98$$

As $16 - X - Y = 5$

On solving, we get

X = 9.03

So $P_{NOCl} = 18.06$

27. $K_p = P_{NH3} \times P_{H2S}$;Pt = 0.614atm

If the equilibrium amounts of NH_3 and H_2S are due solely to the decomposition of NH_4HS (s), the equilibrium pressure of the two gases are equal, and each is ½ of the total pressure.

$P_{NH_3} = P_{H_2S} = 0.614$ atm/2 = 0.307 atm

$Kp = (0.307)^2 = 0.0943$

28. $\log \frac{K_2}{K_1} = \frac{\Delta H°}{2.303\ R}[\frac{1}{300} - \frac{1}{400}]$

$2.303\ R = 2.303 \times 1.987$

$= 4.576$ cal $mol^{-1}\ K^{-1}$.

$\Delta H° = 4576$ cal mol^{-1}

$\log K_2/K_1 = 1000\ (1/1200) = 10/12$

= 5/6.

29. As $K_P = P_{CO_2} = 2.25$ atm

So number of moles of CO_2

$$= \frac{2.25 \times 1}{0.0821 \times 600}.$$

The minimum moles of $CaCO_3$ needed

= 0.0457

The minimum weight of $CaCO_3$ needed

$= 0.0457 \times 100 = 4.57$ g

30. $[SO_2Cl_2]$ = 2.00mol/2.00 L = 1.00 M. The change in $[SO_2Cl_2]$, x, = 0.56 (1.00 M) = 0.56 M

$SO_2Cl_2\ (g) \rightleftharpoons SO_2\ (g) + Cl_2\ (g)$

Initialy 1.00M 0 0

Change –0.56M +0.56M + 0.56 M

At quil. 0.44 M +0.56 M + 0.56 M

$$Kc = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]}$$

$$= \frac{(0.56)^2}{0.44}$$

= 0.7127 = 0.71 M

31. As $PCO << PCO_2$

So $K_P = \frac{PCO_2}{PCO} = \frac{1}{500 \times 10^{-6}} = 2000$

As $2.303\ RT \log_{10} K_P = -\Delta G°_P$

$2.303 \times 8.314 \times T \times \log_{10} 2000 = 20700 + 12T$

On solving, we get

T = 404.3 K

32. Assume NO_2 = X g

Then $N_2O_4 = (100 - X)$ g

Moles of NO_2 = X/46

Moles of $N_2O_4 = \frac{100 - X}{92}$

Mole fraction of NO_2

$= \frac{X/46}{X/46 + (100 - X)/96}$.

$= \frac{X}{46} \times \frac{92}{100 + X} = \frac{2X}{100 + X}$.

Molar mass of mixture

$= \frac{2X}{100 + X} \times 46 + \frac{100 - X}{100 + X} \times 92$

$= \frac{9200}{100 + X}$.

$\frac{9200}{100 + X} = 2 \times 38.3 = 76.6$

$76.6\ X = 9200 - 7660 = 1540$

$X = 20.10$ g

So moles of $NO_2 = \frac{20.10}{46} = 0.436$

33. $H_2O\ (g) \rightleftharpoons H_2 + \frac{1}{2} O_2$

Initially	2 atm	0	0
At eq.	$2 - X$	X	$X/2$

$\frac{X\ (X/2)^{1/2}}{2 - X} = 6.4 \times 10^{-5}$

$\frac{X^{3/2}}{\sqrt{2}\ (2 - X)} = 6.4 \times 10^{-5}$

As dissociation of H_2O is very less so

$P_{H_2O} \approx 2$ atm

that is, $2 - X \approx 2$

$X^{3/2} = 2\sqrt{2} \times 6.4 \times 10^{-5}$

$X^{3/2} = (2 \times 10)^{3/2} \times 10^{-6}$

On solving, we get

$X = 2 \times 16 \times 10^{-4} = 0.0032$

So % of O_2 in the exit stream

$= \frac{0.0032\ 2}{2} \text{x} 100 = 0.08\ \%$

35. For $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$

$K_P = P_{CO_2} = 0.0095$ atm

As atmospheric pressure = 1 atm

So % of CO_2 in air $= \frac{PCO_2}{P_{Total}} \times 100 = 0.95\%$

Therefore, to prevent the decomposition of $CaCO_3$ at 100°C of CO_2 in air must be greater than 0.95%.

CHAPTER 5B

Ionic Equilibrium

Chapter Contents

Solubility product, common ion effect, pH and buffer solutions; Acids and bases (Bronsted and Lewis concepts); Hydrolysis of salts, and Various levels of multiple–choice questions.

IONIC EQUIILIBRIUM

Type of Substances

Substances are of two types:

1. Non–Electrolyte: Their aqueous solution or molten state does not conduct electricity.

   Example, solution of urea, glucose, sugar, glycerine etc.

2. Electrolyte: Their aqueous or molten state conducts electricity.

Strong Electrolyte: These are much ionized in water, and hence show more conduction. Example, Strong acids like HCl, H_2SO_4, HNO_3, strong bases like MOH, $M(OH)_2$ Example, KOH, NaOH etc., and salt of strong acid or strong base like NaCl, CH_3COONa, NH_4X etc.

Weak Electrolyte: These are less ionized in water so show less conduction. Example, weak acids like CH_3COOH, HCN, H_3PO_4, H_2CO_3, weak bases like NH_4OH and their salts like NH_2CN, CH_3COONH_4 etc.,

Degree of Ionization: It is the extent to which an electrolyte gets ionized in a solvent. It is shown by α or x.

$$\alpha = \frac{\text{number of molecules dissociated}}{\text{total number of molecules}}$$

α depends upon

- Nature of solute and solvent: For strong electrolytes, α is more than that for weak electrolytes.
- $\alpha \propto$ Dielectric constant of solvent

  That is, greater the dielectric constant of a solvent more will be ionization of electrolyte in it.
- The degree of dissociation of weak electrolyte $\propto$ Dilution that is α is maximum at infinite dilution.
- $\alpha \propto 1/\text{Concentration}$
- $\alpha \propto$ Temperature

Ostwald Dilution Law

It is law of mass action for weak electrolytes and dilute solutions. It is not applicable for strong electrolytes or highly concentrated solutions.

For a Binary Weak Electrolyte

$$AB \leftrightarrow A^+ + B^-$$

$$\begin{array}{ccc} 1 & 0 & 0 \\ 1-\alpha & \alpha & \alpha \\ (1-\alpha)/V & (\alpha/V) & (\alpha/V) \end{array}$$

$$\text{so} \quad K = \frac{\alpha^2 / V^2}{(1-\alpha)/V} = \frac{\alpha^2}{(1-\alpha)/V}$$

$$K = \frac{\alpha^2}{(1-\alpha)/V} \quad \text{as } 1 >>> \alpha \text{ so } (1-\alpha) = 1$$

$$K = \frac{\alpha^2}{V} \text{ or } \alpha^2 = KV \text{ or } \alpha = \sqrt{KV}$$

$$\alpha \propto = \sqrt{V}$$

that is, at constant temperature, degree of dissociation is directly proportional to the square root of its dilution.

- If 'C' is the concentration then

  $$AB \leftrightarrow A^+ + B^-$$

  $$\begin{array}{ccc} C(1-\alpha) & C\alpha & C\alpha \end{array}$$

  $$K = \frac{C\,\alpha^2}{(1-\alpha)}$$

  $$K = C\,\alpha^2 \qquad \text{or} \qquad \alpha^2 = K/C$$

  $$\alpha = \sqrt{(K/C)}$$

  i.e,. $\alpha \propto \sqrt{1/C}$

  that is, at constant temperature, degree of dissociation is inversely proportional to the square root of its concentration.

- $\alpha = \frac{\lambda v}{\lambda \infty}$ or $\frac{\Lambda v}{\Lambda \infty}$

  Here λv or Λv is equivalent conductivity at V dilution. and $\lambda\infty$ or $\Lambda\infty$ is equivalent conductivity at infinite dilution.

- $\lambda v = Kv \times V$

  Here Kv = specific conductivity

  V = dilution

- $\boldsymbol{\lambda\infty = \lambda c + \lambda a}$

  Here **λc** and **λa** are the ionic mobilities of cation and anion respectively.

Illustrations

1. 0.16 g of N_2H_4 is dissolved in water and the total volume is made up to 500 ml. Calculate the percentage of N_2H_4 that has reacted with water in this solution. The K_b for N_2H_4 is 4.0×10^{-6} M.

Solution

$$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$$

$$\begin{array}{lccc} \text{Before dissociation} & 1 & 0 & 0 \\ \text{After dissociation} & 1-\alpha & \alpha & \alpha \end{array}$$

$$K_b = \frac{C\,\alpha^2}{(1-\alpha)}.$$

$$1 - \alpha = 1$$

$$K_b = C\alpha^2$$

$$[N_2H_4] = C = \frac{0.16 \times 1000}{32 \times 500} = 0.01$$

Given: $K_b = 4 \times 10^{-6}$ M

$$\alpha^2 = \frac{4 \times 10^{-6}}{0.01} = 4 \times 10^{-4}$$

$$\alpha = 2 \times 10^{-2}$$

$$\alpha = 0.02 \text{ or } 2\%$$

2. An aqueous solution of aniline of concentration 0.24 M is prepared. What concentration of sodium hydroxide is needed in this solution so that anilinium ion concentration remains at 1×10^{-8} M? Ka for $C_6H_5NH_3^+$ is 2.4×10^{-5} M.

Solution $C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$

$$K_b = \frac{[C_6H_5NH_3^+]\,[OH^-]}{[C_6H_5NH_2]} \quad \ldots\ldots \text{(i)}$$

$$K_b \text{ for } C_6H_5NH_2 = \frac{K_W}{\text{Ka for } C_6H_5NH_3^+}.$$

$$= \frac{10^{-14}}{2.4 \times 10^{-5}} \quad \ldots\ldots \text{(ii)}$$

As dissociation of $C_6H_5NH_2$ occurs in presence of NaOH so dissociation of $C_6H_5NH_2$ will suppress.

Here $[C_6H_5NH_2] = 0.24$

$$[C_6H_5NH_3^+] = 10^{-8}$$

$$[OH^-] = ?$$

So $\dfrac{10^{-14}}{2.4 \times 10^{-5}} = \dfrac{10^{-8} \times [OH^-]}{0.24}$

$[OH^-] = \dfrac{0.24 \times 10^{-14}}{2.4 \times 10^{-5} \times 10^{-8}} = 0.01$

$[NaOH] = 0.01$ M

3. Nicotinic acid ($Ka = 1.4 \times 10^{-5}$) is represented by the formula HNi**C**. Calculate its per cent dissociation in a solution which contains 0.10 mole of nicotinic acid per 2.0 litre of solution.

Solution

$HNiC \rightleftharpoons H^+ + NiC^-$

$1 \quad 0 \quad 0$

$(1 - \alpha) \quad \alpha \quad \alpha$

$C = \dfrac{0.1}{2} = 5 \times 10^{-2}$ mole litre^{-1}

$Ka = 1.4 \times 10^{-5}$

$Ka = \dfrac{C\alpha^2}{(1 - \alpha)} = C\alpha^2$

(As $1 - \alpha \approx 1$)

$\alpha = \sqrt{(Ka / C)} = \dfrac{\sqrt{(1.4 \times 10^{-5})}}{\sqrt{(5 \times 10^{-2})}}$

$= 1.67 \times 10^{-2}$ or 1.67 %

4. A solution contains 0.1 M H_2S and 0.3 M HCl. Calculate the conc. of S^{2-} and HS^- ions in solution. Given Ka_1 and Ka_2 for H_2S are 10^{-7} and 1.3×10^{-13} respectively.

Solution

$H_2S \rightleftharpoons H^+ + HS^- \qquad Ka_1 = 10^{-7}$

$HS^- \rightleftharpoons H^+ + S^{2-} \qquad Ka_2 = 1.3 \times 10^{-13}$

$HCl \rightarrow H^+ + Cl^-$

Due to common ion effect the dissociation of H_2S is suppressed and the $[H^+]$ in solution is due to HCl.

$Ka_1 = \dfrac{[H^+]\,[HS^-]}{[H_2S]}$

$10^{-7} = \dfrac{[0.3]\,[HS^-]}{[0.1]}$ [as $[H^+]$ from HCl = 0.3]

$[HS^-] = \dfrac{10^{-7} \times 0.1}{0.3} = 3.3 \times 10^{-8}$ M

$Ka_1 = \dfrac{[H^+]\,[HS^-]}{[H_2S]}$ and $Ka_2 = \dfrac{[H^+]\,[S^{2-}]}{[HS^-]}$

$Ka_1 \times Ka_2 = \dfrac{[H^+]^2\,[S^{2-}]}{[H_2S]}$

$10^{-7} \times 1.3 \times 10^{-13} = \dfrac{[0.3]^2\,[S^{2-}]}{[0.1]}$

$[S^{2-}] = \dfrac{1.3 \times 10^{2-} \times 0.1}{0.09} = 1.44 \times 10^{-20}$ M

Common Ion Effect

The value of degree of dissociation for a weak electrolyte is decreased by the addition of a strong electrolyte having common ion.

As a result of this effect the concentration of the uncommon ion of the weak electrolyte decreases.

Example,– (1)

$NH_4OH \leftrightarrow NH_4^+ + OH^-$

Weak

$NH_4Cl \leftrightarrow NH_4^+ + Cl^-$

Common ion

Here α for NH_4OH will be decreased by NH_4Cl.

(2)

$CH_3COOH \leftrightarrow CH_3COO^- + H^+$

$CH_3COONa \leftrightarrow CH_3COO^- + Na$

Common ion

Here α for CH_3COOH will be decreased by CH_3COONa.

- Solubility of a partially soluble salt decreases due to common ion effect. For example, presence of $AgNO_3$ or KCl decreases solubility of AgCl in water.
- Salting out of soap by addition of NaCl.
- Purification of NaCl by passing HCl gas.

Isohydric Solution: These are the solutions having same concentration of common ions.

Ionic Product of Water

It is the product of the molar concentrations of H^+ or H_3O^+ and OH^- ions. It is denoted by Kw.

$H_2O + H_2O \leftrightarrow H_3^+O + OH^-$

$Kw = [H_3^+O] \, . \, [OH^-]$

$[H^+]$ Or

Here Kw = Ionic product of water or auto pro-tolysis constant of watch

- $Kw = Ka.\ K_b$

  $pKw = -\log_{10} Kw$
- $Kw = Ka \times K_b$
- $pKw = pKa + pK_b$
- At 25°C : $Kw = 1 \times 10^{-14}$

  $pKw = 14$

  The value of Kw increases with the increase of temperature.

  For example, at 98°C, Kw is 1×10^{-12}.

pH Scale

It was introduced by Sorrenson to measure acidity or basicity of a solution. pH Potential de – H^+–ion concentration.

It is given as

$[H^+] = 10^{-pH}$

$pH = -\log_{10} [H^+]$

pH of aqueous solution is equal to –ve log of H^+ ($H_3{}^+O$) concentration in mole/litre.

- $pH = \log_{10} \dfrac{1}{[H^+]}$

pH of Weak Acid In case of a weak acid like acetic acid

$CH_3COOH \leftrightarrow CH_3COO^- + H^+$

$1 \quad 0 \quad 0$

$C(1-x) \quad Cx \quad Cx$

$K = Cx^2$

$x = \sqrt{(Ka / C)}$

$[H^+] = Cx = C\sqrt{(Ka/C)} \approx \sqrt{KaC}$

$pH = -\log_{10} Cx$

$pH = -\log_{10} \sqrt{KaC}$

Here C = Molar concentration of acid

x = Degree of dissociation

Ka = Dissociation constant of an acid

pH of Weak Base

$NH_4OH \leftrightarrow NH_4^+ + OH^-$

$1 \quad 0 \quad 0$

$(1-x) \quad Cx \quad Cx$

$[OH^-] = Cx = \sqrt{K_bC}$

$pOH = -\log_{10} Cx$

$pOH = -\log_{10} \sqrt{K_bC}$

Here K_b = dissociation constant of a base.

REMEMBER

- pH of strong acid or base does not depend upon temperature
- pH of weak acid deceases with increase in temperature due to increase in ionization.
- pH of weak base increases with increase in temperature due to increase in ionisation or $[OH^-]$ ion concentration.

pOH

$[OH^-] = 10^{-pOH}$

$pOH = -\log_{10} [OH^-]$ or $\dfrac{1}{\log_{10} [OH^-]}$.

- $pH + pOH = 14$
- $pH + pOH = pKw$
- $pKa = -\log_{10} Ka$
- $pKa \propto \dfrac{1}{Ka} \propto \dfrac{1}{\text{Acidic Strength}}$.
- $pK_b = -\log_{10} K_b$
- $pK_b \propto \dfrac{1}{K_b} \propto \dfrac{1}{\text{Basic strength}}$.
- pK: –ve log of dissociation constant.
- A weak acid has high pK_a
- A weak base has high pK_b.

To Find the Nature of Solution

- If $[H^+] > 10^{-7}$, pH is less than 7 and the solution is acidic.
- If $[H^+] = 10^{-7}$, pH is 7 and the solution is neutral.
- If $[H^+] < 10^{-7}$, pH is more than 7 and the solution is basic.

pH Range of Some Substances

Substance	pH – range
Gastric	1 – 3.0
Soft drink	2 – 4.0
Lemons	2.2 – 2.4
Vinegar	2.4 – 2.4
Urine	4.8 – 8.4
Milk	6.3 – 6.6
Saliva	6.5 – 7.5
Blood	7.3 – 7.5
Sea water	8.5
Tears	7.4

Limitation of pH–Scale

- pH value of the solution does not give us at once idea of the relative strength of the solution.
- pH is zero for 1N solution of strong acid.
- pH is negative for concentration 2N, 3N, 10N etc for strong acids.
- At higher concentration in place of pH Hammet acidity functions are used.

Illustrations

5. How many grams of NaOH must be dissolved in one litre of solution to give it a pH value of 11?

Solution Given pH of solution = 11

$$pH = -\log [H^+]$$

$$11 = -\log [H^+]$$

$$[H^+] = 10^{-11}\ M$$

$$Kw = [H^+]\,[OH^-] = 1 \times 10^{-14}$$

$$[OH^-] = \frac{1 \times 10^{-14}}{10^{-11}} = 1 \times 10^{-3}\ M$$

$$[OH^-] = 1 \times 10^{-3}\ M$$

Strength = Molarity × mol. weight

$= 10^{-3} \times 40$

= 0.04 g / litre.

6. Find the pH of 0.004 M NH_4OH having 3.2 % dissociation.

Solution

$$\begin{array}{llll} NH_4OH \rightarrow & NH_4^+ & + OH^- & \text{(weak base)} \\ c & 0 & 0 & \text{conc. before ionization} \\ c(1-\alpha) & c.\alpha & c.\alpha & \text{conc. after ionization} \end{array}$$

$$[H^+] = c.\alpha = 3 \times 10^{-3} \times \frac{4.3}{100}.$$

$$= 1.29 \times 10^{-4}\ M$$

$$pH = -\log [H^+] = -\log [1.29 \times 10^{-4}]$$

$$pH = 3.8894$$

7. Find the pH of solution obtained by mixing 20 ml of 0.1 M HCl and 30 ml of 0.2 M H_2SO_4

Solution Milli equivalent of H^+ from HCl = $20 \times 0.1 = 2$

Milli equivalent of H^+ from H_2SO_4

$= 30 \times 0.2 \times 2 = 12$

Total milli equiv. of H^+ in solution = 2 + 12

= 14

Total volume of solution = 20 + 30 = 50

$$[H^+] = \frac{M_{eq}}{V_{\text{in ml}}} = \frac{14}{50} = 0.28$$

$$pH = -\log [H^+] = -\log (0.28) = 0.5528$$

8. Calculate the pH of a solution containing 2.0 g of NaOH per litre of water.

Solution As the solution contains 2.0 g of NaOH per

litre of water, its normality $= \frac{2}{40} = \frac{1}{20}$ N

$[OH^-]$ = 1/20 g–ion / litre

$$[H^+]\,[OH^-] = 10^{-14}$$

$$[H^+]\,[1/20] = 10^{-14}$$

$[H^+] = 20 \times 10^{-14} = 2 \times 10^{-13}$ g ion /litre

$$pH = -\log [H^+]$$

$$= -\log [2 \times 10^{-13}]$$

$= – [\log 2 – 13 \log 10]$

$= –[0.3010 – 13]$

$= 12.699$

9. Calculate the pH of a solution obtained by mixing 50 ml of 0.01 M $Ba(OH)_2$ solution with 50 ml water.

Solution

$N_1V_1 = N_2V_2$

$Ba(OH)_2$ mixture

[Normality of solution of $Ba(OH)_2$ = 2 × its molarity, as its mol. wt = 2 × eq. wt]

$0.01 \times 2 \times 50 = N_2 \times (50 + 50)$

(as it is assumed as 100% ionized).

$$N_2 = \frac{0.01 \times 100}{100} = 0.01\text{ N}$$

$[OH^-] = \alpha\,.\,N = 1 \times 0.01 = 10^{-2}$

$pOH = –\log [OH^-] = –\log 10^{-2} = 2 \log 10$

$pOH = 2$

$pH + pOH = 14$

$pH + 2 = 14$

$pH = 12$

10. A 0.100 N NaOH solution was added to 50.0 ml of 0.100 N $HC_2H_3O_2$ solution. What would be the pH of the solution after the addition of (i) 50.0 ml of NaOH solution and (ii) 60.0 ml of NaOH solution?

Solution

(i) The addition of 50.00 ml of 0.100 N NaOH solution represents the end point of the titration. Therefore, the solution will be:

$$\frac{0.00500\text{ mole } NaC_2H_3O_2}{0.100\text{ litre solution}}$$

= 0.0500 M with respect to $NaC_2H_3O_2$.

$$\text{As}\quad K_h = \frac{K_W}{K_b} = \frac{[HC_2H_3O_2]\,[OH^-]}{[C_2H_3O_2^-]}$$

Suppose $X = [HC_2H_3O_2] = [OH^-]$

Since salt is essentially 100% ionized,

$[C_2H_3O_2^-] = 0.05$ mole per litre

$$K_h = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{X^2}{5.0 \times 10^{2-}}\,.$$

On solving,

$X = 5.3 \times 10^{-6}$ mole OH^- per litre

As $[H^+]\,[OH^-] = 1.0 \times 10^{-14}$ at 25°C

$$[H^+] = \frac{1.0 \times 10^{-14}}{5.3 \times 10^{-6}} = 1.9 \times 10^{-9}$$

$$pH = \log_{10} \frac{1}{1.9 \times 10^{-9}} = 8.7$$

(ii) All OH^- ions will originate from the excess of 10.0 ml of 0.100 N NaOH, therefore

$$OH^-] = \frac{(0.010)\,(0.100)\text{ mole}}{0.100\text{ litre}}$$

$= 9.1 \times 10^{-3}$ mole per litre

$$pOH = \log_{10} \frac{1}{9.1 \times 10^{-3}} = 2.04$$

$pH = 14.00 – 2.04 – 11.96$

11. Saccharin ($Ka = 2 \times 10^{-12}$) is a weak acid represented by formula HSa**C**. A 4×10^{-4} mole amount of saccharin is dissolved in 200 cm^3 water of pH 3. Assuming no change in volume, calculate the concentration of SaC^- ions in the resulting solution at equilibrium.

Solution

$$[HSaC] = \frac{\text{mole}}{\text{litre}} = \frac{4 \times 10^{-4}}{200 / 1000} = 2 \times 10^{-3}\text{ M}$$

The dissociation of HSaC takes place in presence of $[H^+] = 10^{-3}$

$$\begin{array}{lccc} & HSaC & \rightleftharpoons H^+ & + SaC^- \\ \text{Conc. before disso.} & 2 \times 10^{-3} & 10^{-3} & 0 \end{array}$$

In presence of H^+ the dissociation of HSaC is almost negligible because of common ion effect. So at equilibrium

$[HSaC] = 2 \times 10^{-3}$

$[H^+] = 10^{-3}$

$$Ka = \frac{[H^+]\,[SaC^-]}{[HSaC]}$$

$$2 \times 10^{-12} = \frac{[10^{-3}]\,[SaC^-]}{2 \times 10^{-3}}$$

$[SaC^-] = 4 \times 10^{-12}$ M

12. An aqueous solution contains 10% ammonia by mass and has a density of 0.99 g cm^{-3}. Calculate hydroxyl and hydrogen ion concentration in this solution. Ka for $NH_4^+ = 5.0 \times 10^{-10}$ M

Solution

$$\frac{\text{Weight of } NH_3}{\text{Weight of solution}} = \frac{10}{100}.$$

As 100 g solution contains 10 g NH_3

$$\text{So } MNH_3 = \frac{10 \times 1000}{17 \times (100/0.99)} = 5.82$$

(as V = mass/density)

$$NH_3 + H_2O \rightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Before diss. $\quad 1 \quad 0 \quad 0$

After diss. $\quad (1 - \alpha) \quad \alpha \quad \alpha$

$[OH^-] = C.\ \alpha = C\sqrt{(K_b / C)} = \sqrt{(K_b\ .\ C)}$

As $\quad C = 5.82$ M

$$K_b = \frac{K_W}{Ka} = \frac{10^{-14}}{5 \times 10^{-10}} = 2 \times 10^{-5}$$

$[OH^-] = \sqrt{[2 \times 10^{-5} \times 5.82]} = 1.07 \times 10^{-2}$ M

$$[H^+] = \frac{10^{-14}}{1.07 \times 10^{-2}} = 0.9268 \times 10^{-12} \text{ M}$$

$pH = -\log_{10} [H^+] = -\log 0.9268 \times 10^{-12}$

$= 12.0330$

13. Calculate the pH at the equivalence point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M NaOH. Ka for acid = 1.9×10^{-5}.

Solution Suppose V ml of acid and V ml of NaOH is used concentration of both acid and NaOH are same.

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

Conc. $\quad \frac{0.1 \times V}{2V} \quad \frac{0.1 \times V}{2V} \quad 0 \quad 0$
before reac.

Conc. after $\quad 0 \quad 0 \quad \frac{0.1 \times V}{2V} \quad \frac{0.1 \times V}{2V}$
reaction

$$[CH_3COONa] = \frac{0.1}{2} = 0.05 \text{ m}$$

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

$[OH^-] = C\ \alpha = C.\sqrt{(K_h / C)} = \sqrt{(K_h .C)}$

$= \sqrt{[(K_W / Ka)\ .C]}$

$$= \frac{\sqrt{(10^{-14} \times 0.05)}}{\sqrt{(1.9 \times 10^{-5})}} = 5.12 \times 10^{-6}$$

pOH = 5.29

pH = 8.71

14. How many moles of calcium hydroxide must be dissolved to produce 250.0 ml of an aqueous solution of pH 10.65? Assume complete dissociation.

Solution pH + pOH = 14

pOH = 14 – pH

= 14 – 10.65 = 3.35

$-\log [OH^-] = 3.35$

$\log [OH^-] = -3.35 = \bar{4}.65$

$[OH^-]$ = Antilog $\bar{4}.65 = 4.47 \times 10^{-4}$ M

$= 4.47 \times 10^{-4}$ mol L^{-1}

Moles of OH^- required for 250 ml

$$= \frac{4.47 \times 10^{-4} \text{ mol } L^{-1}}{(250 \text{ ml} / 1000 \text{ ml}) \text{ L}} = 1.12 \times 10^{-4} \text{ mol}$$

As 1 mol $Ca(OH)_2$ produces 2 mol OH^- ions.

So moles of $Ca(OH)_2$ dissolved

$$= \frac{1.12 \times 10^{-4} \text{ mol}}{2} = 5.6 \times 10^{-5} \text{ mol } Ca(OH)_2$$

15. The pH of the 0.10 M hydrocyanic acid solutions is 5.2. What is the value of Ka for hydrocyanic acid?

Solution $pH = -\log H^+ = 5.2$

$\log [H^+] = -5.2 = \bar{6}.8$

$[H^+]$ = Antilog $\bar{6}.8 = 6.31 \times 10^{-6}$ M

$$HCN \rightleftharpoons H^+ + CN^-$$

$0.1 - 6.31 \times 10^{-6} \quad 6.31 \times 10^{-6} \text{ M} \quad 6.31 \times 10^{-6} \text{ M}$

= 0.1 M

$$Ka = \frac{[H^+]\ [CN^-]}{[HCN]}$$

$$= \frac{(6.31 \times 10^{-6}\,M) \times (6.31 \times 10^{-6}\,M)}{0.1\,M}$$

$$= 3.9816 \times 10^{-10} = 4.0 \times 10^{-10}$$

16. The concentration of HCN and NaCN in a solution is 0.01 M each. Calculate the concentration of hydrogen and hydroxyl ions if the dissociation constant of HCN is 7.2×10^{-10}.

Solution

$$\begin{array}{llll} \text{(i)} & HCN \rightleftharpoons & CN^- + & H^+ \\ & (0.01 - X)\,M & X\,M & X\,M \end{array}$$

$$\begin{array}{llll} \text{(ii)} & NaCN \rightleftharpoons & CN^- + & Na^+ \\ \text{Initial} & 0.01\,M & 0\,M & 0\,M \\ \text{Final} & 0.0\,M & 0.01\,M & 0.01\,M \end{array}$$

So at equilibrium, $[H^+] = X\,M$

$$[CN^-]_{total} = [CN^-]_{acid} + [CN^-]_{salt}$$

$$= X\,M + 0.01\,M = 0.01\,M$$

$$[HCN] = 0.01\,M - X\,M = 0.01\,M$$

$$pH = pKa + \log_{10} \frac{[CN^-]}{[HCN]}.$$

$$= -\log 7.2 \times 10^{10} + \log \frac{1.01\,M}{0.01\,M}$$

$$-\log [H^+] = \log 7.2 \times 10^{-10}$$

$$[H^+] = 7.2 \times 10^{-10}\,M$$

$$[OH^-] = \frac{K_W}{[H^+]}.$$

$$= \frac{1 \times 10^{-14}}{7.2 \times 10^{-10}} = 1.4 \times 10^{-5}\,M$$

Buffer Solution

Buffer solution is the solution whose pH does not change much by the addition of a small amount of a strong acid or a base. It is also called reserve acidity or basicity solution as it resists change of pH value and this action to resists pH change is called Buffer action.

Features:

- It has a definite pH i.e., reserve acidity or basicity.
- It's pH does not change on standing for a long time also.
- It's pH does not change on dilution also.
- It's pH slightly (unnoticeable) changes by the addition of small quantity of a strong acid or base.

Buffer Capacity

Buffer capacity is the ratio of number of moles of the acid or base added in one litre of the solution so as to change its pH by unity. It is denoted by Φ.

$$\Phi = \frac{\text{No. of moles of acid / base added to 1 lit}}{\text{Change in pH}}$$

Or

It is also defined as the amount of a strong acid or strong base needed to change the pH of a buffer by one unit. Suppose we take a buffer solution of volume 1 L with 'q' mole of salt and 'p' mol of salt + acid . The pH of the buffer can be given as follows

$$pH = pK_a + \log \frac{q}{p-q}.$$

On adding 'x' mol of a strong acid (monobasic), the pH changes to

$$pH' = pK_a + \log \frac{q-x}{(p-q+x)}.$$

$$\Delta pH = \log \frac{q}{p-q} - \log \frac{q-x}{(p-q+x)}$$

$$\Delta pH = \log \left(\frac{q}{p-q} \times \frac{(p-q+x)}{(q-x)} \right)$$

$$= \frac{1}{2.303} \ln \left(\frac{q}{p-q} \times \frac{(p-q+\times)}{(q-x)} \right)$$

On differentiating with respect to × we get

$$\frac{d\Delta pH}{dx} = \left(\frac{1}{\frac{q}{(p-q)} \times \left(\frac{p-q+x}{q-x} \right)} \right) \times \frac{q}{p-q}$$

$$\times \frac{[\,(q-x) \times 1 - (p-q+x) \times -1\,]}{(q-x)^2} \times \frac{1}{2.303}$$

$$= \frac{p}{(p-q+x)\,(q-x)\,2.303}$$

On taking the inverse

$$\frac{dx}{d\Delta pH} = \frac{(p-q+x)\,(q-x)\,2.303}{p}$$

Type of Buffer Solution

1. **Acidic Buffer:** It is a solution of a weak acid and its salt with a strong base.

Example,

$CH_3COOH + CH_3COONa$

Phthalic acid + potassium phthalate

Boric acid + Borax

$H_2CO_3 + NaHCO_3$

Citric acid + sodium citrate

2. **Basic Buffer:** It is a solution of a weak base and its salt with a strong acid

   Example,

   $NH_4OH + NH_4Cl$

   Glycine + glycine hydrogen chloride

   Glycerol + glycerine hydrogen chloride

3. **Ampholyte Solution:** Example, Protein and amino acids also act like a buffer solution.

4. A mixture of acidic salt and normal salt of a polybasic acid

   Example,

   $Na_2HPO_4 + Na_3PO_4$

5. Salt of weak acid and weak base (in water)

   Example,

   CH_3COONH_4, NH_4CN

Uses of Buffer

Some of the important uses of buffer are as follows:

(i) To determine pH value with the help of an indicator.

(ii) NH_4Cl + NH_4OH and $(NH_4)_2CO_3$ buffer solution is used to precipitate carbonates of Vth group

(iii) CH_3COOH and CH_3COONa buffer is used to remove PO_4^{-3} in qualitative inorganic analysis after IInd group.

(iv) CH_3COOH and CH_3COONa buffer is used to precipitate lead chromate quantitatively in gravimetric analysis.

(v) They are also used in paper, dye, printing ink, dairy product etc.

(iv) $H_2CO_3 + NaHCO_3$ maintains pH of blood.

Illustrations

17. Calculate the pH of a 0.01 M NH_4OH solution containing 10 mol / litre of NH_4Cl? ($pK_b = 4.76$)

Solution [Conjugate base] = 0.10 M NH_3 in H_2O

[Conjugate acid] = 1.0 M NH_4^+

$$pOH = pK_b + \log \frac{[Salt\ ]}{[Base]}$$

$$= 4.76 + \log \frac{1.0}{0.1}$$

$$= 4.76 + \log 10 = 5.76$$

$$pH = 14 - pOH$$

$$= 14 - 5.76 = 8.24$$

18. What volume of 0.1 M sodium formate solution should be added to 50 ml of 0.05 M formic acid to produce a buffer solution of pH = 4.0; pKa of formic acid = 3.80?

Solution Suppose V ml of 0.1 M HCOONa is mixed to 50 ml of 0.05 M HCOOH.

$$[Molarity] = \frac{\text{Total millimole}}{\text{Total volume}}$$

$$\text{In mixture } [HCOONa] = \frac{0.1 \times V}{(V + 50)}.$$

$$[HCOOH] = \frac{50 \times 0.05}{V + 50}$$

$$pH = -\log Ka + \log \frac{[Salt]}{[Acid]}.$$

$$4.0 = 3.80 + \log_{10} \frac{(0.1 \times V)}{(V + 50)/2.5 / (V + 50)}$$

$$V = 39.62 \text{ ml}$$

19. Calculate the change in pH of 1 litre buffer solution containing 0.1 mole each of NH_3 and NH_4Cl up on addition of;

(i) 0.02 mole of dissolved gaseous HCl

(ii) 0.02 mole of dissolved NaOH.

(Assume no change in volume. $KNH_3 = 1.8 \times 10^{-5}$)

Solution Initial pH of solution when,

$[NH_3] = \frac{0.1}{1}$ and $[NH_4Cl] = \frac{0.1}{1}$

$pOH = -\log_{10} 1.8 \times 10^{-5} + \log_{10} \frac{[Salt]}{[Base]}$.

$= -\log_{10} 1.8 \times 10^{-5} + \log_{10} \frac{0.1}{0.1}$

$pOH = 4.7447$

$pH = 9.2553$

(i) When 0.02 mole of HCl are added,

$$HCl + NH_4OH \rightarrow NH_4Cl + H_2O$$

Mole before diss. 0.02 0.1 0.1
Mole after diss. 0 0.08 (0.1 + 0.02)

As Volume = 1 litre

So $[NH_4OH] = 0.08 / 1$
$[NH_4Cl] = 0.12 / 1$

$pOH_1 = -\log_{10} 1.8 \times 10^{-5} + \log_{10} \frac{0.12}{0.08}$

$pOH_1 = 4.9208$

$pH_1 = 9.0792$

Change in pH = $pH - pH_1 = 9.2553 - 9.0792$

$= +0.1761$

Change in pH = 0.1761 unit i.e., pH decreases

(ii) When 0.02 mole of NaOH are added,

$$NaOH + NH_4Cl \rightarrow NaCl + NH_4OH$$

Mole before diss. 0.02 0.1 0 0.1
Mole after diss. 0 0.08 0.02 0.12

$pOH_2 = -\log_{10} 1.8 \times 10^{-5} + \log_{10} \frac{0.08}{0.12}$

$pOH_2 = 4.5686$

$pH_2 = 9.4314$

Change in pH = $pH - pH_2 = 9.2553 - 9.4314$

$= -0.1761$

Change in pH = 0.1761 that is, pH increases.

20. Calculate the amount of NH_3 and NH_4Cl required to prepare a buffer solution of pH 9.0 when total concentration of buffering reagents is 0.6 mol litre^{-1}. pK_b for $NH_3 = 4.7$, $\log_{10} 2 = 0.30$

Solution $pOH = -\log_{10} K_b + \log_{10} \frac{[Salt]}{[Base]}$.

$5 = 4.7 + \log_{10} \frac{a}{b}$.

$a / b = 2$

So $a = 2b$

Given $a + b = 0.6$
$2b + b = 0.6$
$3b = 0.6$

$b = 0.2$ mole

$= 0.2 \times 17 = 3.4$ g/litre

$a = 0.4$ mole

$= 0.4 \times 53.5 = 21.4$ g/litre

$[Salt] = 0.4$ M

$[Base] = 0.2$ M

21. The pH of 0.05 M aqueous solution of diethyl amine is 12.0. Calculate K_b.

Solution

$$(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$$

Initial conc. 1 0 0

Eq. conc. $(1 - \alpha)$ α α

$[OH^-] = C\,\alpha$

Here C is conc. of base and C = 0.05 M

As $pH = 12$

So $pOH = 2$

$[OH^-] = 10^{-2}$ M

$C\,\alpha = 10^{-2}$

$0.05 \times \alpha = 10^{-2}$ (as C = 0.05)

$\alpha = 0.2$

$$K_b = \frac{C\alpha^2}{(1 - \alpha)} = \frac{0.05 \times (0.2)^2}{(1 - 0.2)}$$

$$= \frac{0.05 \times 0.04}{0.8} = 2.5 \times 10^{-3}$$

22. A solution contains 0.1 M H_2S and 0.3 M HCl. Calculate the conc. of S^{2-} and HS^- ions in solution. Given Ka_1 and Ka_2 for H_2S are 10^{-7} and 1.3×10^{-13} respectively.

Solution

$H_2S \rightleftharpoons H^+ + HS^-$ $\quad Ka_1 = 10^{-7}$

$HS^- \rightleftharpoons H^+ + S^{2-}$ $\quad Ka_2 = 1.3 \times 10^{-13}$

$HCl \rightarrow H^+ + Cl^-$

Due to common ion effect the dissociation of H_2S is suppressed and the $[H^+]$ in solution is due to HCl.

$$Ka_1 = \frac{[H^+]\,[HS^-]}{[H_2S]}$$

$$10^{-7} = \frac{[0.3]\,[HS^-]}{[0.1]} \text{ [as } [H^+] \text{ from HCl} = 0.3]$$

$$[HS^-] = \frac{10^{-7} \times 0.1}{0.3} = 3.3 \times 10^{-8}\text{ M}$$

$$Ka_1 = \frac{[H^+]\,[HS^-]}{[H_2S]} \text{ and } Ka_2 = \frac{[H^+]\,[S^{2-}]}{[HS^-]}$$

$$Ka_1 \times Ka_2 = \frac{[H^+]^2\,[S^{2-}]}{[H_2S]}$$

$$10^{-7} \times 1.3 \times 10^{-13} = \frac{[0.3]^2\,[S^{2-}]}{[0.1]}$$

$$[S^{2-}] = \frac{1.3 \times 10^{2-} \times 0.1}{0.09} = 1.44 \times 10^{-20}\text{ M}$$

23. Two buffers, (X) and (Y) of pH 4.0 and 6.0 respectively are prepared from acid HA and the salt Na**A**. Both the buffers are 0.50 M in H**A**. What would be the pH of the solution obtained by mixing equal volumes of the two buffers? ($K_{HA} = 1.0 \times 10^{-5}$)

Solution $pH = -\log_{10} Ka + \log_{10} \frac{[Salt]}{[Acid]}$.

When pH = 4

$$4 = -\log_{10} 1.0 \times 10^{-5} + \log_{10} \frac{[Salt]}{0.5\text{ M}}.$$

$$4 = 5 + \log_{10} \frac{[Salt]}{0.5\text{ M}}.$$

$$\log_{10} \frac{[Salt]}{0.5\text{ M}} = -1$$

$$[Salt] = 0.1 \times 0.5 = 0.05\text{ M}$$

When pH = 6,

$$6 = -\log_{10} (1.0 \times 10^{-5}) + \log_{10} \frac{[Salt]}{0.5\text{ M}}.$$

$$6 = 5 + \log_{10} \frac{[Salt]}{0.5\text{ M}}.$$

$$\log_{10} \frac{[Salt]}{0.5\text{ M}} = 1$$

$$[Salt] = 10 \times 0.5 = 5\text{ M}$$

Suppose V litre each of both buffers are mixed. The concentration of the salt in this solution will be:

$$[Salt] = \frac{(0.05\text{ M} \times V) + (5\text{ M} \times V)}{2\text{ V}} = \frac{5.05}{2}\text{ M}$$

Concentration of [HA] in mixed buffer

$$= \frac{(0.5\text{ M} \times V) \times (0.5\text{ M} \times V)}{2\text{ V}} = 0.5\text{ M}$$

$$pH = -\log_{10} (1.0 \times 10^{-5}) + \log_{10} \frac{[5.05/2]}{0.5}$$

$$= 5 + 0.7033 = 5.7033$$

Solubility

It is the weight in gm of solute present in 100 ml of solvent . It is denoted by 's' and is expressed in mol per litre or gm per litre. The number of moles of solute in 1 L of saturated solution is known as molar solubility.

Solubility ∝ 1/concentration of common ions
or number of common ions

Example, The solubility of AgCl in water in presence of $AgNO_3$.

Solubility increases due to complex ion formation.

Example, AgCl has more solubility in ammonia due to complex formation.

$AgCl + 2NH_3 \rightarrow Ag(NH_3)_2Cl$

$HgCl_2$ has more solubility in KI due to complex formation (Nesseler's reagent).

$HgI_2 + 2KI \rightarrow K_2HgI_4$

In IInd group analysis SnS, Sb_2S_3 As_2S_3 are soluble in $(NH_4)_2S$ due to complex ion formation.

$SnS + S^{-2} \rightarrow SnS_2^{-2}$

$Sb_2S_3 + 3S^{-2} \rightarrow 2SbS_3^{-3}$

$As_2S_5 + 3S^{-2} \rightarrow 2AsS_4^{-3}$

Simultaneous Solubility: It is the solubility of a solution of two electrolytes having common ions.

Example, (1) $AgBr + AgSCN$

(2) $CaF_2 + SrF_2$

(3) $MgF_2 + CaF_2$

Solubility Product: It is the product of the molar concentrations of ions of an electrolyte in a saturated solution at a particular temperature. It is denoted by Ksp or S.

For a Binary Electrolyte AB:

$AB \leftrightarrow AB \leftrightarrow A^+ + B^-$

Solid un–ionised

$$\text{So } K = \frac{[A^+][B^-]}{[AB]}$$

or $K.[AB] = [A^+][B^-]$

or

$Ksp = [A+] [B–]$ At constant temp.

General Representation

$AxBy \leftrightarrow xA^{+y} + yB^{-x}$

$Ksp = [A+y]x [B–x]y$

Example (1)

$CaF_2 \leftrightarrow Ca^{+2} + 2F^-$

$Ksp = [Ca^+] [F^-]^2$

Example (2)

$Ag_2CrO_4 \leftrightarrow 2Ag^+ + CrO_4^{-2}$

$Ksp = [Ag^+]^2 [CrO_4^{-2}]$

Relation between Solubility(s) and Solubility Product (Ksp)

$AxBy \leftrightarrow xA^{+y} + yB^{-x}$

a 0 0

a – s xs ys

$Ksp = (x\,s)^x. (y\,s)^y$

or

$Ksp = x^x y^y (s)^{x+y}$

If α is given

$Ksp = x^x y^y (\alpha\,s)^{x+y}$

Example $Cu_2Cl_2 \leftrightarrow 2Cu^+ + 2Cl^-$

2s 2s

so $Ksp = 2^2 . 2^2 .(s)^{2+2} = 16\,s^4$

$Fe(OH)_2 \leftrightarrow Fe^{+3} + 3OH^-$

s 3s

$Ksp = 1^1.3^3 (s)^{1+3} = 27\,s^4$

$Al_2(SO_4)_3 \leftrightarrow 2Al^{+3} + 3SO_4^{-2}$

2s 3s

$Ksp = 2^2.3^3.(s)^{2+3} = 108\,s^5$

$Na_3Li_3(AlF_6)_2 \leftrightarrow 3Na^+ + 3Li^{+3} + 2AlF_6^{-3}$

$Ksp = 3^3.3^3.2^2.(s)^{3+3+2} = 2916\,s^8$

Solubility Product and Precipitation

- If Ks.p ≈ Ionic product

  Solution is saturated and for precipitation more solute is to be added.

- If Ionic product > Ks.p

  solution is super saturated so easily precipitated.

- If Ionic product < Ks.p

  Solution is unsaturated so no precipitation takes place.

Application of Solubility Product

(i) In the precipitation of Soap by adding a little Nacl: on adding a little Nacl soap gets precipi-tated as ionic product becomes more then Ksp.

$R–CooNa \rightleftharpoons R–Coo^- + Na^+$

$Ks.p \geq [R–Coo^-] [Na^+]$

on a adding Nacl

$[R–Coo^-] [Na^+] > Ks.p$

(ii) In Analytical Chemistry:

(A) Cation of IInd gp. [$Cu^{2+}, Bi^{+2}, Hg^{2+}, Pb^{2+}, Cd^{+2}$] are precipitatedas S^{-2} by using H_2S + Hcl at lower lenc entration of S^{-2} due to the tact that they have lower Ks.p than other group cations.

$H_2S \rightleftharpoons 2H^+ + S^{-2}$

$HCl \rightleftharpoons H^+ + Cl^-$

Common ions

Here due to commonion effect conc^n π S^{-2} decreases so far other gp. Cations Ks.p > Ionic product hence they cannot be precipitated.

(B) Cations of IIIrd gp. (fe^{3+}, Al^{3+}, Cr^{+3}) are precipitated at low concentration of $\overline{O}H$ due to their lower Ksp than other gp. Cat-ions by using $NH_4OH + NH_4Cl$.

$NH_4OH \rightleftharpoons NH_4 + \overline{O}H$

$NH_4Cl \rightleftharpoons NH_4 + Cl^-$

Common ions

Due to common ions conc^n of $\overline{O}H$ decreases so other gp. Cations cannot be precipitated as for them ksp > Ionic product.

Illustrations

24. The solubility of $Mg(OH)_2$ in water at 25°C is 0.00912 g per litre. Find Ksp for $Mg(OH)_2$ assuming complete ionization.

Solution

$Mg(OH)_2 \rightleftharpoons Mg^{2+} + OH^- + OH^-$

1 mole 1 mole 2 mole

$Ksp = [Mg^{2+}]\,[OH^-]^2$ ……(i)

$$\text{Concentration of } Mg(OH)_2 = \frac{0.00912\text{ g}}{58.3\text{ g /mole}}$$

= 0.000156 mole per litre

Since one mole of $Mg(OH)_2$ yields one mole of Mg^{2+} ion and two moles of OH^- ion, then

$[Mg^{2+}] = 0.000156$ mole per litre

$[OH^-] = 2 \times 0.000156 = 0.000312$ mole per litre

On putting the values in equation (i)

$Ksp = (0.000156) \times (0.000312)^2$

$= 1.52 \times 10^{-11}$ for $Mg(OH)_2$ at 25°C

25. The solubility product of SrF_2 in water is 8×10^{-10}. Find its solubility in 0.1 M NaF aqueous solution.

Solution For SrF_2,

$K_{sp} = [Sr^{2+}]\,[F^-]^2$

Let the solubility of SrF_2 in 0.1 M NaF be X mol L^{-1}.

$8 \times 10^{-10} = (X)\,(2X + 0.1)^2$

(Neglecting X^2 and X^3 terms)

$0.01\,X = 8 \times 10^{-10}$

$X = 8 \times 10^{-8}$ mol L^{-1}.

26. What (H_3O^+) must be maintained in a saturated H_2S solution to precipitate Pb^{2+}, but not Zn^{2+} from a solution in which each ion is present at a concentration of 0.01 M?

(Ksp of H_2S = 1.1×10^{-22}, Ksp of ZnS = 1.0×10^{-21})

Solution For ZnS not to be precipitate from a solution of Zn^{2+} and Pb^{2+}.

$[Zn^{2+}]\,[S^{2-}] <$ Ksp of ZnS

$[10^{-2}]\,[S^{2-}] < 1.0 \times 10^{-21}$

or the maximum $[S^{2-}] = 10^{-19}$ at which ZnS will begin to precipitate or upto this concentration, no precipitation will occur.

$H_2S \rightleftharpoons 2H^+ + S^{2-}$

$[H^+]^2\,[S^{2-}] = 1.1 \times 10^{-22}$

$[H^+]^2\,[10^{-19}] = 1.1 \times 10^{-22}$

$[H^+]^2 = 11 \times 10^{-4}$

$[H^+] = 3.3 \times 10^{-2}$ M

Therefore if $[H^+] = 3.3 \times 10^{-2}$ or slightly higher, the precipitation of ZnS will not take place and only PbS will precipitate.

27. Determine the concentration of NH_3 solution whose one litre can dissolve 0.10 mole AgCl. Ksp of AgCl and K_f of $Ag(NH_3)_2^+$ are 1.0×10^{-10} M^2 and 1.6×10^7 M^{-2} respectively.

Solution $AgCl + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$

$AgCl\,(s) \rightleftharpoons Ag^+ + Cl^-$

$Ksp = [Ag^+]\,[Cl^-]$ ……… (i)

Given $Ag^+ + 2NH_3 \rightleftharpoons Ag\,(NH_3)_2^+$

$$K_f = \frac{[Ag(NH_3)_2^+]}{[Ag^+]\,[NH_3]^2} \quad \text{…… (ii)}$$

From equation (i) and (ii)

$$\text{Ksp} \times K_f = \frac{[Ag(NH_3)_2^+]\,[Cl^-]}{[NH_3]^2}$$

$$1 \times 10^{-10} \times 1.6 \times 10^{7} = \frac{a \times a}{[NH_3]^2}$$

Given: solubility of AgCl = 0.1 M

a = 0.1 M for $Ag(NH_3)_2^+$ and Cl^-

$$[NH_3]^2 = \frac{0.1 \times 0.1}{1.6 \times 10^{-3}} = 6.25$$

$[NH_3] = 2.5$ M

0.2 M NH_3 is needed to dissolve 0.1 M Ag^+ ions, so

$[NH_3] = 2.5 + 0.2 = 2.7$ M

28. Calculate simultaneous solubility of AgCNS and AgBr in a solution of water.

Ksp of AgBr = 5×10^{-13} and Ksp of AgCNS = 1×10^{-12}.

Solution Suppose solubility of AgCNS and AgBr in a solution is X and Y mol litre^{-1} respectively.

$$AgCNS\,(s) \rightleftharpoons Ag^+ + CNS^-$$

[Ion] furnished on dissolution X X

$$AgBr\,(s) \rightleftharpoons Ag^+ + Br^-$$

[Ion] furnished on dissolution Y Y

$[Ag^+] = X + Y$

$[CNS^-] = X$

$[Br^-] = Y$

Ksp of AgCNS = $[Ag^+]\,[CNS^-]$

$1 \times 10^{-12} = (X + Y)\,(X)$ ….. (i)

Ksp of AgBr = $[Ag^+]\,[Br^-]$

$5 \times 10^{-13} = (X + Y)\,(Y)$ …… (ii)

From equation (i) and (ii)

$$\frac{X}{Y} = \frac{10^{-12}}{5 \times 10^{-13}} = 2$$

$X = 2Y$

From equation (i),

$(2Y + Y)\,(2Y) = 1 \times 10^{-12}$

$6Y^2 = 1 \times 10^{-12}$

$Y = 4 \times 10^{-7}$ mol litre^{-1}

From equation (i),

$(X + X/2)\,(X) = 1 \times 10^{-12}$

$X = 8.16 \times 10^{-7}$ mole litre^{-1}

29. Determine the number of mole of AgI which may be dissolved in 1.0 litre of 1.0 M CN^- solution. Ksp for AgI and Kc for $Ag(CN)_2^-$ are $1.2 \times 10^{-17}\ M^2$ and $7.1 \times 10^{19}\ M^{-2}$ respectively.

Solution $AgI\,(s) \rightleftharpoons Ag^+\,(aq) + I^-\,(aq)$

$\text{Ksp} = [Ag^+]\,[I^-] = 1.2 \times 10^{-17}$ ……. (i)

$Ag^+\,(aq) + 2CN^-\,(aq) \rightleftharpoons [Ag(CN)_2]\,(aq)$

$$K_f = \frac{[Ag(CN)_2^-\,]}{[Ag^+]\,[CN^-]^2} = 7.1 \times 10^{19} \quad \text{…… (ii)}$$

Suppose X mole of AgI is dissolved in CN^- solution

$$AgI\,(s) + 2CN^- \rightleftharpoons [Ag(CN)_2^-] + I^-$$

Mole before diss. 1 0 0

Mole after reaction (1 – 2X) X X

From equation (i) and (ii),

$\text{Keq} = \text{Ksp} \times K_f$

$$\text{Keq} = \frac{[Ag(CN)_2^-]\,[I^-]}{[CN^-]^2} = 1.2 \times 10^{-17} \times 7.1 \times 10^{19}$$

$\text{Keq} = 8.52 \times 10^{2}$ ……. (iii)

$$K_{eq} = 8.52 \times 10^{2} = \frac{X\,.\,X}{(1 - 2X)} = \frac{X^2}{(1 - 2X)^2}\,.$$

$$\frac{X}{1 - 2X} = 29.2$$

$X = 29.2 - 58.4X$

X = 0.49 mole

30. The solubility product of $BaSO_4$ is 1.5×10^{-9}. Find out its solubility in (i) Pure water and (ii) 0.10 M $BaCl_2$

Solution (i) In pure water

$BaSO_4\,(s) \rightleftharpoons Ba^{2+}\,(aq) + SO_4^{2-}\,(aq)$

As 1 mole of $BaSO_4$ dissolves to give 1 mole of Ba^{2+} ions and 1 mole of SO_4^{2-} ions. Therefore, if S is the solubility of $BaSO_4$ in moles per litre, then

Solubility $= S = [Ba^{2+}] = [SO_4^{2-}]$

$Ksp = [Ba^{2+}][SO_4^{2-}] = S \times S = S^2$

$S = \sqrt{Ksp} = \sqrt{(1.5 \times 10^{-9})}$

$= 3.87 \times 10^{-5}$ mol L^{-1}

(ii) In 0.1 M $BaCl_2$:

0.1 M $BaCl_2$ dissolves completely to give 0.1 M Ba^{2+} (common ions) and 0.1 M Cl^- ions

$BaCl_2 \rightarrow Ba^{2+} + 2Cl^-$
1 mol 1 mol 2 mol
0.1 M 0.1 M 0.2 M

At equilibrium

$[Ba^{2+}]_{eq}$

$= [Ba^{2+}]$ from $BaCl_2$ added $+ [Ba^{2+}]$ from $BaSO_4$

$= 0.1\ M + S\ M$

$= 0.1\ M$

$[SO_4^{2-}] = S$

$Ksp = [Ba^{2+}][SO_4^{2-}]$

$$[SO_4^{2-}] = S = \frac{Ksp}{[Ba^{2+}]}$$

$$= \frac{1.5 \times 10^{-9}}{0.1\ M} = 1.5 \times 10^{-8}\ M$$

31. A solution has 0.05 Mg^{2+} and 0.05 M NH_3. Calculate the concentration of NH_4Cl required to prevent the formation of $Mg(OH)_2$ in this solution. Ksp of $Mg(OH)_2 = 9.0 \times 10^{-12}$ and ionization constant of $NH_3 = 1.8 \times 10^{-5}$.

Solution $Mg(OH)_2\ (s) \rightleftharpoons Mg^{2+}\ (aq) + 2OH^-\ (aq)$

$Ksp = [Mg^{2+}][OH^-]^2$

$$[OH^-]^2 = \frac{Ksp}{[Mg^{2+}]} = \frac{9.0 \times 10^{-12}}{0.05\ M} = 180 \times 10^{-12}$$

$[OH^-] = \sqrt{(180 \times 10^{-12})} = 13.4 \times 10^{-6}\ M$

Therefore, $[OH^-]$ concentration cannot be more than 13.4×10^{-6} M.

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

$MNH_4^+ = MNH_4Cl$

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$$Keq = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

$$[NH_4^+] = \frac{[NH_3] \times Keq}{[OH^-]}$$

$$= \frac{0.05\ M \times 1.8 \times 10^{-5}}{13.4 \times 10^{-6}} = 0.067\ M$$

Concentration of NH_4Cl needed = 0.067 M

32. Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.05 mol L^{-1} of NH_4OH and 0.25 mol L^{-1} of NH_4Cl. Calculate the concentration of aluminium and magnesium ions in solution.

Ksp $Al(OH)_3 = 6 \times 10^{-32}$

K_b $NH_4OH = 1.8 \times 10^{-5}$

Ksp $Mg(OH)_2 = 6 \times 10^{-10}$

Solution $pOH = \log_{10} \frac{[Salt]}{[Base]} - \log K_b$

$$-\log_{10}[OH^-] = \log_{10} 0.25 - \log_{10} \frac{1.8 \times 10^{-5}}{0.05}$$

$$\log_{10}[OH^-] = \log_{10} \frac{1.8 \times 10^{-5}}{5}$$

$[OH^-] = 0.36 \times 10^{-5}$ mol L^{-1}

$$[Al^{3+}] = \frac{Ksp\ Al(OH)_3}{[OH^-]^3}$$

$$= \frac{6 \times 10^{-32}}{(0.36 \times 10^{-5})^3}.$$

$= 1.29 \times 10^{-10}$ mol L^{-1}

$$[Mg^{2+}] = \frac{Ksp\ Mg(OH)_2}{[OH^-]^2}$$

$$= \frac{6 \times 10^{-10}}{(0.36 \times 10^{-5})^2} = 46.3 \text{ mol } L^{-1}$$

Salt Hydrolysis

When a salt is added in water ions of the salt interact with water to cause acidity or basicity in aqueous solution. This ionic interaction is called salt hydrolysis. Interaction of cation is cationic hydrolysis and interaction of anion is anionic hydrolysis.

- Hydrolysis is reverse of neutralization and an endothermic process.
- If hydrolysis constant is K_h and neutralization constant is Kn.

  $Kn = 1/K_h$
- A solution of the salt of strong acid and weak base is acidic and for it pH < 7 or $[H^+] > 10^{-7}$

  Example, $FeCl_3$ (weak base + strong acid): Solution is acidic and involves cationic hydrolysis
- A solution of the salt of strong base and weak acid is basic and for it pH > 7 or $[H^+] < 10^{-7}$

  Example, KCN (strong base + weak acid): Solution is basic and involves anionic hydrolysis.
- A solution of the salt of weak acid and weak base –

  If $Ka > K_b$ it is acidic

  If $Ka < K_b$ it is basic

  If $Ka = K_b$ it is neutral
- CH_3COONH_4 (weak acid + weak base): Solution is neutral and involves both cationic and anionic hydrolysis
- A solution of the salt of strong acid and strong base is neutral or pH = 7 or

  $[H^+] = 10^{-7}$
- A salt of strong acid and strong base is never hydrolyzed however, ions are hydrated.

  Example, K_2SO_4 (however, strong base + strong acid)

Degree of Hydrolysis: It is the amount or fraction of the salt which is hydrolysed. It is denoted by h.

$$h = \frac{\text{No. of moles of salt hydrolysed}}{\text{Total moles of the salt taken}}$$

Various Expressions for Kh, h and pH for Different Type of Salts:

1. For the salt of weak acid and strong base (KCN)

   $K_h = \frac{Kw}{Ka}$

   $h = \sqrt{(K_h / C)}$

   $h = \sqrt{(Kw / Ka.C)}$

   $pH = ½ [pKw + pKa + \log C]$

   $pOH = ½ [pKw – pKa – \log C]$
2. For the salt of strong acid and weak base ($FeCl_3$)

   $K_h = \frac{Kw}{K_b}$

   $h = \sqrt{(K_h / C)}$

   $h = \sqrt{(Kw/K_b.C)}$

   $pH = ½ [pKw – pK_b – \log C]$
3. For the salt of weak acid and weak base (NH_4Cn)

   $K_h = \frac{Kw}{Ka\,K_b}$

   $h = \sqrt{(Kw/Ka.K_b)}$

   $pH = ½ [pKw + pKa – pK_b]$

Illustrations

33. Calculate hydrolysis constant of salt containing NO_2^- ion. Given the Ka for $HNO_2 = 4.5 \times 10^{-10}$.

Solution

NO_2^- ion hydrolysis as

$$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$$

$$K_H = \frac{[HNO_2]\,[OH^-]}{[NO_2^-]} \quad \ldots\ldots (1)$$

$$Kw = [H^+]\,[OH^-] \quad \ldots\ldots.. (2)$$

HNO_2 ionizes as follows:

$$HNO_2 \rightleftharpoons H^+ + NO_2^-$$

$$Ka = \frac{[H^+]\,[NO_2^-]}{[HNO_2]} \quad \ldots\ldots.. (3)$$

From equations (1) and (3)

$$K_H = \frac{Kw}{Ka} = \frac{1 \times 10^{-14}}{45 \times 10^{-10}} \cdot$$

$$= 2.22 \times 10^{-5}$$

34. Calculate for 0.01 N solution of sodium acetate,

a. Hydrolysis constant

b. Degree of hydrolysis

c. pH

Given Ka = 1.9

Solution

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

Before hydrolysis 1 0 0

After hydrolysis $(1 – \alpha)$ α α

(a) $K_h = \frac{K_W}{Ka} = \frac{10^{-14}}{1.9 \times 10^{-5}} = 5.26 \times 10^{-10}$

(b) $\alpha = \sqrt{(K_h / C)}$

$$= \frac{\sqrt{(5.26 \times 10^{-10})}}{\sqrt{0.01}} = 2.29 \times 10^{-4}$$

(c) $[OH^-]$ from NaOH, a strong alkali = $C\alpha$

$= 0.01 \times 2.29 \times 10^{-4}$

$= 2.29 \times 10^{-6}$ M

pOH = 5.64

pH = 8.36

35. Calculate the percentage hydrolysis in 0.003 M aqueous solution of NaOCN. Ka for HOCN $= 3.33 \times 10^{-4}$.

Solution $NaOCN + H_2O \rightleftharpoons NaOH + HCN$

$$\alpha = \sqrt{(K_h / C)} = \frac{\sqrt{K_W}}{\sqrt{(Ka \, . \, C)}}$$

$$= \frac{\sqrt{(10^{-14})}}{\sqrt{(3.33 \times 10^{-4} \times 0.003)}}$$

$h = 10^{-4}$

% hydrolysis $= 10^{-4} \times 100 \qquad = 10^{-2}$

36. Ka for butyric acid is 2.0×10^{-5}. Calculate pH and hydroxyl ion concentration in 0.2 M aqueous solution of sodium butyrate.

Solution

$NaBu + H_2O \rightleftharpoons NaOH + BuH$

Conc. before hydrolysis 1 0 0

Conc. after hydrolysis $1 - \alpha$ α α

$[OH^-] = C\,\alpha = C.\sqrt{(K_h / C)} = \sqrt{(K_h .C)}$

$= \sqrt{[(K_W / Ka) .C]}$

$$[OH^-] = \frac{10^{-14} \times 0.2}{2 \times 10^{-5}} = \sqrt{10^{-10}} = 10^{-5}$$

pOH = 5

pH + pOH = 14

So pH = 14 – 5 = 9

37. Ka for ascorbic acid (HAsC) is 5×10^{-5}. Calculate the hydrogen ion concentration and percentage of hydrolysis in an aqueous solution in which the concentration of AsC^- ions is 0.02 M.

Solution $AsC^- + H_2O \rightleftharpoons HAsC + OH^-$

$[OH^-] = C\,\alpha = C.\sqrt{(K_h / C)} = \sqrt{(K_h .C)}$

$= \sqrt{[(K_W / Ka) .C]}$

$$= \frac{\sqrt{(10^{-14} \times 0.02)}}{\sqrt{(5 \times 10^{-5})}} = 2 \times 10^{-6}$$

$$[H^+] = \frac{1 \times 10^{-14}}{2 \times 10^{-6}} = 5 \times 10^{-9}$$

$$\alpha = \sqrt{(K_h / C)} = \frac{\sqrt{K_W}}{\sqrt{(Ka \times C)}} \, .$$

$$= \frac{\sqrt{10^{-14}}}{\sqrt{(5 \times 10^{-5} \times 0.02)}} = 10^{-4}$$

= 0.01 %

38. Calcium lactate is a salt of weak acid and represented as $Ca(LaC)_2$. A saturated solution of $Ca(LaC)_2$ contains 0.13 mole of salt in 0.50 litre solution. The pOH of this 5.60. Assuming complete dissociation of salt, calculate Ka of lactic acid.

Solution

$Ca(LaC)_2 + 2H_2O \rightleftharpoons Ca(OH)_2 + 2HLAC$

$2LaC^- + 2H_2O \rightleftharpoons 2OH^- + 2HLaC$

Before hydrolysis 1 0 0

After hydrolysis $(1 - \alpha)$ α α

$$[Ca(LaC)_2] = \frac{0.13}{0.5} = 0.26 \text{ M}$$

$[LaC] = 0.26 \times 2 = 0.52$ M

(as 1 mole $Ca(LaC)_2$ gives 2 mole LaC.)

$[OH^-] = C\,\alpha = C.\sqrt{(K_h / C)} = \sqrt{(K_h .C)}$

$$= \frac{\sqrt{(K_W \, x.C)}}{\sqrt{Ka}}$$

Here C is the concentration of anion which undergoes hydrolysis

$$10^{-5.60} = \frac{\sqrt{(10^{-14} \times 0.52)}}{\sqrt{Ka}}$$

$Ka = 8.25 \times 10^{-4}$

ACID AND BASES

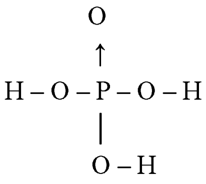
Arrhenius Concept of Acid and Base

According to it "Acids are H^+ ion donor in water and bases are OH^- ion donor in water".

1. **Acid:**

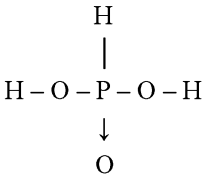
- $HA + H_2O \rightarrow A^- + H_3O^+$ Hydronium ion or Hydrated proton
- Water can accept H^+ to form hydronium ion (H_3O^+) due to hydrogen bonding.
  Example,– [$H_5O_2^+$, $H_7O_3^+$]
- H^+ can hold water molecule by hydrogen bond as it has high heat of hydration.
  Example, – HNO_3, H_2SO_4, HX
- H_3O^+ has sp^3 hybridization and trigonal pyramidal shape.
- Number of H^+ donated = Basicity
  or protosity of the acid
  Example,

1. H_3PO_4 (tribasic)



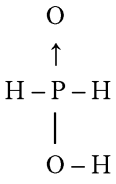
$$\begin{array}{c} O \\ \uparrow \\ H-O-P-O-H \\ | \\ O-H \end{array}$$

2. H_3PO_3 (dibasic)



$$\begin{array}{c} H \\ | \\ H-O-P-O-H \\ \downarrow \\ O \end{array}$$

3. H_3PO_2



$$\begin{array}{c} O \\ \uparrow \\ H-P-H \\ | \\ O-H \end{array}$$

2. **Base:**

$B.OH + H_2O \rightarrow B^+ + H_3O_2^-$ [other $H_5O_3^-$]

Example, NaOH, KOH etc.

Strength of Acid and Base

- Acidic strength α Ka
  Dissociation const. of acid
- Base strength α Kb
  Dissociation const. of base
- Relative strength = $\sqrt{(K_1 / K_2)}$

$H_3PO_4 \xleftrightarrow{K_1} H_2PO_4^- + H^+$ or H_3O^+

$H_2PO_4^- \xleftrightarrow{K_2} HPO_4^{-2} + H^+$

$HPO_4^- \xleftrightarrow{K_3} PO_4^{-3} + H^+$

Here $K_1 > K_2 >> K_3$ so the correct acidic strength order is

$H_3PO_4 > H_2PO_4^- > HPO_4^{-2}$

- As negative charge develops the removal of H^+ becomes more and more difficult so acidic nature decreases.

REMEMBER

This concept fails to explain acidic and basic nature in case of $AlCl_3$, BX_3, NH_3 etc.

Bronsted Lowry Concept or Proton Concept

1. **Acid:** Acids are Proton or H^+ donor.

$HA \rightarrow A^- + H^+$
Acid conjugate base

Example, – $HX \rightarrow H^+ + X^-$
Conjugate base

$H_2SO_4 \rightarrow H^+ + HSO_4^-$
acid conjugate base

$HNO_3 \rightarrow H^+ + NO_3^-$

2. **Base:** Bases are proton or H^+ acceptor.

Base + H^+ → (Base H)$^+$
or proton conjugate base
given by acid

Example,. – $OH^- + H^+ \rightarrow H_2O$
Base conjugate acid

Amphoteric or Ampholyte Substances

Such substances can behave both like an acid and a base that is, can donate or accept H^+ or proton.

Example,– (1)

$$\underset{\text{Conjugate acid}}{NH_4^+} \xleftarrow{+H^+} \underset{\text{amphoteric}}{NH_3} \xrightarrow{-H^+} \underset{\text{conjugate base}}{NH_2^-}$$

Example, (2)

$$\underset{\text{Conjugate acid}}{H_3O^+} \xleftarrow{+H^+} \underset{\text{substance}}{H_2O} \xrightarrow{-H^+} \underset{\text{conjugate base}}{OH^-}$$

Some other examples are HSO_4^-, HCO_3^-, $H_2PO_4^-$, HPO_4^{2-}, $H_2PO_3^-$, HS^- and $HC_2O_4^-$

> **REMEMBER**
>
> $H_2PO_2^-$ and HPO_3^{2-} are only bronsted bases as H_3PO_2 and H_3PO_3 are monobasic and dibasic acid respectively so they can release only one and two H^+ respectively.

Lewis Concept of Acid and Base

1. **Lewis Acid**

   Lewis acids are electron deficient species which accept electron pair.

Example,

- Cations

  $-\underset{|}{C^+}-$, $NO_2^+ + X^+$

- Electron deficient central atom

  $\underset{4}{\underset{\downarrow}{BeX_2}}$, $\underset{6}{\underset{\downarrow}{BX_3}}$, $\underset{6}{\underset{\downarrow}{FeX_3}}$, $\underset{6}{\underset{\downarrow}{AlX_3}}$ $\underset{4}{\underset{\downarrow}{SnCl_2}}$, $\underset{4}{\underset{\downarrow}{ZnCl_2}}$

- Central atom with multiple bonds only

  $O = C = O$, $O = S = O$, $S = C = S$

- If in a molecule central atom has vacant 'd'–orbital. It can accept more than eight electrons that is, expansion of octate state so it can behave as a lewis acid.

Example (1)

$$\underset{\text{Lewis acid}}{PX_5} + \underset{\text{Lewis base}}{X^-} \rightarrow PX_6^-$$

Example (2)

$$\underset{\text{Lewis acid}}{SiX_4} + 2X^- \rightarrow SiX_6^{-2}$$

- Some Other Examples:

  SnX_4, PX_3, GeX_4, SF_4, SeF_4, $TeCl_4$

- Elements with an electron sextet (Example, O, S etc.)

Strength of Lewis Acid

Lewis acid strength ∝ Electronegativity difference

Example, $\underset{\text{Acidic nature}}{\xrightarrow{AF_3 \quad AlCl_3 \quad AlBr_3 \quad AlI_3}}$

In case of Boron halide (BX_3)

$BI_3 > BBr_3 > BCl_3 > BF_3$

No back bonding   less back bonding   max back bonding

Here, fluorine shifts its electron pairs back to boron atom as in F–atom due to its small size and more electron density ($2p^5$) there is more $e^- - e^-$ repulsion but in case of B atom size is large and 2p–orbital is almost vacant.

The decreasing order of strength of some Lewis acids:

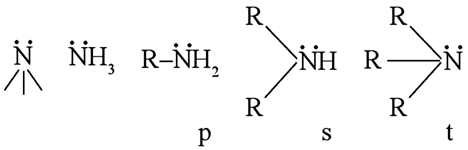
BX_3 , AlX_3, FeX_3, GaX_3, SbX_5, InX_3, SnX_4, AsX_5, ZnX_2, HgX_2

2. **Lewis Base:** These are electron efficient species which donate lone pair of electrons.

   Any anion or molecule with octet state and central atom with lone pair of electrons is a Lewis base as it can donate its lone pair.

   Example, – X^-, OH^-, CN^-

   Example,



$\ddot{P}H_3$ $\quad H-\underset{\cdot\cdot}{\ddot{O}}-H \quad R-\underset{\cdot\cdot}{\ddot{O}}-H \quad R-\underset{\cdot\cdot}{\ddot{O}}-R$

Some multiple bonded molecules which form complexes with transition metals. Example, CO, NO, C_2H_4 etc.

Strength of Lewis Base

Lewis base ∝ 1 / Electronegativity difference

Example,

$$NH_3 > NI_3 > NBr > NCl_3 > NF_3$$

Less electronegativity difference

REMEMBER

CO, RCH = CH_2, RC ≡ CH are border line Lewis bases.

Factors Effecting Acidic Strength:

- Acidic strength ∝ Electronegativity difference

  Example (1)

  $HF > H_2O > NH_3 > CH_4$

  As electronegativity of F > O > N > C

  $HNO_3 > H_2CO_3 > H_3BO_3$

  As electronegativity of N > C > B

  Example (2)

  $HClO > HBrO > HIO$

  $HClO_3 > HBrO_3 > HIO_3$

  As electronegativity of Cl > Br > I.

- Acidic strength ∝ Size of central atom or easy removal of H^+

  Example,

  $HF < HCl < HBr < HI$

  $H_2O < H_2S < H_2Se$

  $NH_3 < PH_3 < AsH_3 < SbH_3$

- Strength of oxyacids ∝ Oxidation number of central atom

  Example (1)

$$HO\overset{+1}{X} < H\overset{+4}{X}O_2 < H\overset{+5}{X}O_3 < H\overset{+7}{X}O_4$$

$$\xrightarrow[\text{Increasing order of acidic nature}]{\hspace{7cm}}$$

  Example (2)

$$\overset{-1/3}{N_3}H < H_2\overset{+1}{N_2}O_2 < H\overset{+3}{N}O_2 < H\overset{+5}{N}O_3$$

REMEMBER

$H_3PO_2 > H_3PO_3 > H_3PO_4$

Effect of Solvent on Acidic Strength: A solvent also effects acidic strength and it is called leveling effects.

Example (1) – CH_3COOH

CH_3COOH behaves like a weak acid in water but in liquid ammonia it is a strong acid as ammonia has more tendency than water to accept H^+.

Example,

$$\underset{\text{Acid}}{CH_3COOH} + \underset{\text{Base}}{H_2O} \longleftrightarrow \underset{\text{C.B}}{CH_3COO^-} + \underset{\text{C.A.}}{H_3O^+}$$

$$\underset{\text{Acid}}{CH_3COOH} + \underset{\text{Base}}{NH_3} \rightarrow \underset{\text{C.B}}{CH_3COO^-} + \underset{\text{C.A}}{NH_4^+}$$

CH_3COOH in HF behaves like a base as HF is stronger acid than it.

$$\underset{\text{Base}}{CH_3COOH} + \underset{\text{Acid}}{HF} \rightarrow \underset{\text{C.A}}{CH_3C\ OO^+H_2} + \underset{\text{C.B}}{F^-}$$

Example (2) – HNO_3

HNO_3 is although a strong acid in water but a weak acid in CH_3COOH and a base in HF.

- $HClO_4$ (the strongest acid) becomes a weak acid in HF.

Some important acids in the decreasing order of acidic strength:

$HClO_4$, $HClO_3$, HI, H_2SO_4, HBr, HCl, H_3O^+, HNO_3, HF, HSO_4^-, H_3PO_4, HCOOH, CH_3COOH, H_2CO_3, H_2S, NH_4^+, HCN, C_6H_5OH, H_2O, R – OH, HC ≡ CH, NH_3, $H_2C = CH_2$, CH_4, C_2H_6, C_6H_{12} (Cyclo hexane)

The strength of conjugate base will be in increasing order for the above acidic strength order that is,

ClO_4^-, ClO_3^- , I^-, H_2O, NO_3^-, F^-, SO_4^{2-}, $H_2PO_4^-$, $HCOO^-$, CH_3COO^-, HCO_3^-, HS^-, NH_3, CN^-, $C_6H_5O^-$, ^-OH, ^-OR, $^-C \equiv CH$, NH_2^-, $^-CH = CH_2$, $^-CH_3$, $^-C_2H_5$, $^-C_6H_{11}$,

Enhance Your Knowledge

- According to Ingold concept an electrophile is an acid while a nucleophile is a base.

Example, $AlCl_3$ (El) is an acid and NH_3 (Nu) is a base.

- In the reaction $I_2 + I^- \rightarrow I_3^-$ the lewis base is I^-.
- $[Fe(H_2O)_6]^{3+} + H_2O \rightarrow [Fe(H_2O)_5OH]^{2+} + H_3O^+$
  Acid Base C.B. C.A.
- $[Zn(H_2O)_5OH]^{2+} + H_3O^+ \rightarrow [Zn(H_2O)_6]^{3+} + H_2O$
  Base Acid C.A. C.B.
- The reaction of a cation or anion with water accompanied by cleavage of O – H bond is called salt hydrolysis.

Solved Problems from the IITs

1. The solubility of $Mg(OH)_2$ in pure water is 9.57×10^{-3} g L^{-1}. Calculate its solubility in g L^{-1} in 0.02 M $Mg(NO_3)_2$ solution.

[IIT 1986]

Solution Solubility of $Mg(OH)_2$ in pure water

$= 9.57 \times 10^{-3}$ g L^{-1}

$= \dfrac{9.57 \times 10^{-3}}{\text{Mol. mass}}$ mol L^{-1}

$= \dfrac{9.57 \times 10^{-3}}{58} = 1.65 \times 10^{-4}$ mol L^{-1}

$$Mg(OH)_2 \rightleftharpoons \underset{S}{Mg^{2+}} + \underset{2S}{2OH^-}$$

$K_S = [Mg^{2+}]\,[OH^-]^2$

$= S \times (2S)^2 \quad = 4S^3$

$= 4 \times (1.65 \times 10^{-4})^3$

$= 17.9685 \times 10^{-12}$

Let S' be the solubility of $Mg(OH)_2$ in presence of $Mg(NO_3)_2$.

As $[Mg^{2+}] = (S' + c) = (S' + 0.02)$

$[OH'] = 2S'$

So $K_S = (S' + 0.02)\,(2S')^2$

$17.9685 \times 10^{-12} = 4\,(S')^2\,(S' + 0.02)$

$\dfrac{17.9685 \times 10^{-12}}{4} = (S')^3 + 0.02\,(S')^2$

On neglecting $(S')^3$ we get,

$4.4921 \times 10^{-12} = 0.02\,(S')^2$

$(S')^2 = \dfrac{4.4921}{0.02} \times 10^{-12}$

$S' = 14.9868 \times 10^{-6}$ mol L^{-1}

Solubility of $Mg(OH)_2$ in g L^{-1} = S' × M

$= 14.9868 \times 10^{-6} \times 58$

$= 8.69 \times 10^{-4}$ g L^{-1}

2. What is the pH of the solution when 0.2 mole of hydrochloric acid is added to one litre of a solution containing 1 M acetic acid and acetate ion? Assume that the total volume is one litre. Ka for $CH_3COOH = 1.8 \times 10^{-5}$.

[IIT 1987]

Solution On adding HCl, the free hydrogen ions combine with CH_3COO^- ions to form CH_3COOH. Thus, the concentration of acetic acid increases while that of CH_3COO^- ions decreases.

$[CH_3COOH] = (0.2 + 1) = 1.2$ mol litre^{-1}

$[\text{Salt}] = (1 - 0.2) = 0.8$ mol litre^{-1}

According to Henderson's equation

$pH = \log_{10} \dfrac{[\text{Salt}]}{[\text{Acid}]} - \log Ka$

$= \log_{10} \dfrac{0.8}{1.2} - \log_{10} 1.8 \times 10^{-5}$

$= \log_{10} 2 - \log_{10} 3 - \log_{10} 1.8 \times 10^{-5}$

$= 4.5687$

3. How many gram moles of HCl will be required to prepare one litre of a buffer solution (having NaCN and HCN) of pH 8.5 using 0.01 g formula mass of NaCN? Ka for HCN = 4.1×10^{-10}?

[IIT 1988]

Solution Let 'X' moles of HCl be added. It combines with NaCN to form HCN.

$$\begin{array}{lllll} \mathrm{NaCN} + \mathrm{HCl} & \rightarrow & \mathrm{NaCl} + \mathrm{HCN} \\ \mathrm{X} \quad \mathrm{X} & & \qquad\quad \mathrm{X} \end{array}$$

$[\mathrm{NaCN}] = (0.01 - \mathrm{X})$

$[\mathrm{HCN}] = \mathrm{X}$

$$\mathrm{pH} = \log_{10} \frac{[\mathrm{NaCN}]}{[\mathrm{HCN}]} - \log_{10} \mathrm{Ka}$$

$$8.5 = \log_{10} \frac{0.01 - \mathrm{X}}{\mathrm{X}} - \log_{10} 4.1 \times 10^{-10}$$

$$\log_{10} \frac{(0.01 - \mathrm{X})}{\mathrm{X}} = 8.5 + 0.6127 - 10.0$$

$$\frac{(0.01 - \mathrm{X})}{\mathrm{X}} = 0.1296$$

$$\mathrm{X} = \frac{0.01}{1.1296} = 0.0089 \text{ mole}$$

4. Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.05 mol L^{-1} of $\mathrm{NH_4OH}$ and 0.25 mol L^{-1} of $\mathrm{NH_4Cl}$. Calculate the concentration of aluminium and magnesium ions in solution.

Ksp $\mathrm{Al(OH)_3} = 6 \times 10^{-32}$

$\mathrm{K_b}$ $\mathrm{NH_4OH} = 1.8 \times 10^{-5}$

Ksp $\mathrm{Mg(OH)_2} = 6 \times 10^{-10}$

[IIT 1989]

Solution $\mathrm{pOH} = \log_{10} \frac{[\mathrm{Salt}]}{[\mathrm{Base}]} - \log \mathrm{K_b}$

$$-\log_{10} [\mathrm{OH^-}] = \log_{10} \frac{0.25}{0.05} - \log_{10} 1.8 \times 10^{-5}$$

$$\log_{10} [\mathrm{OH^-}] = \log_{10} \frac{1.8 \times 10^{-5}}{5}$$

$[\mathrm{OH^-}] = 0.36 \times 10^{-5}$ mol L^{-1}

$$[\mathrm{Al^{3+}}] = \frac{\mathrm{Ksp\ Al(OH)_3}}{[\mathrm{OH^-}]^3}$$

$$= \frac{6 \times 10^{-32}}{(0.36 \times 10^{-5})^3} \cdot$$

$= 1.29 \times 10^{-10}$ mol L^{-1}

$$[\mathrm{Mg^{2+}}] = \frac{\mathrm{Ksp\ Mg(OH)_2}}{[\mathrm{OH^-}]^2}$$

$$= \frac{6 \times 10^{-10}}{(0.36 \times 10^{-5})^2} = 46.3 \text{ mol L}^{-1}$$

5. What is the pH of a 1.0 M solution of acetic acid? To what volume of one litre of this solution be diluted so that the pH of the resulting solution will be twice the original value? Given $\mathrm{Ka} = 1.8 \times 10^{-5}$.

[IIT 1990]

Solution As degree of dissociation $(\alpha) = \sqrt{}(\mathrm{Ka/C})$

$= \sqrt{}(1.8 \times 10^{-5} / 1)$

$= 4.2426 \times 10^{-3}$

$[\mathrm{H^+}] = \mathrm{C} \times \alpha$

$= 1 \times 4.2426 \times 10^{-3}$

$= 4.2426 \times 10^{-3}$ mol L^{-1}

$\mathrm{pH} = -\log_{10} [\mathrm{H^+}]$

$= -\log_{10} 4.2426 \times 10^{-3}$

$= 2.3724$

So pH of the acetic acid solution after dilution

$= 2 \times 2.3724 = 4.7448$

New $[\mathrm{H^+}] = 10^{-4.7448} = 1.8 \times 10^{-5}$

Suppose the new concentration is $\mathrm{C_0}$.

$$\begin{array}{lccc} & \mathrm{CH_3COOH} \rightleftharpoons & \mathrm{H^+} + & \mathrm{CH_3COO^-} \\ \text{At. eq.} & \mathrm{C_0} - 1.8 \times 10^{-5} & 1.8 \times 10^{-5} & 1.8 \times 10^{-5} \end{array}$$

$$\text{As } \mathrm{Ka} = \frac{[\mathrm{H^+}]\,[\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]}$$

$$= \frac{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}{(\mathrm{C_0} - 1.8 \times 10^{-5})} = 1.8 \times 10^{-5}$$

So $\mathrm{C_0} = 3.6 \times 10^{-5}$

Suppose the new volume is V litre.

$1 \times 1 = 3.6 \times 10^{-5} \times \mathrm{V}$

$$\mathrm{V} = \frac{1}{3.6 \times 10^{-5}} = 2.78 \times 10^4 \text{ litre}$$

6. A certain weak acid has $\mathrm{Ka} = 1.0 \times 10^{-4}$. Calculate the equilibrium constant for its reaction with a strong base.

[IIT 1991]

Solution $\mathrm{HA} + \mathrm{BOH} \rightleftharpoons \mathrm{BA} + \mathrm{H_2O}$

Weak Strong

$HA + B^+ + OH^- \rightleftharpoons B^+ + A^- + H_2O$

$HA + OH^- \rightleftharpoons A^- + H_2O$

$$K = \frac{[A^-]}{[HA]\,[OH^-]}.$$

For the following reaction,

$$K_h = \frac{[HA]\,[OH^-]}{[A^-]}$$

So $K = \frac{1}{K_h}$.

$$K_h = \frac{K_W}{Ka} = \frac{10^{-14}}{1.0 \times 10^{-4}} = 10^{-10}$$

$$K = \frac{1}{10^{-10}} = 10^{10}$$

7. The solubility product of $Ag_2C_2O_4$ at 25°C is 1.29×10^{-11} mol³ L⁻³. A solution of $K_2C_2O_4$ containing 0.1520 mole in 500 ml of water is shaken with excess of Ag_2CO_3 till the following equilibrium is reached.

$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$

At equilibrium, the solution contains 0.0358 mole of K_2CO_3. Assuming the degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be equal, calculate the solubility product of Ag_2CO_3.

[IIT 1991]

Solution $Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$

Initial	0.1520 mole	0
At. eq.	(0.1520 – 0.0358) = 0.1162 mole	0.0358 mole
Conc.	2 × 0.1162 = 0.2324 M	2 × 0.0358 = 0.0716 M

$Ksp\ Ag_2C_2O_4 = [Ag^+]^2\,[C_2O_4^{2-}]$

$[Ag^+] = [Ksp\ Ag_2C_2O_4 / [C_2O_4^{2-}]\,]^{1/2}$

$Ksp\ Ag_2CO_3 = [Ag^+]^2\,[CO_3^{2-}]$

$[Ag^+] = [Ksp\ Ag_2CO_3 / [CO_3^{2-}]]^{1/2}$

so $[Ksp\ Ag_2C_2O_4 / [C_2O_4^{2-}]\,]^{1/2}$

$= [Ksp\ Ag_2CO_3 / [CO_3^{2-}]]^{1/2}$

$$Ksp\ Ag_2CO_3 = \frac{Ksp\ Ag_2C_2O_4 \times [CO_3^{2-}]}{[C_2O_4^{2-}]}$$

$$= Ksp\ Ag_2C_2O_4\ \frac{[K_2CO_3]}{[K_2C_2O_4]}.$$

$$= 1.29 \times 10^{-11} \times \frac{0.0716}{0.2324}$$

$= 3.97 \times 10^{-12}$ mol³ L⁻³

8. The Ksp of $Ca(OH)_2$ is 4.42×10^{-5} at 25°**C.** 500 ml of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4 M NaOH. How much $Ca(OH)_2$ in mg is precipitated?

[IIT 1992]

Solution Suppose 'S' is the solubility of $Ca(OH)_2$ in saturated solution.

$$\underset{S}{Ca(OH)_2} \rightleftharpoons \underset{S}{Ca^{2+}} + \underset{2S}{2OH^-}$$

$Ksp\ Ca(OH)_2 = [Ca^{2+}]\,[OH^-]^2$

$4.42 \times 10^{-5} = S \times 4S^2$

$4.42 \times 10^{-5} = 4S^3$

$S = 0.0223$ mol L⁻¹

After mixing the two solutions, the total volume becomes one litre.

$$[Ca^{2+}] = \frac{0.0223}{1000} \times 500 = 0.01115 \text{ mol L}^{-1}$$

$$[OH^-] = \underset{[\text{From } (Ca(OH)_2]}{\frac{0.0223 \times 2 \times 500}{1000}} + \underset{[\text{From NaOH}]}{\frac{0.4 \times 500}{1000}}$$

$= 0.2223$ mol L⁻¹

Under the high concentration of OH^- ions, some $Ca(OH)_2$ will be precipitated.

$[Ca^{2+}]_{left}\,[OH^-]^2 = Ksp$

$$[Ca^{2+}]_{left} = \frac{4.42 \times 10^{-5}}{(0.2223)^2}$$

$= 8.94 \times 10^{-4}$ mol L⁻¹

Moles of $Ca(OH)_2$ precipitated

= Moles of Ca^{2+} precipitate

$= [Ca^{2+}]_{Initial} - [Ca^{2+}]_{left}$

$= 0.01115 - 8.94 \times 10^{-4}$

$= 111.5 \times 10^{-4} \times 8.94 \times 10^{-4}$

$= 102.56 \times 10^{-4}\ \text{M} = 102.56 \times 10^{-4} \times 74\ \text{g}$

$= 7589.44 \times 10^{-4}\ \text{g}$

$= 758.944\ \text{mg}$

9. An aqueous solution of metal bromide, MBr_2 (0.05 M) is saturated with H_2S. What is the minimum pH at which MS will precipitate? Ksp for MS = 6.0×10^{-21}, concentration of saturated H_2S = 0.1 M. ($K_1 = 10^{-7}$ and $K_2 = 1.3 \times 10^{-13}$ for H_2S).

[IIT 1993]

Solution Minimum concentration of S^{2-} ions required to precipitate MS is

$$[S^{2-}] = \frac{\text{Ksp MS}}{[M^{2+}]}$$

$$= \frac{6.0 \times 10^{-21}}{0.05} = 1.2 \times 10^{-19}\ \text{M}$$

H_2S ionizes in solution in following steps:

$H_2S \rightleftharpoons H^+ + HS^-$; $K_1 = 10^{-7}$

$HS^- \rightleftharpoons H^+ + S^{2-}$; $K_2 = 1.3 \times 10^{-13}$

$$\text{As } K_1 = \frac{[H^+]\,[HS^-]}{[H_2S]}$$

$$K_2 = \frac{[H^+]\,[S^{2-}]}{[HS^-]}$$

$$\text{So } K_1 K_2 = \frac{[H^+]^2\,[S^{2-}]}{[H_2S]}$$

$$[H^+]^2 = \frac{K_1 K_2\,[H_2S]}{[S^{2-}]}$$

$$= \frac{10^{-7} \times 1.3 \times 10^{-13} \times 0.1}{1.2 \times 10^{-19}}$$

$= 1.08 \times 10^{-2}$

$[H^+] = 1.04 \times 10^{-1}$

$pH = -\log_{10}[H^+]$

$= -\log_{10}(1.04 \times 10^{-1})$

$= 0.98$

10. The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M $NaHCO_3$ solution should be mixed with a 10 ml sample of blood which is 2 M in H_2CO_3, in order to maintain a pH of 7.47? Ka for H_2CO_3 in blood is 7.8×10^{-7}.

[IIT 1993]

Solution Suppose V ml of 5 M $NaHCO_3$ solution be mixed.

Total volume = (V + 10) ml

Concentration of H_2CO_3 in the solution becomes

$$[NaHCO_3] = \frac{5 \times V}{(V + 10)}\ \text{M}$$

$$[H_2CO_3] = \frac{2 \times 10}{(V + 10)}\ \text{M}$$

According to Henderson's equation,

$$pH = -\log_{10} Ka + \log_{10} \frac{[NaHCO_3]}{[H_2CO_3]}$$

$$7.4 = -\log_{10} 7.8 \times 10^{-7} + \log_{10} \frac{5 \times V}{(V + 10)} \times \frac{(V + 10)}{2 \times 10}$$

$$= -\log_{10} 7.8 \times 10^{-7} + \log_{10} \frac{V}{4}$$

$$\log_{10} \frac{V}{4} = 7.4 + \log_{10} 7.8 \times 10^{-7}$$

V = 78.32 ml

11. Find the pH of an aqueous solution of 1.0 M ammonium formed assuming complete dissociation. (pKa of formic acid = 3.8 and pK_b of NH_3 = 4.8.)

[IIT 1995]

$HCOONH_4 + HOH \leftrightarrow HCOOH + NH_4OH$

pH for a salt of weak acid and weak base

$pH = ½\,[\log_{10} K_b - \log_{10} Ka - \log Kw]$

$= ½\,[pKa + pKw - pK_b]$

$= ½\,[3.8 + 14 - 4.8]$

$= 6.5.$

12. The ionization constant of NH_4^+ in water is 5.6×10^{-10} at 25°C. The rate constant for the reaction of NH_4^+ and OH^- to form NH_3 and H_2O at 25°C is 3.4×10^{-10} litre mol^{-1} sec^{-1}. Find the rate constant for proton transfer from water to NH_3.

[IIT 1996]

$$NH_4^+ + H.OH \longleftrightarrow NH_4OH + H^+$$
$$Ka = 5.6 \times 10^{-10}$$

$$NH_3 + HOH \underset{k_2}{\overset{k_1}{\rightleftarrows}} NH_4^+ + OH^- \quad K_b = 3.4 \times 10^{10}$$

$$K\,(NH_3) = \frac{K_1}{K_2} = \frac{Kw}{Ka\,(NH_4^+)}.$$

$$\frac{K_1}{3.4 \times 10^{10}} = \frac{1 \times 10^{-14}}{5.6 \times 10^{-10}}.$$

$K_1 = 6.07 \times 10^5$

13. For 0.50 M aqueous solution of sodium cyanide, (pK_b of CN^- is 4.70), calculate (i) hydrolysis constant (ii) degree of hydrolysis (iii) pH

[IIT 1996]

Solution

(i) $K_h = \frac{K_W}{Ka} = \frac{K_W \times K_b}{K_W}$

(As $K_a \times K_b = K_W$)

So $K_h = K_b = 2 \times 10^{-5}$

(ii) $h = \sqrt{}(K_h / c) = \sqrt{}(2 \times 10^{-5} / 0.5)$

$= 6.3 \times 10^{-3}$

(iii) $[OH^-] = ch = 0.5 \times 6.3 \times 10^{-3}$

$[OH^-] = 3.15 \times 10^{-3}$

$pOH = 2.5$

$pH = 14 - 2.5 = 11.5$

14. What is the pH of a 0.5 M aqueous NaCN solution? pK_b of CN^- is 4.70.

[IIT 1996]

Solution $pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log_{10} M$

$pK_a + pK_b = 14$

$pK_a + 4.7 = 14$

$pK_a = 9.3$

$pH = \frac{1}{2} \times 14 + \frac{1}{2} \times 9.3 + \frac{1}{2} \times \log_{10} 0.5$

$= 7 + 4.65 - 0.15$

$= 11.5$

15. An acid type indicator, HIn differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio $[In^-] / [HIn]$ is greater than 10 or smaller than 0.1 what would be the minimum change in pH of the solution to observe a complete colour change ($Ka = 1.0 \times 10^{-5}$)?

[IIT 1997]

Solution pH of the two given acidic buffers is as follows:

$$pH = pKa + \log_{10} \frac{[Salt]}{[Acid]}.$$

Case I: $pH = -\log_{10} 1 \times 10^{-5} + \log_{10} 10$

$= 5 + 1 = 6$

Case II: $pH = -\log_{10} 1 \times 10^{-5} + \log_{10} 0.1$

$= 5 - 1 = 4$

So the minimum change in pH = 6 – 4 = 2

16. What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH = 2) is mixed with 300 ml of an aqueous solution of NaOH (pH = 12)?

[IIT 1998]

Solution

As pH of HCl = 2

So $[HCl] = 10^{-2}$ M

pH of NaOH = 12

$[NaOH] = 10^{-2}$ M

$$HCl + NaOH \rightleftharpoons NaCl + H_2O$$

M_{eq} 0 100×10^{-2}

after reaction = 1

$[OH^-]$ after reaction $= \frac{1}{500}$.

$= 2 \times 10^{-3}$ M

$pOH = -\log_{10} [OH^-]$

$= -\log_{10} 2 \times 10^{-3} = 2.7$

$pH = 14 - 2.7 = 11.3$

17. Given $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$,

$K_C = 6.2 \times 10^{-8}$ and Ksp of AgCl is 1.8×10^{-10} at 298 K. Calculate concentration of the complex in 1 M aqueous ammonia.

[IIT 1998]

Solution $AgCl \rightleftharpoons Ag^+ + Cl^-$

On adding ammonia solution, complex formation takes place.

$$\underset{(X-Y)}{Ag^+} + \underset{1}{2NH_3} \rightleftharpoons \underset{Y}{[Ag(NH_3)_2]^+} \quad \ldots.(i)$$

Here

X = Solubility of AgCl in NH_3

Y = Amount of complex formed

Ksp of AgCl = $[Ag^+]\,[Cl^-]$

$1.8 \times 10^{-10} = (X - Y) . X$ ……(ii)

K_C for equation (i)

$$= \frac{[Ag(NH_3)_2]^+}{[Ag^+]\,[NH_3]^2}.$$

$$\frac{1}{6.2 \times 10^{-8}} = \frac{Y}{(X - Y) \times 1} \quad \ldots\ldots.(iii)$$

On solving equation (ii) and (iii), we obtain

Y = 0.0539 M.

18. The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6} M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8.

[IIT 1999]

Solution $Pb(OH)_2 \rightleftharpoons Pb^{2+} + 2OH^-$

$Ksp = [Pb^{2+}]\,[OH^-]^2$

$= 6.7 \times 10^{-6} \times (2 \times 6.7 \times 10^{-6})^2$

$= 4 \times (6.7 \times 10^{-6})^3$

$= 1.2 \times 10^{-15}$

Solubility of $Pb(OH)_2$ in buffer system of pH 8.

pH of buffer solution = 8

pOH = 6

$[OH^-] = 10^{-6}$

$$[Pb^{2+}] = \frac{1.2 \times 10^{-15}}{(10^{-6})_2} = 1.2 \times 10^{-3}\text{ M}$$

19. The average concentration of 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 SO_2 in water at 298 K is 1.3653 mol litre^{-1} and the pKa of H_2SO_3 is 1.92, estimate the pH of rain on that day.

[IIT 2000]

Solution pKa = 1.92

Ka = Antilog (–1.92) = 0.012

$$\begin{array}{llll} & H_2SO_3 & \rightleftharpoons\ 2H^+ & +\ SO_3^{2-} \\ t=0 & C & 0 & 0 \\ t_{eq} & C - C\alpha & 2C\alpha & C\alpha \end{array}$$

$$Ka = \frac{[H^+]^2\,[SO_3^{2-}]}{[H_2SO_3]}$$

$$0.012 = \frac{(2C\alpha)^2 \times C\alpha}{C(1-\alpha)} = \frac{4C^2\alpha^3}{(1-\alpha)} = 4C^2\alpha^3$$

$0.012 = 4 \times (1.3653)^2 \times \alpha^3$

$\alpha = 0.117$

$[H^+] = 2C\alpha$

$= 2 \times 1.3653 \times 0.117$

$= 0.3194$

$pH = -\log_{10} \times 0.3194$

$= 0.495$

20. 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 6g of NaOH is added to the above solution, determine final pH. Assume there is no change in volume on mixing. Ka for acetic acid is 1.75×10^{-5} M.

[IIT 2002]

Solution

(a) Concentration of HCl and CH_3COOH after mixing will be 0.1 M.

$$\begin{array}{llll} & CH_3COOH & \rightleftharpoons CH_3COO^- & + H^+ \\ t=0 & 0.1 & 0 & 0.1\text{ (from HCl)} \\ t_{eq} & 0.1 - X & X & 0.1 + X \end{array}$$

$$Ka = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]}$$

$$1.75 \times 10^{-5} = \frac{X \times (0.1 + X)}{(0.1 - X)}$$

On solving, we get

$X = 1.75 \times 10^{-5}$

$[H^+] = 0.1 + X = 0.1$ M

$pH = -\log_{10} [0.1] = 1$

Degree of dissociation of acetic acid

$= \frac{1.75 \times 10^{-5}}{0.1} = 1.75 \times 10^{-4}$

(b) Number of moles of NaOH added $= \frac{6}{40}$

$= 0.15$

$CH_3COOH + HCl + NaOH \rightleftharpoons$

t = 0   0.1   0.1   0.15

0.05   0   0

$CH_3COONa + NaCl + H_2O$

0   0   0

0.05   0   0

$$pH = pKa + \log_{10} \frac{[Salt]}{[Acid]}.$$

$$= -\log_{10} 1.75 \times 10^{-5} + \log_{10} \frac{0.05}{0.05}$$

$= 4.757$

21. Will the pH of water be same at 4°C and 25°C? Explain.

[IIT 2003]

Solution

$K_W = [H^+] [OH^-]$

At 25°C $[H^+] = [OH^-] = 1.01 \times 10^{-7}$ M

$pH = -\log_{10} [H^+]$

$= -\log_{10} [10^{-7}] = 7$

At 4°C, ionization of water will be less than that at 25°C.

As at 25°C $K_W = [H^+] [OH^-]$ will be less than 10^{-14} so pH of water will be more than 7 at 4°C.

22. 0.1 M NaOH is titrated with 0.1 M HA till the end point; Ka for HA is 5.6×10^{-6} and degree of hydrolysis is less compared to one. Calculate pH of the resulting solution at the end point.

[IIT 2004]

Solution Neutralization of HA with NaOH may be given as,

$HA + NaOH \rightarrow NaA + H_2O$

Concentration of salt will be 0.1 / 2 M that is, 0.05 M, as volume will be double. pH of salt after hydrolysis may be calculated as,

$pH = \frac{1}{2} [pK_W + pKa + \log C]$ .....(i)

$pK_W = 14$

$pKa = -\log_{10} Ka$

$= -\log_{10} (5.6 \times 10^{-6}) = 5.2518$

$\log_{10} C = \log_{10} 0.05 = -1.3010$

On putting the values of pK_W, pKa and $\log_{10} C$ in equation (i), we obtain

$pH = \frac{1}{2} [14 + 5.2518 - 1.3010]$

$= 8.9754$

23. 0.1 mol of methyl amine ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mol of HCl and the solution is diluted to 1 litre. Determine the hydrogen ion concentration of the resulting solution.

[IIT 2005]

Solution

	CH_3NH_2 +	HCl →	$CH_3N^+H_3Cl^-$
Initially	0.1 mol	0.08 mol	0 mol
On completion	0.02 mol	0 mol	0.08 mol

This resulting solution is a basic buffer for which

$$pOH = pK_b + \log_{10} \frac{[Salt]}{[Base]}$$

$$= -\log_{10} 5 \times 10^{-4} + \log_{10} \frac{0.08}{0.02}$$

$= 3.3 + 0.6 = 3.9$

$pH = 14 - 3.9 = 10.1$

$H^+ = 8 \times 10^{-11}$ M

MULTIPLE-CHOICE QUESTIONS

Straight Objective Type Questions (Single Choice only)

1. At 90°C, pure water has $[H_3O^+]$ 10^{-6} mole litre^{-1}. What is the value of Kw at 90°C?

   a. 10^{-8} b. 10^{-6}
   c. 10^{-12} d. 10^{-14}

2. Which of the following has the highest pH ?

   a. 0.1 M NaOH
   b. 0.1 M CH_3COOH
   c. 0.01 M NaOH
   d. 0.1 M HCl

3. Which among the following is the least soluble?

   a. MnS (Ksp = 7×10^{-16})
   b. FeS (Ksp = 4×10^{-19})
   c. PtS (Ksp = 8×10^{-73})
   d. NiS (Ksp = 3×10^{-12})

4. Of the given anions, the strongest bronsted base is

   a. ClO_4^- b. ClO_3^-
   c. ClO_2^- d. ClO^-

5. The conjugate acid of O^{2-} ion is

   a. H_2O b. H^+
   c. H_3O^+ d. OH^-

6. The pH of a 10^{-8} molar solution of HCl in water is

   a. –8 b. 8
   c. between 6 and 7 d. between 7 and 8

7. A acidic buffer solution can be prepared by mixing the solutions of

   a. sodium chloride and sodium hydroxide
   b. sulphuric acid and sodium sulphate
   c. ammonium chloride and ammonium hydroxide
   d. ammonium acetate and acetic acid

8. At 25°C, the pH of pure water is 7. It dissociates as $H_2O\,(l) + H_2O\,(l) \leftrightarrow H_3O^+ + {}^-OH$, $\Delta H° = -13.7$ Kcal mol^{-1}. pH water of 37°C is expected to be

   a. > 7 b. $= 7$
   c. < 7 d. none of these

9. Molten sodium chloride conducts electricity due to the presence of

   a. free ions
   b. free molecules
   c. free electrons
   d. atoms of sodium and chlorine

10. Conjugate base of hydrazoic acid is

    a. HN_3^- b. N_2^-
    c. Azide ion d. Nitride ion

11. The precipitate of CaF_2 (Ksp = 1.7×10^{-10}) is obtained when equal volumes of the following are mixed

    a. 10^{-2} M Ca^{2+} + 10^{-3} M F^-
    b. 10^{-3} M Ca^{2+} + 10^{-5} M F^-
    c. 10^{-4} M Ca^{2+} + 10^{-4} M F^-
    d. 10^{-5} M Ca^{2+} + 10^{-3} M F^-

12. Out of Ca^{2+}, Al^{3+}, Cr^{3+}, Mg^{2+} and Zn^{2+}, the reagents NH_4Cl and aqueous NH_3 will precipitate

    a. Ca^{2+}, Al^{3+} b. Al^{3+}, Cr^{3+}
    c. Bi^{3+}, Mg^{2+} d. Mg^{2+}, Zn^{2+}

13. A certain weak acid has a dissociation constant of 1.0×10^{-4}. the equilibrium constant for its reaction with a strong base is

    a. 1.0×10^{10} b. 1.0×10^{14}
    c. 1.0×10^{-10} d. 1.0×10^{-4}

14. Which of the following compounds can form a buffer solution?

    a. Na_2HPO_4 and NaH_2PO_4
    b. HCl and NH_4Cl
    c. CH_3COOH and HCOOH
    d. Na_3PO_4 and NaOH

15. The compound that is not a Lewis acid is

    a. $SnCl_4$ b. $BeCl_2$
    c. BF_3 d. $AlCl_3$

16. 10 ml of 0.2 M acid is added to 250 ml of a buffer solution with pH = 6.34. The pH of the solution becomes 6.32. The buffer capacity of the solution is

    a. 0.4 b. 0.3
    c. 0.2 d. 0.1

17. The conjugate acid of NH_2^- is

a. NH_4^+
b. NH_3
c. NH_2OH
d. N_2H_4

18. The solubility products of $Al(OH)_3$ and $Zn(OH)_2$ are 8.5×10^{-23} and 1.8×10^{-14} respectively. If NH_4OH is added to a solution containing Al^{3+} and Zn^{2+} ions, then substance precipitated that is

a. $Zn(OH)_2$
b. $Al(OH)_3$
c. both (a) and (b)
d. none of these

19. The best indicator for detection of end point in titration of a weak acid and a strong base is

a. methyl red (5 to 6)
b. methyl orange (3 to 4)
c. phenolphthalene (8 to 9.6)
d. bromothymol blue (6 to 7.5)

20. The pKa of acetylsalicylic acid (aspirin) is 3.5×10^{-5}. The pH of gastric juice in human stomach is about 2 – 3 and the pH in the small intestine is about 8. Aspirin will be

a. ionized to the stomach and almost unionized in the small intestine
b. ionized in the small intestine and almost unionized in the stomach
c. unionized in small intestine and in the stomach
d. completely ionized in the small intestine and in the stomach

21. The pKa of acetyl salicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2 – 3 and pH in the small intestine is about 8. Aspirin will be

a. ionized in the small intestine and almost unionized in the stomach
b. unionized in the small intestine and in the stomach
c. completely ionized in the small intestine and in the stomach.
d. ionized in the stomach and almost unionized in the small intestine.

22. The aqueous solution of NH_4CN is slightly alkaline because

a. it is a salt
b. CN^- ion hydrolyses to a greater extent than NH_4^+ ion.
c. NH_4^+ ion hydrolyses to a greater extent than CN^- ion.
d. both hydrolyses to an equal extent

23. The compound whose 0.1 M solution is basic is

a. ammonium acetate
b. ammonium sulphate
c. sodium acetate
d. ammonium chloride

24. Which among the following acts as a basic buffer?

a. $NH_4Cl + NH_4OH$
b. $NaCl + NaOH$
c. $NH_4Cl + CH_3COOH$
d. $CH_3COONa + CH_3COOH$

25. Amongst the following hydroxides, the one which has the lowest value of Ksp at ordinary temperature (about 25°C) is

a. $Mg(OH)_2$
b. $Ca(OH)_2$
c. $Ba(OH)_2$
d. $Be(OH)_2$

26. The strongest Bronsted base among the following ions is

a. CH_3O^-
b. $C_2H_5O^-$
c. $(CH_3)_2CHO^-$
d. $(CH_3)_3CO^-$

27. The pH of the neutralization point of 0.1 N ammonium hydroxide with 0.1 NHCl is

a. 1
b. 6
c. 9
d. 7

28. The following reactions are known to occur in the body

$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^{-1}$

If CO_2 escapes from the system

a. pH will decrease
b. Hydrogen ion concentration will diminish
c. H_2CO_3 concentration will remain unchanged
d. the forward reaction will be favoured.

29. The following equilibrium is established when hydrogen chloride is dissolved in acetic acid.

$HCl + CH_3COOH \leftrightarrow Cl^- + CH_3COOH_2^+$

The set that characterizes the conjugate acid base pair is

a. (HCl, CH_3COOH) and ($CH_3COOH_2^+$, Cl^-)
b. (HCl, $CH_3COOH_2^+$) and (HCl, $CH_3COOH_2^+$) and (CH_3COOH, Cl^-)
c. ($CH_3COOH_2^+$, HCl) and (Cl^-, CH_3COOH)
d. (HCl, Cl^-) and ($CH_3COOH_2^+$, CH_3COOH)

30. Which of the following are Lewis acids?

(i) BF_3
(ii) H_2O
(iii) HSO_4^-
(iv) SO_3

a. (i) and (iii)
b. (i) and (ii)
c. (i) and (iv)
d. (iii) and (iv)

31. The pKa pf HCN is 9.30. The pH of a solution prepared by mixing 2.5 moles of KCN and 2.5 moles of HCN in water and making up the total volume to 500 ml is

a. 9.30
b. 8.30
c. 7.30
d. 10.30

32. What is the pH of a 0.25 M weak acid that is 2.2 % ionazied ?

a. 0.60
b. 2.00
c. 1.00
d. 2.26

33. Fear or excitement, generally causes one to breathe rapidly and it results in the decrease of CO_2 concentration in blood. In what way will it change the pH of blood?

a. pH will increase
b. pH will decrease
c. no change
d. pH will adjust to 7.

34. Which of the following is correct order of increasing acidity?

a. HI < HBr > HCl < HF
b. HF < HCl < HBr < HI
c. HF > HCl > HBr > HI
d. HF > HCl < HBr > HI

35. The pH of a 0.1 M aqueous solution of a weak acid (HA) is 3. What is its degree of dissociation?

a. 1%
b. 10%
c. 50%
d. 25%

36. Ammonium cyanide is a salt of NH_4OH of Kb = 2.5 × 10^{-5} and HCN of Ka = 4.0 × 10^{-10}. The hydrolysis constant of NH_4CN at 25°C is

a. 4.6
b. 4.4
c. 2.4
d. 1.4

37. If the acids HA and HB have dissociation constants 1 × 10^{-3} and 1 × 10^{-5} respectively, then

a. HA is five times stronger than HB
b. HA is ten times stronger than HB
c. HA is ten times weaker than HB
d. HA is five times weaker than HB

38. The dissociation constant of two acids HA_1 and HA_2 are 3.0 × 10^{-4} and 1.8 × 10^{-5} respectively. The relative strengths of the acids is

a. 1:16
b. 1:4
c. 4:1
d. 16:1

39. The strongest Bronsted base in the following anion is

a. ClO^-
b. ClO_2^-
c. ClO_3^-
d. ClO_4^-

40. When solid potassium cyanide is added in water, then its

a. pH will decrease
b. pH will increase
c. electrical conductivity will not change
d. pH will remain the same

41. The solubility of CuBr is 2 × 10^{-4} mol L^{-1} at 25°C. The Ksp value for CuBr is

a. 4 × 10^{-6}
b. 4 × 10^{-16}
c. 4 × 10^{-11}
d. 4 × 10^{-8}

42. The solubility of MX_2 type electrolyte is 0.5 × 10^{-4} mol L^{-1}. The value of Ksp of the electrolyte is

a. 1.35 × 10^{-13}
b. 25 × 10^{-10}
c. 5 × 10^{-13}
d. 5 × 10^{-18}

43. The solubility product of $PbCl_2$ at 20°C is 1.5 × 10^{-4}. Its solubility is

a. 3.45 × 10^{2} mol L^{-1}
b. 3.34 × 10^{4} mol L^{-1}
c. 3.34 × 10^{-2} mol L^{-1}
d. 3.85 × 10^{-4} mol L^{-1}

44. Which has highest pH?

a. CH_3COOK
b. Na_2CO_3
c. NH_4Cl
d. $NaNO_3$

45. How do you differentiate between Fe^{3+} and Cr^{3+} in group III?

a. By increasing NH_4^+ ion concentration
b. By decreasing OH^- ion concentration
c. By taking excess of NH_4OH
d. Both (a) and (b)

46. 0.005 M acid solution has 5 pH. The percentage ionization of acid is

a. 0.8 %
b. 0.6 %
c. 0.4 %
d. 0.2 %

47. Which one of the following order of acid strengths is correct?

a. RCOOH > HC ≡ CH > HOH > ROH
b. RCOOH >HOH > HC ≡ CH > ROH
c. RCOOH > ROH > HOH > HC ≡ CH
d. RCOOH > HOH > ROH > HC ≡ CH

48. The concentrations of H^+ and OH^- of a 0.1 aqueous solution of 2% ionized weak acid are [ionic product of water = 1 × 10^{-14}]

a. 3 × 10^{-2} M and 5 × 10^{-13} M
b. 0.1 × 10^{-3} M and 3 × 10^{-11} M

c. 0.2×10^{-3} M and 5×10^{-11} M
d. 2×10^{-3} M and 5×10^{-12} M

49. When rain is accompanied by thunderstorm, the collected rain water will have a pH value

a. slightly lower than that of rain water without thunderstorm
b. which depends on the amount of dust in air
c. slightly higher than that of rain water without thunderstorm
d. uninfluenced by the occurrence of thunderstorm

50. The pH value of an acid is 5 and its concentration is 1 M. What is the value of Ka for the acid?

a. 10^{-5} **b.** 10^{-10}
c. 10^{-7} **d.** 10^{-8}

51. Which of the following is not a buffer solution?

a. 0.05 M $KClO_4$ + 0.05 M $HClO_4$
b. 2 M $C_6H_5NH_2$ + 2 M $C_6H_5{}^+NH_3Br$
c. 0.8 M H_2S + 0.8 M KHS
d. 3 M H_2CO_3 + 3 M $KHCO_3$

52. The conjugate base of $H_2PO_4^-$ is

a. HPO_4^{2-} **b.** H_3PO_4
c. PO_4^{3-} **d.** P_2O_5

53. A rapid change of pH near stiochiometric point of an acid–base titration is the basis of indicator detection. The pH of solution is related to the ratio of concentrations of conjugate acid [HIn] and base forms of the indicator by the expression

a. $\log \frac{[In^-]}{[HIn]} = pH - pK_{In}$

b. $\log \frac{[HIn^-]}{[In]} = pH - pK_{In}$

c. $\log \frac{[HIn^-]}{[In]} = pK_{In} - pH$

d. $\log \frac{[In^-]}{[HIn]} = pK_{In} - pH$

54. Two solutions A and B are prepared by adding NaOH and HCl acid into water respectively. The ionic product of water will

a. increase in B and decrease in A
b. increase in A and B
c. remain the same in two solutions
d. increase in A and decrease in B

55. Dimethyl glyoxime gives a red precipitate with Ni^{2+}, which is used for its detection. To get this precipitate readily, the best pH range is

a. 0.1 **b.** 2.3
c. 9.11 **d.** 3.6

56. The molar solubility of a sparingly used soluble salt MX_4 is 'S'. The corresponding solubility product is Ksp. The value of 'S' is given in terms of Ksp by the relation

a. $S = (Ksp / 128)^{1/4}$ **b.** $S = (256\ Ksp)^{1/5}$
c. $S = (Ksp / 256)^{1/5}$ **d.** $S = (128\ Ksp)^{1/5}$

57. The conjugate base of OH^- is

a. H_2O **b.** O^{2-}
c. O^- **d.** O_2

58. What is the correct relationship between the pHs of isomolar solutions of sodium oxide (pH_1), sodium sulphide (pH_2), sodium selenide (pH_3) and sodium telluride (pH_4)?

a. $pH_1 > pH_2 \approx pH_3 > pH_4$
b. $pH_1 < pH_2 < pH_3 < pH_4$
c. $pH_1 < pH_2 < pH_3 \approx pH_4$
d. $pH_1 > pH_2 > pH_3 > pH_4$

59. When 10 mL of 0.1 M acetic acid (pKa = 5.0) is titrated against 10 mL of 0.1 M ammonia solution (pKb = 5.0) the equivalence point occurs at pH

a. 5.0 **b.** 6.0
c. 9.0 **d.** 7.0

60. H_2S gas when passed through a solution of cations containing HCl precipitates the cations of second group of qualitative analysis but not those belonging to the fourth group. It is because

a. Solubility product of group II sulphides is more than that of group IV sulphides
b. Presence of HCl increases the sulphide ion concentration
c. Sulphides of group IV cations are unstable in HCl.
d. Presence of HCl decreases the sulphide ion concentration

61. A solution has pH = 5, it is diluted 100 times, then it will become:

a. Neutral **b.** More acidic
c. Basic **d.** Unaffected

62. A buffer solution has equal volume of 0.2 M NH_4OH and 0.02 M NH_4Cl. The pK_b of the base is 5. The pH is

a. 4 **b.** 10
c. 7 **d.** 9

63. Solubility product of a salt AB is 1×10^{-8} M^2 in a solution in which the concentration of A^+ ion is 10^{-3}

M. The salt will precipitate when the concentration of B^- ion is kept

a. $< 10^{-8}$ M
b. $> 10^{-5}$ M
c. Between 10^{-8} M to 10^{-7} M
d. Between 10^{-7} M to 10^{-6} M

64. Choose the correct order arranged in decreasing order of basicity.

a. $OH^- > CH_3O^- > CH \equiv\equiv C^-$
b. $CH \equiv C^- > CH_3O^- > OH^-$
c. $CH_3O^- > OH^- > CH \equiv C^-$
d. $CH_3O^- > CH \equiv C^- > OH^-$

65. In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (molecular mass = 283) the equilibrium which sets in is

$AgIO_3\,(s) \rightleftharpoons Ag^+\,(aq) + IO_3^-\,(aq)$

If the solubility product constant Ksp of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 ml of its saturated solution?

a. 2.83×10^{-3} g
b. 1.0×10^{-7} g
c. 1.0×10^{-4} g
d. 28.3×10^{-2} g

66. The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be

a. 5.0×10^{15}
b. 5.0×10^{-15}
c. 0.2×10^{5}
d. 5.0×10^{-5}

67. The pKa of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50 % of the acid is ionized is

a. 2.5
b. 9.5
c. 7.0
d. 4.5

68. Degree of hydrolysis of a salt of weak acid and a strong base is given by

a. $x = \sqrt{(C / K_h)}$
b. $x = \sqrt{(K_h / C)}$
c. $x = (K_h K_b / C)$
d. $x = \sqrt{(K_b / C)}$

69. 100 cc of HCl of pH value 1 is mixed with 100 cc of distilled water. The pH of the resultant solution is

a. 1.3
b. 1.7
c. 2.3
d. 1.9

70. The pKa of a weak acid, HA is 4.80. The pK_b of a weak base, BOH is 4.78. The pH of an aqueous solution of the corresponding salt, BA will be

a. 9.58
b. 4.79
c. 7.01
d. 9.22

Brainteasers Objective Type Questions (Single choice only)

71. A certain buffer solution contains equal concentration of X^- and HX. The Kp for X^- is 10^{-10}. The pH of the buffer is

a. 6
b. 10
c. 4
d. 14

72. What is the decreasing order of strength of the bases?

$OH^-, NH_2^-, H - C \equiv C^-$ and $CH_3 - CH_2^-$?

a. $CH_3 - CH_2^- > NH_2^- > H - C \equiv C^- > OH^-$
b. $H - C \equiv C^- > CH_3 - CH_2^- > NH_2^- > OH^-$
c. $OH^- > NH_2^- > H - C \equiv C^- > CH_3 - CH_2^-$
d. $NH_2^- > H - C \equiv C^- > OH^- > CH_3 - CH_2^-$

73. The dissociation constants of acids HA and HB are 3.2×10^{-4} and 2×10^{-5} respectively. The ratio of the strengths HA to HB will be

a. 4:1
b. 1:4
c. 16:1
d. 1:16

74. Which of the following solutions will have pH close to 1.0?

a. 100 ml of (M/10) 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/10) HCl + 25 ml of (M/5) NaOH

75. A base dissolved in water, yields a solution with a hydroxyl ion concentration of 0.05 mol L^{-1}. The solution is

a. acid
b. neutral
c. basic
d. either (a) and (b)

76. The pH of the solution, produced when an aqueous solution of pH 5 is mixed with an equal volume of an aqueous solution of pH 3, is

a. 3.3
b. 4.3
c. 2.5
d. 6.3

77. 75 ml of 0.2 M HCl is mixed with 25 ml of 1 M HCl. To this solution, 300 ml of distilled water is added. What is the pH of the resultant solution?

a. 1
b. 2
c. 4
d. 0.2

78. The pH of a buffer solution, containing 0.2 mole per litre of CH_3COONa and 1.5 mol L^{-1} of CH_3COOH is (Ka for acetic acid is 1.8×10^{-5})

a. 3.45 **b.** 4.87
c. 5.48 **d.** 9.23

79. At 295 K, solubility of AgCl is 1.435×10^{-3} gL^{-1}. Its solubility product is (take molecular weight of AgCl = 143.32)

a. 10^{-12} **b.** 10^{-10}
c. 10^{-6} **d.** 10^{-16}

80. The solubility product of AgI at 25°C is 1.0×10^{-16}. The solubility of AgI in 10^{-4} N solution of KI at 25°C is approximately.

a. 1.0×10^{-6} **b.** 1.0×10^{-8}
c. 1.0×10^{-12} **d.** 1.0×10^{-16}

81. 100 ml of 0.015 M HCl solution is mixed with100 ml of 0.005 M HCl. What is the pH of the resultant solution?

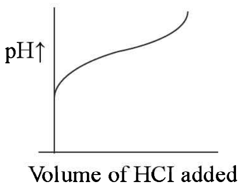
a. 2.5 **b.** 1.5
c. 2 **d.** 1

82. What is the pH of 0.01 M glycine solution? For glycine $Ka_1 = 4.5 \times 10^{-3}$ and $Ka_2 = 1.7 \times 10^{-10}$ at 298 K

a. 6.94 **b.** 7.06
c. 5.06 **d.** 8.02

83. When 100 ml of 0.1 M NaCN solution is titrated with 0.1 HCl solution the variation of pH of solution with volume of HCl added will be

a.



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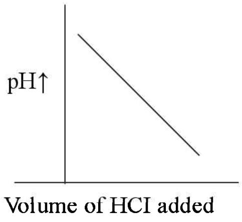

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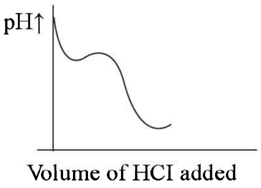

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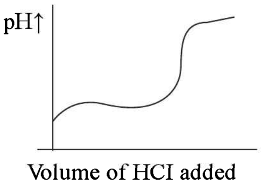


84. 50 ml of 0.1 M HCl and 50 ml of 0.2 M NaOH are mixed. The pH of the resulting solution is

a. 12.7 **b.** 10.17
c. 11.7 **d.** 1.30

85. 0.365 g of HCl gas was passed through 100 cm^3 of 0.2 M NaOH solution. The pH of the resulting solution would be

a. 1 **b.** 8
c. 7 **d.** 13
e. 9

86. The Ka value of formic acid and acetic acid are respectively 1.77×10^{-4} and 1.75×10^{-5}. the ratio of the acid strength of 0.1 N acids is

a. 0.1 **b.** 0.3
c. 3.178 **d.** 100

87. On adding 0.1 M solution each of Ag^+, Ba^{2+}, Ca^{2+} ions in a Na_2SO_4 solution, species first precipitated is (Ksp $BaSO_4 = 10^{-11}$, Ksp $CaSO_4 = 10^{-6}$, Ksp $Ag_2SO_4 = 10^{-5}$)

a. $CaSO_4$ **b.** Ag_2SO_4
c. $BaSO_4$ **d.** All of these

88. The Ksp of $Mg(OH)_2$ is 1×10^{-12}. 0.01 M Mg^{2+} will precipitate at the limiting pH of

a. 3 **b.** 5
c. 8 **d.** 9

89. 20 ml of 0.5 N HCl and 35 ml of 0.1 N NaOH are mixed. The resulting solution will

a. Turn methyl orange red
b. Turn phenolphthalein solution pink
c. Be neutral
d. Be basic

90. 1 litre of 0.5 M KCl solution is electrolysed for one minute in a current of 16.08 mA. Considering 100 % efficiency, the pH of resulting solution will be

a. 7 **b.** 9
c. 8 **d.** 10

91. The hydrogen ion concentration of a 10^{-8} M HCl aqueous solution at 298 K ($Kw = 10^{-14}$) is

a. 9.525×10^{-8} M **b.** 1.0×10^{-8} M
c. 1.0×10^{-6} M **d.** 1.0525×10^{-7} M

92. 40 ml of 0.1 M ammonia solution is mixed with 20 ml of 0.1 M HCl. What is the pH of the mixture? (pKb of ammonia solution is 4.74)

a. 5.74 **b.** 9.26
c. 4.56 **d.** 7.06

93. HA is a weak acid. The pH of 0.1 M HA solution is 2. What is the degree of dissociation (α) of HA?

a. 0.1 **b.** 0.2
c. 0.4 **d.** 0.51

94. At 25°C the value of pK_b (K_b being the dissociation constant as a base) for NH_3 in aqueous solution is 4.7. What is the pH of a 0.1 M aqueous solution of NH_4Cl with 0.01 M NH_3 (approximately)?

a. 9 **b.** 8.3
c. 9.6 **d.** 10

95. A weak acid, HA has a Ka of 1.00×10^{-5}. If 0.100 mol of this acid is dissolved in one litre of water, the percentage of acid dissociated at equilibrium is closest to

a. 99.0 % **b.** 1.00 %
c. 99.9 % **d.** 0.100 %

96. The aqueous solutions of HCOONa, $C_6H_5NH_3Cl$ and KCN are respectively

a. Basic, acidic, basic
b. Basic, neutral, neutral
c. Acidic, acidic, basic
d. Acidic, basic, neutral
e. Basic, neutral, basic

97. Which is the best choice for weak base–strong acid titration?

a. Methyl acid
b. Phenolphthalein
c. Litmus
d. Phenol acid

98. Addition of sodium acetate to 0.1 M acetic acid will cause

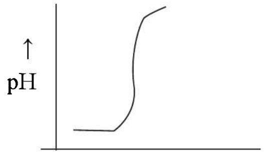
a. Increase of pH
b. No change in pH
c. Change in pH that cannot be predicted
d. Decrease in pH

99. Solubility product of Mg $(OH)_2$ at ordinary temp. is 1.96×10^{-11} . pH of a saturated soln. of $Mg(OH)_2$ will be–

a. 10.53 **b.** 6.78
c. 3.56 **d.** 3.66

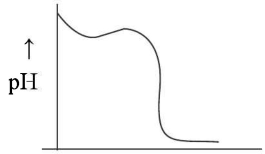
100. Which one is the correct graph for the corresponding acid base titration?

a.



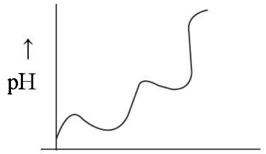
Volume of strong base added to a monobasic strong acid

b.



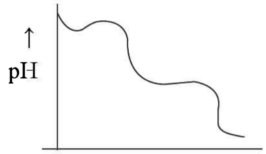
Volume of strong base added to a monobasic weak acid

c.



Volume of strong base added to a weak dibasic acid

d.



Volume of strong base added to a weak diacidic base

101. The pH of a solution obtained by mixing 50 ml of 1 N HCl and 30 ml of 1 N NaOH is [log 2.5 = 0.3979]

a. 11.045 **b.** 0.6021
c. 2.768 **d.** 1.0009
e. 14. 897

102. A buffer solution is prepared by mixing equal concentration of acid (ionization constant K_α) and a salt . The pH of buffer is

a. $14 - pK_\alpha$ **b.** $pK_\alpha + 7$
c. pK_α **d.** $pK_\alpha + 1$

103. Equimolar solutions of the following were prepared in water separately. Which one of the solutions will record the highest pH?

a. $MgCl_2$ **b.** $CaCl_2$
c. $SrCl_2$ **d.** $BaCl_2$

104. The values pf Kp_1 and Kp_2 for the reactions

$X \rightleftharpoons Y + Z$ ……..(1)

$A \rightleftharpoons 2B$ ……….(2)

are in ratio of 9:1. If degree of dissociation of X and A be equal, then total pressure at equilibrium (1) and (2) are in the ratio:

a. 36:1 **b.** 1:1

c. 3:1 **d.** 1:9

105. For a concentrated solution of a weak electrolyte A_xB_y of concentrated 'C', the degree of dissociation α is given as

a. $\alpha = (K_{eq} / C^{xy})$

b. $\alpha = (K_{eq} / Cxy)$

c. $\alpha = K_{eq} / C^{x+y-1} x^x y^y)^{1/(x+y)}$

d. $\alpha = K_{eq} C / (xy)$

e. $\alpha = K_{eq} / C(x + y)$

106. The solubility of $BaSO_4$ in water is 2.33×10^{-3} g–L^{-1}. Its solubility product will be (molecular weight of $BaSO_4 = 233$)

a. 1×10^{-10} **b.** 1×10^{-15}

c. 1×10^{-5} **d.** 1×10^{-20}

107. If Ksp of $PbBr_2$ is 8×10^{-5} and it is 80% dissociated in solution find its solubility?

a. 0.027 m/L **b.** 0.038 m/ L

c. 0.017 m/L **d.** 0.034 m/L

108. Ascorbic acid, $H_2C_6H_6O_6$, is a polyprotic acid containing two ionizable hydrogens. K_{a1} is 8.0×10^{-5} and K_{a2} is 1.6×10^{-12}. Calculate the pH of a 2.0×10^{-3} M solution of ascorbic acid.

a. 3.40 **b.** 0.340

c. 2.70 **d.** 0.270

109. The solubility products of CuS, Ag_2S and HgS are respectively 10^{-37}, 10^{-49} and 10^{-54}. The solubilities (in mol.lit^{-1}) of these sulphides are in the descending order,

a. CuS > Ag_2S > HgS

b. Ag_2S > HgS > CuS

c. HgS > Ag_2S > CuS

d. Ag_2S > CuS > HgS

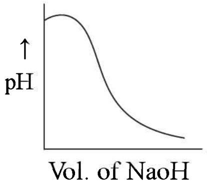
110. Equal volumes of three acid solutions of pH 3, 4, and 5 are mixed in a vessel. What will be the H^+ ion concentration in the mixture?

a. 3.7×10^{-3} M **b.** 1.11×10^{-3} M

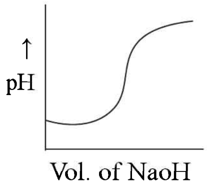
c. 1.11×10^{-4} M **d.** 3.7×10^{-4} M

111. Which one of these curves represents the graph of pH during the titration of NaOH and HCl (aq) here

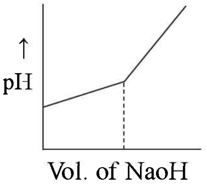
a.



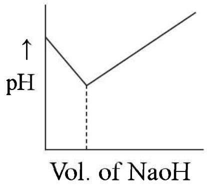
b.



c.



d.



112. From the following chemical reactions determine the relative Bronsted–Lowry acid strengths (Strongest to weakest).

$HClO_4 (aq) + H_2O (l) \rightarrow H_3O^+ (aq) + ClO_4^- (aq)$

$HNO_2 (aq) + H_2O (l) \rightleftharpoons H_3O^+ (aq) + NO_2^- (aq)$

a. $HClO_4 > HNO_2 > H_3O^+$

b. $HClO_4 > H_3O^+ > HNO_2$

c. $H_3O^+ > HNO_2 > HClO_4$

d. $H_3O^+ > HClO_4 > HNO_2$

113. Four species are listed below:

(I) HCO_3^- (II) H_3O^+

(III) HSO_4^- (IV) HSO_3F

Which one of the following is the correct sequence of their acid strength?

a. IV < II < III < I

b. II < III < I < IV

c. I < III < II < IV

d. III < I < IV < II

114. What is the pH of a solution prepared by mixing 100 ml of 0.020 M $Ca(OH)_2$ with 50.00 ml of 0.100M NaOH? Assume that the volumes are additive.

a. 10.87
b. 11.78
c. 12.00
d. 12.78

115. Para–Aminobenzoic acid (PABA), p $H_2NC_6H_4(COOH)$, is used in some sunscreens and hair conditioning products. Calculate the pH of an aqueous solution with [PABA] = 0.030 M and Ka = 2.2×10^{-5}.

a. 2.09
b. 4.98
c. 6.18
d. 3.09

116. Three sparingly soluble salts A_2X, AX and AX_3 have the same solubility product. Their solubilities will be in the order

a. $AX_3 > AX > A_2X$

b. $AX_3 > A_2X > AX$

c. $AX > AX_3 > A_2X$

d. $AX > A_2X > AX_3$

117. At 25°C, the pH of a vinegar solution is 2.60. What are the values of $[H_3O^+]$ and $[OH^-]$ in the solution?

a. 2.51×10^{-3} M, 3.99×10^{-12} M

b. 2.30 M, 12.40 M

c. 3.51×10^{-4} M, 3.99×10^{-10} M

d. 2.51×10^{-3} M, 1.28×10^{-4} M

118. Which of the following are weak diprotic acids?

a. Hydrocyanic acid – HCN, sulphuric acid – H_2SO_4, phosphoric acid – H_3PO_4

b. Carbonic acid – H_2CO_3, oxalic acid – $H_2C_2O_4$, sulphurous acid – H_2SO_3

c. Formic acid – HCOOH, acetic acid – CH_3COOH, benzoic acid – C_6H_5COOH

d. Carbonic acid – H_2CO_3, hydrosulphuric acid – H_2S, acetic acid – CH_3COOH

119. Which of the following salts are acidic?

a. NH_4Cl, $CuCl_2$, $AlCl_3$

b. LiCl, NaCl, KCl

c. NaCl, NH_4Cl, Na_2CO_3

d. $NaCH_3CO_2$, KCH_3CO_2, $RbCH_3CO_2$

120. An acidic solution at 25°C will have a hydronium ion concentration ______ and a pH value of _______.

a. $[H_3O^+] < 1 \times 10^{-7}$ M, pH < 7.00

b. $[H_3O^+] < 1 \times 10^{-7}$ M, pH > 7.00

c. $[H_3O^+] > 1 \times 10^{-7}$ M, pH < 7.00

d. $[H_3O^+] > 1 \times 10^{-7}$ M, pH > 7.00

121. The decreasing order of acidic nature of H_2SO_4 (I), H_3PO_4 (II), and $HClO_4$ (III) is

a. I > II > III
b. I > III > II
c. III > I > II
d. III > II > I

122. Arrange the following 0.5 M aqueous solutions in order of increasing pH

NaOH, HBr, $NaCH_3CO_2$, KBr, NH_4Br

a. HBr, NH_4Br, KBr, $NaCH_3CO_2$, NaOH

b. NaOH, $NaCH_3CO_2$, KBr, NH_4Br, HBr

c. NaOH, $NaCH_3CO_2$, NH_4Br, KBr, HBr

d. HBr, KBr, NH_4Br, $NaCH_3CO_2$, NaOH

123. The pH values of 2 M solutions of CH_3COOH (I), CH_3COOK (II), CH_3COONH_4 (III), and KOH (IV) will be in the order

a. IV > III > II > I
b. IV > II > III > I
c. I > III > II > IV
d. II > I > III > IV

124. P_3Q_2 is a sparingly soluble salt of molar mass M $(g.mol^{-1})$ and solubility × $g.lit^{-1}$. The ratio of the molar concentration of Q^{3-} to the solubility product of the salt is

a. $\frac{1}{54}\ \frac{M^4}{x^4}$
b. $\frac{M^3}{27\,x^3}$.
c. $\frac{M^3}{{}^2/27^{1/2}\,x^{3/2}}$
d. $54\,\frac{x^5}{M^5}$.

125. An acidic solution at 25°C has

a. $[H_3O^+] = [OH^-] > 1 \times 10^{-7}$ M

b. $[H_3O^+] < 1 \times 10^{-7}\ M > [OH^-]$

c. $[H_3O^+] > [OH^-] > 1 \times 10^{-7}$ M

d. $[H_3O^+] > 1 \times 10^{-7}\ M > [OH^-]$

126. Consider the following:

(I) KCl
(II) NH_4Cl
(III) KCN
(IV) HCl

The correct sequence in the order of increasing pH of 0.2 M solution of these compounds will be

a. III < II < I < IV

b. IV < II < I < III

c. IV < III < II < I

d. IV < I < II < III

127. 0.15 mole of pyridinium chloride has been added to 500 cm³ of 0.2 M pyridine solution. What is the pH of the resulting solution assuming no change in volume? (K_b for pyridine = 1.5×10^{-9} M)

a. 5 **b.** 6
c. 7 **d.** 8

128. What quantity of sodium acetate must be added to 1.00 litre of a 0.200 ?M acetic acid

($K_a = 1.8 \times 10^{-5}$) solution to form a buffer of pH = 4.30?

a. 7.18×10^{-2} moles
b. 3.62×10^{-5} moles
c. 7.18 ×v 10^{-3} moles
d. 4.15×10^{-9} moles

129. $K_{sp} = 1.39 \times 10^{-8}$ at 25 °C for PbI_2 . What is the concentration of lead ion (Pb^{2+}) in a solution containing 0.15 ?M NaI?

a. 3.25×10^{-2} M **b.** 1.18×10^{-4} M
c. 6.18×10^{-7} M **d.** 9.27×10^{-8} M

130. In a 50mL of 0.1 M HCl solution, 10 mL of 0.1 M NaOH is added and the resulting solution is diluted to 100mL. Wha is change in pH of the HCl solution ?

a. 4.04 **b.** 0.4
b. 0.1 **d.** 0.2

Multiple Correct Answer Type Questions

131. For a series of weak bases of the same concentration, which statement is/are incorrect?

a. The rate of production of hydroxide ion increases with pK_b.

b. The larger the value of pK_b the more exothermic is the reaction of the base with water.

c. The pOH of water is larger in all cases.

d. The larger the value of pK_b the smaller the value of pH.

132. $Mg(OH)_2$ is a slightly soluble salt with a K_{sp} of 1.8×10^{-11}. If a solution is 0.15 M in $Mg(NO_3)_2$ and 0.15 M in NH_3 ($K_b = 1.8 \times 10^{-5}$), which statement is/ are incorrect?

a. $Mg(OH)_2$ will not precipitate because of the presence of the weak acid NH_4^+.

b. Addition of HCl to the solution decreases the solubility of $Mg(OH)_2$.

c. The concentration of OH^- will bwe larger than of NH_4^+

133. Equimolar solution of AOH and BOH are prepared. The I.P. of A and B are 5.1 and 13.0 eV respectively. The EN of A and B are 0.9 and 3.2 respectively. From the data, pick out the correct statements

a. BOH solution will have a pH > 7

b. solution of BOH will give effervescence with sodium carbonate

c. treatment of NH_4Cl with AOH will lead to evolution of NH_3.

d. phenolphthalein will give pink colour with AOH solution.

134. A solution contains 0.01 M each of NaCl and Na_2CrO_4 solid $AgNO_3$ is gradually added to it. Which is/ are not true?

[Given Ksp(AgCl) = 1.7×10^{-10} M²; Ksp($Ag_2Cr_2O_4$) = 1.9×10^{-12} M³]

a. CrO_4^{2-} ions are precipitated first

b. Cl^- ions are precipitated first

c. the second ion states precipitating when half of the first ion is precipitate

d. both Cl^- and CrO_4^{2-} ions are precipitated together

135. Which one of the following statement is/are true?

a. pH + pOH = 14 for all aqueous solutions

b. pH of 1×10^{-8} M HCl is 8

c. conjugate base of $H_2PO_4^-$ is HPO_4^{2-}

d. 96,500 coulombs of electricity when passed through a $CuSO_4$ solution deposits 1 gram equivalent of copper at the cathode.

136. Equal volumes of the following Ca^{2+} and F^- solutions are mixed. In which of the solutions will precipitation occurs?

[Ksp of $CaF_2 = 1.7 \times 10^{-10}$]

a. 10^{-2} M Ca^{2+} + 10^{-5} M F^-
b. 10^{-3} M Ca^{2+} + 10^{-3} M F^-
c. 10^{-4} M Ca^{2+} + 10^{-2} M F^-
d. 10^{-2} M Ca^{2+} + 10^{-3} M F^-

137. An acid base indicator (Ka = 10^{-5}) has its pH range 4.4 – 6. The correct statement amongst the following is/are

a. the indicator will be suitable for the titration of a strong acid against a weak base

b. the acidic colour of the indicator will predominate if the concentration of acidic form is 6 times more than that of the basic form.

c. the indicator will be suitable for the titration of a weak acid against a strong base

d. the basic colour of the indicator will prevail when concentration of basic form will be at least 10 times more than that of the acidic form.

138. If S and Ksp be the solubility and solubility product respectively, then

a. for AgCl: $S = \sqrt{Ksp}$ and for $Al(OH)_3$: $S = \sqrt[3]{(Ksp / 9)}$

b. for $CaSO_4$: $S = \sqrt{Ksp}$ and for KI_3: $S = \sqrt{Ksp}$

c. for $Ca_3(PO_4)_2$: $S = \sqrt[5]{(Ksp / 108)}$ and for AgI: $S = \sqrt{Ksp}$

d. for Bi_2S_3 and for $Ca_3(PO_4)_2$ both : $S = \sqrt[5]{(Ksp / 108)}$

139. Which of the following statement is/are incorrect?

a. Solubility of AgCl is less in 0.5 M KCl solution than pure water

b. Solubility of AgCl is more in 0.5 M $CaCl_2$ than water

c. Solubility of AgCl is more in 1 M $AgNO_3$ than pure water

d. Solubility of AgCl is more in NH_3 than H_2O

140. Complex formation in a solution results in

a. change in solubility of sparingly soluble salt

b. change in pH of solution

c. not change in freezing point

d. change in chemical nature

141. $A(OH)_2$ is a partially soluble substance and its Ksp value is 4×10^{-12}, which of the following statement is/are correct?

a. the solubility is unaffected by pH of the medium

b. its solubility has been decreased in a buffered medium at pH at 1 L

c. its solubility has been increased in a buffered medium having pH at 9

d. its saturated solution has pH is equal to 10.3

142. The acid ionization (hydrolysis) constant of Zn^{2+} is 1.0×10^{-9}. Which of the following statement are incorrect.

a. the $[H_3O^+]$ ion concentration in 0.001 M $ZnCl_2$ solution is 1.0×10^{-4}.

b. the pH of 0.001 M $ZnCl_2$ solution is 6.

c. the basic dissociation constant of $Zn(OH)^+$ is 1.0×10^{-5}.

d. the basic dissociation constant of $Zn(OH)^+$ is 1.0×10^{5}.

143. Which of the following solution(s) have pH between 6 and 7?

a. 2×10^{-6} M KOH **b.** 2×10^{-6} M HCl

c. 10^{-8} M HCl **d.** 10^{-12} M KOH

144. Which of the following solutions will have no effect on pH on dilution?

a. 0.3 M CH_3COOK

b. 2.4 M CH_3COONH_4

c. 0.2 M NH_4OH + 0.2 M NH_4Cl

d. 0.3 M H_2CO_3 + 0.3 M $NaHCO_3$

145. During the titration of a mixture of NaOH, Na_2CO_3 and inert substances against HCl

a. phenolphthalein can be used to detect the end point when half equivalent of Na_2CO_3 and full equivalent NaOH is consumed

b. phenolphthalein can be used to detect the second end point

c. methyl orange can be used to detect the final end point

d. methyl orange can be used to detect the first end point

146. Which of the following solution will have pH close to 7?

a. 10 ml of M/10 HCl + 100 ml of M/10 $Mg(OH)_2$

b. 100 ml of M/10 H_2SO_4 + 50 ml of M/10 NaOH

c. 200 ml of M/10 KCl + 200 ml of M/10 NaOH

d. 2 M solution of CH_3COONH_4 ($K_a = K_b$)

147. 100 ml solution having 0.2 M HA (weak acid, Ka = 1.0×10^{-5}) and 0.2 N NaA, 200 ml of 0.1 M NaOH has been added. Furthermore, diluted to 1L. Which of the following statement is correct?

a. initially, the solution have pH equal to 3.

b. in the final solution, the concentration of $[OH^-]$ is 10^{-9} M.

c. after the addition of NaOH, the pH of solution increase by four unit

d. after the addition of base, the solution losses buffering action and restores after the addition of acid

148. Which statement is/are not true about buffers?

a. Buffers consists of a strong acid and its conjugate base

b. Buffers have a pH of 7.

c. Buffers resist change in pH upon addition of small amounts of strong acid or strong base.

d. A buffer does not change pH on addition of a strong acid or strong base.

149. Solubility (S) of calcium phosphate (molecular mass, M) is 'x' g per 100 ml at 300 K, its solubility product at 300 K will be approximately

a. $10^7 (x / M)^5$

b. $10^6 (x / M)^5$

c. $10^8 (x / M)^5$

d. $108\ S^5$

150. Acetic acid and aq. NH_3 are weak monobasic acid and weak monoacidic base respectively and Ka of acetic acid is equal to K_b of aq. NH_3. Which of the following statements are correct?

a. all the above mixing would result in neutral solution having pH = 7 at 25°C

b. if aq. NH_3 is exactly half neutralized by HCl, then pOH of resulting solution is equal to pK_b.

c. if acetic acid is exactly half neutralized by NaOH, then pH of resulting solution is equal to pKa.

d. if acetic acid is exactly neutralized by aq. NH_3 then pH of resulting solution is equal to ½ pkw.

151. Equal volumes of following solutions are mixed, in which case the pH of resulting solution will be average value of pH of two solutions?

a. pH = 3 (HNO_3) and pH = 5 (HNO_3)

b. pH = 2 (HNO_3) and pH = 12 (KOH)

c. pH = 4.5 (CH_3COOH) and pH =9.5 (NH_3) (aq) (K_a CH_3COOH = K_b NH_4OH)

d. pH = 3 (HCN) and pH = 11 (NaOH) (K_a of HCN = 10^{-10})

152. Which one of the following statement is/are incorrect?

a. Bronsted–Lowry theory could not explain the acidic nature of BCl_3

b. the pH of 0.01 M NaOH solution is 2.

c. the ionic product of water at 25°C is 10^{-10} $mol^2\ lit^{-2}$.

d. the pH of a solution can be calculated using the equation pH = log [H^+]

153. What is/are correct expression for the weak acid HA?

a. $pKa = 14 - pK_b$

b. $pKa = \log_{10} Ka$

c. $pKa = pH - \log_{10} \{[A^-] / [HA]\}$

d. $Ka = [H_3O^+]\ [A^-] / [Ha]$

154. Which of the following statements about pH and H^+ ion concentration is/are correct?

a. addition of one drop of concentrated HCl in NH_4OH solution decreases pH of the solution.

b. a solution of the mixture of one equivalent of each of CH_3COOH and NaOH has a pH of 7.

c. pH of pure neutral water is not zero.

d. a cold and concentrated H_2SO_4 has lower H^+ ion concentration than a dilute solution of H_2SO_4.

155. Which one of the following is/are buffer solution?

a. 0.8 M H_2S + 0.8 M KHS

b. 2M $C_6H_5NH_2$ + 2M $C_6H_5\overset{+}{N}H_3Br^-$

c. 3M H_2CO_3 + 3M $KHCO_3$

d. 0.05 M $KClO_4$ + 0.05 M $HClO_4$

156. In the reaction:

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5\,(OH)]^{2+} + H_3O^+$$

a. $[Fe(H_2O)_6]^{3+}$ is an acid

b. $[Fe(H_2O)_6]^{3+}$ is a base

c. $[Fe(H_2O)_5\,(OH)]^{2+}$ is a conjugate acid

d. $[Fe(H_2O)_5\,(OH)]^{2+}$ is a conjugate base

157. Which of the following solution will have pH = 13 on assuming complete dissociation

a. 100 ml of solution of 0.1 N $Mg(OH)_2$

b. 0.56 g of KOH in 100 ml solution

c. 4 g of NaOH in 500 ml solution.

d. 100 ml of solution of 0.05 M $Mg(OH)_2$

158. Factor influencing the degree of dissociation of a weak electrolyle is

a. Dilution

b. Temperature

c. Presence of common ions

d. Nature of solvent

159. Acid strength can be directly proportional to

a. Ka
b. pH
c. pOH
d. H^+

160. Which of the following mixtures can act as buffer?

a. H_2CO_3 + KOH (2 : 5 : 1 molar ratio)

b. H_2CO_3 + KOH (2 : 5 : 3 molar ratio)

c. $NH_4OH + HNO_3$ (6 : 4 molar ratio)

d. $NH_4OH + HNO_3$ (3 : 5 molar ratio)

Linked-Comprehension Type Questions

Comprehension 1

According to Bronsted concept acid is proton donor while base is proton accepter. According to Lewis an acid is electron deficient and electron accepter while a base is electron efficient and electron donor. The acidic strength depends upon electro negativity difference, oxidation number etc.

161. From the following chemical reactions determine the relative Bronsted–Lowry acid strengths (strongest to weakest).

$$HClO_4\,(sol) + CH_3COOH\,(l) \rightarrow CH_3C_2(OH)_2^+\,(sol) + ClO_4^-\,(aq)$$

$$H_2SO_4\,(sol) + CH_3COOH\,(l) \rightleftharpoons CH_3C(OH)_2^+\,(sol) + HSO_4^-\,(sol)$$

a. $HClO_4 > CH_3C(OH)_2^+ > H_2SO_4$

b. $HClO_4 > CH_3COOH > H_2SO_4$

c. $HClO_4 > H_2SO_4 > CH_3C(OH)_2^+$

d. $HClO_4 > H_2SO_4 > CH_3COOH$

162. For Cu^{2+} and CO_2, which will behave as a Lewis acid toward OH^- in water?

a. Only CO_2

b. Only Cu^{2+}

c. Neither Cu^{2+} nor CO_2

d. Both Cu^{2+} and CO_2

163. Identify the set of Lewis acids:

a. $CH_3^-, NH_2^-, OH^-, F^-$

b. $H_3PO_4, H_2PO_4^-, HPO_4^-, PO_4^{3-}$

c. $BH_3, BF_3, Cu^{2+}, CO_2$

d. Cl^-, OH^-, NH_3, H_2O

164. From the following chemical reactions determine the relative Bronsted–Lowry base strengths (strongest to weakest).

$$HNO_3\,(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3(aq)$$

$$HF\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + F^-\,(aq)$$

a. $F^- > H_2O > NO_3^-$

b. $F^- > NO_3^- > H_2O$

c. $HNO_3 > H_3O^+ > HF$

d. $NO_3^- > H_2O > F^-$

Comprehension 2

pH scale was introduced by Sorenson to measure acidity or basicity of a solution. pH value of a solution does not instantaneously give us an idea of the relative strength of the solution. At higher concentration, in place of pH, Hammelt acidity functions are used. Buffer solution is the solution whose pH, on addition of a small amount of strong acid or a base, does not change much.

165. The degree of dissociation of a weak monoprotic acid can be given as:

a. $\alpha = \dfrac{1}{1 + 10^{(pKa + pH)}}$

b. $\alpha = \dfrac{1}{1 + 10^{(pKa - pH)}}$

c. $\alpha = \dfrac{1}{1 + 10^{(pH - pKa)}}$

d. $\alpha = \dfrac{1}{1 + 10^{(pKa\,/\,pH)}}$

166. Given a solution of acetic acid. How many times of the acid concentration, acetate salt should be added to obtain a solution with pH = 7.0? [K_a for dissociation of $CH_3COOH = 1.8 \times 10^{-5}$]

a. 170 times
b. 137 times
c. 173 times
d. 172 times

167. pH = 7.40 K_1 of $H_2CO_3 = 4.5 \times 10^{-7}$. What will be the ratio of $[HCO_3^-]$ to $[H_2CO_3]$?

a. 11.3
b. 1.13
c. 1.23
d. 1.31

Comprehension 3

For a general reaction given, below the value of solubility product can be given as:

$$\begin{array}{lccc} A_xB_y & \rightleftharpoons xA^{+y} & + & yB^{-x} \\ a & 0 & & 0 \\ a-s & x\,s & & y\,s \end{array}$$

$K_{sp} = (x\ s)^x . (y\ s)^y$

or

$K_{sp} = x^x y^y\ (s)^{x+y}$

Solubility product gives us not only an idea about the solubility of an electrolyte in a solvent but also helps in explaining concept of precipitation and calculation of H^+ ion, OH^- ion.It is also useful in qualitative analysis for the identification and separation of basic radicals

168. Which metal sulphides can be precipitated from a solution that is 0.01 M in Mn^{2+}, Zn^{2+}, Pb^{2+} and Cu^{2+} and 0.10 M in H_2S at a pH of 1.0?

Metal sulphide	Ksp
MnS	3×10^{16}
ZnS	3×10^{-2}
PbS	3×10^{-7}
CuS	6×10^{-16}

a. CuS **b.** MnS
c. ZnS, PbS, CuS **d.** PbS, CuS

169. Potassium chromate is slowly added to a solution containing 0.20 M $AgNO_3$ and 0.20 M $Ba(NO_3)_2$. Describe what happens if the Ksp for Ag_2CrO_4 is 1.1×10^{-12} and the Ksp of $BaCrO_4$ is 1.2×10^{-10}.

a. The Ag_2CrO_4 precipitates first out of solution and then $BaCrO_4$ precipitates.

b. The $BaCrO_4$ precipitates first out of solution.

c. Both Ag_2CrO_4 and $BaCrO_4$ precipitate simultaneously out of solution.

d. Neither Ag_2CrO_4 nor $BaCrO_4$ precipitates out of solution.

170. What is the molar solubility of $Cu(OH)_2$ in 1.0 M NH_3 if the deep blue complex ion $Cu(NH_3)_4^{2+}$ forms? The Ksp for $Cu(OH)_2$ is 1.6×10^{-19} and the K_f for $Cu(NH_3)_4^{2+}$ is 1.1×10^{13}.

a. 7.1×10^{-4} M **b.** 7.6×10^{-3} M
c. 6.7×10^{-3} M **d.** 5.6×10^{-3} M

171. The solubility product of AgI in water is 4.9×10^{-11} at a given temperature. The solubility of AgI in 0.001 M KI solution is

a. 7.0×10^{-7} **b.** 4.8×10^{-3}
c. 7.0×10^{-8} **d.** 5.9×10^{-10}

Comprehension 4

Salt hydrolysis is a phenomenon in which the cation or anion or both of a salt react with water to produce acidity or basicity. The extent of hydrolysis is measured in terms of degree of hydrolysis (h). For various type of salts there are different relations to find K_H (Hydrolysis constant) h, and pH of the aqueous solution.

172. The hydrolysis const for $ZnBr_2$ can be given as

a. $k_h = \frac{K_w}{K_b}$ **b.** $k_h = \frac{K_w}{K^2_b}$
c. $k_h = \frac{K_b}{K^2_w}$ **d.** $k_h = \frac{K^2_w}{K_b}$

173. Which of the following salts on dissolving in water produce acidic solution

(i) KCN
(ii) $NaNO_3$
(iii) NH_4Cl
(iv) $KHSO_4$

a. (ii), (iii), (iv) **b.** (ii), (iii)
c. (iii), (iv) **d.** (iii)

174. Find the pH of 0.012 M solution of NH_4CN if K_a for HCN and K_b for NH_3 are 6.2×10^{-10} and 1.6×10^{-5} respectively

a. 8.2 **b.** 9.2
c. 4.8 **d.** 5.8

175. At 298 K the value of ionization constant of anilinium hydroxide is 4.6×10^{-10} and that of ionic product of water 1×10^{-14}, the value of degree of hydrolysis constant is nearly?

a. 0.415 % **b.** 4.15 %
c. 0.163% **d.** 0.217 %

Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given. Mark

a. if A and R both are correct and R is the correct explanation of A;

b. if A and R both are correct but R is not the correct explanation of A;

c. A is true but R is false;

d. A is false but R is true,

e. A and R both are false.

176. **(A):** The pH of a buffer solution containing equal moles of acetic acid and sodium acetate is 4.8 (pKa of acetic acid is 4.8)

(R): The ionic product of water at 25°C is 10^{-14} $mol^2\ lit^{-2}$

177. **(A):** In the titration of Na_2CO_3 with HCl using methyl orange indicator, the volume of the acid required at the equivalence point is twice that of the acid required using phenolphthalene indicator.

(R): Two moles of HCl are required for complete neutralization of one mole of Na_2CO_3.

178. **(A):** Solubility of $CaSO_4$ in 0.1 M K_2SO_4 is 10^{-8} M hence its K_{sp} is 10^{-16}

(R): Since for $CaSO_4 K_{sp} = (s)^2$

179. **(A):** According to principle of common ion effect, the solubility of HgI_2 is expected to be less in an aqueous solution of KI than in water. But HgI_2 dissolves in an aqueous solution of KI to form a clear solution.

(R): Iodide ion, I^- is highly polarisable.

180. **(A):** On dissolving AgCl in 0.1 M solution of NaCl, $CaCl_2$ and NH_3 solution the solubility is lowest in NH_3.

(R): AgCl form complex with NH_3 in aqueous solution.

181. **(A):** The addition of a small amount of a 'neutral' electrolyte (one that does not share a common ion) such as NaCl to a dilute solution of acetic acid, will cause an increase in the degree of dissociation of the acid.

(R): Due to the increased ionic strength, the mean ionic activity coefficient of H_3O^+ and CH_3COO^- will increase.

182. **(A):** On addition of NH_4Cl to NH_4OH solution, pH decreases but remains greater than 7.

(R): Addition of NH_4^+ ion decreases ionization of NH_4OH thus, $[OH^-]$ is decreased, hence, pH decreases.

183. **(A):** The pH range of any indicator is form

$pK_{In} -\ 1$ to $pK_{In} + 1$

(R): As the pH of the indicator can be given as follows

$$pH = pK_{In} + \log \frac{(ln^-)}{(Hln)}$$

As pH range depends upon the ratio of $[ln^-]$ to [Hln] which can not have value 10 to 1/10 for all indicators.

184. **(A):** 0.33 M solution of KCN is more basic than 0.33 M solution of KF.

(R): 0.33 M solution of KCN is more basic than 0.33 M solution of CH_3COOK.

185. **(A):** On mixing equal volumes of 1M HCl and 2 M CH_3COONa , an acidic buffer solution is formed.

(R): Resultant mixture contains CH_3COOH and CH_3COONa which are parts of acidic buffer.

186. **(A):** H_3PO_3 is a dibasic acid.

(R): There are two hydrogen atoms directly attached to phosphorus

187. **(A):** Sodium carbonate can be titrated against sulphuric acid by using either phenolphthalene or methyl orange as indicator.

(R): The volume of sulphuric acid required to produce colour change for the two indicators is different.

188. **(A):** A mixture of the solutions of a weak acid and its sodium salt acts as a good buffer.

(R): The ratio of the salt to the acid in the mixture does not change substantially when small amount of acid or base is added to the buffer.

189. **(A):** pH of an amphiprotic anion always independent of concentration.

(R): pH of amphiprotic anion can be given by ½ $[p^{k1} + p^{k2}]$. Here p^{k1} and p^{k2} are the dissociation constants of the acid in which amphiprotic anion is formed.

190. **(A):** In the volumetric estimation of iron (II) in acid solution in the presence of excess chloride by titration with permaganate solution, excess phosphoric acid and manganese (II) sulphate are added to the solution containing iron (II) before the titration.

(R): Phosphoric acid complexes the iron (III) produced by the oxidation, and manganese (III) depresses the reduction potential of permanganate.

191. **(A):** When 0.1 M diprotic weak acid H_2X dissociates with its dissociation constants $K_{a1} = 10^{-4}$ and $K_{a2} = 10^{-12}$, then $[X^{-2}]$ is almost equal to 10^{-12} M.

(R): Since $K_{a2} << K_{a1}$ for 0.1 M so H_2X so $[X^{-2}]$ is negligible w.r.t. $[HX^-]$. Hence $[X^{-2}] \approx K_{a2}$

192. **(A):** On mixing 500 mL of 10^{-6}M Ca^{2+} ion and 500 mKL of 10^{-6} MF^- ion, the precipitate of CaF_2 will be obtained.

$K_{sp}\ (CaF_2) = 10^{-18}$

(R): If Ksp is greater than ionic product, precipitate will be obtained.

Matrix-Match Type Questions

193. Match the following:

Column I (Titration)	**Column II (Indication used)**
A. Strong acid vs Strong base	(p) Phenol phthalein
B. Weak acid vs strong base	(q) Methyl red
C. Strong acid vs weak base	(r) Methyl orange
D. Weak acid vs weak base	(s) No indicator

194. Match the following:

Column I (Buffer)	**Column II**
A. $H_2CO_3 + NaHCO_3$	(p) Removal of PO_4^{3-}
B. CH_3COO + CH_3COONa	(q) Precipitate of hydroxides of Fe^{+3}, Al^{+3}, Cr^{+3}
C. $NH_4OH + NH_4Cl$	(r) Precipitate of Lead chromate
D. $H_2PO_4^- + HPO_4^{2-}$	(s) Maintain pH of Blood

195. Match the following:

Column I (Buffer)	**Column II**
A. 1×10^{-8} M KOH	(p) 1.3
B. 1×10^{-8} M HBr	(q) pH = 6.95
C. 1 M HCl + 1 M NaOH	(r) pH = 7.0414
D. 0.02 M H_2SO_4	(s) pH = 7
	(t) acidic solution

196. Match the effect of addition of 0.1 M NaOH to 0.1 M, 50 mL H_3PO_4 Ka_1, Ka_2, Ka_3 are the I, II, III ionization constant of H_3PO_4 respectively

Column I (Buffer)	**Column II**
A. 150 mL of NaOH	(p) $pH = p^{K}a_2$
B. 75 mL of NaOH	(q) $pH = p^{K}a_1$
C. 25 mL of NaOH	(r) $pH = 7 + \frac{1}{2}[p^{K}a_3 + \log C]$
D. 100 mL of NaOH	(s) $pH = \dfrac{P^{K}a_2 + P^{K}a_3}{2}$

197. Match the following:

Column I	**Column II**
A. $CuSO_4$	(p) Cationic interaction
B. Na_2CO_3	(q) Anionic interaction
C. $FeCl_3$	(r) Ph > 7
D. K_2SO_4	(s) Ph < 7
	(t) No ionic interaction

198. Match the following:

Column I	**Column II**
A. Ostwald's dilution law	(p) $\alpha = \sqrt{K}/ C = \sqrt{KV}$
B. Ionic product	(q) $\dfrac{\text{No .of molecules dissociated}}{\text{Total No. of moles taken}}$
C. Catalyst	(r) Helps in attaining equilibrium at appropriate time.
D. Degree of ionization	(s) $[H_3O^+]\,[OH^-]$
	(t) Increases with the increase of temperature

199. Match the following:

Column I	**Column II**
A. CCl_4	(p) Lewis acid
B. $AlCl_3$	(q) Lewis base
C. NH_3	(r) Bronsted acid
D. $HClO_4$	(s) Bronsted base
	(t) Neither lewis acid nor lewis base

200. Match the following:

Column I	**Column II**
A. 0.5 M NO_3 + 0.1 M NH_4OH	(p) 7
B. 0.1 M KCl + 0.1 M KNO_3	(q) greater then 7
C. 0.2 M NaOH + 0.5 M HCOOH	(r) between 1 to 7
D. 0.1 NH_4Cl + 0.1 M KOH	(s) 0.7

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201. The solubility of A_2X_3 is y mol dm^{-3}. Its solubility product is

a. $6y^4$
b. $64\ y^4$
c. $36\ y^5$
d. $108\ y^5$

[IIT 1997]

202. If pKb for fluoride ion at 25°C si 10.83, the ionization constant of hydrofluoric acid at this temperature is

a. 1.74×10^{-5}
b. 3.52×10^{-3}
c. 6.75×10^{-4}
d. 5.38×10^{-2}

[IIT 1997]

203. Which of the following statement is correct?

1. the pH of 1.0×10^{-8} M solution of HCl is 8
2. the conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
3. autoprotolysis constant of water increases with temperature
4. when a solution of a weak monoprotic acid is titrated against a strong base at half neutralization point, pH = (1/2) pKa.

a. 2, 3
b. 1,2,3
c. 3, 4
d. 2,3,4

[IIT 1998]

204. A buffer solution can be prepared from a mixture of

1. sodium acetate and acetic acid in water
2. sodium acetate and hydrochloric acid in water
3. ammonia and ammonium chloride in water

205. ammonia and sodium hydroxide in water.

a. 1,3,4
b. 2,3,4
c. 1,2,4
d. 1,2,3

[IIT 1999]

206. The pH 0.1 M solution the following salts increases in the order

a. NaCl < NH_4Cl < NaCN < HCl
b. HCl < NH_4Cl < NaCl < NaCN
c. NaCN < NH_4Cl < NaCl < HCl
d. HCl < NaCl < NaCN < NH_4Cl

[IIT 1999]

207. r a sparingly soluble salt A_pB_q, the relationship of its solubility product (Ls) with its solubility (S) is

a. $Ls = S^{p+q}.\ p^p\ .q^q$
b. $Ls = S^{p+q}.\ p^q\ .q^p$
c. $Ls = S^{pq}.\ p^p\ .q^q$
d. $Ls = S^{pq}.\ (pq)^{p+q}$

[IIT 2001]

208. Identify the correct order of solubility of Na_2S, CuS and ZnS in aqueous medium

a. Na_2S > CuS > ZnS
b. CuS > ZnS > Na_2S
c. Na_2S > ZnS > CuS
d. ZnS > Na_2S > CuS

[IIT 2002]

209. Identify the correct order of solubility of Na_2S, CuS and ZnS in aqueous medium

a. Na_2S > CuS > ZnS
b. CuS > ZnS > Na_2S
c. Na_2S > ZnS > CuS
d. ZnS > Na_2S > CuS

[IIT 2002]

210. A solution which is 10^{-3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{-16} M sulphide ion. If Ksp of MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-23}, 10^{-20} and 10^{-54} respectively, which one will precipitate first?

a. MnS
b. FeS
c. ZnS
d. HgS

[IIT 2003]

211. A weak acid HX has the dissociation constant 1×10^{-5} M. It forms a salt NaX on reaction with alkali. The degree of hydrolysis of 0.1 M solution of NaX is

a. 0.1 %
b. 0.01 %
c. 0.0001 %
d. 0.150 %

[IIT 2004]

212. When 0.1 mole of CH_3NH_2 (ionization constant $K_b = 5 \times 10^{-4}$) is mixed with 0.08 mol HCl and the volume is made up of 1 litre. Find the $[H^+]$ of resulting solution.

a. 8×10^{-2}
b. 2×10^{-11}
c. 1.23×10^{-4}
d. 8×10^{-11}

[IIT 2005]

213. $Ag^+ + NH_3 \leftrightarrow [Ag(NH_3)^+]$;

$K_1 = 3.5 \times 10^{-3}$

$[Ag(NH_3)]^+ + NH_3 \leftrightarrow [Ag(NH_3)_2]^+$;

$K_2 = 1.7 \times 10^{-3}$

Then the formation constant of $[Ag(NH_3)_2]^+$ is

a. 6.08×10^{-6}
b. 6.08×10^{6}
c. 6.08×10^{-9}
d. None

[IIT 2006]

214. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature 'T' are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15}, respectively. Solubilities (mol dm^{-3}) of the sales at temperature 'T' are in the order

a. $MX > MX_2 > M_3X$

b. $M_3X > MX_2 > MX$

c. $MX_2 > M_3X > MX$

d. $MX > M_3X > MX_2$

[IIT 2008]

215. 2.5 mL of 2/5 M weak monoacidic base ($K_{b1} \times 10^{-12}$ at 25°C) is titrated with 2/15 M HCl in water at 25°C. The concentration of H+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C)

a. 3.7×10^{-13} M **b.** 3.2×10^{-7} M

b. 3.2×10^{-2} M **d.** 2.7×10^{-2} M

[IIT 2008]

216. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4}. The pH of a 0.01 M solution of its sodium salt is

a. 6 **b.** 8

c. 7 **d.** 4

[IIT 2009]

ANSWERS

Straight Objective Type Questions

1. c	**2.** a	**3.** c	**4.** d	**5.** d	**6.** c	**7.** d	**8.** c	**9.** a	**10.** c	**11.** a	**12.** b
13. a	**14.** a	**15.** a	**16.** a	**17.** b	**18.** b	**19.** c	**20.** b	**21.** a	**22.** b	**23.** c	**24.** a
25. d	**26.** d	**27.** b	**28.** b	**29.** d	**30.** c	**31.** a	**32.** d	**33.** c	**34.** b	**35.** a	**36.** d
37. b	**38.** c	**39.** a	**40.** b	**41.** d	**42.** c	**43.** c	**44.** b	**45.** d	**46.** d	**47.** d	**48.** d
49. a	**50.** b	**51.** a	**52.** a	**53.** a	**54.** c	**55.** c	**56.** c	**57.** b	**58.** d	**59.** d	**60.** d
61. a	**62.** b	**63.** b	**64.** b	**65.** a	**66.** b	**67.** b	**68.** b	**69.** a	**70.** c		

Brainteasers Objective Type Questions

71 c	**72** a	**73** a	**74** d	**75** c	**76** a	**77** a	**78** b	**79** b	**80** c	**81** c	**82** b
83 c	**84** a	**85** d	**86** c	**87** c	**88** d	**89** a	**90** c	**91** d	**92** c	**93** a	**94** b
95 b	**96** a	**97** a	**98** a	**99** a	**100** d	**101** b	**102** c	**103** d	**104** a	**105** c	**106** a
107 d	**108** a	**109** d	**110** d	**111** b	**112** b	**113** a	**114** d	**115** d	**116** d	**117** a	**118** b
119 a	**120** c	**121** c	**122** a	**123** b	**124** a	**125** d	**126** b	**127** a	**128** a	**129** c	**130** b

Multiple Correct Answer Type Questions

131. a, b, c	**132.** a, c, d	**133.** b, c, d	**134.** a, c, d	**135.** a, c, d	**136.** c, d	**137.** a, b, d
138. b, c, d	**139.** b, c	**140.** a, b, d	**141.** b, c, d	**142.** a, d	**143.** b, c	**144.** b, c, d
145. a, c	**146.** b, c, d	**147.** b, c, d	**148.** a, b, d	**149.** a, d	**150.** b, c, d	**151.** b, c
152. b, c, d	**153.** a, c, d	**154.** a, c, d	**155.** a, b, c	**156.** a, d	**157.** a, b, d	**158.** a, b, c, d
159. a, c, d	**160.** a, c					

Linked-Comprehension Type Questions

Comprehension 1

161. a **162.** d **163.** c **164.** a

Comprehension 2

165. b **166.** c **167.** a

Comprehension 3

168. c **169.** a **170.** b **171.** a

Comprehension 4

172. d **173.** c **174.** b **175.** a

Assertion Reason Answers

176 b **177** b **178** d **179** b **180** d

181 a **182** a **183** d **184** b **185** a

186 a **187** d **188** a **189** a **190** a

191 a **192** d

Matrix-Match Type Questions

193. A – (p, q, r), B – (p), C – (q, r), D – (s)

194. A – (s), B – (p, r), C – (q), D – (s)

195. A – (r), B – (q, t), C – (s), D – (p, t)

196. A – (r), B – (p), C – (q), D – (s)

197. A – (p, s), B – (q, r), C – (p, s), D – (t)

198. A – (p), B – (s, t), C – (r),D – (q, t)

199. A – (t), B – (p), C – (q, r, s), D – (r)

200. A – (s), B – (p), C– (r), D – (q)

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201. d **202.** c **203.** a **204.** **205.** d **206.** b **207.** a **208.** c **209.** c

210. a **211.** b **212.** d **213.** a **214.** **215.** **216.** b

Hints and Explanations

1. For pure water, $[H_3O^+] = [OH^-]$

   $Kw = 10^{-6} \times 10^{-6} = 10^{-12}$

2. Based have higher pH than acids; stronger is the base still higher is the pH.

   W = *Zit* (Z is the ECE)

3. Solubility product α solubility

   PtS having least Ksp is least soluble here.

4. Among the given oxyacids HClO is the weakest as acidity depends on the oxidation state (+1 in HClO, which is lowest). Hence its conjugate base (ClO^-) is the strongest one.

5. $OH^- \leftrightarrow H^+ + O^{2-}$

   Conjugate acid of O^{2-} ion is OH^-.

6. Molar conc. of HCl = 10^{-8}

   pH = 8.

   But this cannot be possible as pH of an acidic solution can not be more than 7. Here we have to consider $[H^+]$ coming from H_2O to find Ph value.

7. Weak acid (CH_3COOH) + its conjugate base (CH_3COO^- from CH_3COONH_4) forms acid buffer

9. In molten state the cations and anions become free and flow of current is due to migration of these ions in opposite directions in the electric field.

10. $HN_3 \rightarrow H^+ + N_3^-$

    Hydrazoic acid conjugate base

    (Azide ion)

11. Calculate the ionic product $[Ca^{2+}][F^-]^2$ in each case and see that ionic product must exceed Ksp for pre-

cipitation. Concentration of each ion is halved due to dilution effect

12. $NH_4Cl + NH_4OH$ precipitate radical of group III viz., Al^{3+} and Cr^{3+}

13. The equilibrium constant for the neutralization of a weak acid with a strong base can be given as,

$$K = \frac{Ka}{Kw} = \frac{1.0 \times 10^{-4}}{1.0 \times 10^{-14}} = 1.0 \times 10^{10}$$

14. $H_2PO_4^- \leftrightarrow H^+ + HPO_4^-$

acid salt

15. Sn in $SnCl_4$ has its octet completed while the central atoms in other molecules have incomplete octet.

17. NH_2^- (base) + $H^+ \rightarrow NH_3$ (conjugate acid)

19. The pH of the solution at the equivalence point is greater than 7 due to salt hydrolysis. So an indicator giving colour on the basic side will be suitable.

21. Gastric juice is acidic so the ionization of aspirin is suppressed where as small intestine has basic medium therefore aspirin is more ionized.

23. CH_3COONa give basic solution as it is a salt of weak acid and strong base.

24. Weak base (NH_4OH) + salt of a strong acid (NH_4Cl)

25. Solubility of hydroxide of group 2 elements increases down the group. Therefore $Be(OH)_2$ has lowest solubility and have lowest solubility product.

26. The corresponding acids are

a. CH_3OH **b.** C_2H_5OH

c. $(CH_3)_2CHOH$ **d.** $(CH_3)_3COH$.

Among 1°, 2° and 3° alcohols, the order of acidity is 1° > 2° > 3°.

As A weak acid has a strong conjugate base. Therefore (D) is the strongest conjugate base.

27. $NH_4OH + HCl \rightarrow NH_4Cl$

NH_4Cl is a salt of weak base and strong acid, so it gives the acidic solution with pH < 7.

28. This is according to Le–Chatelier's principle

29. $HCl + CH_3COOH \leftrightarrow Cl^- + CH_3COOH_2^+$

Acid Base Conj.base Conj. acid

30. BF_3 and SO_3 are Lewis acids because they can accept electron pairs.

31. In the Henderson's equation,

pH = pKa + log [Salt] / [Acid]

when [Salt] = [Acid]

pH = pKa = 9.30

33. pH of blood remains same because it has a buffer solution of H_2CO_3 / HCO_3^-.

34. In a group of periodic table, there is a gradual increase in acid strength with an increase in atomic size.

As the order of atomic size of the given species is F < Cl < Br < I, therefore correct order of increasing acidity is HF < HCl < HBr < HI.

35. As pH = 3

So $[H^+] = 1 \times 10^{-3}$

$\alpha = [H^+] / C$

$= 1 \times 10^{-3} / 0.1$

$= 0.01$

α % = 1 %.

36. $(Kh) = \dfrac{Kw}{Ka \times Kb}$.

$$= \frac{1.0 \times 10^{-14}}{(4.0 \times 10^{-10}) \times (1.8 \times 10^{-5})} = 1.4$$

37. $$\frac{\text{Strength of HA} = \sqrt{K_{HA}}}{\text{Strength of HB} = \sqrt{K_{HB}}}$$

$$\frac{\sqrt{1 \times 10^{-3}}}{\sqrt{1 \times 10^{-5}}} = \sqrt{100} = 10.$$

Thus HA is ten times stronger than HB.

38. $HA_1 / HA_2 = \sqrt{(Ka_1 / Ka_2)}$

$= \sqrt{(3.0 \times 10^{-4} / 1.8 \times 10^{-5})}$

$= \sqrt{(300 / 18)}$

$\approx 4 : 1$

39. According to the Bronsted–Lowry theory an acid is a substance which has a tendency to lose proton, while base is a substance which has a tendency to gain proton. Thus, ClO^- has maximum ability to gain proton, therefore ClO^- anion is the strongest Bronsted base.

40. KCN (aq) $\leftrightarrow K^+ + CN^-$ and

$CN^- + HOH \leftrightarrow HCN + OH^-$

Since in this reaction, the pH will increase due to increase in OH^- ion concentration.

41. Solubility product of binary salt $Ksp = S^2$

$= (2 \times 10^{-4})^2 = 4 \times 10^{-8}$.

42. MX_2 gives three ions after dissociation, thus it is ternary salt.

The solubility product of ternary salt (Ksp)

$= 4S^3 = 4 \times (0.5 \times 10^{-4})^3 = 5 \times 10^{-13}$

43. $PbCl_2$ gives three ions after dissociation, therefore it is ternary salt.

The solubility of a ternary salt (S)

$= (Ksp / 4)^{1/3} = (1.5 \times 10^{-4} / 4)^{1/3}$

$= 3.34 \times 10^{-2}$ mol L^{-1}.

44. Na_2CO_3 is salt of weak acid H_2CO_3 and strong base NaOH, therefore, has pH more than 7. Also, it dissociate to give two moles of NaOH (Alkaline solution).

$Na_2CO_3 + 2H_2O \rightarrow 2NaOH + 2H_2CO_3$

45. In group III, addition of NH_4Cl increases NH_4^+ ion concentration and decreases OH^- ion concentration produced from NH_4OH due to common ion effect.

46. As pH = 5

So $[H^+] = 1 \times 10^{-5}$

$\alpha = [H^+] / C$

$= 1 \times 10^{-5} / 0.005$

$= 0.002$

so $\alpha \% = 0.2 \%$

47. The higher value of pKa of a compound, lower is its strength.

The values of pKa for CH_3COOH, HOH, C_2H_5OH and $HC \equiv CH$ are 4.75, 15.7, 16 and 25 respectively.

The correct order of acidic strengths is

$RCOOH > HOH > ROH > HC \equiv CH$.

48. The concentration of $[H^+] = C \times \alpha$

$= 0.1 \times 0.02 = 2 \times 10^{-3}$ M.

concentration of $[OH^-] = \dfrac{Kw}{[H^+]} = \dfrac{1 \times 10^{-14}}{2 \times 10^{-3}}$

$= 5 \times 10^{-12}$ M.

49. The rain water is generally pure. But when rain drops fall they dissolve various hazardous gases on the way, due to which their pH increases. And when rain is accompanied by thunderstorm the gases do not completely dissolve, because of high random momentum of gaseous molecules in air.

When rain is accompanied by thunderstorm, the collected rain water will have a pH value slightly lower than that of rain water without thunderstorm.

50. $pH = -\log \sqrt{Ka} \times C$

$5 = -\log \sqrt{Ka} \times 1$

$5 = -\frac{1}{2} \log Ka$

$\log Ka = -10$

$Ka = 10^{-10}$

51. A buffer solution is prepared by mixing a weak acid with its salt of a strong base or by mixing a weak base with its salt of a strong acid.

Hence 0.05 M $KClO_4$ and 0.05 M $HClO_4$ are very dilute, therefore it is not a buffer solution.

52. The conjugate base is formed by the removal of H^+ from acid i.e., $H_2PO_4^- \rightarrow HPO_4^{2-} + H^+$. Thus HPO_4^{2-} is the conjugate base of $H_2PO_4^-$.

53. The dissociation reaction for acid is

$HIn \leftrightarrow H^+ + In^-$.

Thus acid dissociation constant

$(K_{In}) = \dfrac{[H^+]\,[In^-]}{[HIn]}$ or $[H^+] = K_{In} \times \dfrac{[HIn]}{[In^-]}$

Taking logarithem on both sides,

$\log H^+ = \log K_{In} + \log \dfrac{[HIn]}{[In^-]}$

taking negative sign on both side, we get

$pH = pK_{In} + \log \dfrac{[In^-]}{[HIn]}$ or $\log \dfrac{[In^-]}{[HIn]} = pH - pK_{In}$

54. NaOH is base and HCl is an acid, therefore their solutions in water become basic and acidic respectively. The value of ionic product of water does not change in acidic and basic solution. Thus ionic product of water remains same in these two solutions.

56. $MX_4 \rightarrow M^{4+}(aq) + 4X^-(aq)$

The solubility product of MX_4 (Ksp)

$= S \times (4S)^4$

$Ksp = 256 \times S^5$

$S = (Ksp / 256)^{1/5}$

60. H_2S being a weak acid does not dissociate appreciably in presence of HCl and thus $[S^{2-}]$ becomes less due to common ion effect (H^+).

61. As pH = 5

$[H_3O^+] = 10^{-pH} = 10^{-5}$ M

$M_1 = 10^{-5}$ let $V_1 = \times$

$M_2 = ?\ V_2 = 100x$

According to dilution law

$M_1V_1 = M_2V_2$

$10^{-5} \times = M_2 100\ x$

$\frac{10^{-5}\ x}{100\ x} = M_2$

$= 10^{-7}\ M = M_2$

$[H_3O^+] = 10^{-7}\ M + 10^{-7}\ M$

(from water) $= 2 \times 10^{-7}$ M

$pH = -\log [H_3O^+]$

$= -\log 2 \times 10^{-7} = 6.69$

Hence, the solution becomes almost neutral

62. $pOH = pK_b + \log_{10} \frac{[Salt]}{[Base]}$.

$= 5 + \log_{10} \frac{0.02}{0.2} = 5 + (-1) = 4$

$pH = 14 - pOH$

$= 14 - 4 = 10$

63. $Ksp\ [AB] = [A^+]\ [B^-] = 10^{-8}$

Putting $[A^+] = 10^{-3}$ M, we have $[B^-] = 10^{-5}$ M

AB will precipitate out if ionic product is greater than solubility product.

Thus precipitation $[B^-] > 10^{-5}$ M.

64. As stronger the acid, weakest is the conjugate base. So decreasing order of basicity is

$CH \equiv C^- > CH_3O^- > OH^-$.

65. $AgIO_3\ (s) \rightleftharpoons Ag^+\ (aq) + IO_3^-\ (aq)$

Let the solubility of $AgIO_3$ be 'S'.

$Ksp = [Ag^+]\ [IO_3^-]$

$1.0 \times 10^{-8} = S^2$

$S = 10^{-4}$ mol / litre

$= \frac{10^{-4} \times 283}{1000} \times 100$

$= 283 \times 10^{-5}$

$= 2.83 \times 10^{-3}$ g / 100 ml

66. $H_2A \rightleftharpoons HA^- + H^+$

$K_1 = \frac{[HA^-]\ [H^+]}{[H_2A]}$ ……… (1)

$HA^- \rightleftharpoons H^+ + A^{2-}$

$K_2 = \frac{[H^+]\ [A^{2-}]}{[HA^-]}$ ……… (2)

For the reaction

$H_2A \rightleftharpoons 2H^+ + A^{2-}$

$K = \frac{[H^+]^2\ [A^{2-}]}{[H_2A]} = K_1 \times K_2$

$= 1 \times 10^{-5} \times 5 \times 10^{-10}$

$= 5 \times 10^{-15}$

67. For buffer solution

$pH = pKa + \log_{10} \frac{[Salt]}{[Acid]}$.

$= 4.5 + \log_{10} \frac{[Salt]}{[Acid]}$.

As HA is 50% is ionized so [salt] = [acid]

$pH = 4.5$

$pH + pOH = 14$

$pOH = 14 - 4.5 = 9.5$

68. If C is the initial concentration and 'x' is the degree of hydrolysis, then the degree of hydrolysis of NH_4Cl.

$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

$C(1 - x) \qquad Cx \qquad Cx$

$K_h = \frac{Cx^2}{1 - x}$.

$x = \sqrt{}(K_h / C)$

69. pH = 1 means $[H^+] = 10^{-1}$ M.

On adding equal amount of water $[H^+] = 10^{-1} / 2$

$pH = -\log_{10} (10^{-1} / 2) = 1 + \log_{10} 2$

$= 1 + 03 = 1.3$

70. It is a salt of weak acid and weak base.

$[H^+] = \sqrt{}[(K_w \times Ka)/ K_b]$

On solving, we get

pH = 7.01.

Brainteasers Objective Type Questions

71. For a basic buffer,

$pH = 14 - pKb - \log \frac{[salt]}{[base]}$

$= 14 - (- \log 10^{-10}) - \log 1$

$pH = 4$

72. As the strength of conjugate base α 1/acidic strength As acidic strength is

$HOH > HC \equiv CH > NH_3 > CH_3 - CH_3$

So

$CH_3 - CH_2^- > NH_2^- > H - C \equiv C^- > OH^-$

73. $\frac{\text{Strength of HA}}{\text{Strength of HB}} = \frac{\sqrt{K_{HA}}}{\sqrt{K_{HB}}}$

$$\frac{\sqrt{3.2 \times 10^{-4}}}{\sqrt{2 \times 10^{-5}}} = \frac{\sqrt{32}}{\sqrt{2}} = \frac{\sqrt{16}}{\sqrt{1}} = \frac{4}{1}$$

i.e., strength of HA : strength of HB = 4 : 1

74. $MH^+ = \frac{M_1V_1 - M_2V_2}{V_1 + V_2}$

$= \frac{0.1 \times 75 - 0.2 \times 25}{100} = \frac{7.5 - 5.0}{100}$

$MH^+ = 2.5 / 100 = 2.5 \times 10^{-2} M$

$= 25 \times 10^{-3} M$

$pH = -\log [H^+] = -\log (25 \times 10^{-3})$

$= -1.398 + 3 = 1.602$

i.e., in this case, pH is close to 1.

75. $[H^+] = \frac{Kw}{[OH^-]} = \frac{1 \times 10^{-14}}{0.05} = 2 \times 10^{-13} \text{ mol L}^{-1}$

$pH = -\log [H^+] = -\log [2 \times 10^{-13}]$

$= -\log 2 - \log 10^{-13} = -\log 2 - (-13) \log 10$

$= -0.3010 + (13 \times 1) = 12.7.$

Hence the value of pH is greater than 7, thus the solution is basic.

76. Given : pH of first solution = 5

Or $[H^+] = 10^{-5}$ M and pH of second solution

= 3

Or $[H^+] = 10^{-3}$ M

On mixing the given solution, in equal volumes, the average hydrogen ion concentration $[H^+]$

$= \frac{10^{-5} + 10^{-3}}{2}$

$= 5.05 \times 10^{-4}$ M.

$pH = -\log_{10} [H^+] = -\log_{10} [5.05 \times 10^{-4}]$

$= -0.7033 - (-4) = 4 - 0.7033 = 3.2967$

= 3.3.

77. $M_R = \frac{M_1 V_1 + M_2 V_2}{\text{Total volume}}$

$= \frac{0.2 \times 75 + 1 \times 25}{400} = 1 / 10$

= 0.1

so net $[H^+] = 0.1$ hence pH = 1.

78. The strength of acid (pKa) = $-\log (1.8 \times 10^{-5})$

= 4.745.

According Henderson–Hasselbalch equation for acidic buffer that

$PH = pKa + \log \frac{[\text{salt}]}{[\text{acid}]} = 4.745 + \log \frac{0.2}{0.15}$

$= 4.745 + \log 1.3333 = 4.745 + 0.125$

= 4.87.

79. Solubility of AgCl (S) = $\frac{\text{solubility of AgCl}}{\text{Mol. wt. of AgCl}}$

$= \frac{1.435 \times 10^{-3}}{143.32} = 10^{-5} \text{ mol L}^{-1}$

AgCl gives two ions after dissociation, thus it is a binary salt.

The solubility product of a binary salt (Ksp) = $S^2 = (10^{-5})^2 = 10^{-10}$

80. Solubility product of AgI (Ksp) = $[Ag^+] [I^-]$

$= 1.0 \times 10^{-16} \text{ mol}^2 \text{ L}^{-2}$

and concentration of KI = 10^{-4} N

In 10^{-4} N AgI, concentration of iodide ion $[I^-] = 10^{-4}$ N

The solubility product of AgI in 10^{-4} N AgI solution (Ksp) = $[Ag^+] [Cl^-]$

$= (S) (S + 10^{-4})$ (due to common ion effect)

$= (S) (10^{-4})$ $[S <<< 10^{-4}]$

or $1.0 \times 10^{-16} = (S) (10^{-4})$

$S = \frac{1.0 \times 10^{-16}}{10^{-4}} = 1.0 \times 10^{-12}.$

81. $M_R = \frac{M_1 V_1 + M_2 V_2}{\text{Total volume}}$

$= \frac{100 \times 0.015 + 100 \times 0.005}{200}$

= 1 / 100

i.e., $[H^+] = 1/100 = 0.01$

so pH = 2

82. Dissociation constant of glycine

(K) = $Ka_1 \times Ka_2$

$= (4.5 \times 10^{-3}) \times (1.7 \times 10^{-10}) = 7.65 \times 10^{-13}$

the hydrogen ion concentration of glycine $[H^+] = \sqrt{}K.C$

$= \sqrt{}(7.65 \times 10^{-13} \times 0.01) = \sqrt{7.65} \times 10^{-15}$

$= 0.87 \times 10^{-7}$ mol L^{-1}.

Therefore pH value of the glycine = $-\log [H^+]$

$= -\log [0.87 \times 10^{-7}] = 7 + 0.06 = 7.06$

84. 50 ml of 0.1 M HCl = 50 × 0.1 = 5 millimoles

50 ml of 0.2 NaOH = 50 × 0.2 = 10 illimoles

Millimoles of NaOH left after neutralization = 5

Volume of solution = 100 ml.

Molar conc. of NaOH

$$= \frac{5}{100} = 5 \times 10^{-2} \text{ M}$$

$pOH = -\log_{10} (5 \times 10^{-2})$

$$= \log_{10} \frac{1}{5 \times 10^{-2}} = \log_{10} 20 = 1.301$$

pH = 14 – 1.301 = 12.699 = 12.70.

85. 0.365 g HCl = $\frac{0.365}{36.5}$ mole = 0.01 mole

100 cm^3 of 0.2 M NaOH

$$= \frac{0.2}{1000} \text{ x } 100 = 0.02 \text{ mole}$$

NaOH left un–neutralised = 0.01 mole

Volume of solution = 100 ml

So molarity of NaOH in the solution

$$= \frac{0.01}{100} \times 1000 = 0.1 \text{ M} = 10^{-1} \text{ M}$$

As $[H^+] = \frac{10^{-14}}{10^{-1} \text{ M}} = 10^{-13}$ M

So pH = 13.

86. $HCOOH / CH_3COOH$

= √(Ka for formic acid / Ka for acetic acid)

$= \sqrt{}(1.77 \times 10^{-4} / 1.75 \times 10^{-5})$

= √(10 / 1)

= 3.178 / 1

= 3.178

87. Ksp for $Ag_2SO_4 = [Ag^+]^2 [SO_4^{2-}]$

$[SO_4^{2-}]$ for precipitation of Ag_2SO_4

$$> \frac{Ksp}{[Ag^+]^2} = \frac{10^{-5}}{(0.1)^2} = 10^{-3} \text{ M}$$

Similarly, $[SO_4^{2-}]$ for precipitation of $BaSO_4$

$$> \frac{Ksp}{[Ba^{2+}]} = \frac{10^{-11}}{0.1} = 10^{-10} \text{ M}$$

$[SO_4^{2-}]$ for precipitation of $CaSO_4$

$$> \frac{Ksp}{[Ca^{2+}]} = \frac{10^{-6}}{0.1} = 10^{-5} \text{ M}$$

So minimum $[SO_4^{2-}]$ needed for precipitation is for $BaSO_4$.

88. Ksp for $Mg(OH)_2 = [Mg^{2+}] [OH^-]^2$

$10^{-12} = (0.01) [OH^-]^2$

$[OH^-]^2 = 10^{-10}$ M

$[OH^-] = 10^{-5}$ M

$[H^+] = 10^{-9}$ M

So pH = 9.

89. 20 ml of 0.5 N HCl have 20 × 0.5 milli eq. = 10 milli eq. of HCl

15 ml of 0.1 N NaOH have 35 × 0.1 milli eq. = 3.5 milli eq. of NaOH

Thus 3.5 milli eq. of NaOH will neutralize 3.5 milli eq. of HCl

(10 – 3.5) = 6.5 milli eq of HCl will be left.

Therefore solution will be acidic and it will turn methyl orange red.

90. The redox changes are

$K^+ + e \rightarrow K$ [at cathode]

$2H_2O \rightarrow 4H^+ + O_2 + 4e$ [at anode]

W / E = it / 96500

Eq. of K^+ lost = equivalent of H^+ formed

$$= \frac{it}{96500} = \frac{16.08 \times 10^{-3} \times 1 \times 60}{96500} = 10 \times 10^{-6}$$

$$[H^+] = \frac{10 \times 10^{-6}}{10^3} = 10 \times 10^{-9} = 10^{-8}$$

pH = 8.

91. $HCl \rightarrow H^+ + Cl^-$

$$\begin{array}{ccccc} & & 10^{-8} & & \\ H_2O & \leftrightarrow & H^+ & + & OH^- \\ & & 10^{-8} + a & & a \end{array}$$

$Kw = [H^+]\,[OH^-]$

$10^{-14} = (10^{-8} + a) \times a$

$a = 0.95 \times 10^{-7}$

$[H^+] = 10^{-8} + 0.95 \times 10^{-7} = 1.05 \times 10^{-7}$

92. According to Handerson–Hasselbalch equation

$$pOH = pK_b + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]}$$

At half stage of titration

[Salt] = [Base]

$pOH = pK_b = 4.74$

$pH = 14 - pOH$

$= 14 - 4.74 = 9.26$

93. As pH = 2

So $[H^+] = 10^{-2}$ M

$$\begin{array}{lll} HA & \rightleftharpoons & H^+ + A^- \\ C \text{ mol } L^{-1} & & \\ C\,(1-\alpha) & C\alpha & C\alpha \end{array}$$

$[H^+] = C\alpha$

$\alpha = [H^+] / C = 10^{-2} / 10^{-1}$

$= 10^{-1} = 0.1$ M.

94. At 25°C, pK_b for $NH_3 = 4.7$ (in aq. solution)

$[NH_4Cl] = 0.1$ M and $[NH_3] = 0.01$ M

For basic buffer,

$$pOH = pK_b + \log_{10} \frac{[\text{Conjugate acid } B^+]}{[\text{Weak base BOH}]}$$

$$pOH = 4.7 + \log_{10} \frac{0.1}{0.01}\ .$$

$= 4.7 + \log(10) = 5.7$

$pH + pOH = 14$

$pH = 14 - 5.7 = 8.3$

95. Molar conc. of the given solution = 0.100 M

$$\begin{array}{lcccc} & HA & \rightleftharpoons & H^+ & + \ A^- \\ \text{Initial conc.} & C \text{ mol } L^{-1} & & & \\ \text{After diss.} & C - C\alpha & & C\alpha & C\alpha \\ & = C(1-\alpha) & & & \end{array}$$

$$K_a = \frac{C\alpha \,.\, C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} = C\alpha^2$$

$\alpha = \sqrt{(K_a / C)}$

$= \sqrt{[(1.0 \times 10^{-5}) / (0.1)]} = 10^{-2}$

So % dissociation = $10^{-2} \times 100 = 1\%$.

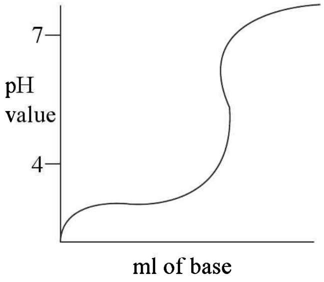
96. HCOONa, being salt of weak acid and strong base, solution is basic.

$C_6H_5NH_3Cl$, being salt of weak acid and strong acid, solution is acidic.

KCN, being salt of strong base and weak acid, solution is basic.

97. pH curve of strong acid with a weak base is vertical over the pH range of

4 to 7.



The indicator that shows colour change within this range is suitable. Methyl red (pH range 4.4–6.5) is the best choice.

98. Due to common ion effect of acetate ion further ionization of acetic acid is reduced, which leads to decrease in H^+ concentration in solution, and hence increase in pH of the solution.

99. $Mg(OH)_{2(s)} \rightleftharpoons Mg^{2+} + 2OH^-$

$$K_{sp} = \frac{[Mg]^{2+}\,[OH]^-}{[Mg(OH)_2]}$$

$= 1.96 \times 10^{-11}$

$x \times (2x)^2 = 1.96 \times 10^{-11}$ (concentration of solid is unity)

$4x^3 = 1.96 \times 10^{-11}$

$$x = \left(\frac{1.96 \times 10{-}11}{4}\right)^{1/3}$$

$x = (4.9 \times 10^{-11})^{1/3} = 1.6 \times 10^{-4}$

So, OH^- concentration $= 2 \times 1.6 \times 10^{-4}$

i.e., $[OH^-] = 3.2 \times 10^{-4}$

Now, $pOH = -\log [OH^-]$

$= -\log [3.2 \times 10^{-4}]$

$= 4 - 0.505 = 3.495$

As $pH = 14 - 3.495 = 10.505$

101. No of milli equivalent of NaOH = 30 ×1 =30

No of milli equivalent of HCl = 50 × 1 =50

As, NO of milli equivalent of HCl left after titration = 50 – 30 = 20

Total volume of the mixture = 50 + 30 = 80

i.e., 20 milli equivalent or 0.02 equivalent of HCl are present in 80 ml.

So, 250 milli equivalent or 0.25 equivalent of HCl are present in 1000 ml or 1 litre.

i.e., 025 N HCl ≈ 0.25 MNaOH (Monobasic)

So, $[H^+] = 0.25$ M

$pH = -\log_{10} [0.25]$

$pH = -\log_{10} [2.5 \times 10^{-1}]$

$pH = 1 - \log_{10} 2.5$

$pH = 1 - 0.3979$

$pH = 0.6021$

102. pH of buffer is

$$pH = pK_\alpha + \log \frac{[\text{salt}]}{[\text{acid}]}$$

Since, [salt] = [acid] , $pH = pK_{\alpha'}$

103. Equimolar solutions of the given chlorides when prepared in water forms their respective hydroxides. $Be(OH)_2$ is amphoteric, but the hydroxides of other alkaline earth metals are basic. The basic strength increases down the group. Therefore higher the basic character higher will be the pH.

104. $X \rightleftharpoons Y + Z$ …….(i)

$A \rightleftharpoons 2B$ …….(ii)

	$X \rightleftharpoons$	Y +	Z
Initially	1	0	0
At. eq.	$1 - \alpha$	α	α

Total No. of moles at equilibrium

$= 1 - \alpha + 2\alpha = 1 + \alpha$

	$A \rightleftharpoons$	$2B$
Initially, when t = 0	1	0
At. eq.	$1 - \alpha$	2α

Total no. of moles at equilibrium

$= 1 - \alpha + 2\alpha = 1 + \alpha$

$$K_{P1} = \frac{P_Y \times P_Z}{P_X}$$

$$= \frac{[(\alpha / 1 + \alpha) P_1]\,[(\alpha / 1 + \alpha) \times P_1]}{[1 - \alpha / 1 + \alpha] \times P_1}$$

$$\frac{K_{P2}}{P_A} = (p_B)^2 = \frac{[(2\alpha / 1 + \alpha) \times P_2]^2}{[1 - \alpha / 1 + \alpha] \times P_2}$$

$$\frac{K_{P1}}{K_{P2}} = \frac{P_1}{4P_2} .$$

$$\frac{P_1}{P_2} = \frac{36}{1} = 36 : 1$$

105.

A_xB_y	$\rightleftharpoons$ xA^{y}	+ yB^{x-}	
C	0	0	(Initially)
$C(1 - \alpha)$	$Cx\alpha$	$Cy\alpha$	(At equilibrium)

As $$K_{eq} = \frac{(Cx\alpha)^x (Cy\alpha)^y}{C(1 - \alpha)}$$

For concentrated solution of weak electrolyte , α is very small. Therefore , $(1 - \alpha) \approx 1$.

So, $$\alpha = \left(\frac{K_{eq}}{C^{x+y-1.}\, x^x \cdot y^y} \right)^{\frac{1}{x+y}}$$

106. Solubility of $BaSO_4$ (S) $= \dfrac{\text{solubility of } BaSO_4}{\text{Mol. wt. of } BaSO_4}$

$= \dfrac{2.33 \times 10^{-3}}{233} = 0.01 \times 10^{-3}$ mol L^{-1}

$BaSO_4$ gives two ions after dissociation, thus it is a binary salt.

$(Ksp) = S^2 = (0.01 \times 10^{-3})^2 = (1 \times 10^{-5})^2$

$= 1 \times 10^{-10}$.

109. $S_{CuS} = (10^{-37})^{1/2} = 10^{-18.5}$;

$S_{HgS} = (10^{-54})^{1/2} = 10^{-27}$

K_{sp} of $Ag_2S = 4s^3 = 10^{-49}$

$S^3 = \dfrac{10^{-49}}{4} = 0.025 \times 10^{-48}$

$S = 0.292 \times 10^{-16}$.

Thus $Ag_2S > CuS > HgS$.

110. $pH = -\log_{10} [H^+]$

$[H^+] = 10^{-pH}$

$[H^+]$ of solution 1 = 10^{-3}

$[H^+]$ of solution 2 = 10^{-4}

$[H^+]$ of solution 3 = 10^{-5}

Total concentration of $[H^+]$

$= 10^{-3}(1 + 1 \times 10^{-1} + 1 \times 10^{-2})$

$$= 10^{-3}\left(\frac{1}{1} + \frac{1}{10} + \frac{1}{100}\right)$$

$$= 10^{-3}\left(\frac{111}{100}\right) = 1.11 \times 10^{-3}$$

Therefore, H^+ ion concentration in mixture of equal volume of these acid solutions

$$= \frac{1.11 \times 10^{-3}}{3} = 3.7 \times 10^{-4}\ M$$

113. Here the correct order is IV < II < III < I.

116. $A_2X \leftrightarrow 2A^+ + X^{-2}$

$\qquad 2S \quad S$

$Ksp = (2S)^2 (S) = 4S^3$

$S = [Ksp/4]^{1/3}$

$AX \leftrightarrow A^+ + X^-$

$\qquad S_1 \quad S_1$

$Ksp = (S_1)^2$

$S_1 = (Ksp)^{1/2}$

$AX_3 \leftrightarrow A^{+3} + 3X^-$

$\qquad S_2 \quad 3S_2$

$Ksp = (S_2)(3S_2)^3 = 27S_2^{\,4}$

$S_2 = [Ksp / 27]^{1/4}$

Thus, it is clear that $S_1 > S > S_2$

121. Acidic strength of oxyacids increases with increase in electronegativity of the non–metal and its oxidation number. thus the order is

$HClO_4$ (III) > H_2SO_4 (I) > H_3PO_4 (II)

123. Solution of I is acidic (pH < 7), solution of II is basic (ph > 7), solution of III is neutral (pH = 7) while solution of IV is strongly basic (pH >> 7).

Thus the order of pH is IV > II > III > I

124. $P_3Q_2(s) \leftrightarrow 3P^{2+} + 2Q^{3-}$.

Solubility = × / M mol lit^{-1}

$[P^{2+}] = \frac{3x}{M}$ mol lit^{-1}; $[Q^{3-}] = \frac{2x}{M}$

$K_{sp} = (3x / M)^3 (2x / M)^2 = 108\, x^5 / M^5$

$$\frac{[Q^{3-}]}{K_{sp}} = \frac{2x}{M} \cdot \frac{M^5}{108\, x^5} = \frac{1}{54}\,\frac{M^4}{x^4}.$$

127. $pOH = pK_b + \log_{10}\frac{[Salt]}{[Base]}$.

$$= -\log_{10}(1.5 \times 10^{-9}) + \log_{10}\frac{0.15}{500 \times 0.2 \times 10^{-3}}.$$

$= 9 - \log_{10} 1.5 + \log_{10} 1.5 = 9$

pH = 14 – 9 = 5.

130. $$[H^+] = \frac{\text{remaining mili eq. of } H^+}{\text{total volume (in mL)}}$$

$$= \frac{40}{100} = \frac{4}{10}$$

Hence pH = 1– log 4 = 1 – 0.6

= 0.4

Multiple Correct Answer Type Questions

135. The 10^{-8} M solution of HCl is very dilute.

And the contribution of H^+ ions, due to self ionization of water, cannot be neglected. Therefore, $[H^+]$total = $[H^+]$ (from HCl+ water) = $10^{-8} + 10^{-7} = 10^{-7}(10^{-1} + 1)$

$= 10^{-7}(0.1 + 1) = 10^{-7} \times 1.1$.

$pH = -\log[H^+] = -\log(1.1 \times 10^{-7}) = 6.96$.

So option (B) is not true, while rest are true.

143. pH of 10^{-8} M HCl is not 8 but it is less than 7 because in this case contribution of H^+ from water can not be neglected.

So total $H^+ = 10^{-8}$ (from acid) + 10^{-7} (from water)

$= 10^{-8}(1 + 10)$

$= 11 \times 10^{-8}$ M

$pH = -\log[H^+] = -\log[11 \times 10^{-8}]$

$= -[\log 11 + \log 10^{-8}]$

$= -[1.0414 - 8]$

$= 6.9586 \simeq 6.96$

154. CH_3COOH is weak acid while NaOH is strong base, so one equivalent of NaOH can not be neutralized with one equivalent of CH_3COOH. Therefore the solution of one equivalent of each does not have pH value as 7. That is it is incorrect

160. As KOH, HNO_3 are limiting reagents here.

166. uppose the concentration of the acetate salt added is × times the concentration of acetic acid solution of obtain pH = 7. Then $[CH_3COO^-]$

$= x \times [CH_3COOH]$

$$\frac{[CH_3COO^-]}{[CH_3COOH]} = x$$

Now, for acid buffer, $pH = pK_a + \log \frac{[salt]}{[acid]}$

$7 = -\log (1.8 \times 10^{-5}) + \log x$

$7 = 4.76 + \log \times$ or $\log \times = 2.24$

$x = 1.73 \times 10^2 = 173$ times

167. $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

$$K_1 = \frac{[H^+]\,[HCO_3^-]}{[H_2CO_3]}$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{K_1}{[H^+]}$$

pH = 7.40 means $-\log [H^+] = 7.4$

or $\log [H^+] = -7.4 = 8.6$

$[H^+] = 3.981 \times 10–8$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{4.5 \times 10^{-7}}{3.981 \times 10^{-8}}$$

$= 11.3$

171. $AgI \rightleftharpoons Ag^+ (s) + I^- (s)$

$Ksp = S^2$

$S = \sqrt{(Ksp)} = \sqrt{(4.9 \times 10^{-11})} = \sqrt{(49 \times 10^{-12})}$

$= 7 \times 10^{-6}$

In 0.001 M KI,

$Ksp = (7 \times 10^{-6})\,(7 \times 10^{-6})\,(10^{-2})$

$= 49 \times 10^{-14}$

$S = \sqrt{Ksp} = \sqrt{(49 \times 10^{-14})} = 7.0 \times 10^{-7}$

172. $Zn^{2+} + 2H_2O \rightleftharpoons Zn\,(OH)_2 + 2H^+$

$$K_h = \frac{[Zn(OH)_2[H^+]^2}{[Zn\,(OH)]_2}$$

$Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2OH^-$

$$K_b = \frac{[Zn^{2+}]\,[OH^-]^2}{[Zn(OH)_2]}$$

$$= \text{Hence } K_h = \frac{K^2_w}{K_b}$$

174. $pH = 7 + ½\,[pK_a - pK_b]$

$= 7 + ½\,[\log K_a + \log K_b]$

$= 7 + ½\,[-\log(6.2 \times 10^{-10)} + \log (1.6 \times 10^{-5})]$

$= 7 + ½\,[(10 - 0.7924) + (-5 + 0.2041)]$

$= 9.21$

175. Aniline hydrochloride ($C_6H_5NH_3Cl^-$) is a salt of weak base ($C_6H_5NH_2$) and strong acid (HCl) so for it

$C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + H_3O^+$

or $C_6H_5NH_3 \rightleftharpoons CH_5NH2 + H^+$

$$K_h = \frac{K_w}{K_b} = \frac{1.02 \times 10^{-14}}{5.93 \times 10^{-10}}$$

$= 1.72 \times 10^{-5}$

$$h = \sqrt{\frac{Kh}{c}} = \sqrt{\frac{1.72 \times 10^{-5}}{10}}$$

$= 4.15 \times 10^{-3}$

$= 4.15 \times 10^{-3} \times 100\% = 0.415\ \%$

184. As CN^- is more basic than F^- and $CH3COO^-$

187. It can be titrated only by basic nature indicator.

190. Both assertion and reason is correct and give correct explanation.

201. $A_2B_3 \leftrightarrow 2A^{+3} + 3B^{-2}$

2S 3S

$Ksp = [A^{+3}]^2\,[B^{-2}]^3 = (2S)^2\,(3S)^3$

$Ksp = 108\ S^5$

202. $pKa = 14 - pKb = 14 - 10.83 = 3.17$

$Ka = \text{Antilog}\ (-\ pKa)$

$Ka = \text{Antilog}\ (-3.17) = 6.75 \times 10^{-4}$

203. pH of 10^{-8}M HCl is not 8 but it is less than 7.

Only choices 2, 3 are correct.

205. In all the 1, 2, 3 buffer solution is prepared. In choice 2, when CH_3COONa reacts with HCl it forms $CH_3COOH + NaCl$.

206. HCl : Strong acid

NH_4Cl : Salt of weak base + strong acid → it gives acidic solution.

NaCl : Salt of strong base + strong base → it gives neutral solution with pH = 7.

NaCl : Salt of strong base + weak acid → it gives basic solution with pH > 7.

Thus the increasing order of pH is

$HCl < NH_4Cl < NaCl < NaCN$

207. $Ap\,Bq \leftrightarrow pA^{q+} + B^{p-}$

$\qquad\qquad pS \qquad qS$

Ksp or Ls = $[A^{q+}]^p \,.\, [B^{p-}]^q$

$= (pS)^p.(qS)^q = p^p.\ S^p.\ q^q.\ S^q$

$Ls = S^{\,p+q}.\ p^p.\ q^q$

208. $Ag_2S \rightarrow 2Ag + S^{-2}$.

Solubility product of this reaction

$(Ksp) = [Ag]^2\,[S^{-2}]$

solubility of each product is S, then solubility product (Ksp) = $(2S)^2 \times (S)$

$256 \times 10^{-6} = 4S^2 \times S$

$256 \times 10^{-6} = 4S^3$

$$S^3 = \frac{256 \times 10^{-6}}{4} = 64 \times 10^{-6}$$

$S = \sqrt[3]{(64 \times 10^{-6})} = 4 \times 10^{-2}$.

209. $[Pb^{2+}] = 1.3 \times 10^{-3}$ M

$[I^-] = 2 \times 1.3 \times 10^{-3}$ M

$= 2.6 \times 10^{-3}$ M

$Ksp = [Pb^{2+}]\,[I^-]^2$

$= (1.3 \times 10^{-3})\,(2.6 \times 10^{-3})^2$

$= 8.8 \times 10^{-9}$.

$PbI_2 \rightarrow Pb^{2+} + 2I^-$

210. The one with lowest value of Ksp, i.e., HgS will precipitate out first.

211. Hydrolysis reaction is

$X^- + H_2O \rightarrow HX + OH^-$

For a salt of weak acid and strong base

As $K_h = \dfrac{K_W}{Ka} = ch^2$

$$\frac{10^{-14}}{10^{-5}} = 0.1 \times h^2$$

$h^2 = 10^{-8}$

$h = 10^{-4}$

So % hydrolysis = $10^{-4} \times 100 = 10^{-2} = 0.01$

212. CH_3NH_2 (base) on reaction with HCl (acid) to give a salt of weak base and strong acid as $CH_3NH_3^+Cl^{-1}$.

$$CH_3NH_2 \ + \ HCl \ \rightarrow \ CH_3NH_3^+Cl^-$$

At t = 0 $\quad$ 0.1 mole $\quad$ 0.08 mole $\quad$ 0

After $\quad$ (0.1 – 0.08) $\qquad$ 0.08 mole

reac. $\quad$ = 0.02 mole

So, it acts as basic buffer solution due to presence of base and salt is solution of one litre.

$$pOH = -\log_{10} K_b + \log_{10} \frac{[Salt]}{[Base]}\ .$$

$$= -\log_{10} K_b + \log_{10} \frac{[CH_3NH_3^+\,Cl^-]}{[CH_3NH_2]}$$

$$= -\log_{10} 5 \times 10^{-4} + \log_{10} \frac{[0.08]}{[0.02]}$$

$$= -\log_{10} 5 + 4 \log_{10} 10 + \log_{10} \frac{[0.08]}{[0.02]}$$

$= -0.699 + 4 + 0.602 = 3.9030$

pH = 14 – pOH

= 14 – 3.903 = 10.097

$10.097 = -\log_{10} [H^+]$

$[H^+] = 8.0 \times 10^{-11}$

213. (i) $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+$,

$k_1 = 3.5 \times 10^{-3}$

(ii) $[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$

$k_2 = 1.7 \times 10^{-3}$

According to these reactions

$$k_1 = \frac{[Ag(NH_3)]^+}{[Ag^+]\,[NH_3]} \quad \ldots\ldots \text{(i)}$$

$$k_2 = \frac{[Ag(NH_3)_2]^+}{[Ag(NH_3)]^+\,[NH_3]} \quad \ldots\ldots. \text{(ii)}$$

For the formation of $[Ag(NH_3)_2]^+$

$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH)_2]^+$

Formation constant (K)

$$= \frac{[Ag(NH_3)_2]^+}{[Ag^+]\,[NH_3]^2} \quad \ldots.. \text{(iii)}$$

From equation (i) and (ii)

$K = k_1 \times k_2$

$= 3.5 \times 10^{-3} \times 1.7 \times 10^{-3}$

214. $MX \rightleftharpoons M^+ + X^-$

Solubility of $MX(s_1) = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4}$

$MX_2 \rightleftharpoons M^+ + 2X^-$

Solubility of $MX_2(s_2) = 4s_2^3 = K_{sp}$

$$s_2 = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{3.2\times 10^{-14}}{4}\right)^{1/3}$$

$= 2 \times 10^{-5}$

$M_3X \rightleftharpoons 3M^+ + X_3^-$

Solubility of $M_3X(s_3) = 27s_3^4$

$= 2.7 \times 10^{-15}$

$= s_3 = 10^{-4}$

$s_1 > s_3 > s_2$

$\Rightarrow MX > M_3X > MX_2$

215. $BOH + HCl \rightarrow BCl$ **c.** $+ H_2O$

$B^+ + H_2O \rightleftharpoons BOH + H^+$

$C(1-h) \qquad Ch \qquad Ch$

For titration

$N_{acid} \times V_{acid} = N_{base} \times V_{base}$

$$\frac{2}{15}\times V = 2.5\times\frac{2}{5}$$

Hence V = volume of HCl used = 7.5 mL.

In resulting solution,

Concentration of salt [BCl]

$$= \frac{2}{5\times 2.5/10} = \frac{2}{20} = 0.1$$

$$\text{As } \frac{Ch^2}{1-h} = \frac{K_w}{K_b}$$

$$\text{or } h = \sqrt{\frac{K_w}{K_b\times C}} = \sqrt{\frac{10^{-14}}{10^{-12}\times 0.1}}$$

$$\text{So} \quad h = \sqrt{\frac{1}{10}}$$

Now, as $[H^+] = Ch$

$= 0.1 \times \sqrt{\frac{1}{10}}$

$= 0.1 \times 0.316$

$= 3.16 \times 10^{-2}$ M

So $[H^+] \approx 3.2 \times 10^{-2}$

Numericals for Practice

1. 20 ml 0.5 M solution of a weak acid HA and 20 ml 1.0 M HCl are mixed together 1.2 g NaOH of them dissolved into it. If pH of the resulting solution is 5.5, pKa of the weak acid is

a. 4.8	**b.** 5.2
c. 9.0	**d.** 7

2. The pKa of HCN is 9.30. The pH of a solution prepared by mixing 1.5 moles of KCN and 1.5 moles of HCN in water and making up the total volume to 500 ml is

a. 7.0	**b.** 4.7
c. 8.3	**d.** 9.3

3. The formation constant of the complex $[Ag(NH_3)_2]^+$ at 25°C is 1.0×10^8. In a solution prepared by mixing 1.0×10^{-3} mole of $AgNO_3$ and 1.0 lit of 0.1 M NH_3 solution, the $[Ag^+]$ is about

a. 1.0×10^{-10} M	**b.** 1.0×10^{-8} M
c. 1.0×10^{-9} M	**d.** 10.6×10^{-8} M

4. The solubility of calcium arsenate in pure water at 25°C is 9.0×10^{-5} mol/lit. The solubility product, K_{sp} at this temperature is

a. 6.4×10^{-19}	**b.** 7.6×10^{-19}
c. 6.4×10^{19}	**d.** 6.4×10^{-20}

5. The solubility product values of barium sulphate and barium carbonate are 1.0×10^{-10} and 5.0×10^{-9} respectively. When the two salts are equilibrated in pure water the ratio of $[SO_4^{2-}] / [CO_3^{2-}]$ is

a. 0.05	**b.** 0.02
c. 0.002	**d.** 0.01

6. The solubility product of Ag_2CrO_4 at 25°C is 1.686×10^{-12}. The $[Ag^+]$ in a solution of 0.02 M Na_2CrO_4 is

a. 4.56×10^{-5} M

b. 4.56×10^{-6} M

c. 9.1×10^{-6} M

d. 9.1×10^{-5} M

7. A buffer solution is prepared by mixing 0.02 M benzoic acid solution and sodium benzoic solution to give a pH of 5.4. K_a of benzoic acid = 6.4×10^{-15}. The proportion , [acid] / [salt] in which the two solutions have to be mixed is

a. 1.0	**b.** 0.5
c. 0.3	**d.** 0.7

8. In a saturated solution of silver chromate in pure water at 25°C, the concentration of chromate ion is 2×10^{-4} mol.lit^{-1}. The solubility product of silver chromate is

a. 3.2×10^{-10}
b. 3.2×10^{-11}
c. 4×10^{-8}
d. 2.3×10^{-12}

9. The approximate pH of a saturated solution of H_2S in water ($[H_2S] = 0.1$ M) at 25°C is (K_1, $H_2S = 1.0 \times 10^{-7}$, K_2, $H_2S = 1.3 \times 10^{-13}$)

a. 3.0
b. 4.0
c. 5.0
d. 2.0

10. 25.0 ml of 0.05 M H_2SO_5 is added to 0.10 M NaOH solution. The resulting solution has a pH of 10.6. The volume of NaOH solution taken is

a. 25.0 ml
b. 25.1 ml
c. 25.2 ml
d. 25.52 ml

11. The degree of hydrolysis of 0.10 M aniline acetate (aq) is ($K_a = 1.75 \times 10^{-5}$ and $K_b = 4.0 \times 10^{-10}$)

a. 0.3484
b. 0.9564
c. 0.4584
d. 0.5444

12. Assume the ionic product of water to be 10^{-14} at a certain temperature. The dissociation constant of water (in mol lit^{-1}) at the same temperature is roughly

a. 3.6×10^{-17}
b. 1.8×10^{-16}
c. 8.1×10^{-16}
d. 10^{-16}

13. What is the minimum pH range over which an acid–base indicator HIn ($K_{In} = 10^{-5.5}$) may be effectively used, if the colour is distinctly discemable, when the concentration ratio $[In^-] / [HIn]$ is ≥ 10 or ≤ 0.1?

a. 4.5 to 6.5
b. 4.0 to 6.0
c. 5.0 to 6.0
d. 5.5 to 6.5

14. Blood is buffered with CO_2 and HCO_3^-. What is the ratio of the base concentration to the acid (i.e., CO_2 (aq.) + H_2CO_3) concentration to maintain the pH of blood at 7.4? The first dissociation constant of H_2CO_3 ($H_2CO_3 \leftrightarrow H^+ + HCO_3^-$) is 4.2×10^{-7} where the H_2CO_3 is assumed to include CO_2 (aq.) i.e., dissolved CO_2.

a. 1.06
b. 10.6
c. 108
d. 106

5. The first and the second dissociation constants of H_2S are respectively 10^{-7} and 10^{-14} (approximate). The pH of a 0.1 M H_2S solution is roughly

a. 2.0
b. 3.0
c. 3.5
d. 4.0

16. Two weak monobasic acids HA and HB have dissociation constants 4×10^{-6} and 1×10^{-8} respectively. The hydrogen ion concentration ratio for HA and HB is roughly

a. 5 : 1
b. 20 : 1
c. 100 : 1
d. 400 : 1

17. pH of the solution prepared by mixing 5ml of N/10 CH_3COOH and 5 ml of N/10 NaOH solution is (Assume the Ka of CH_3COOH is 10^{-5})

a. 7
b. 5.16
c. 1.3
d. 8.84

18. How many times (approximately) should an extremely weak monobasic acid, HA, be diluted, so that the hydrogen ion concentration is reduced to ¼ of that in the original solution?

a. 2
b. 4
c. 8
d. 16

19. In an acid–base titration, 24.9 ml of 0.1 M HCl are added to 25.0 ml of 0.1 M NaOH. 0.2 ml more of HCl is then added. The change in pH between these two stages of titration is approximately

a. –7.6
b. +7.0
c. –6.6
d. +6.0

20. The acid dissociation constant, K_a of H_2O_2 is 10^{-12}. The pH of a '11.2 volume' solution of H_2O_2 is approximately

a. 2.0
b. 3.0
c. 4.0
d. 6.0

21. If 0.1 M solution of a weak acid is 8% ionized. Then Ka for the acid is approximately

a. 6.4×10^{-2}
b. 6.4×10^{-3}
c. 6.4×10^{-4}
d. 6.4×10^{-6}

22. Ka for a weak acid is 4.0×10^{-5}. pH of 0.001 M of the same acid is

a. 4.3
b. 3.7
c. 2.7
d. 3.5

23. pKa of acetic acid is 4.7. If 60 mL of 0.02 M acetic acid is mixed with 60 mL of 0.01 M NaOH, the pH of the solution is

a. 2.7
b. 4.7
c. 6.7
d. 8.7

24. In a 0.1 N solution of acetic acid the degree of ionization is 0.015. The OH^- ion concentration is

a. 6.66×10^{-12}
b. 0.666×10^{-12}
c. 66.6×10^{-12}
d. 0.06×10^{-12}

25. One litre of water contains 10^{-7} moles of H^+ ions. The percentage degree of ionization of water is

a. 1.6×10^{-7}
b. 1.8×10^{-7}
c. 3.6×10^{-7}
d. 36×10^{-9}

26. pH of $Ba(OH)_2$ is 12. Its solubility product is

a. 5×10^{-7} **b.** 0.5×10^{-7}
c. 5×10^{-6} **d.** 4×10^{-6}

27. pH of 0.01 M $(NH_4)_2SO_4$ and 0.02 M NH_4OH buffer [pKa (NH_4^+) =9.26] is

a. 9.26 + log 2 **b.** 9.26
c. 4.74 + log 2 **d.** 4.74

28. The solubility product of A_2X_3 is 1.08×10^{-23}. Its solubility will be

a. 1.0×10^{-3} M **b.** 1.0×10^{-4} M
c. 1.0×10^{-5} M **d.** 1.0×10^{-6} M

29. M(OH)x has Ksp = 4×10^{-12} and solubility 10^{-4} M, x is

a. 1 **b.** 2
c. 3 **d.** 4

30. The number of H^+ ions present in 1 cm^3 of a solution whose pH is 10 is

a. 10^{-10} **b.** 10^{-13}
c. 6.02×10^{10} **d.** 6.02×10^{13}

31. What is the pH value at which $Mg(OH)_2$ begins to precipitate from a solution containing 0.10 M Mg^{+2} ion? Ksp of $Mg(OH)_2$ is 1×10^{-11}.

a. 3 **b.** 6
c. 9 **d.** 11

32. For preparing a buffer solution of pH 6 by mixing sodium acetate and acetic acid, the ratio of the concentration of salt and acid should be

(Ka = 10^{-5})

a. 1 : 10 **b.** 10 : 1
c. 100 : 1 **d.** 1 : 100

33. 50 litres of 0.1 M HCl are mixed with 50 litres of 0.2 M NaOH. The pOH of the resulting solution is

a. 12.70 **b.** 12.34
c. 8.7 **d.** 4.2

34. The pH of 0.05 M aqueous solution of diethylamine is 12. Its Kb is

a. 2×10^{-3} **b.** 2.5×10^{-3}
c. 3×10^{-3} **d.** 4.5×10^{-3}

35. The degree of ionization of water was found to be 1.8×10^{-9}. The Ka (ionization constant) of water is

a. 1.8×10^{-9} **b.** 1.8×10^{-16}
c. 1.0×10^{-14} **d.** cannot be calculated.

36. In the titration of 50.00 mL of 0.250 M NH_3 (K_b = 1.8×10^{-5}) with 0.500 M HCl, what is the equivalence point pH? (Note : remember to account for dilution.)

a. 2.5 **b.** 5.02
c. 6.69 **d.** 7.87

37. The solubility product of P_2Q_3 is 1.08×10^{-23}. Its solubility will be

a. 1.0×10^{-3} M **b.** 1.0×10^{-8} M
c. 1.0×10^{-5} M **d.** 1.0×10^{-6} M

38. The number of OH^- ions in 1 mL of solution and having present pH value 4

a. 6.02×10^{8} **b.** 6.02×10^{23}
c. 6.02×10^{10} **d.** 6.02×10^{13}

39. The solubility (in mole/litre) of AgCl in 0.1 M KCl solution is (Given K_{sp} of AgCl = 1.6×10^{-10})

a. 1.6×10^{-9} **b.** 1.6×10^{-5}
c. 1.32×10^{-5} **d.** 1.6×10^{-10}

40. What is the pH of a solution composed of 0.20 M NH_3 and 0.15 M NH_4Cl ? K_b forNH$_3$ is 1.8×10^{-5}.

a. 2.15 **b.** 4.62
c. 8.26 **d.** 9.38

ANSWER KEYS

Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.
1.	b	2.	d	3.	c	4.	a	5.	b
6.	c	7.	b	8.	b	9.	b	10.	c
11.	d	12.	b	13.	a	14.	b	15.	d
16.	b	17.	d	18.	d	19.	c	20.	d
21.	c	22.	b	23.	b	24.	a	25.	b
26.	a	27.	b	28.	c	29	b	30.	c
31.	c	32.	b	33.	a	34.	b	35.	b
36.	d	37.	c	38.	d	39.	a	40.	d

Hints and Explanations

3. $K_f = \dfrac{[Ag\,(NH_3)_2\,]^+}{[Ag^+]\,[NH_3]^2}$

Initial conc. $[Ag^+] = 1 \times 10^{-3}$ M

$[NH_3] = 0.1$ M

K_f has a high value and $[NH_3]$ is in excess and so the $[Ag(NH_3)_2]^+$ may be taken as equal to 1×10^{-3}.

$1 \times 10^8 = \dfrac{1 \times 10^{-3}}{X\,(0.1)^2}$

$X = 1 \times 10^{-9}\ M = [Ag^+]_{eq}$

4. $Ca_3\,(AsO_4)_2 \leftrightarrow 3Ca^{2+} + 2AsO_4^{3-}$

$[Ca^{2+}] = 3s$

$[AsO_4^{3-}] = 2s$

If the solubility is s moles lit^{-1}, then

$K_{sp} = [3s]^3\,[2s]^2 = 108\ s^5$

$= 108 \times (9.0 \times 10^{-5})^5$

$= 6.37 \times 10^{-19}$

$= 6.4 \times 10^{-19}$

5. $K_{sp1} = [Ba^{2+}]\,[SO_4^{2-}]$

$K_{sp2} = [Ba^{2+}]\,[CO_3^{2-}]$

$\dfrac{K_{sp1}}{K_{sp2}} = \dfrac{[SO_4^{2-}]}{[CO_3^{2-}]} = \dfrac{1 \times 10^{-10}}{5 \times 10^{-9}} = 0.02$

6. $Ag_2CrO_4 \leftrightarrow 2Ag^+ + CrO_4^{2-}$

$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = 1.686 \times 10^{-12}$

$= [Ag^+]^2 \times 0.02$

$[Ag^+] = 9.1 \times 10^{-6}$ M

7. $pH = pKa + \log \dfrac{[salt]}{[acid]}$

$\log \dfrac{[acid]}{[salt]} = pKa - pH$

$= -\log\,(6.4 \times 10^{-5}) - 4.5$

$= -0.3$

$[acid] / [salt] = 0.5$

8. $Ag_2CrO_4 \leftrightarrow 2Ag^+ + CrO_4^{2-}$

$K_{sp} = (2 \times 2 \times 10^{-4})^2\,(2 \times 10^{-4})$

$= 32 \times 10^{-12}$

$= 3.2 \times 10^{-11}$

9. $H_2S \leftrightarrow H^+ + HS^-$

The second dissociation constant is small and can be neglected for approximate calculation of $[H^+]$.

So $1.0 \times 10^{-7} = \dfrac{[H^+]\,[HS^-]}{0.1} = \dfrac{[H^+]^2}{0.1}$

$[H^+] = 1.0 \times 10^{-4}$ M

pH = 4.0

10. $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O.1$

So 25 ml of 0.05 M H_2SO_4 requires 25.0 ml of 0.10 M NaOH solution.

pH = 10.6

$-\log\,[H^+] = 10.6$

$\log\,[H^+] = -10.6 = \bar{1}1.4$

Taking antilog, $[H^+] = 2.5 \times 10^{-11}$ M

So $[OH^-] = \dfrac{10^{-14}}{2.5 \times 10^{-11}} = \dfrac{1}{2.5} \times 10^{-3}$ M

Taking the total volume as 50 ml,

number of moles of NaOH required for 50 ml

$= \dfrac{1}{2.5} \times 10^{-3} \times \dfrac{50}{1000}$.

For 0.10 M NaOH solution

$0.1 \times \dfrac{V}{1000} = \dfrac{1}{2.5} \times 10^{-3} \times \dfrac{50}{1000}$.

$V = \dfrac{50 \times 10^{-3}}{2.5 \times 0.1} = 0.2$ ml

Volume of NaOH to be added = 25 + 0.2

= 25.2 ml

11. For the salt of a weak acid and weak base

$K_h = \dfrac{K_w}{K_a\,K_b} = \dfrac{h^2}{(1-h)^2}$.

$h / 1 - h = \sqrt{(K_w / K_a\,K_b)}$

$= (10^{-14} / 1.75 \times 4.0 \times 10^{-15})^{1/2}$

$= 1.195$

So $h = \dfrac{1.195}{2.195} = 0.5444$

12. $H_2O \leftrightarrow H^+ + OH^-$

$$K_a = \frac{[H^+]\,[OH^-]}{[H_2O]} = \frac{10^{-14}}{55.5}$$

$= 1.8 \times 10^{-16}$ mol lit^{-1}

13. $HIn \leftrightarrow H^+ + In^-$.

$$pH = pK_{In} + \log \frac{[In^-]}{[HIn]} = 5.5 + \log \frac{[In^-]}{[HIn]} .$$

The required upper limit of pH = $5.5 + \log_{10} = 6.5$.

The required lower limit = $5.5 + \log 0.1 = 4.5$.

The minimum pH range is therefore 4.5 to 6.5.

14. $[H^+]$ in blood = $10^{-7.4} = 3.98 \times 10^{-8}$

$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$

$$\frac{[H^+]\,[HCO_3^-]}{[H_2CO_3]} = 4.2 \times 10^{-7};$$

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{4.2 \times 10^{-7}}{[H^+]}$$

$$= \frac{4.2 \times 10^{-7}}{3.98 \times 10^{-8}} = 10.55 = 10.6$$

15. $K_1 >>> K_2$. Therefore $[H^+]$ is primarily decided by the first dissociation.

$H_2S \leftrightarrow H^+ + HS^-;\ K_1 = 10^{-7}$

Conc: $(0.1 - x)\quad x \quad x$

$$\frac{x^2}{0.1 - x} = 10^{-7};\ \frac{x^2}{0.1} = 10^{-7}$$

$x^2 = 10^{-8}$; $x = 10^{-4}$

$[H^+] = 10^{-4}$

so pH = 4.0

16. Acid HA: $HA \leftrightarrow H^+ + A^-$

$c(1 - \alpha) \quad \alpha c \quad \alpha c$

$K_I = 4 \times 10^{-6} \approx \alpha_1{}^2 c$

$$\alpha_1{}^2 = \frac{4 \times 10^{-6}}{c}$$

$$\alpha_1 = \frac{2 \times 10^{-3}}{c^{1/2}}$$

$[H^+]_1 = \alpha_1 c = 2 \times 10^{-3} \times c^{1/2}$

Similarly, for the acid HB,

$[H^+]_{II} = \alpha_{II}\, c = 1 \times 10^{-4} \times c^{1/2}$,

the concentrations of HA and HB, being the same (equal to c).

$$\frac{[H^+]_I}{[H^+]_{II}} = \frac{2 \times 10^{-3} \times c^{1/2}}{1 \times 10^{-4} \times c^{1/2}} = 20$$

19. I stage of titration: excess concentration of NaOH ≈ 0.1 ml of 0.1 M NaOH dilute to 50 ml

$$= 0.1 \times \frac{0.1}{50}\ M = 2 \times 10^{-4}\ M$$

$[OH^-] = 2 \times 10^{-4}$

pOH = 4 – 0.3010 = 3.6990

pH = 14 – 3.6990 = 10.3010

II stage of titration : excess concentration of HCl ≈ 2×10^{-4} M

pH = 3.6990

$\Delta pH = 3.6990 - 10.3010 = -6.6020 = -6.6$

20. 11.2 volume H_2O_2 solution is 1 M.

$H_2O_2 \leftrightarrow HO_2^- + H^+$

$K_a \approx \alpha^2 c = \alpha^2 \times 1 = 10^{-12}$

$\alpha = 10^{-6}$

$[H^+] = \alpha c = 10^{-6} \times 1 = 10^{-6}$

pH = 6.0

21. For a weak acid

$Ka = C \times \alpha^2$

$\alpha = 8 / 100 = 0.08$

$Ka = 0.1 \times 0.08 \times 0.08$

$= 6.4 \times 10^{-4}$

22. $[H_3O^+] = C \times \alpha$

$Ka = C \times \alpha^2$

$\alpha = \sqrt{(Ka / C)} = \sqrt{[(4.0 \times 10^{-5})/0.001]} = 0.2$

$[H_3O^+] = 0.001 \times 0.2 = 0.0002$

$pH = -\log(0.0002) = 3.7$

23. 60 ml of 0.01 M NaOH neutralizes 60 ml of 0.01 M acetic acid

CH_3COOH in the solution

$$= \frac{60 \times 0.01}{120} = 0.005\ M$$

$$pH = pKa + \log_{10} \frac{[Salt]}{[Acid]} .$$

$$[CH_3COONa] = \frac{0.01}{2} = 0.005$$

$$= 4.7 + \log_{10} \frac{[Salt]}{[Acid]} .$$

$$= 4.7 + \log_{10} \frac{0.005}{0.005} = 4.7$$

24. $[H^+]$ ion concentration = 0.1×0.015

$= 1.5 \times 10^{-3}$ g ion / litre

$[OH^-] = \dfrac{1 \times 10^{-14}}{1.5 \times 10^{-3}} = 0.666 \times 10^{-11}$

$= 6.66 \times 10^{-12}$

25. One litre of water ≡ 1000 g of water

$\equiv \dfrac{1000}{18} = 55.5$ moles

55.5 moles of H_2O contains 10^{-7} moles of H^+ ions

100 moles of H_2O contains = $\dfrac{10^{-7} \times 100}{55.5}$

$= 1.8 \times 10^{-7}$ moles of H^+ ions

26. $A_2X_3 \leftrightarrow 2A^{+3} + 3X^{-2}$

2S 3S

$Ksp = [A^{+3}]^2\,[X^{-2}]^3$

$= (2S)^2\,(3S)^3 = 108\,S^5$

$S = \left(\dfrac{Ksp}{108}\right)^{1\backslash 5} = \left(\dfrac{1.08 \times 10^{-23}}{180}\right)^{1/5}$

$S = [10^{-25}]^{1/5} = 10^{-5}$

29. $M(OH)x \leftrightarrow M^{+x} + \times OH^-$

10^{-4} 10^{-4} $x\ x\ 10^{-4}$

$Ksp = [M^{+x}]\,[OH^-]^x = 4 \times 10^{-12}$

$[10^{-4}]\,[x \times 10^{-4}]^x = 4 \times 10^{-12}$

$[x \times 10^{-4}]^x = 4 \times 10^{-8}$

it holds good if x = 2

30. pH = 10 means

$[H^+] = 10^{-10}$ mol $L^{-1} = 10^{-13}$ g ions/cc

$= 10^{-13} \times (6.02 \times 10^{23})$ ions/cc

$= 6.02 \times 10^{10}$ ions/cc

31. When $Mg(OH)_2$ starts undergoing precipitation, then

$[Mg^{+2}]\,[OH^-]^2$ = Ksp of $Mg(OH)_2$

$[0.1]\,[OH^-]^2 = 1 \times 10^{-11}$

$[OH^-] = 10^{-5}$ M

now pOH = $-\log [OH^-] = -\log 10^{-5} = 5$

pH = 14 – pOH = 14 – 5 = 9

32. $pH = pKa + \log \dfrac{[Salt]}{[Acid]}$

$\log \dfrac{[Salt]}{[Acid]} = pH - pKa = 6 - 5 = 1$

$[pKa = -\log Ka = -\log 10^{-5} = 5]$

$\dfrac{[Salt]}{[Acid]} = \text{antilog}\,(1) = 10$

33. $M\,(H^+) = \dfrac{M_1V_1\,(\text{base}) - M_2V_2\,(\text{acid})}{V_1 + V_2}$

$= \dfrac{0.2 \times 50 - 0.1 \times 50}{100} = 5 \times 10^{-2}$

$pH = -\log [H^+] = -\log (5 \times 10^{-2})$

$= 1.301$

Now, pH + pOH = 14

pOH = 14 – pH

= 14 – 1.301

= 12.69

34. pH = 12 $[H^+] = 10^{-12}$

Now $[OH^-] = \dfrac{10^{-14}}{[H^+]} = \dfrac{10^{-14}}{10^{-12}} = 10^{-2}$ M

= 0.01 M

$(C_2H_5)_2\,NH + H_2O \leftrightarrow (C_2H_5)_2\,\overset{+}{NH} + OH^-$

initial molar conc 0.05 0 0

At ≡m 0.05 – 0.01 0.010.01

$Kb = \dfrac{[OH^-]^2}{[(C_2H_5)_2\,NH]} = \dfrac{(0.01)^2}{0.04}$

$= \dfrac{10^{-4} \times 10^2}{4} = \dfrac{10^{-2}}{4}$

$= 2.5 \times 10^{-3}$

35. $H_2O \leftrightarrow H^+ + OH^-$

$C = \dfrac{1000}{18} = 55.55$ M

$Ka = \dfrac{[H^+]\,[OH^-]}{[H_2O]} = \dfrac{C\alpha \,.\, C\alpha}{C}$

$= C\alpha^2$

$Ka = 55.55 \times (1.8 \times 10^{-9})^2$

$= 1.8 \times 10^{-16}$

37. $P_2Q_3 \equiv 2P^{3+} + 3Q^{2-}$

2S 3S

$\text{Ksp} = [P^{3+}]^2\,[Q^{2-}]^3$

$[2S]^2 \qquad [3S]^3$

$= 108\ S^5$

$$S = \left(\frac{\text{Ksp}}{108}\right)^{1/5} = \left(\frac{1.08 \times 10^{-23}}{108}\right)^{1/5}$$

$= [10\text{–}25]^{1/5} = 10^{-5}$

$S = 10^{-5}\ M$

38. As pH = 4

$H^+ = 10^{-4}$

Since $[H^+]\,[OH^-] = 10^{-14}$

$$[OH^-] = \frac{10^{-14}}{[H+]} = \frac{10^{-14}}{10^{-4}} = 10^{-10}\,g\,\frac{\text{ion}}{\text{litre}}$$

$[OH^-] = 6.023 \times 10^{23} \times 10^{-10}$

$= 6.023 \times 10^{13}$ ion/litre.

$$= \frac{6.023 \times 10^{13}\ \text{ion}}{1000\text{mL}}$$

$= 6.023 \times 10^{10}$ ion/ mL.

CHAPTER 6

Electrochemistry

Chapter Contents

Electrochemical cells and cell reactions; Standard electrode potentials; Nernst equation and its relation of ΔG; Electrochemical series, emf of galvanic cells; Faraday's laws of electrolysis; Electrolytic conductance, specific, equivalent and molar conductivity, Kohlrausch's laws Concentration cells and Various levels of multiple-choice questions.

ELECTROCHEMISTRY

Electrochemistry is the branch of the science that deals with the transformation of chemical energy into electrical energy and vice versa or it deals with the relationship between electrical and chemical energy produced in a redox reaction.

ELECTROLYSIS

Here direct current is used to cause a non-spontaneous chemical reaction due to it chemical decomposition of electrolytes takes place or It is the flow of electrons across the boundary followed by a chemical reaction that is, redox reaction. It occurs in electrolytic cell and it takes place at electrodes.

- The electrode which is connected to the positive pole of the battery is known as anode or positive electrode.
- At anode, de-electronation of anions or oxidation takes place.

$A- \rightarrow A + e^-$

- The electrode which is connected to the negative pole of the battery is known as cathode or negative electrode.
- At cathode, electronation of cation or reduction takes place.

$B^+ + e^- \rightarrow B$

- It is interesting to note that the current enters the electrolyte through cathode while leaves through anode.
- The electrolyte as a whole remains neutral during the process of electrolysis as equal number of charges are neutralized at the electrodes.
- Electrodes are two types: (i) Inert and (ii) Active
- If inert electrode is used, the products formed at cathode and anode depends upon nature of electrolytes.
- If active electrode is used at cathode metal deposits and at anode metal is dissolved.

Example, If Ni deposits at cathode, it is called electroplating.

- When fused salts are electrolyzed by using inert electrodes they ionize into their constituent elements.

  Example, $NaCl \rightarrow Na + ½\ Cl_2$

  $NiCl_2 \rightarrow Ni + Cl_2$
- When fused salts are electrolyzed by using active electrodes anode get dissolved due to formation of ions while cathode increases due to deposition of metal on it.
- During electrolysis of aq. solution of $AgNO_3$ the concentration of $AgNO_3$ is found to be same before and after electrolysis.
- During the electrolysis of aqueous solution of salts having NO_3^- , SO_4^{2-} (oxo anions) only water molecule undergo oxidation to liberate O_2 at anode.
- During electrolysis of aqueous solution of alkali or alkaline earth metals, only water molecules undergo reduction to liberate hydrogen at cathode.

Feature	Cathode	Anode
Sign	Negative as attached to negative end of external battery	Positive as attached to positive end of external battery
Direction of movement of electrons	Into the cell	Out of the cell
Direction of movement of ions	Cations	Anions
Half-reaction	Reduction	Oxidation

Examples of Electrolysis

(i) Electrolysis of Molten or Fused NaCl:

Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

Cathode: $2Na^+ + 2e^- \rightarrow Na\ (s)$

Net reaction:

$2Na^+ + 2Cl^- \rightarrow Cl_2\ (g) + 2Na\ (s)$

(ii) Electrolysis of Aqueous NaCl Solution

$NaCl \rightarrow Na^+ + Cl$

$2Cl^- \rightarrow Cl_2 + 2e^-$ at +ve electrode

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

$2H^+ + 2e^- \rightarrow H_2$ at –ve electrode

As NaOH is in solution so pH increases.

At anode, Cl^- donate e^- as $E_{O.P.}$ or $Cl^- > E_{O.P.}$ of OH^-

At cathode, H^+ accept e^- as $E_{R.P.}$ of $H^+ > E_{R.P.}$ of Na^+

O_2 is not formed at anode here as over voltage is very high for it.

(iii) Electrolysis of H_2SO_4:

For pure H_2SO_4 electrolysis is not possible due to absence of ions.

$H_2SO_4 \leftrightarrow 2H^+ + SO_4^{-2}$

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

H_2 at –ve $\quad O_2$ at +ve

Solution becomes colourless and pH decreases as H_2SO_4 is formed.

If further electrolysis is done O_2 is released at anode and H_2 is released at cathode.

$$2H_2O \rightarrow \underset{\text{‘g’}}{O_2} + \underset{\text{‘aq’}}{4H^+} + 4e^-\ E = -1.23\ V$$

Electrolysis of some electrolytes

S. No	Electrolytes	Electrodes		Products		Electrode reactions	
		Anode	cathode	At anode	At cathode	At anode	At cathode
1	NaCl (fused)	Pt	Pt	Cl_2	Na	$2Cl^- \rightarrow Cl_2 + 2e$-	$Na^+ + e- \rightarrow Na$
2	$MgCl_2$ (fused)	Graphite	Steel	Cl_2	Mg	$2Cl^- \rightarrow Cl_2 + 2e^-$	$Mg^{2+} + 2e- \rightarrow Mg$

3	Al_2O_3 (fused) + cryolite	Graphite	Graphite	F_2	Al	$2F^- \rightarrow F_2 + 2e^-$	$Al^{3+} + 3e^- \rightarrow Al$
4	$NiCl_2$ (fused)	Pt	Pt	Cl_2	Ni	$2Cl^- \rightarrow Cl_2 + 2e^-$	$Ni^{2+} + 2e^- \rightarrow Ni$
5	NaCl (aq)	Pt	Pt	O_2, Cl_2	H_2	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $2Cl^- \rightarrow Cl_2 + 2e^-$	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
6	$AgNO_3$ (aq)	Pt Ag	Pt Pt	O_2 O_2, Ag^+	Ag Ag	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $Ag \rightarrow Ag^+ + e^-$	$Ag^+ + e^- \rightarrow Ag$ $Ag^+ + e^- \rightarrow Ag$
7	$CuSO_4$ (aq)	Pt	Pt	O_2	Cu	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	$Cu^{2+} + 2e^- \rightarrow Cu$
8	50% H_2SO_4 (aq)	Pt	Pt	$H_2S_2O_8$	H_2	$2HSO_4^- \rightarrow H_2S_2O_8 + 2e^-$	$2H^+ + 2e^- \rightarrow H_2$
9	K_2SO_4 (aq)	Pt	Pt	O_2	H_2	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
10	$CuCl_2$ (molten)	Pt Cu	Pt Pt	Cl_2 Cu^{2+}	Cu Cu	$2Cl^- \rightarrow Cl_2 + 2e^-$ $Cu \rightarrow Cu^{2+} + 2e^-$	$Cu^{2+} + 2e^- \rightarrow Cu$ $Cu^{2+} + 2e^- \rightarrow Cu$

REMEMBER

- The apparatus used for measurement of quantity of electricity is called Coulomefer.
- The amount of ion discharged doing electrolysis is independent of resistance of solution and temprature of bath.
- The art of electroplating was given by Faraday.

Product of Electrolysis

According to preferential discharge theory the ion will discharge first which required less energy. The potential at which ion get discharged is called deposition potential or discharge potential.

Discharge potential = Electrode potential + Over voltage

FARADAY'S LAWS OF ELECTROLYSIS

Faraday's First Law of Electrolytes

According to the first law, "The amount of substance or quantity of chemical reaction at electrode is directly proportional to the quantity of electricity passed into the cell".

$$W \text{ or } m \propto q$$

$$\text{or } W \propto It$$

$$W = Zit$$

$$Z = \frac{M}{nf}$$

Z = Electrochemical equivalence

M = molar mass

F = 96500

n = Number of electrons transfer

q = amount of charge utilized

Electrochemical equivalent is the amount of the substance deposited or liberated by one ampere current passing for one second (that is, one coulomb, $I \times t = Q$) or one coulomb of charge.

One gm equivalent of any substance is liberated by one faraday.

$$\text{Eq. Wt.} = Z \times 96500$$

$$\frac{W}{E} = \frac{q}{96500}$$

$$w = \frac{E.\ q.}{96500}$$

$$w = \frac{E\,i\,t}{96500}$$

As $w = a \times l \times d$ that is, area × length × density

Here a = area of the object to be electroplated

d = density of metal to be deposited

l = thickness of layer deposited

Hence from here we can predict charge, current strength time, thickness of deposited layer etc.

REMEMBER

One Faraday: One faraday is the quantity of charge carried by one mole of electrons.

$$E \propto Z$$

$$E = FZ$$

$$I\,F = 1.6023 \times 10^{-19} \times 6.023 \times 10^{23}$$

$$= 96500 \text{ Coulombs}$$

Faraday's Second Law of Electrolytes

According to the second law, "When the same quantity of electricity is passed through different electrolytes, the amounts of the products obtained at the electrodes are directly proportional to their chemical equivalents or equivalent weights".

As $\frac{W}{E} = \frac{q}{96500}$ = No. of equivalents constant

So

$$\frac{E_1}{E_2} = \frac{M_1}{M_2} \text{ or } \frac{W_1}{W_2} = \frac{Z_1 It}{Z_2 It} = \frac{Z_1}{Z_2}$$

E_1 = equivalent weight mass

E_2 = equivalent weight mass

W or M = mass deposited

From this law, it is clear that 96500 coulomb of electricity gives one equivalent of any substance Example, 1F = 1 gm eq

Application of Faraday's Laws

- It is used in electroplating of metals.
- In is used in the extraction of several metals in pure form.
- It is used in the separation of metals form non-metals.
- It is used in the preparation of compounds

REMEMBER

Current Efficiency

It is the ratio of the mass of the products actually liberated at the electrode to the theoretical mass that could be obtained

$$\text{C.E.} = \frac{\text{desired extent}}{\text{Theoretical extent of reaction}} \times 100\%$$

Illustrations

1. A solution of a salt of a metal of atomic weight 112 was electrolysed for 150 minutes with a current of 0.15 amperes. The weight of metal deposited was 0.783 mg. Find the equivalent weight and valency of the metal in the salt.

Solution Given: I = 0.15 ampere

$t = 150 \times 60$ seconds

$Q = I \times t$

$Q = 0.15 \times 150 \times 60$ coulombs

$= 1350$ coulombs

1350 coulombs of electricity deposit = 0.783 gm of metal

96540 coulombs of electricity

$$= \frac{0.783 \times 96540}{1350} \text{ gm } = 55.97 \text{ gm of metal}$$

Equivalent weight of metal = 55.97

$$\text{Valency of metal} = \frac{\text{Atomic weight}}{\text{Equivalent weight}}.$$

$$= \frac{112}{55.97} = 2$$

2. A current of 3.7 amperes is passed for 360 minutes between nickel electrodes of a 2 M solution of $Ni(NO_3)_2$. What will be the molarity of the solution at the end of the electrolysis? (At. wt. of Ni = 58.70)

Solution $Ni^{2+} + 2e^- \rightarrow Ni\ (s)$

$$w = \frac{E.\ i.\ t}{F}$$

$$= \frac{58.70 \times 3.7 \times 360 \times 60}{96500 \times 2} = 24.307 \text{ g}$$

Number of moles of Ni deposited

$$= \frac{24.307}{58.70} = 0.414 \text{ mole}$$

Molarity of remaining solution = 2.0 – 0.414

= 1.586 M

3. How many grams of silver could be plated out on a serving tray be electrolysis of a solution containing silver in +1 oxidation state for a period of 8.0 hours at a current of 8.46 amperes? What is the area of the tray if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm^3.

Solution $Ag^+ + 1e^- \rightarrow Ag\ (s)$

$$\text{Wt. of Ag} = \frac{E.\ i.\ t}{F}$$

$$= \frac{107.9 \times 8.46 \times 8 \times 60 \times 60}{96500} = 272.43 \text{ g}$$

$$\text{Volume of Ag} = \frac{\text{Wt. of Ag}}{\text{density}} = \frac{272.43}{10.5} = 25.94 \text{ ml}$$

$$\text{Area of tray} = \frac{\text{Volume}}{\text{Thickness}} = \frac{25.94}{0.00254}.$$

= 10212.6 cm^2

4. A copper coulometer and a silver coulometer were connected in series. The copper coulometer contained a 5% solution of $CuSO_4.5H_2O$ while the silver coulometer contained a 2% solution of $AgNO_3$. A current of 0.01 ampere was passed through the coulometers for 30 minutes. What was the ratio of the masses of Cu and Ag deposited at the cathode of the two coulometers respectively?

Solution W = Z. i. t

For copper

$$W = \frac{31.75}{96500} \times 0.01 \times 30 \times 60$$

= 0.0059 g

For silver

$$W = \frac{108}{96500} \times 0.01 \times 30 \times 60$$

= 0.0201 g

Thus ratio of the masses of Cu and Ag deposited at the cathode is

0.0059 : 0.0201 = 1 : 3.407

5. When an aqueous solution of copper (II) sulphate, CuSO4 is electrolyzed copper metal is deposited

$Cu^{2+}\ (aq) + 2e^- \rightarrow Cu\ (s)$

If a constant current was passed for 5.0 hour, 404 mg of copper metal was deposited, what must have been the current?

Solution According to Faraday's first law of electrolysis,

m = Z. i. t

$$404 \times 10^{-3} \text{ g} = \frac{63 \text{ g C}^{-1}}{2 \times 96500} \times i \times 5 \times 60 \times 60$$

$$i = \frac{0.404 \times 2 \times 96500}{63 \times 5 \times 60 \times 60}$$

= 0.0682 ampere

6. How long will it take 5 amperes of current to deposit 2 g of copper from a solution of copper sulphate? (Equivalent wt. of Cu = 32, F = 96500 C)

Solution W = Z . i. t

$$2 \text{ g} = \frac{32 \text{ g}}{96500 \text{ C}} \times 5 \text{ amp} \times t$$

$$t = \frac{2 \times 96500}{32 \times 5}$$

= 1206.25 s.

7. During the electrolysis of an aqueous solution of NaCl 10.3 g of chlorine was liberated. Calculate the volume of hydrogen that would be liberated at 20°C and 740 mm of Hg pressure from acidulated water, when the same quantity of current as that used in the electrolysis of NaCl was passed.

Solution

According to Faraday's law of electrolysis, as the current passed will be the same

$$\frac{\text{Weight of } H_2 \text{ liberated}}{\text{Eq. weight of } H_2} = \frac{\text{Weight of } Cl_2 \text{ liberated}}{\text{Eq. weight of } Cl_2}$$

$$\frac{\text{Weight of } H_2 \text{ liberated}}{1} = \frac{10.3}{35.5}.$$

$$\text{Weight of } H_2 \text{ liberated} = \frac{10.3}{35.5}\ \text{g}$$

As 2 g of H_2 occupies 22400 cc at NTP

$$\text{So } \frac{10.3}{35.5}\ \text{g occupies } \frac{22400 \times 10.3}{2 \times 35.5} = 3249 \text{ cc}$$

The volume of H_2 at 20°C and 740 mm of Hg pressure will be from

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V = \frac{3249 \times 760 \times 293}{273 \times 740} = 3582 \text{ cc}$$

ELECTRICAL CONDUCTANCE

Here, conductance is due to movement of ions through electrodes. It involves transfer of matter and ions. It occurs in small magnitude. Besides nature of material, the magnitude of conductivity also depends upon temperature and pressure at which the measurements are made.

- The conductivity of electrolytic solutions depends upon
  - (a) Nature of electrolyte
  - (b) Size of ions produced and their solvation (hydration)
  - (c) Nature of solvent and its viscosity
  - (d) Concentration of the electrolytes
  - (e) Temperature (direct relation)
- Electronic conductance through metals is known as metallic or electronic conductance and it is due to the moment of electrons the conductivity of metals depends upon:
  - (a) Nature of structure of metal
  - (b) Number of valence electrons per atom
  - (c) Density of metal
  - (d) Temperature (inverse relation)
- As the electrons enter at one end go out at the other end, the composition of the metallic conductor remains unchanged. In contrast to electrolytic conductance, electronic conductance decreases with increase in temperature.

Ohm's Law

According to Ohm's law,

$$\frac{E}{I} = \text{constant (R)}$$

or

$$I = \frac{E}{R}$$

E = potential, R = resistance

Unit : Ω ohms

Resistance (R)

It offers obstruction to the passage of electric current. It is directly proportional to the length (l) and inversely proportional to the area of cross section (a) of the conductor.

$$R \alpha 1/a \text{ or } R = \frac{\varrho l}{a}$$

Specific Resistance (ϱ)

The resistance offered by one cm^3 of the conductor is known as specific resistance.

If l = 1 cm

If a = 1 cm^2

$R = \varrho$

$\varrho = R.\frac{a}{l}$ ohm. cm.

Conductance (C)

It is ease of flow of electric current through the conductor and it is reciprocal of resistance.

$$C = \frac{1}{R}\ \Omega^- \text{ (mho)}$$

$1S = 1\ \Omega^-$

siemens

Specific Conductance (k, kappa)

It is the reciprocal of specific conductance.

$$k = \frac{1}{\varrho} = \frac{1}{R} \cdot \frac{l}{a}$$

$\frac{l}{a}$ = cell constant

Unit: $\Omega^{-} cm^{-1}$

- If 'l' and 'a' are unity then conductance of one c.c. is called specific conductance or conductivity

Cell Constant

$$\text{Cell constant} = \frac{\text{Specific conductance}}{\text{Measured conductance}}$$

Conductance is measured by using wheat stone bridge method (for R) and 1N or .01 N KCl solution for [l/a]

Effect of Dilution on specific Conductance

The number of current carrying particles or ions per ml decrease on dilution and specific conductivity, being the conductance of one centimeter cube of solution, decreases with dilution.

Equivalent Conductivity

The conductivity of all the ions produced when one gram equivalent of an electrolyte is dissolved in V ml of solution is called equivalent conductivity. It is denoted by λv or Λv.

λ or $\Lambda = k \times V$.

Unit: $\Omega^{-1} c. m^2$

As $\frac{W}{E} = \frac{NV}{1000}$

So $\lambda = \frac{k \times 1000}{N}$

- The equivalent conductivity increases with increase of dilution.

Molar Conductivity

The conductivity of all the ions produced when one mole of an electrolyte is dissolved in V ml of solution is known as molar conductivity.

$$\lambda m \text{ or } \Lambda m = \frac{1000 \times k \times V}{\text{M (molarity)}}$$

Factors Affecting the Molar Conductivity (Λm)

- **Nature of Electrolyte**: Strong electrolytes like HCl, H_2SO_4, NaOH, KOH, KNO_3, KCl, NH_4NO_3 etc., are completely ionized in aqueous solution so have high value of molar conductivity.

As weak electrolytes like H_2CO_3, CH_2COOH, NH_4OH etc., are ionized to lesser extent in aqueous solution so have lower value of molar conductivity.

- **Temperature**

$\Lambda m \propto$ Temperature

As the increase of temperature decreases inter ionic attractions, solvation of ions, viscosity and increases kinetic energy of ions and their speed so Λm increases with the increase of temperature.

- **Dielectric Constant of Solvent**: Higher the value of dielectric constant of a solvent, the more is the value of molar conductivity as it decreases inter ionic attractions.

- $K = \frac{C. (\Lambda^{o}/\Lambda_{M})_2}{1 - \Lambda^{o}/\Lambda_{M}}$.

- **Viscosity of Solvent**

$\Lambda m \ \alpha \ 1/\eta$

that is, higher the value of viscosity lower is the value of molar conductivity.

Effect of Dilution on Molar Conductivity

Molar conductivity increases with dilution as degree of dissociation of electrolyte increase with dilution. At ∞ Dilution Λ is maximum i.e., Λ_∞ is maximum.

$$\alpha = \frac{\Lambda v}{\Lambda_\infty}$$

- **Concentration of the Solution**

As the concentrated solutions of strong electrolytes have significant inter ionic attractions, which reduces the speed of ions so lowers the value of molar conductivity. As the dilution decreases such attractions so increases the value of molar conductivity.

The limiting value of Λm (Λm^∞ the molar conductivity at zero concentration or at infinite dilution) can be obtained by extrapolating the graph shown below.

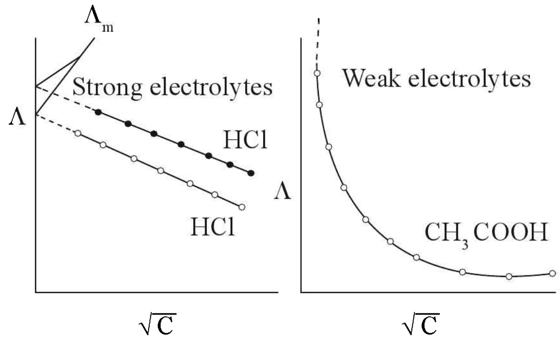


Fig (a) Fig (b)

Variation of molar conductance (Λ) with square root of concentration $\sqrt{C}$ (a) Strong electrolytes and (b) Weak electrolytes

The variation in molar conductance with concentration is different for strong and weak electrolytes.

Debye–Huckel–Onsagar Equation

It shows a relation between molar conductivity at a particular concentration and molar concentration at infinite dilution as follows:

$\Lambda m = \Lambda m^{\infty} - b\sqrt{C}$

or

$\mu = \mu_{\infty} - b\sqrt{C}$

Here, b = Constant,

C = Concentration;

Λm^{∞} or μ_{∞} = Molar conductance at infinity.

Λm or μ = Molar conductance at other dilutions The value of b for a given solvent and temperature depends upon the nature of electrolyte that is, the charges on cation and anion produced after dissociation (thus NaCl, $CaCl_2$, $MgSO_4$ are known as 1–1, 2–1 and 2–2 electro lies respectively). All electrolytes of a particular type have same value of b. The value of b is obtained from the slope value.

Kohlrausch Law

Kohlrausch examined Λ° or Λ^{∞} values for a number of strong electrolytes and observed certain regularities. He noted that the difference in Λ° of the electrolytes NaX and KX for any X in nearly constant.

On the basis of these observations he introduced **Kohlrausch law of Independent Migration of ions.** The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. that is, at infinite dilution, the contribution of any ion towards equivalent conductance is constant; it does not depend upon presence of any ion.

For any electrolyte:

$P_X Q_Y \rightleftharpoons XP^{+y} + YQ^{-X}$

$\Lambda^{\circ} = X\lambda^{\circ}_{+} + Y\lambda^{\circ}_{-}$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$\Lambda^{\infty}_m (CH_3COOH) = (\Lambda^{\infty}_{H} + \Lambda^{\infty}_{Cl^-}) + (\Lambda^{\infty}_{CH_3COO^-} + \Lambda^{\infty}_{Na^+})$

$-(\Lambda^{\infty}_{Na^+} - \Lambda^{\infty}_{Cl^-})$

$= \Lambda^{\infty}_{HCl} + \Lambda^{\infty}_{CH_3COONa} - \Lambda^{\infty}_{Nacl}$

Application of Kohlrausch's Law

1. Determination of $\Lambda^{\circ}B$ of a weak electrolyte:

In case of weak electrolytes, the degree of ionization increases which increases the value of Λm. However, it cannot be obtained by extrapolating the graph. The limiting value, Λm^{∞}, for weak electrolytes can be obtained by Kohlrausch law.

for example in case of NH_4OH

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$\Lambda^{\infty}_m (NH_4OH) = (\Lambda^{\infty}_{NH_4} + \Lambda^{\infty}_{Cl^-}) + (\Lambda^{\infty}_{Na^+} + \Lambda^{\infty}_{\overline{OH}})$

$-(\Lambda^{\infty}_{Na^+} - \Lambda^{\infty}_{Cl^-})$

$= \Lambda^{\infty}_{NH_4Cl} + \Lambda_{NaoH} - \Lambda^{\infty}_{Nacl}$

2. To determine degree of dissociation and equilibrium constant of weak electrolyte:

$$\begin{array}{cccc} CH_3COOH & \rightleftharpoons & CH_3COO^- \; + & H^+ \\ C & & 0 & 0 \\ C - C\alpha & & C\alpha & C\alpha \end{array}$$

Here C = Initial concentration

α = Degree of dissociation

$\alpha = \frac{\Lambda^{\circ}}{\Lambda_M}$.

Here Λ° or Λ^{∞} = Molar conductance at infinite dilution or zero concentration.

Λ_M = Molar conductance at given conc. C

$$K = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]}$$

$$K = \frac{C\alpha \,.\, C\alpha}{C(1-\alpha)}$$

$$K = \frac{C\alpha^2}{1 - \alpha}.$$

$$K = \frac{C.\ (\Lambda^o/\Lambda_M)^2}{(1 - \Lambda^o/\Lambda_M)}.$$

$$= \frac{C\ (\Lambda^o)^2}{\Lambda^o\ (\Lambda^o - \Lambda_m)}$$

These are Ostwald's relations.

3. To determine solubility of salt and K_{sp}:

$AgCl\ (s) \rightleftharpoons Ag^+ + Cl^-$

$$\Lambda^o = \frac{1000\ K}{M}$$

$$\Lambda^o = \lambda^o Ag^+ + \lambda^o Cl^-$$

$$M = \frac{1000\ K}{\Lambda^o}$$

Here M = Solubility of AgCl

Solubility product:

$Ksp = [Ag^+]\ [Cl^-]$

As $[Ag^+] = [Cl^-]$

$$Ksp = \frac{1000\ K}{\Lambda^o} \times \frac{1000\ K}{\Lambda^o}$$

$$Ksp = (1000\ K/\Lambda^o)^2$$

Illustrations

8. Calculate the equivalent conductivity of 1M H_2SO_4 solution, if its conductivity is 26×10^{-2} $ohm^{-1}\ cm^{-1}$. (Atomic weight of sulphur = 32)

Solution $N = nM = 2 \times 1\ M = 2N$

As H_2SO_4 is a diprotic acid so n = 2

k = Specific conductivity = $26 \times 10^{-2}\ ohm^{-1}\ cm^{-1}$

$$\Lambda eq = \frac{1000\ k}{N} = ohm^{-1}\ cm^2\ equiv^{-1}$$

$$= \frac{1000 \times 26 \times 10^{-2}}{2N}$$

$$= 1.3 \times 10^2\ ohm^{-1}\ cm^2\ equiv^{-1}$$

9. If Λ^∞_m of HCl, NaCl and CH_3COONa are 425, 128 and 96 $\Omega^{-1}\ cm^2\ mol^{-1}$ respectively, calculate the value of Λ^∞_m for acetic acid.

Solution $\Lambda^\infty_{m\ CH3COOH} = \Lambda^\infty_{m\ CH3COOH} + \Lambda^\infty_{m\ HCl} - \Lambda^\infty_{mNaCl}$

$= 96.0 + 425.0 - 128.0$

$= 393.0\ \Omega^{-1}\ cm^2\ mol^{-1}$

10. A salt solution of 0.30 N placed in a cell whose electrodes are 1.9 cm apart and 3.6 cm^2 in area offers a resistance pf 20 Ω. Calculate equivalent conductivity of solution.

Solution $R = 20\ \Omega, l = 1.9\ cm$

$a = 3.6\ cm^2,\ N = 0.30\ N$

$$\text{Cell constant} = \frac{l}{a} = \frac{1.9}{3.6} = 0.528\ cm^{-1}$$

Specific conductance (k) = conductance × cell constant = (1/R) × cell constant

$= (1/20) \times 0.528$

$= 0.0264\ s\ cm^{-1}$

$$\Lambda_{eq} = \frac{k \times 1000}{N} = \frac{0.0264 \times 1000}{0.30}$$

$= 88\ s\ cm^2\ eq^{-1}$.

11. 0.05 M NaOH solution offered a resistance of 31.16 Ω in a conductivity cell at 298 K. If cell constant is 0.367 cm^{-1}. Find out the molar conductivity of NaOH solution.

Solution $$\text{Conductivity (k)} = \frac{\text{Cell constant}}{R}$$

$$= \frac{0.367}{31.16} = 0.0118\ s\ cm^{-1}$$

$$\Lambda_m = \frac{k \times 1000}{M} = \frac{0.0118 \times 1000}{0.05}$$

$= 236\ s\ cm^2\ mol^{-1}$

12. The molar conductivities of CH_3COOH at 25°C at the concentration of 0.1 M and 0.001 M are 5.20 and 49.2 $s\,cm^2\,mol^{-1}$ respectively. Calculate the degree of dissociation of CH_3COOH at these concentrations. (Λ^∞_m (CH_3COOH) = 390.7 s $cm^2\ mol^{-1}$)

Solution $$\text{Degree of dissociation } (\alpha) = \frac{\Lambda^c_m}{\Lambda^\infty_m}$$

$$= \frac{5.20}{390.7} = 0.013 = 1.3\%$$

$$0.001\text{ M} = \frac{49.2}{390.7} = 0.125 = 12.5\%$$

Electrochemical Cell or Galvanic Cell or Voltaic Cell

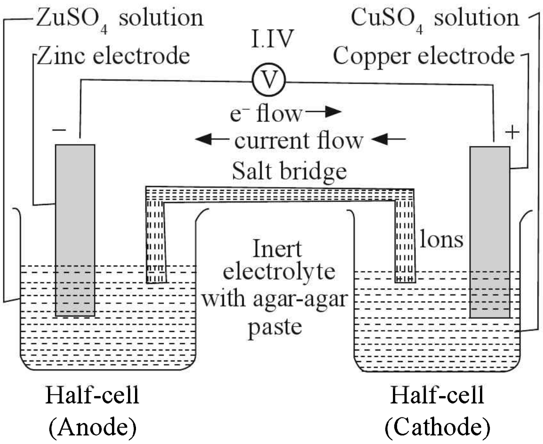
It is the device in which the decrease of free energy during the indirect redox reaction is made to convert chemical energy into electrical energy.

Galvanic and Voltaic developed such devices therefore these cells are also known as Galvanic cells or Voltaic cell or Redox cells.

Feature	Cathode	Anode
Sign	Positive due to consumption of electrons	Negative due to release of electrons
Reaction	Reduction	Oxidation
Movement of electrons	Into the cell	Out of cell

Electrochemical Cell	Electrolytic Cell
It is a combination of two half cells, containing the same or different electrodes in the same or different electrolytes.	It is a single cell containing the same electrodes present in the same electrolyte.
Anode is negative, cathode is positive	Anode is positive, cathode is negative
Electrons move from anode to cathode in external circuit	Electrons enter through cathode and leave through anode.
It converts chemical energy into electrical energy, produced as a result of redox reaction.	It converts electrical energy into chemical energy. Energy is supplied to the electrolytic solution to bring about the redox reaction.
Cell reaction is spontaneous.	Cell reaction is non spontaneous.
Salt bridge is required.	No salt bridge is required.

Galvanic or Daniel cell



DANIEL CELL

- The Daniel cell is a typical galvanic cell. It is designed to make use of the spontaneous redox reaction between zinc and cupric ion to produce an electric current.
- The Daniel cell can be conventionally represented as

$$\text{Zn (s)} \mid \text{ZnSO}_4\text{ (aq)} \underset{\text{Saltbridge}}{\mid\mid} \text{CuSO}_4\text{ (aq)} \mid \text{Cu(s)}$$

- The Daniel cell reaction is represented as

$$\text{Zn (s)} + \text{Cu}^{2+}\text{ (aq)} \rightarrow \text{Zn}^{2+}\text{ (aq)} + \text{Cu (s)}$$

- In Daniel cell, electrons flow from zinc electrode to copper electrode through external circuit while metal ions flow form one half cell to the other through salt bridge.
- Here current flows from copper electrode to zinc electrode that is, cathode to anode in external circuit.
- Daniel cell is a reversible cell while a voltaic cell may be reversible or irreversible.

A voltaic cell is reversible only when it satisfies following conditions:

- The emf of external source is more than that of voltaic cell so that current may flow from external source into the voltaic cell and cell reaction can be reversed.
- If emf of voltaic cell is more than that of external source current flows from voltaic cell into external source.

Saltbridge

It maintains electrical neutrality in two compartments by allowing movement of anions towards anodic compartment and cations towards cathodic compartment.

- It is a glass tube having KCl, KNO_3, ammonium nitrate in a gelatin gel or agar–agar past.
- The gelatin gel allows ionic movement through it but prevents any kind of mixing.
- In case of KCl or ammonium nitrate, the ionic mobility of cation and anion are same.

Function of a Saltbridge

- A salt bridge acts as an electrical contact between the two half-cells.
- It prevents mechanical flow of solution but it provides free path for the migration of ions to maintain an electric current through the electrolyte solution. It prevents the accumulation of charges.
- A salt bridge helps in maintaining the charge balance in the two half cells.
- A salt bridge minimizes/eliminates the liquid junction potential.

Liquid Junction Potential: The unequal rates of migration of the cations and anions across a liquid-liquid junction give rise to a potential difference across the junction. This potential difference across the liquid-liquid junction is called liquid junction potential.

REMEMBER

- If salt bridge is removed the emf of the cell drops to zero.

Electrodes or Half Cells

- An electrode and the solution in which it is dipped is called a half-cell.
- Half cells are called anodic half cells and cathodic half cells.
- The electrode at which oxidation takes place is called anode.
- The electrode at which reduction takes place is called cathode.
- Anode is positively charged and cathode is negatively charged in electrolytic cell.
- In voltaic cell anode has negative charge as the electron will flow from it.
- In voltaic cell cathode has positive charge as the electrons are drawn from it.
- At anode deelectronation or oxidation occurs as the elements goes into the solution due to loss of electrons by ions.
- At cathode electronation or reduction process occurs as ions gain electron and get discharged here.

Types of Electrodes or Half Cells

The various types of electrodes which are frequently used in the electrochemical cells are as follows:

1. **Metal-Metal Ion Electrode**: It includes a metal strip dipped in the solution of its own cations.

   Example, Zn/Zn^{2+}, Cu/Cu^{2+}, Ag/Ag^{+} etc.

2. **Amalgam Electrode:** It is similar to metal-metal ion type electrode, but here, metal is replaced by its amalgam with Hg. This is done to improve the activity of metal.

   Example, $Zn – Hg/Zn^{2+}$

3. **Gas Electrode**: It involves the inert metal foil like Pt immersed in the solution capable of furnishing ions of gas.

   Example, Pt, H_2/H^+ and Pt, Cl_2/Cl^-

4. **Metal-Metal Insoluble Salt-Salt Anion**: This type of electrode includes metal in contact with its sparingly soluble salt and aqueous solution of solution salt containing same anion.

   Example, $Hg– Hg_2Cl_2$ (s) – KCl (aq) Calomel electrode

   $Pb– PbSO_4$ (s) – K_2SO_4 (aq)

5. **Redox Electrode**: This electrode includes a platinum wire dipped in a solution of mixture of the two salts of the same metal but with different oxidation states.

   Example, Pt, Fe^{2+}/Fe^{3+}.

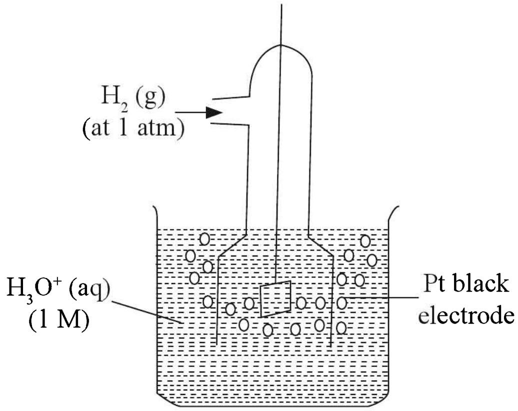
6. **Glass Electrode**:

   It consists of a thin walled glass bulb made out of special types of low melting glass.

Glass electrodes are not affected by oxidizing and reducing agents and are not easily poisoned so they are finding great applications, in industry, in analytical chemical and biological laboratories in the measurement of pH.

Glass electrode gives very good results for pH value ranging between 0 and 6. For solutions of high alkalinity, high accuracy is not obtained.

7. Standard Hydrogen Electrode (SHE):



Hydrogen electrode

A hydrogen electrode in which pressure of hydrogen gas is maintained at 1 atm and the concentration of H^+ ions in the solution is 1 M, is called a standard hydrogen electrode (SHE).

SHE half reaction	Electrode potential
$H_2 \rightarrow 2H^+ + 2e^-$	0.0 V (Anode)
$2H^+ + 2e^- \rightarrow H_2$	0.0 V (Cathode)

- The emf of a standard hydrogen electrode is taken as 0.00 V at all temperature.
- It is a reversible electrode.
- It is used as a reference electrode.
- A saturated calomel electrode is also used as a secondary reference electrode. It has a potential of –0.24 volt.

8. Electrode Potential or Single Electrode Potential:

It is the tendency of an electrode to accept or to lose electrons.

When a metal strip M is placed in contact with the solution of its own ions M^{n+}, an electrical potential difference is set up between the metal strip and the solution due to either of the two tendencies.

Oxidation: $(M \leftrightarrow M^{n+} + ne^-)$

Reduction: $(M^{n+} + ne^- \leftrightarrow M)$

- The electrical potential difference between metal strip and solution is known as half cell electrode potential (E).
- Single electrode potential cannot be measured experimentally.
- The potential difference between two single electrodes can be measured by using Potentiometer.
- The tendency of oxidation can be represented by oxidation potential (E_{oxi}).
- The tendency of reduction can be represented by reduction potential (E_{red}).
- Oxidation potential of element is same in magnitude but opposite in sign to the reduction potential, that is, ($E_{red} = -E_{oxi}$). Therefore, by conventions, the electrode potentials (E) are represented by their reduction potentials E_{red}.
- E_{red} values vary with the concentration of the ions in solution at particular temperature. The reduction potential of the electrode at standard state conditions (1 molar conc. of the ions, 298 K and 1 atm pressure) is called Standard reduction potential (E°).
- The absolute values of E° for any electrode can not be determined because it is impossible to work with single half cell hence the E° values are determined with respect to standard hydrogen electrode (SHE) whose standard electrode potential (E°) is taken to be zero by conventions.
- E° is an intensive property like temperature or molar volume. This means that E° is same for half cell reaction whether it is represented as

  $2X^+ + 2e^- \rightarrow X_2$

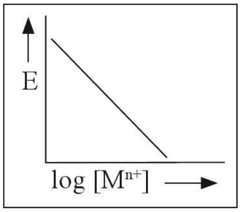
  $X^+ + e^- \rightarrow \frac{1}{2} X_2$.
- E° values are not thermodynamic functions and may not be added directly. However, they can be calculated from free energy which is extensive property.

The value of electrode potential developed on an electrode depends upon

- Temperature of the system.
- Concentration of ions in solutions.
- Chemical nature of the metal or non metal
- Number of electrons transferred in the half cell reaction
- It does not depend upon length of electron.

Types Of Electrode Potential

(i) **Oxidation Potential**: When electrode is negatively charged with respect to solution then it acts as anode and oxidation takes place here.



$M \rightarrow M^{n+} + ne^-$

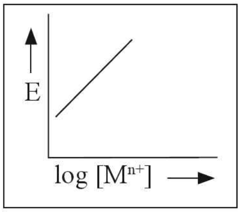
$$E_{OX} = E^\circ_{OX} - \frac{2.303\ RT}{nF} \cdot \log_{10} [M^{n+}]$$

Here

Intercept = E°_{OX}

$$\text{Slope} = \frac{-2.303\ RT}{nF}$$

(ii) **Reduction potential**: When electrode is positively charged with respect to solution then it acts as cathode and reduction takes place here.



$M^{n+} + ne^- \rightarrow M$

$$E_{red} = E^\circ_{red} \frac{-2.303\ RT}{nF} \log_{10} \frac{1}{[M^{n+}]} .$$

$$E_{red} = E^\circ_{red} + \frac{2.303\ RT}{nF} \log_{10} [M^{n+}]$$

Here

Intercept = E°_{red}

$$\text{Slope} = \frac{2.303\ RT}{nF}$$

EMF of the Cell or Cell Voltage

It is the potential difference between the two terminals of the cell when no current is drawn from it. It is measured with the help of potentiometer or vacuum tube voltmeter.

Calculation of the EMF of the Cell

Mathematically, it may be expressed as

$$E_{cell} \text{ or EMF} = [E_{red} \text{ (cathode)} - E_{red} \text{ (anode)}]$$

$$E^\circ_{cell} \text{ or EMF}^\circ$$

$$= [E^\circ_{red} \text{ (cathode)} - E^\circ_{red} \text{ (anode)}]$$

- For cell reaction to occur the E_{cell} should be positive. This can happen only if E_{red} (cathode) > E_{red} (anode).
- E°cell must be positive for a spontaneous reaction.
- Rate of reaction is directly proportional to the emf of the cell.
- The emf of the cell depends on the intensity of the reaction in the cell.
- It measures free energy change for maximum convertibility of heat into useful work.
- It causes flow of current from higher value of E° electrode to lower E° value electrode.

Difference between EMF and Cell Potential

EMF	**Cell potential**
It is measured by potentiometer.	It is measured by voltmeter.
It is potential difference between two electrodes when no current is flowing in the circuit	It is potential difference between two electrodes when current is flowing through the circuit
It is maximum voltage obtained from cell	It is less than maximum voltage
It corresponds to maximum useful work obtained from galvanic cell.	It does not correspond.

Nernst Equation

This equation gives the relationship between electrode potential and concentration of ions in the solution.

Or

It shows the dependency of electrode potential on the concentration of the ions with which the electrode is reversible.

For a single electrode involving the reduction process,

$M^{n+} + ne^- \rightarrow M$

The Nernst equation is

$$E = E^\circ + \frac{2.303\ RT}{nF} \log_{10} \frac{[M^{n+}]}{[M]}$$

or

$$E = E^\circ \frac{-2.303\ RT}{nF} \log_{10} \frac{[M]}{[M^{n+}]}.$$

At 25°C or 298 K

$$E = E^\circ + \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log_{10} \frac{[M^{n+}]}{[M]}$$

$$E = E^\circ + \frac{0.059}{n} \log_{10} \frac{[M^{n+}]}{[M]}$$

or

$$E = E^\circ - \frac{0.059}{n} \log_{10} \frac{[M]}{[M^{n+}]}.$$

Here R = Gas constant

T = Absolute temperature

E° = emf of the cell

E = Electrode potential of cell

F = Faraday number

n = number of electrons transferred

- If electrode is solid its active mass is taken as one.
- For an electrochemical cell having net reaction

$$xA + yB \xrightarrow{ne^-} mC + nD,$$

The emf can be calculated as

$$Ecell = E^\circ cell + \frac{0.059}{n} \log \frac{[A]^x\ [B]^y}{[C]^m\ [D]^n}$$

In using the above equation, the following facts should be kept in mind.

- Concentration or activity of gases is expressed in terms of their partial pressures.
- n, the number of electrons transferred should be calculated from the balanced net cell reaction
- Concentration or activity of solids in taken to be unity.

Equilibrium Constant and Cell Potential

$E_{cell} = E^\circ_{cell} - 0.0591/n \log Q$

At equilibrium

$E_{cell} = 0, Q = K$

$$0 = E^\circ_{cell} - \frac{0.0591}{n} \log_{10} K$$

$$\log_{10} K = \frac{E^\circ_{cell} \cdot n}{0.0591}.$$

- **Relationship between free energy change (ΔG) and cell potential (E)**: Electrical work done in one second is equal to electrical potential multiplied by total charge passed. If we want to obtain maximum work from a galvanic call then charge has to be passed reversibly. The reversible work done by a galvanic cell is equal to decrease in its Gibbs energy and therefore, if the emf (it is the potential of the cell when no current is drawn) of the cell is E and nF is the amount of charge passed and ΔG is the Gibbs energy of the reaction then

$\Delta G = -nF\ Ecell$

for standard state conditions,

$\Delta G^\circ = -nF\ E^\circ cell$

Thermodynamics Relationship of Cell

(i) **Gibbs-Helmholtz equation:**

$$\Delta G = \Delta H + T \left(\frac{\partial}{\partial T} \Delta G\right)_P$$

Here ΔH = Change in enthalpy

T = Temperature

(ii) Temperature Coefficient:

$$\Delta G = \Delta H + T \left(\frac{\partial}{\partial T} \Delta G\right)_P$$

$$-n FE_{cell} = \Delta H + T \left[\frac{\partial}{\partial T} (-nF\ E_{cell})\right]_P$$

$$\Delta H = -nF\ E_{cell} + nFT \left(\frac{\partial}{\partial T} E_{cell}\right)_P$$

$$\left(\frac{\partial}{\partial T} E_{cell}\right)_P = \text{Temperature coefficient}$$

(iii) Change in Entropy:

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

$\Delta G - \Delta H = -T\Delta S$ ……. (i)

$$\Delta G = \Delta H + T \left(\frac{\partial}{\partial T} \Delta G\right)_P$$

$$\Delta G - \Delta H = T \left(\frac{\partial}{\partial T} \Delta G\right)_P \quad \text{…… (ii)}$$

From equation (i) and (ii), we get

$$-T\Delta S = T\left(\frac{\partial}{\partial T}\Delta G\right)_P$$

$$\Delta S = -\left(\frac{\partial}{\partial T}\Delta G\right)_P$$

$$\Delta S = +nF\left(\frac{\partial}{\partial T}E_{cell}\right)_{P'}$$

Concentration Cells

Concentration cell is one in which emf arises as a result of different concentrations of the same electrolyte in the component half-cells.

- The two solutions are connected by a salt bridge and the electrodes are joined by a piece of metallic wire.
- The reduction occurs in the more concentrated compartment while oxidation occurs in the diluted compartment.

$$E = E^\circ - \frac{2.303\,RT}{nF}\log\frac{[C_2]}{[C_1]}$$

or

$$E = E^\circ + \frac{2.303\,RT}{nF}\log\frac{[C_1]}{[C_2]}$$

Concentration cells are of following two types:

(i) Electrode concentration cell

(ii) Electrolyte concentration cell

(i) Electrode Concentration Cell: When emf is produced between two similar electrodes at different concentrations dipped in the same solution of electrolyte.

Pt, $H_2\ (p_1)\ |\ H^+\ |\ H_2\ (p_2)$, Pt

Anode Cathode

At anode: $\frac{1}{2}H_2\ (p_1) \rightarrow H^+ + 1e^-$

At cathode: $H^+ + 1e^- \rightarrow \frac{1}{2}H_2\ (p_2)$

Cell reaction: $\frac{1}{2}H_2\ (p_1) \rightarrow \frac{1}{2}H_2\ (p_2)$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{1}\log_{10}(p_2/p_1)^{1/2}$$

$$E_{cell} = \frac{0.0591}{2}\,.\,\log_{10}\frac{p_1}{p_2}\,.$$

(ii) Electrolyte Concentration Cell: When identical electrodes are dipped into the solutions of same electrolyte of different concentration, emf produced due to the difference in concentration is called liquid-junction potential. This type of cell is called electrolyte concentration cell.

$Cu\ |\ Cu^{2+}\ (C_1)\ ||\ Cu^{2+}\ (C_2)\ |\ Cu$

(–)	Salt	(+)
Anode	bridge	Cathode

At anode: $Cu \rightarrow Cu^{2+}\ (C_1) + 2e^-$

At Cathode: $Cu^{2+}\ (C_2) + 2e^- \rightarrow Cu$

Cell Reaction: $Cu^{2+}\ (C_2) \rightarrow Cu^{2+}\ (C_1)$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\,.\,\log_{10}\frac{C_2}{C_1}\,.$$

$$E_{cell} = \frac{0.0591}{2}\log_{10}\frac{C_2}{C_1}\,.$$

Illustrations

13. If $E^\circ Fe^{2+}/Fe = -0.441$ V and $E^\circ Fe^{3+}/Fe^{2+} = 0.771$ V, the standard EMF of the reaction will be

$Fe + 2Fe^{3+} \rightarrow 3Fe^{2+}$

Solution $E^\circ Fe^{2+}/Fe = -0.441$ V

$E^\circ Fe^{3+}/Fe^{2+} = 0.771$ V

If $E^\circ cell = E^\circ OPFe/Fe^{2+} + E^\circ RPFe^{3+}/Fe^{2+}$

$= +0.441 + 0.771 = 1.212$ V

Illustrations

14. For a Ag-Zn button cell, net reaction is

$Zn(s) + Ag_2O\ (s) \rightarrow ZnO\ (s) + 2Ag\ (s)$

$\Delta G^\circ_f\ (Ag_2O) = -11.21$ kJ mol^{-1}

$\Delta G^\circ_f\ (ZnO) = -318.3$ kJ mol^{-1}

Find the E°cell of the button cell here.

Solution $\Delta G^\circ = \Delta G_f\ (ZnO) - \Delta G_f\ (Ag_2O)$

$= -318.30 + 11.21 = -307.09$ kJ

$= -307.09 \times 10^3$ J

$\Delta G^\circ = -nFE^\circ cell$

$-307.09 \times 10^3 = -2 \times 96500 \times E^\circ cell$

$E^\circ cell = 1.591$ V

Illustrations

15. The observed emf of the cell

Pt | H_2 (1 atm) | H^+ (3×10^{-4} M) || H^+ (M_1) | H_2 (1 atm) | Pt

is 0.154 V. Calculate the value of M_1 and pH of cathodic solution.

Solution $E_{cell} = 0.0591 \log_{10} \frac{M_1}{3 \times 10^{-4}}$.

$$\log_{10} \frac{M}{3 \times 10^{-4}} = \frac{0.154}{0.0591} = 2.6058$$

$$\frac{M_1}{3 \times 10^{-4}} = 4.034 \times 10^2$$

$$M_1 = 4.034 \times 10^2 \times 3 \times 10^{-4}\ M$$

$$= 0.121\ M$$

$$pH = -\log_{10} [H^+] = -\log_{10} 0.121 = 0.917$$

16. Calculate the cell potential for the cell containing 0.10 M Ag^+ and 4.0 M Cu^{2+} at 298 K.

Given $E°Ag^+/Ag = 0.80$ V

$E°Cu^{2+}/Cu = 0.34$ V

Solution Cu (s) | Cu^{2+} (4.0 M) || Ag^+ (0.1 M) | Ag (s)

Here n = 2;

$$E = E°_{cell} + \frac{0.0591}{2} \log \frac{[Ag^+]^2}{[Cu^{2+}]}$$

$$= 0.80 - 0.34 + \frac{0.0591}{2} \log_{10} \frac{[0.1]^2}{[4.0]}$$

$$= 0.46 + 0.0295 \times \log_{10} 2.5 \times 10^{-3}$$

$$= 0.46 - 0.07676 = 0.3832\ V$$

17. Calculate the e.m.f of the following cell at 298 K.

Zn | Zn^{2+} (0.1 M) || Ag^+ (0.01 M) | Ag

Given: $E°Zn^{2+}/Zn = -0.76$ C

$E°Ag^+/Ag = +0.80$ V

Solution $E_{cell} = E°_{cell} + \frac{0.0591}{n} \log \frac{[Ag^+]^2}{[Zn^{2+}]}$

$$= 0.80 - (-0.76) + \frac{0.0591}{2} \log_{10} \frac{[0.01]^2}{[0.1]}$$

$$= 1.56 + \frac{0.0591}{2} \log_{10} 1 \times 10^{-3}$$

$$= 1.56 - 0.08865 = 1.471\ V$$

18. Find the EMF of the following cells:

Fe | Fe^{2+} || Sn^{2+} | Sn $E°_{Fe} = -0.44$ V

a = 0.6 a = 0.2 $E°_{Sn} = +0.14$ V

Solution Fe | Fe^{2+} || Sn^{2+} | Sn

$$E°_{cell} = E°_R - E°_L$$

$$= 0.14 - (-0.44) = 0.58\ V$$

Cell reaction

$$Fe + Sn^{2+} \rightarrow Fe^{2+} + Sn$$

According to Nernst's equation,

$$E = E° - \frac{0.059}{N} \log_{10} \frac{[Fe^{2+}]}{[Sn^{2+}]}$$

$$= 0.58 - \frac{0.059}{2} \log_{10} \frac{0.6}{0.2}$$

$$= 0.58 - 0.0295 \log_{10} 3$$

$$= 0.58 - 0.0295 \times 0.4771$$

$$= 0.58 - 0.014$$

$$= 0.566\ V$$

19. Find the pH of the following half-cell

Pt H_2/H_2SO_4.

The oxidation electrode potential = 0.3 V.

Solution $H_2 \rightarrow 2H^+ + 2e^-$

$$E = E° - \frac{0.059}{N} \log_{10} \frac{[H^+]^2}{[H_2]}$$

$$0.3 = 0 - \frac{0.059}{2} \log_{10} [H^+]^2$$

$$-\log [H^+] = \frac{0.3}{0.059} = 5.08$$

$$pH = 5.08$$

20. Calculate the cell potential of the given cell at 25°C. (R = 8.31 J K^{-1} mol^{-1}, F = 96500 C mol^{-1}).

$Ni (s) | Ni^{2+} (0.01 M) || Cu^{2+} (0.1 M) | Cu(s)$

Given: $E^o Cu^{2+}/Cu = +0.34$ V

$E^o Ni^{2+}/Ni = -0.25$ V

Solution $E_{cell} = E^o_{cell} + \frac{2.303\ RT}{nF} \log_{10} \frac{[Cu^{2+}]}{[Ni^{2+}]}$

$$= 0.34 - (-0.25) + \frac{2.303 \times 8.31 \times 298}{2 \times 96500} \log \frac{0.1}{0.01}$$

$$= 0.59 + \frac{0.0591}{2} \log_{10} 10 = 0.6195 \text{ V}$$

21. The emf of a cell corresponding to the reaction,

$Zn + 2H^+ (aq) \rightarrow$

Zn^{2+} (0.1 M) + H_2 (g) 1 atm

is 0.28 volt at 25°C. Write the half cell reactions and calculate the pH of the solution at the hydrogen electrode.

$E^o Zn^{2+}/Zn = -0.76$ volt

$E^o H^+/H_2 = 0$

Solution $E^o_{cell} = 0.76$ volt

According to Nernst equation,

$$E_{cell} = E^o_{cell} - \frac{0.0591}{2} \log_{10} \frac{[Zn^{2+}][H_2]}{[H^+]^2}$$

$$0.28 = 0.76 - \frac{0.0591}{2} \log_{10} \frac{(0.1) \times 1}{[H^+]^2}$$

$$\log_{10} \frac{0.1}{[H^+]^2} = \frac{2 \times 0.48}{0.0591}$$

$$\log_{10} 0.1 - \log_{10} [H^+]^2 = 16.2436$$

[As $-\log_{10} [H^+] = pH$]

$$2\ pH = 16.2436 - \log_{10} 0.1$$

$$pH = \frac{17.2436}{2} = 8.6218$$

22. A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-6} M hydrogen ions. The EMF of the cell is 0.118 V at 25°C. Calculate the concentration of hydrogen ions at the positive electrode.

Solution Suppose $[H^+]$ at the cathode = X mol litre^{-1}

$E_2 = E^o + 0.059 \log_{10} X$ .... (i)

$E_1 = E^o + 0.059 \log_{10} 10^{-6}$ ...... (ii)

Subtracting equation (ii) from (i),

$$E_2 - E_1 = 0.059 (\log_{10} X - \log_{10} 10^{-6})$$

$$0.118 = 0.059 (\log_{10} X + 6)$$

$$X = 10^{-4}$$

$[H^+] = 10^{-4}$ mole litre^{-1}

23. To find the standard potential of M^{3+}/M electrode, the following cell is constituted:

$Pt | M | M^{3+}(0.0018\ mol^{-1}L) || Ag^+(0.01\ mol^{-1}\ L) | Ag$

The emf of this cell is found to be 0.42 volt. Calculate the standard potential of the half reaction.

$M^{3+} + 3e^- \rightarrow M$, $EAg^+/Ag = 0.80$ volt.

Solution The cell reaction is

$M + 3Ag^+ \rightarrow 3Ag + M^{3+}$

According to Nernst equation

$$E_{cell} = E^o_{cell} - \frac{0.0591}{3} \log_{10} \frac{[M^{3+}]}{[Ag^+]^3}.$$

$$0.42 = E^o_{cell} - \frac{0.0591}{3} \log_{10} \frac{(0.0018)}{(0.01)^3}$$

$$= E^o_{cell} - 0.064$$

$$E^o_{cell} = (0.42 + 0.064) = 0.484 \text{ volt}$$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$E^o_{anode} = E^o_{cathode} - E^o_{cell}$$

$$= (0.80 - 0.484) = 0.32 \text{ volt.}$$

ELECTROCHEMICAL SERIES

Reaction (oxidized form)	Reduced form	ε°/V
$Li^+ + e^-$	Li (s)	–3.05
$K^+ + e^-$	K (s)	–2.93
$Ca^{2+} + 2e^-$	Ca (s)	–2.87
$Na^+ + e^-$	Na (s)	–2.71
$Mg^{2+} + 2e^-$	Mg (s)	–2.36
$Al^{3+} + 3e^-$	Al (s)	–1.66
$Zn^{2+} + 2e^-$	Zn (s)	–0.76
$Cr^{3+} + 3e^-$	Cr (s)	–0.74
$Fe^{2+} + 2e^-$	Fe (s)	–0.44
$Ni^{2+} + 2e^-$	Ni (s)	–0.25
$Sn^{2+} + 2e^-$	Sn (s)	–0.14
$Pb^{2+} + 2e^-$	Pb (s)	–0.13
$2H^+ + 2e^-$	H_2 (g)	0.00
AgBr (s) + e^-	Ag (s) + Br^-	0.10
AgCl (s) + e^-	Ag (s) + Cl^-	0.22
$Cu^{2+} + 2e^-$	Cu (s)	0.34
$Cu^+ + e^-$	Cu (s)	0.52
$I_2 + 2e^-$	$2I^-$	0.54
O_2 (g) + $2H^+ + 2e^-$	H_2O_2	0.68
$Fe^{3+} + e^-$	Fe^{2+}	0.77
$Ag^+ + e^-$	Ag (s)	0.80
$2Hg^{2+} + 2e^-$	Hg_2^{2+}	0.92
$NO_3^- + 4H^+ + 3e^-$	NO (g) + $2H_2O$	0.97
$Br_2 + 2e^-$	$2Br^-$	1.09
MnO_2 (s) + $4H^+ + 2e^-$	$Mn^{2+} + 2H_2O$	1.23
O_2 (g) + $4H^+ + 4e^-$	$2H_2O$	1.23
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$2Cr^{3+} + 7H_2O$	1.33
Cl_2 (g) + $2e^-$	$2Cl^-$	1.36
$Au^{3+} + 3e^-$	Au (s)	1.40
$MnO_4^- + 8H^+ + 5e^-$	$Mn^{2-} + 4H_2O$	1.51
$H_2O_2 + 2H^+ + 2e^-$	$2H_2O$	1.78
$Co^{3+} + e^-$	Co^{2+}	1.81
F_2 (g) + $2e^-$	$2F^-$	2.87
Decreasing strength of oxidising agent	Decreasing strength of reducing agent	

It is the arrangement of various electrodes or elements in the increasing order of their standard reduction potential or decreasing order of their standard oxidation potential. It is called electromotive or activity series of the elements

Features of Electrochemical Series

- Metals with positive E°_{op} or negative E°_{rp} are strongly electro positive and have more reactivity. It means a lower placed element or metal is replaced by upper placed or higher element while higher element can be coated by lower metal.

  Example, (i) $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

  Here Cu is replaced by Zn due to more oxidation potential or reactivity of Zn, while Zn is coated by Cu.

  Zn – Cu couple is also coated by Cu. Here, solution turns from blue to colourless and rod becomes Reddish brown from Gray white.

  (ii) $Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag$

Here solution becomes colourless to blue and rod becomes reddish brown to white.

- Metals above H_2 can easily replace H_2 from acid, bases etc. due to there more positive E°_{op} or reactivity

  For example,

  $Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$

$E^\circ_{O.P.}$ of Mg > $E^\circ_{O.P.}$ of H_2

$R - OH + Na \rightarrow R - ONa + H^+$

- Lower placed metals (Cu Hg Ag Pt Au) to H_2 can not do that as $E^\circ_{O.P.}$ of H_2 is more than their E°_{op}

  $Cu + H_2SO_4 \rightarrow$ no reaction

- Oxides of lower metals (Cu, Hg, Ag, Pt, Au) are easily reduced by H_2 or Carbon as they are unstable thermally due to positive E°_{rp} they also decomposed on heating.
- More $E^\circ_{O.P.}$ means ease of tendency to oxidize that is, reducing agents while more $E^\circ_{R.P.}$ means ease to be reduce that is, oxidizing agents. It means metal above hydrogen having positive $E^\circ_{O.P.}$ are reducing agents.

  Reducing property $\propto E^\circ_{O.P.}$

For example, Li is the strongest reducing agent due to maximum $E^\circ_{O.P.}$

For example, If for A is $E^\circ_{O.P.}$ is –0.44 V and for B, E is –0.28 V than A is better reducing agent than B.

- Metals (Cu Hg Ag Pt Au) having high $E^\circ_{R.P.}$ are oxidizing agents. and they have tendency to be reduced

  For example, Oxidizing power $\propto E_{R.P.}$

  $F_2 > Cl_2 > Br_2 > I_2$

  $\longrightarrow$

  Oxidizing power decreases

  HI > HBr > HCl > HF

  $\longrightarrow$

  Reducing power decreases

  As $E^\circ_{O.P.}$ of $I^- > Br^- > Cl^- > F^-$

- Elements with more positive $E^\circ_{R.P.}$ will be discharged first at cathode i.e., discharging order increases from Li to F (for M^+).

  Increasing order of deposition of some cation

Li^+, K^+, Ca^{+2}, Na^+, Mg^{+2}, Al^{+3}, Zn^{+2}, Fe^{+2}, H^+, Cu^{+2}, Ag^+, Au^{+3}

- In case of negative ions, anion with stronger reducing nature is discharged first at anode

  Discharging order $\propto \dfrac{1}{\text{Value of } E^\circ_{R.P.}}$

  Increasing order of discharge of some anion

  $SO_4^{-2} < NO_3^- < OH^- < Cl^- < Br^- < Cl^-$

- Hydroxides of upper metals are strongly basic and their salts do not undergo hydrolysis while hydroxides of lower metals are weakly acidic and their salts undergo hydrolysis.

Enhance Your Knowledge

Primary Cells

- In such cells redox reaction occurs only once so cells can not be recharged again.
- The Cell become dead after some time as electrode reactions cannot be reversed.

  Example, Dry cell, mercury cell

Dry Cell

- It is compact form of Lechlanche cell.
- It has anode of Zn-container and cathode of graphite rod surrounded by MnO_2 + Carbon.
- Here a paste of NH_4Cl and $ZnCl_2$ is filled in between the electrodes.

Cell Reactions

At anode

$Zn\ (s) \rightarrow Zn^{+2}\ (aq) + 2e^-$

At cathode

$2MnO_2\ (s) + 2NH_4^+\ (aq) + 2e^- \rightarrow$

$Mn_2O_3\ (s) + 2NH_3\ (g) + H_2O$

- Zn^{+2} combines with NH_3 to form diammine Zn(II) cation.
- Dry cell has short life as NH_4Cl (acidic) corrodes the Zn-container even if the cell is not in use.
- The cell potential is 1.25 to 1.5 volt

Mercury Cell

- In commonly used mercury cell the reducing agent is zinc and the oxidizing agent is mercury (II) oxide.
- **Cell Reactions**

At anode:

$Zn\ (Hg) + 2OH^- \rightarrow ZnO\ (s) + H_2O + 2e^-$

At cathode:

$HgO + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$

The overall reaction is

$Zn(Hg) + HgO\ (s) \rightarrow ZnO\ (s) + Hg(l)$

- The cell potential is approximately 1.35 V and remains constant throughout its life as overall reaction does not involve any ion, whose concentration can change during its life time. It is used in hearing aids, watches etc.

Secondary Cell

- It can be recharged by passing current to use again as electrode reactions are reversible. Example, lead storage battery, Ni-Cd storage cell.

Batteries

Electrochemical cell used as battery. The voltage provided by the battery is sum of individual voltage of cells.

Types of Batteries: Batteries are of following types:

(i) **Lead Storage Batteries**: Six cells are connected in series each cell provided 2V so total volt provided by the battery is 12 V. The anode, a series of lead grids packed with spongy lead and cathode, a series of grids packed with lead dioxide 38% by weight H_2SO_4 act as electrolyte.

Cell reaction (When discharging takes place)

At anode:

$$Pb\,(s) + HSO_4^-\,(aq) \rightarrow PbSO_4\,(s) + 2H^+ + 2e^-$$

$E° = 0.296$ V

At cathode:

$$PbO_2\,(g) + 3H^+\,(aq) + HSO_4^-\,(aq) + 2e^- \rightarrow$$
$$2PbSO_4\,(s) + 2H_2O\,(l),\ E° = 1.628\text{ V}$$

Net reaction

$$Pb\,(s) + PbO_2\,(s) + 2H^+ + 2HSO_4^-\,(aq) \rightarrow$$
$$2PbSO_4\,(s) + 2H_2O\,(s),\ E° = 1.924\text{ V}$$

Nickel-Cadmium Cell:

- A rechargeable nickel-cadmium cell is a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide.

Fuel Cell

- The best example of fuel cell is Hydrogen–oxygen fuel cell

$$2H_2 + O_2 \rightarrow 2H_2O$$

- Astronauts (Apollo moon flight) used H_2, O_2 fuel cell
- It is pollution free, continuous source of energy and highly efficient.

Cell Reactions

At anode

$$2H_2\,(g) + 4OH^-\,(aq) \rightarrow 4H_2O\,(l) + 4e^-$$

At cathode

$$O_2\,(g) + 2H_2O\,(l) + 4e^- \rightarrow 4OH^-\,(aq)$$

Net reaction is

$$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(l)$$

- ***Requirement:*** It should have compactness, lightness, ruggedness and not much volume drop during use.
- The thermodynamic efficiency of fuel cells is the ratio of the electrical fee energy to the ΔH of the reaction.

$$\eta = \frac{\Delta G}{\Delta H}$$

- **Rusting or Corrosion of Metals**

It is the destruction of metal on reaction with environment. It is reverse extraction of metals and it is a redox process.

Example, Rust of iron is $Fe_2O_3 . xH_2O$

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$$

$Fe(OH)_2$ dehydrates and oxidizes into FeO $Fe(OH)_3$, then finally into rust by dehydration.

- An electrochemical cell known as corrosion cell is developed at the surface of iron.

Anode-Pure iron

Cathode-impure surface

Electrolyte

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$SO_2 + H_2O \rightarrow H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$$

Anode reaction

$$Fe \rightarrow Fe^{2+} + 2e^-$$

Cathode reaction

$$2H^+ + 2e^- \rightarrow 2H$$

$$2H + \tfrac{1}{2}O_2 \rightarrow H_2O$$

Net reaction

$Fe + 2H^+ + ½\, O_2 \rightarrow Fe^{2+} + H_2O$

At surface

$2Fe^{2+} + ½\, O_2 + 2H_2O \rightarrow Fe_2O_3 + 4H^+$

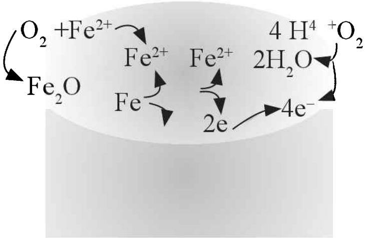
$Fe_2O_3 + xH_2O \rightarrow Fe_2O_3\,.xH_2O$

Net reaction at surface

$2Fe^{2+} + ½\, O_2 + (x + 2)H_2O \rightarrow$

$Fe_2O_3.xH_2O + 4H^+$

Rust



Oxidation: $Fe\ (s) \rightarrow Fe^{2+}\ (aq)\ +2e^-$

Reducation: $O^2\ (g) + 4H^+(aq) + 4e^- \rightarrow 2H_2\ O(1)$

Atomospheric Oxidation: $2Fe^{2+}\ (aq) + 2H_2\ O\ (1) + 1/2\ O \rightarrow Fe_2\ O_3(s) + 4H^+(aq)$

Factors Promoting Corrosion

Reactivity of metal, presence of impurities, presence of air and moisture, strains in metal and presence of electrolyte etc.

Prevention of Corrosion

Sacrifical protection: By covering the surface of iron with a layer of metal which is more active than iron thus prevents the iron from losing electrons (Plating metal with a thin layer of less easily oxidizable metal like Mg, Zn, Sn)

Galvanization

- By covering iron with more active metal like zinc. The layer of Zn on the iron surface when comes in contact with moisture, oxygen and CO_2 in air, a protective invisible thin layer of basic zinc carbonate $ZnCO_3.\ Zn(OH)_2$ is formed due to which the galvanized iron sheets lose their lusture and tends to protect it from further corrosion.
- Iron can be coated with Cu or by Sn. Now if the coating is broken, iron is exposed and being more reactive than iron, Cu and Sn corrode more rapidly.

Electrical Protection

Cathodic Protection More electropositive metals like Zn, Mg or Al may be connected with the iron pipes buried in the moist soil, canals, storage tanks etc.

Using Anti-rust Solutions These are alkaline phosphate and alkaline chromate solutions. The alkaline nature of solutions prevents availability of H^+ ions. On the surface of iron, a protective, insoluble thin film of iron phosphate is formed. These are used in car radiators etc., to prevent rusting.

Solved Problems from the IITs

1. Calculate the electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50%. If the potential drop across the cell is 3.0 volt, how much energy will be consumed?

[IIT 1990]

Solution The reduction reaction is as follows:

$C_6H_5NO_2\ +\ 3H_2 \rightarrow C_6H_5NH_2 + 2H_2O$

123 g	6 g
1 mole	3 mole

Hydrogen required for reduction of 12.3/123 or 0.1 mole of nitrobenzene

$= 0.1 \times 3 = 0.3$ mole

Amount of charge required for liberation of 0.3 mole of hydrogen

$= 2 \times 96500 \times 0.3 = 57900$ coulomb

Actual amount of charge required as efficiency is 50%

$= 2 \times 57900 = 115800$ coulomb

Energy consumed = 115800 × 3.0 = 347400 J

= 347.4 kJ

2. The standard reduction potential of Cu^{2+}/Cu and Ag^+/Ag electrodes are 0.337 and 0.799 volt respectively. Construct a galvanic cell using these electrodes so that its standard emf is positive. For what concentration of Ag^+ will the emf of the cell at 25°C be zero if concentration of Cu^{2+} is 0.01 M?

[IIT 1990]

Solution Given $E^\circ Cu^{2+}/Cu = 0.337$ V

$E^\circ Ag^+/Ag = 0.799$ V.

The standard emf will be positive if Cu/Cu^{2+} is anode and Ag^+/Ag is cathode. The cell may be represented as follows:

$Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$

The cell reaction is as follows:

$Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$

E°_{cell} = Oxidation Potential of anode + Reduction Potential of cathode

$= -0.337 + 0.799$

$= 0.462$ Volt

According to Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log_{10} \frac{[Cu^{2+}]}{[Ag^+]^2}.$$

When $E_{cell} = 0$

$$E^\circ_{cell} = \frac{0.0591}{2} \log_{10} \frac{[Cu^{2+}]}{[Ag^+]^2}.$$

$$\log_{10} \frac{[Cu^{2+}]}{[Ag^+]^2} = \frac{0.462 \times 2}{0.0591} = 15.6345$$

$$\frac{[Cu^{2+}]}{[Ag^+]^2} = 4.3102 \times 10^{15}$$

$$[Ag^+]^2 = \frac{0.01}{4.3102 \times 10^{15}}.$$

$= 0.2320 \times 10^{-17}$

$= 2.320 \times 10^{-18}$

$[Ag^+] = 1.523 \times 10^{-9}$ M

3. A current of 1.70 ampere is passed through 300 ml of 0.160 M solution of zinc sulphate for 230 seconds with a current efficiency of 90%. Calculate the molarity of Zn^{2+} ions after the deposition of zinc. Assume the volume of the solution to remain constant during electrolysis.

[IIT 1991]

Solution Amount of charge passed = 1.70 × 230 coulomb

Amount of actual charge passed

$$= \frac{90}{100} \times 1.70 \times 230$$

= 351.9 coulomb

Number of moles of Zn deposited by passing 351.9 coulomb of charge

$$= \frac{1}{2 \times 96500} \times 351.9 = 0.000182$$

Molarity of Zn^{2+} ions after deposition of zinc

$$= [0.160 - \frac{0.000182 \times 1000]}{300} \text{ M}$$

= 0.154 M.

4. Zinc granules are added in excess to 500 ml of 1.0 M nickel nitrate solution at 25°C until the equilibrium is reached. If the standard reduction potentials of Zn^{2+}/Zn and Ni^{2+}/Ni are –0.75 and –0.24 volt respectively, find out the concentration of Ni^{2+} ions in solution at equilibrium.

[IIT 1991]

Solution The reaction is

$Zn\ (s) + Ni^{2+}\ (aq) \rightleftharpoons Zn^{2+}\ (aq) + Ni\ (s)$

The cell involving this reaction would be

$Zn\ (s) \mid Zn^{2+}\ (aq) \parallel Ni^{2+}\ (aq) \mid Ni\ (s)$

$E^\circ_{cell} = -0.24 + 0.75 = 0.51$ volt

$$\log_{10} K_{eq} = \frac{nFE^\circ}{2.303\ RT} = \frac{nE^\circ}{0.0591}.$$

$$= \frac{2 \times 0.51}{0.0591} = 17.25$$

So $K_{eq} = 1.78 \times 10^{17}$

Suppose 'X' is the concentration of Ni^{2+} that have been reduced to nickel at equilibrium.

$$\underset{}{Zn\ (s)} + \underset{(1.0 - X)}{Ni^{2+}\ (eq)} \rightleftharpoons \underset{X}{Zn^{2+}\ (aq)} + Ni\ (s)$$

$$K_{eq} = \frac{[Zn^{2+}]}{[Ni^{2+}]} = \frac{X}{(1 - X)} = 1.78 \times 10^{17}$$

X = 1.0 M.

So $(1 - X) = [Ni^{2+}] = \frac{1.0}{1.78 \times 10^{17}}$.

$= 5.6 \times 10^{-18}$ M

5. An aqueous solution of sodium chloride on electrolysis gives H_2 (g), Cl_2 (g) and NaOH according to the reaction:

$2Cl^- (aq) + 2H_2O \rightarrow$

$2OH^- (aq) + H_2 (g) + Cl_2 (g)$

A direct current of 25 ampere with a current efficiency 62% is passed through 20 litre of NaCl solution (20% of mass). Write down the reactions taking place at the anode and cathode. How long will it take to produce one kg of Cl_2? What will be the molarity of the solution with respect to hydroxide ion? Assume no loss due to evaporation.

[IIT 1992]

Solution Reactions at anode and cathode are as follows:

$2Cl^- \rightarrow Cl_2 + 2e^-$ (at anode)

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (at cathode)

1 Kg of $Cl_2 = \frac{1000}{71.0} = 14.08$ mole

Charge to produce one mole of Cl_2

$= 2 \times 96500$ coulomb

Charge to produce 14.08 mole of Cl_2

$= 2 \times 96500 \times 14.08$ coulomb

Effective current $= \frac{62}{100} \times 25.0 = 15.5$ ampere

Time $= \frac{\text{Charge}}{\text{Current}}$.

$= \frac{2 \times 96500 \times 14.08}{15.5}$

= 175318.7 second = 48.699 hour

OH^- ions produced = 2 × moles of Cl_2

$= 2 \times 14.08 = 28.16$ mole

Molarity $= \frac{\text{Mole}}{\text{Volume}}$.

$= \frac{28.16}{20} = 1.408$ M

6. For the galvanic cell

Ag | AgCl (s), KCl (0.2 M) || KBr (0.001 M), AgBr (s) | Ag

Calculate the emf generated and assign correct polarity to each electrode for the spontaneous process after taking into account in the cell reaction at 25°C.

Given, $Ksp_{AgCl} = 2.8 \times 10^{-10}$,

$Ksp_{AgBr} = 3.3 \times 10^{-13}$

[IIT 1992]

Solution E_{cell} = E (Oxidation potential of L.H.S electrode) + E (Reduction potential of R.H.S electrode)

$= E^\circ$ (Oxidation potential of Ag/Ag^+) – 0.0591 log $[Ag^+]_{L.H.S}$ + E° (Reduction potential of Ag^+/Ag) + 0.0591 log $[Ag^+]_{R.H.S}$

$$= 0.0591 \log_{10} \frac{[Ag^+]_{R.H.S}}{[Ag^+]_{L.H.S}}$$

(As $E^\circ Ag/Ag^+ + E^\circ Ag^+/Ag = 0$)

$$= 0.0591 \log_{10} \frac{Ksp_{AgBr}/[Br^-]}{Ksp_{AgCl}\,[Cl^-]}$$

$$= 0.0591 \log_{10} \frac{3.3 \times 10^{-13}}{0.001} \times \frac{0.2}{2.8 \times 10^{-10}}.$$

= –0.0371 volt

As the cell potential is negative, so the cell reaction is non-spontaneous. For spontaneous reaction, emf should be positive.

Hence the correct cell reaction is as follows:

Ag | AgBr, KBr || KCl, AgCl | Ag
Anode Cathode

7. The standard reduction potential for the half cell having reaction,

$NO_3^- (aq) + 2H^+ (aq) + e^- \rightarrow$

$NO_2 (g) + H_2O$

is 0.78 volt.

(i) Calculate the reduction potential in 8 MH^+.

(ii) What will be the reduction potential of the half cell in a neutral solution?

Assume all other species to be at unit concentration.

[IIT 1993]

Solution $E_{red} = E^\circ_{red} + \frac{0.0591}{n} \log_{10} [H^+]^2$

$= 0.78 + \frac{0.0591}{2} \log_{10} (8)^2$

$= 0.78 + 0.0591 \times 3 \times 0.3010$

$= 0.833$ volt

(ii) $E_{red} = 0.78 + \frac{0.0591}{2} \log_{10} (10^{-7})^2$

(For neutral solution $[H^+] = 10^{-7}$ M)

$= 0.78 - 0.0591 \times 7$

$= 0.367$ volt.

8. Chromium metal can be plated out from an acidic solution containing CrO_3 according to the following reaction: $CrO_3 + 6H^+ + 6e^- \rightarrow Cr + 3H_2O$

Calculate the mass of chromium plated out by 24000 coulomb. How long will it take to plate out 1.5 g of chromium using 12.5 ampere current?

[IIT 1993]

Solution $CrO_3 + 6H^+ + 6e^- \rightarrow Cr + 3H_2O$

6 × 96500 C   1 mole 52 g

Mass of chromium plated out by 24000 coulomb charge

$= \frac{52}{6 \times 96500} \times 24000 = 2.155$ g

Charge required for plating out 1.5 g of chromium

$= \frac{6 \times 96500}{52} \times 1.5 = 16701.92$ coulomb

$\text{Time} = \frac{\text{Charge}}{\text{Current}}$.

$= \frac{16701.92}{12.5} =$ 1336.15 second

$= 22.27$ minute

9. The standard reduction potential of Ag^+/Ag electrode at 298 K is 0.799 volt. Given for AgI, $K_{sp} = 8.7 \times 10^{-17}$, evaluate the potential of the Ag^+/Ag electrode in a saturated solution of AgI. Also find the standard reduction potential of the $I^- / AgI / Ag$ electrode.

[IIT 1994]

Solution In the saturated solution of AgI, the half cell reactions are

$AgI + e^- \rightarrow Ag + I^-$ (Cathode-reduction)

$Ag \rightarrow Ag^+ + e^-$ (Anode-oxidation)

The cell reaction is

$AgI \rightarrow Ag^+ + I^-$

$E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} + 0.0591 \log_{10} [Ag^+]$

$[Ag^+][I^-] = K_{sp}(AgI) = [Ag^+]^2 = [I^-]^2$

So $[Ag^+]^2 = 8.7 \times 10^{-17}$

$[Ag^+] = \sqrt{(8.7 \times 10^{-17})} = 9.3 \times 10^{-9}$

On putting the value of $E^\circ Ag^+/Ag$ and $[Ag^+]$, we get

$E\, Ag^+/Ag = 0.799 - 0.0591 \log_{10} (9.3 \times 10^{-9})$

$= 0.324$ volt

$E^\circ_{cell} = 0.0591 \log_{10} K_{sp}(AgI)$

$= 0.0591 \log_{10} (8.7 \times 10^{-17})$

$= -0.95$ volt

E°_{cell} = Oxidation potential of anode

+ Reduction potential of cathode

Reduction potential of cathode $E^\circ I^- / Ag^+ / Ag$

$= -0.95 - (-0.799)$

$= -0.95 + 0.799$

$= -0.151$ volt

10. The Edison storage cell is represented as

$Fe(s) \mid FeO(s) \mid KOH(aq) \mid Ni_2O_3(s) \mid Ni(s)$

The half cell reactions are:

$Ni_2O_3(s) + H_2O(l) + 2e^- \rightarrow 2NiO(s) + 2OH^-$

$E^\circ = +0.40$ volt

$FeO(s) + H_2O(l) + 2e^- \rightarrow Fe(s) + 2OH^-$

$E^\circ = -0.87$ volt

(a) What is the cell reaction?

(b) What is the emf of the cell? How does it depend on the concentration of KOH?

(c) What is the maximum amount of energy that can be obtained from one mole of Ni_2O_3?

[IIT 1994]

Solution Actual half reactions are:

$Fe + 2OH^- \rightarrow FeO + H_2O + 2e^-$

(Anode-Oxidation)

$Ni_2O_3 + H_2O + 2e^- \rightarrow 2NiO + 2OH^-$

(Cathode-Reduction)

So the cell reaction is:

(a) $Fe + Ni_2O_3 \rightarrow FeO + 2NiO$

(b) $E_{cell} = E^\circ_{cell} - \dfrac{0.0591}{2} \log_{10} \dfrac{[NiO]^2\,[FeO]}{[Fe]\,[Ni_2O_3]} = E^\circ_{cell}$

Since $\dfrac{[NiO]^2\,[FeO]}{[Fe]\,[Ni_2O_3]} = 1$ as all are solids

$= 0.87 + 0.40 = 1.27$ volt

The emf of the cell is independent of KOH concentration.

(c) Maximum amount of electrical energy

$= n\,f\,E^\circ$

$= 2 \times 96500 \times 1.27$

$= 245.11$ kJ

11. An excess of liquid mercury is added to an acidified solution of 1.0×10^{-3} M Fe^{3+}. It is found that 5% of Fe^{3+} remains at equilibrium at 25°C. Calculate E° Hg_2^{2+}/Hg assuming that the only reaction that occurs is

$2Hg + 2Fe^{3+} \rightarrow Hg_2^{2+} + 2Fe^{2+}$

(Given $EFe^{3+}/Fe^{2+} = 0.77$ volt)

[IIT 1995]

Solution $2Hg \quad + \quad 2Fe^{3+} \rightarrow Hg_2^{2+} \quad + \quad 2Fe^{2+}$

$$\text{At eq. Excess} \quad \frac{10^{-3} \times 5}{100} \quad \frac{10^{-3} \times 95}{2 \times 100} \quad \frac{10^{-3} \times 95}{100}$$

At eq. $E_{cell} = 0$

$$0 = E^\circ_{cell} - \frac{0.0591}{2} \log_{10} \frac{[Hg_2^{2+}]\,[Fe^{2+}]^2}{[Fe^{3+}]^2}$$

$= (E^\circ\, Hg/Hg_2^{2+} + E^\circ\, Fe^{3+}/Fe^{2+})$

$$- \frac{0.0591}{2} \log_{10} \frac{\dfrac{(10^{-3} \times 95)}{2 \times 100}\,(10^{-3} \times 95\ 100)^2}{(10^{-3} \times 5\ 100)^2}$$

$$E^\circ Hg/Hg_2^{2+} = -0.77 + \frac{0.0591}{2} \log_{10} \frac{(95)^3 \times 10^{-5}}{25 \times 2}$$

$= -(0.77 + 0.0226)$

$= -0.7926$ volt

$E^\circ Hg_2^{2+}/Hg = +0.7926$ volt

12. The standard reduction potential for Cu^{2+}/Cu is +0.34 V. Find the reduction potential at pH = 14 for the above couple. K_{sp} of $Cu(OH)_2$ is 1.0×10^{-19}.

[IIT 1996]

Solution $Cu^{2+} + 2e^- \rightarrow Cu \quad E^\circ = +0.34$ V ... (i)

For $Cu(OH)_2$

$K_{sp} = 1.0 \times 10^{-19}$

$[Cu^{2+}]\,[OH^-]^2 = 1.0 \times 10^{-19}$

As pH of the solution is 14

So $[OH^-] = 1$ M

$[Cu^{2+}] = 10^{-19}$

According to Nernst's equation for (i)

$$E = E^\circ - \frac{0.059}{N} \log_{10} \frac{[Cu]}{[Cu^{2+}]}$$

$$= 0.34 - \frac{0.059}{2} \log_{10} \frac{1}{10^{-19}}$$

$$= 0.34 - \frac{0.059}{2} \times 19$$

$= -0.22$ V

13. How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8.0 hours at a current of 8.46 amperes. What is the area of the tray if the thickness of the silver plating is 0.00254 cm? Density of silver is 10.5 g/cm³.

[IIT 1997]

Solution Mass of silver deposited (W) = Z × C × t

$$W = \frac{E \times C \times t}{F}$$

(As Z = E/F)

$$W = \frac{107.8 \times 8.46 \times 8 \times 60 \times 60}{96500}$$

$= 272.178$ g

$$\text{Volume of silver} = \frac{\text{Weight}}{\text{Density}}$$

$$= \frac{272.178}{10.5} = 25.92 \text{ cc}$$

$$\text{Surface area} = \frac{\text{Volume}}{\text{Thickness}}$$

$$= \frac{25.92 \text{ cc}}{0.00254} \text{ cm}$$

$= 10205.43 = 1.02 \times 10^4$ cm^2

14. Electrolysis of a solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2 as per the reaction

$Mn^{2+}(aq) + 2H_2O \rightarrow$

$MnO_2(s) + 2H^+(aq) + H_2(g)$

Passing a current of 27 A for 24 hours gives one Kg of MnO_2. What is the value of current efficiency.

[IIT 1997]

Solution Wt. of MnO_2 (w) $= \frac{E.I.t}{F}$

$$1000 = \frac{87 \times I \times 24 \times 60 \times 60}{2 \times 96500}$$

I = 25.67 ampere

$$\text{Current efficiency} = \frac{25.67 \times 100}{27} = 95\%$$

15. Calculate the equilibrium constant for the reaction:

$Fe^{2+} + Ce^{4+} \leftrightarrow Fe^{3+} + Ce^{3+}$.

Given: $E°Ce^{+4}/Ce^{+3} = 1.44$ V

$E°Fe^{+3}/Fe^{+2} = 0.68$ V

[IIT 1997]

Solution $\log K_C = \frac{n}{0.0591} \times E°_{cell}$

$$= \frac{1}{0.0591} \times 0.76 = 12.8813$$

K_C = antilog of 12.8813

$K_C = 7.608 \times 10^{12}$

16. Calculate the equilibrium constant for the reaction, $2Fe^{3+} + 3I^- \rightarrow 2Fe^{2+} + I_3^-$. The standard reduction potentials in acidic conditions are 0.77 and 0.54 V respectively for Fe^{3+}/Fe^{2+} and I_3^-/I^- couples.

[IIT 1998]

Solution Oxidation half $3I^- \rightarrow I_3^- + 2e^-$

Reduction half $[Fe^{3+} + e^- \rightarrow Fe^{2+}] \times 2$

Cell reaction $Fe^{3+} + 3I^- \rightarrow 2Fe^{2+} + I_3^-$

Here n = 2, $E_{cell} = 0.77 - 0.54 = 0.23$ V

According to Nernst equation,

$$E = E_{cell} - \frac{0.0591}{n} \log_{10} K_C$$

At equilibrium E = 0

$$\text{So } 0 = 0.23 - \frac{0.0591}{2} \log_{10} K_C$$

On solving, we get

$K_C = 6.26 \times 10^7$

17. Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell $Ag \mid Ag^+$ (saturated Ag_2CrO_4 solution) $\parallel Ag^+$ (0.1 M) $\mid$ Ag. is 0.164 V at 298 K.

[IIT 1998]

Solution $E_{cell} = \frac{0.0591}{1} \log_{10} \frac{[Ag^+]_{R.H.S}}{[Ag^+]_{L.H.S}}$

$$0.164 = \frac{0.0591}{1} \log_{10} \frac{0.1}{[Ag^+]_{L.H.S}}$$

$[Ag^+]_{L.H.S} = 1.66 \times 10^{-4}$ M

$$[CrO_4^{2-}] = \frac{1.66 \times 10^{-4}}{2}$$

$Ksp\ (Ag_2CrO_4) = [Ag^+]\ [CrO_4^{2-}]$

$$= (1.66 \times 10^{-4})^2 \times \frac{1.66 \times 10^{-4}}{2}$$

$= 2.287 \times 10^{-12}$ mol^3 L^{-3}

18. The following electrochemical cell has been set up,

Pt (1) | Fe^{3+}, Fe^{2+} (a = 1) || Ce^{4+}, Ce^{3+} (a = 1) Pt (2)

$E°\ (Fe^{3+}/Fe^{2+}) = 0.77$ V

$E°\ (Ce^{4+}/Ce^{3+}) = 1.61$ V

If an ammeter is connected between the two platinum electrodes, predict the direction of flow of current. Will the current increase or decrease with time?

[IIT 2000]

Solution Current will flow from higher reduction potential electrode to lower reduction potential electrode, that is, from Pt (2) electrode to Pt (1) electrode.

$E^\circ_{cell} = 1.61 - 0.77 = 0.84$ volt

19. Copper sulphate solution (250 ml) was electrolyzed using a platinum anode and a copper cathode. A constant current of 2 Ampere was passed for 16 minutes. It was found that after electrolysis the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with.

[IIT 2000]

Solution As number of Faraday passed through the aqueous solution of $CuSO_4$

$$= \frac{I \times t}{96500} = \frac{(2 \times 10^{-3}) \times 16 \times 60}{96500}$$

$= 1.98 \times 10^{-5}$

So number of equivalents of $CuSO_4$ involved in electrolysis from 1 litre solution

$= 4 \times 1.98 \times 10^{-5} = 7.92 \times 10^{-5}$

As after electrolysis, the absorbance reduces to 50% so initial number of equivalents of $CuSO_4$ per litre

$= 2 \times 7.92 \times 10^{-5}$

$= 1.584 \times 10^{-4}$

Normality of $CuSO_4$ solution $= 1.584 \times 10^{-4}$ N

20. The standard potential of the following cell is 0.23 V at 15°C and 0.21 V at 25°C

$Pt\ H_2\ (g)\ |\ HCl\ (aq)\ ||\ AgCl\ (s)\ |\ Ag\ (s)$

(i) Write cell reaction.

(ii) Calculate ΔH° and ΔS° for the cell reaction by assuming that these quantities remain uncharged in the range 15°C to 35°C.

(iii) Calculate the solubility of AgCl in water at 25°C. Given the standard reduction potential of the Ag^+/Ag couple is 0.80 volt at 25°C.

[IIT 2001]

Solution

(i) Electrode process

$\frac{1}{2} H_2 \rightarrow H^+ + e^-$ (Anode)

$AgCl + e^- \rightarrow Ag + Cl^-$ (Cathode)

Net reaction is:

$\frac{1}{2} H_2 + AgCl \rightleftharpoons H^+ + Ag + Cl^-$

(ii) As $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$-22195 = \Delta H^\circ - 288 \times \Delta S^\circ$

$-20265 = \Delta H^\circ - 308 \times \Delta S^\circ$

On solving we get

$\Delta S^\circ = -96.5$ J

$\Delta H^\circ = 49.987$ kJ

(iii) $E = E^\circ - \frac{0.0591}{n} \log_{10} Q$

At eq. $E = 0,\ Q = K = [Ag^+]\ [Cl^-]$

$$0 = (0.8 - 0.22) + \frac{0.0591}{1} \log_{10} Ksp$$

$$\frac{(-0.8 + 0.22)}{0.0591} = \log_{10} Ksp$$

$Ksp = 1.47 \times 10^{-10}$

Solubility (S) $= \sqrt{Ksp}$

$= \sqrt{(1.47 \times 10^{-10})}$

$= 1.21 \times 10^{-5}$ M

21. Two students use same stock solution of $ZnSO_4$ and a solution of $CuSO_4$. The emf of one cell is 0.03 V higher than that of other. The concentration of $CuSO_4$ in the cell with higher emf value is 0.5 M. Calculate the concentration of $CuSO_4$ in the other cell. ($\frac{2.303\ RT}{F} = 0.06$)

[IIT 2003]

Solution

Student I.

$Zn\ (s)\ |\ ZnSO_4\ (C_1)\ ||\ 0.5\ M\ CuSO_4\ |\ Cu\ (s)$

$$E_1 = E^\circ - \frac{0.06}{2} \log_{10} \frac{C_1}{0.5} \quad \text{......(i)}$$

Student II

$Zn\ (s)\ |\ ZnSO_4\ (C_1)\ ||\ CuSO_4\ (C_2)\ |\ Cu\ (s)$

$$E_2 = E^\circ - \frac{0.06}{2} \log_{10} \frac{C_1}{C_2} \quad \text{......(ii)}$$

On subtracting equation (ii) from (i), we get

$$E_1 - E_2 = \frac{0.06}{2}\left[\log_{10}\frac{C_1}{C_2} - \log_{10}\frac{C_1}{0.5}\right]$$

$$0.03 = \frac{0.06}{2}\left[\log_{10}(0.5/C_2)\right]$$

$$1 = \log\frac{0.5}{2}$$

$$C_2 = 0.05\ \text{M}$$

22. Find the equilibrium constant for the reaction,

$In^{2+} + Cu^{2+} \rightleftharpoons In^{3+} + Cu^{+}$ at 298 K.

Given: $ECu^{2+}/Cu^{+} = 0.15$ V

$E^{\circ}\, In^{2+}/In^{+} = -0.4$ V

$E^{\circ} In^{3+}/In^{+} = -0.42$ V

[IIT 2004]

Solution

The given reversible reaction is obtained as follows:

$Cu^{2+} + e^{-} \rightarrow Cu^{+}$; $\quad \Delta G^{\circ} = -0.15$ F

$In^{2+} + e^{-} \rightarrow In^{+}$; $\quad \Delta G^{\circ} = +0.40$ F

$In^{+} \rightarrow In^{3+} + 2e^{-}$; $\quad \Delta G^{\circ} = -0.84$ F

The net reaction is

$Cu^{2+} + In^{2+} \rightleftharpoons In^{3+} + Cu^{+}$; $\quad \Delta G^{\circ} = -0.59$ F

As $\Delta G^{\circ} = -nFE^{\circ}$

So $-nFE^{\circ} = -0.59$ F

$E^{\circ} = 0.59$ volt

Equilibrium constant is calculated as:

$$K = \text{antilog}\,\frac{nE^{\circ}}{0.059}\,.$$

$$= \text{antilog}\,\frac{1 \times 0.59}{0.059} = 10^{10}$$

23. For the reaction

$Ag^{+}(aq) + Cl^{-}(aq) \rightleftharpoons AgCl\,(s)$

Given:

Species	ΔG°_{f} (kJ/mol)
Ag^{+} (aq)	+77
Cl^{-} (aq)	–129
AgCl (s)	–109

Write the cell representation of above reaction and calculate E°_{cell} at 298 K.

Also find the solubility product of AgCl.

(b) If 6.539×10^{-2} g of metallic zinc is added to 100 ml saturated solution of AgCl. Find the value of $\log_{10}\frac{[Zn^{2+}]}{[Ag^{+}]^2}$.

How many moles of Ag will be precipitate in the above reaction?

Given that:

$Ag^{+} + e^{-} \rightarrow Ag$; $E^{\circ} = 0.80$ V

$Zn^{2+} + 2e^{-} \rightarrow Zn$; $E^{\circ} = -0.76$ V

(Atomic mass of Zn = 65.39)

[IIT 2005]

Solution

The reaction is as follows:

At anode:

$Ag\,(s) + Cl^{-}(aq) \rightarrow AgCl\,(s) + e^{-}$

At cathode:

$Ag^{+}(aq) + e^{-} \rightarrow Ag\,(s)$

The net reaction is as follows:

$Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl\,(s)$

Cell representation is as follows:

$Ag\,(s)\,|\,AgCl\,(s)\,|\,Cl^{-}(aq)\,||\,Ag^{+}(aq)\,|\,Ag\,(s)$

$\Delta G^{\circ} = \Delta G^{\circ}_{f}(AgCl) - [\Delta G^{\circ}_{f}(Ag^{+}) + \Delta G^{\circ}_{f}(Cl^{-})]$

$= -109 - (-129 + 77)$

$= -57$ kJ/mol $= -57000$ J/mol

$\Delta G^{\circ} = -n\,F\,E^{\circ}_{cell}$

$-57000 = -1 \times 96500 \times E^{\circ}_{cell}$

(as n = electrons transferred = 1)

$$E^{\circ}_{cell} = \frac{57000}{96500} = 0.59 \text{ volts}$$

$$E^{\circ}_{cell} = \frac{0.0591}{n}\log_{10} K_C$$

$$E^{\circ}_{cell} = \frac{0.0591}{n}\log_{10}\frac{[AgCl]}{[Ag^{+}]\,[Cl^{-}]}$$

$$E^{\circ}_{cell} = \frac{0.0591}{1}\log_{10}\frac{1}{Ksp}$$

[As [AgCl (s)] = 1 and $Ksp = [Ag^{+}]\,[Cl^{-}]$]

$0.59 = -0.059 = \log_{10} Ksp$

$\log_{10} Ksp = -10$

$Ksp = 10^{-10}$

(b) When Zn is added to 100 ml of saturated AgCl solution.

$2Ag^+ + Zn\ (s) \rightleftharpoons 2Ag\ (s) + Zn^{2+}$

$Ag^+ + e^- \rightleftharpoons Ag;\ E^\circ = 0.80\ V$

$Zn^{2+} + 2e^- \rightleftharpoons Zn;\ E^\circ = -0.76\ V$

$E^\circ_{cell} = E^\circ\ Ag^+ \mid Ag\ (s) - E^\circ\ Zn^{2+} \mid Zn\ (s)$

$= 0.80 - (-0.76) = 1.56\ V$

$$E^\circ_{cell} = \frac{0.0591}{n} \log_{10} \frac{[Zn^{2+}]}{[Ag^+]^2}$$

$$1.56 = \frac{0.0591}{2} \log_{10} \frac{[Zn^{2+}]}{[Ag^+]^2}$$

$$\log_{10} \frac{[Zn^{2+}]}{[Ag^+]^2} = 52.9$$

As the value of equilibrium constant is very high so the reaction moves in forward direction completely.

$[Ag^+] = \sqrt{(10^{-10})} = 10^{-5}$

(As $Ksp = 10^{-10} = [Ag^+]\ [Cl^-]$)

Ag^+ in 100 ml of solution

$$= \frac{10^{-5} \times 100}{1000} = 10^{-6}$$

24. We have taken a saturated solution of AgBr. Ksp of AgBr is 12×10^{14}. If 10^{-7} mole of $AgNO_3$ are added to 1 litre of this solution find conductivity (specific conductance) of this solution in terms of $10^{-7}\ S\ m^{-1}$ units.

Given $\lambda^\circ(Ag^+) = 6 \times 10^{-3}\ Sm^2\ mol^{-1}$,

$\lambda^\circ(Br^-) = 8 \times 10^{-3}\ S\ m^2\ mol^{-1}$,

$\lambda^\circ\ (NO_3^-) = 7 \times 10\ S\ m^2\ mol^{-1}$.

[IIT 2006]

The solubility of AgBr in presence of 10^{-7} molar $AgNO_3$ is 3×10^{-7} M.

Therefore $[Br^-] = 3 \times 10^{-4}\ m^3$, $[Ag^+] = 4 \times 10^{-4}\ m^3$ and $[NO_3^-] = 10^{-4}\ m^3$

Therefore $K_{total} = KBr^- + KAg^+ + KNO_3^- = 55\ Sm^{-1}$

MULTIPLE-CHOICE QUESTIONS

Straight Objective Type Questions (Single Choice only)

1. The standard reduction potentials at 298 K for the following half reactions are given against each

$Zn^{2+} (aq) + 2e \leftrightarrow Zn (s)$ –0.762
$Cr^{3+} (aq) + 2e \leftrightarrow Cr (s)$ –0.740
$2H^+ (aq) + 2e \leftrightarrow H_2 (g)$ 0.000
$Fe^{3+} (aq) + 2e \leftrightarrow Fe^{2+} (aq)$ 0.770

Which is the strongest reducing agent?

a. $H_2 (g)$
b. Cr (s)
c. Zn (s)
d. Fe^{2+} (aq)

2. A solution containing one mole per litre of each $Cu(NO_3)_2$; $AgNO_3$; $Hg_2(NO_3)_2$; is being electrolyzed by using inert electrodes. The values of standard electrode potentials in volts (reduction potentials) are

$Ag / Ag^+ = +0.80$, $2Hg / Hg_2^{++} = +0.79$

$Cu / Cu^{++} = +0.34$, $Mg / Mg^{++} = –2.37$

With increasing voltage, the sequence of deposition of metals on the cathode will be

a. Cu, Hg, Ag
b. Ag, Hg, Cu, Mg
c. Mg, Cu, Hg, Ag
d. Ag, Hg, Cu

3. The reaction

$\frac{1}{2} Hg_2(g) + AgCl(s) = H^+(aq) + Cl^–(aq) + Ag(s)$

occurs in the galvanic cell

a. Pt | H_2(g) | KCl (solution) | AgCl (s) | Ag
b. Pt | H_2(g) | HCl (solution) | AgCl (s) | Ag
c. Pt | H_2(g) | HCl (solution) | $AgNO_3$ (solution) | Ag
d. Ag | AgCl (s) | KCl (solution) | $AgNO_3$ (solution) | Ag

4. An electrochemical cell reaction is: Pt, H_2 (1 atm) | HCl (0.1 M) || CH_3COOH (0.1 M) | H_2 (1 atm), Pt. The emf of this cell will not be zero, because

a. emf depends upon molarities of acids used
b. pH of 0.1 M HCl and 0.1 M CH_3COOH is not same
c. acids used in two compartments are different
d. temperature is constant

5. When a lead storage battery is discharged

a. lead is formed
b. lead sulphate is consumed
c. SO_2 is evolved
d. sulphuric acid is consumed

6. The volume of gas measured at NTP, liberated at anode from the electrolysis of Na_2SO_4 solution by a current of 5.0 Å passed for 3 minutes 13s.

a. 224 ml
b. 112 ml
c. 56 ml
d. none of these

7. A solution of sodium sulphate in water is electrolyzed using inert electrodes. The products at the cathode and anode are respectively

a. O_2, H_2
b. O_2, Na
c. O_2, SO_2
d. H_2, O_2

8. The standard oxidation potential E° for the half reactions are as

$Zn \rightarrow Zn^{2+} + 2e–$; $E° = + 0.76$ V

$Fe \rightarrow Fe^{2+} + 2e–$; $E° = + 0.41$ V

The EMF for the cell reaction

$Fe^{2+} + Zn \rightarrow Zn^{2+} + Fe$ is

a. + 1.17 V
b. –0.35 V
c. + 0.35 V
d. 0.117 V

9. 2.At 25°C, the EMF of the cell

Pt, H_2 (1 atm) | 10^{3+} M KOH || 0.1 M HCl | H_2 (1 atm), Pt is equal to

a. +0.591 V
b. –1.182 V
c. +1.182 V
d. + 10 V

10. When a copper wire is placed in a solution of $AgNO_3$, the solution acquires blue colour. This is due to the formation of

a. Cu^+ ions
b. Cu^{2+} ions
c. soluble complex of copper with $AgNO_3$
d. $Cu^–$ ion by the reduction of Cu.

11. The standard reduction potential for

Fe^{2+} / Fe and Sn^{2+} / Sn electrodes are –0.44 and –0.14 volt respectively. For the cell reaction:

$Fe^{2+} + Sn \rightarrow Fe + Sn^{2+}$

The standard emf is

a. +0.30 V **b.** –0.58 V
c. + 0.58 V **d.** –0.300 V

12. A metal wire (M) dipped into 40 mL 1.0 M solution of its M^{2+} ion has a potential of 29.5 milli volt at 25°C. How much volume of water be added to the metal ion solution so that when it is combined with standard hydrogen electrode, no current flows?

a. 1000 ml **b.** 400 ml
c. 350 ml **d.** 0 ml

13. Of the following metals that cannot be obtained by the electrolysis of the aqueous solution of their salts are

a. Ag and Mg **b.** Ag and Al
c. Mg and Al **d.** Cu and Cr

14. A certain current liberates 0.504 g of hydrogen in 2 hour. The amount (or mass) of copper deposited at the cathode during the electrolysis of $CuSO_4$ (aq) solution by the same current flowing for the same time is (atomic masses H = 1.0, Cu = 63.5)

a. 16.0 g **b.** 32.0 g
c. 8.6 g **d.** 1.60 g

15. A solution of Na_2SO_4 in water is electrolyzed using inert electrodes. The product at the cathode and the anode are respectively.

a. O_2, H_2 **b.** O_2, SO_2
c. H_2, O_2 **d.** O_2, Na

16. If a current of 80.0 microampere is drawn from a cell for 100 days, then the number of faradays involved is

a. 7.16×10^{-4} **b.** 7.16×10^{-3}
c. 14.32×10^{-3} **d.** 3.46×10^{-3}

17. Specific conductance of 0.01 N solution of an electrolyte is 0.00419 mho cm^{-1}. The equivalent conductance of this solution will be:

a. 4.19 mho cm^2

b. 419 mho cm^2

c. 0.0419 mho cm^2

d. 0.209 mho cm^2

18. The oxidation state of oxygen in O_2PtF_6 is

a. zero **b.** – ½
c. + ½ **d.** +1

19. In the reaction,

$3Br_2 + 6CO_3^{2-} + 3H_2O \rightarrow 5Br^- + BrO_3^- + 6HCO_3^-$

a. bromine is oxidized and carbonate is reduced

b. bromine is reduced and water is oxidized

c. bromine is neither reduced nor oxidized

d. bromine is both reduced and oxidized.

20. A dilute aqueous solution of Na_2SO_4 is electrolyzed using platinum electrodes. The product at the anode and cathode are

a. O_2, H_2 **b.** $S_2O_8^{2-}$, Na
c. O_2, Na **d.** $S_2O_8^{2-}$, H_2

21. One mole of a metal ion carries two Faradays of electricity. In the ground state ten orbitals are occupied by electron in the metal ion. The spin only magnetic moment of the metal ion and its atomic number will be respectively, equal to

a. 1.73 BM and 21

b. 1.73 BM and 19

c. 0.0 BM and 20

d. 2.82 BM and 21

22. The specific conductance of 0.1 N KCl solution at 23°C is 0.012 ohm^{-1} cm^{-1}. The resistance of cell containing the solution at the same temperature was found to be 55 ohm. The cell constant will be

a. 0.142 cm^{-1} **b.** 0.616 cm^{-1}
c. 6.16 cm^{-1} **d.** 616 cm^{-1}

23. The equivalent conductance of Ba^{2+} and Cl^- are respectively 127 and 76 ohm^{-1} cm^2 $equiv^{-1}$ at infinite dilution. The equivalent conductance (in ohm^{-1} cm^2 $equiv^{-1}$) of $BaCl_2$ at infinite dilution will be

a. 139.5 **b.** 203
c. 279 **d.** 101.5

24. Cu^+ (aq) is unstable in solution and undergoes simultaneous oxidation and reduction according to the reaction,

$2Cu^+ (aq) \leftrightarrow Cu^{2+} (aq) + Cu (s)$

choose correct E° for above reaction if:

$E^\circ\ Cu^{2+}/Cu = 0.34$ V and $E^\circ\ Cu^{2+}/Cu^+ = 0.15$ V

a. –0.38 V **b.** +0.49 V
c. +0.38 V **d.** –0.19 V

25. The electrode potentials of half-cell reactions are: $Zn \rightarrow Zn^{2+} + 2e^-$; E = –0.76 V and $Fe \rightarrow Fe^{2+} + 2e^-$; E = 0.41 V. The emf of the cell $Fe^{2+} + Zn \rightarrow Zn^{2+} + Fe$ is

a. + 0.35 V **b.** –1.17 V
c. –0.35 V **d.** + 1.17 V

26. A Daniell cell is represented as

Zn (s) + Cu^{2+} (aq) → Cu (s) + Zn^{2+} (aq). The value of standard free energy change in the cell is (E° cell = 1.1 V)

a. 200 kJ **b.** – 300 kJ
c. –212.3 kJ **d.** 312.3 kJ

27. Given E° Fe^{2+}/ Fe = –0.44 V and E° Fe^{3+}/ Fe^{2+} = 0.77 V

Fe^{2+}, Fe^{3+} and Fe are placed together then:

a. Fe^{3+} increases
b. Fe^{3+} decreases
c. $[Fe^{3+}]/[Fe^{2+}]$ remains unchanged
d. Fe^{2+} decreases

28. One faraday of electricity is passed separately through one litre of one molar aqueous solution of (i) $AgNO_3$ (ii) $SnCl_4$ and (iii) $CuSO_4$. The number of moles of Ag, Sn, and Cu deposited at cathode are respectively

a. 1.0, 0.25, 0.5
b. 1.0, 0.5, 0.25
c. 0.5, 1.0, 0.25
d. 0.25, 0.5, 1.0

29. The charge required to liberate 112 ml of hydrogen from acidified water is

a. 1 F **b.** 2 F
c. 96500 C **d.** 965 C

30. Which of the following condition will increase the voltage of the cell, represented by the reaction Cu (s) + $2Ag^+$ (aq) → Cu^{2+} (aq) + 2Ag (s) ?

a. increase in the concentration of Ag^+ ions
b. increase in the dimensions of silver electrode
c. increase in the dimensions of copper electrode
d. increase in the concentration of Cu^{2+} ions

31. In electrolyses of NaCl when Pt electrode is taken then H_2 is liberated at cathode while with Hg cathode it forms sodium amalgam because:

a. Hg is more inert than Pt
b. more voltage is required to reduce H^+ at Hg than at Pt
c. Na is dissolved in Hg while it does not dissolve in Pt
d. conc. of H^+ ions is larger when Pt electrode is taken.

32. Consider the following four electrodes:

A = Cu^{2+} (0.0001 M) | Cu (s)
B = Cu^{2+} (0.1 M) | Cu (s)
C = Cu^{2+} (0.01 M) | Cu (s)
D = Cu^{2+} (0.001 M) | Cu (s)

If the standard reduction potential of Cu^{2+} | Cu is +0.34 V, the reduction potentials (in volts) of the above electrodes following the order ……..

a. A > D > C > B
b. A > B > C > D
c. C > D > B > A
d. B > C > D > A

33. What is the oxidation number of iron in the compound $[Fe(H_2O)_5(NO)^+]^{2+}$?

a. +5 **b.** +7
c. +3 **d.** +1

34. For a cell given below

Ag | Ag^+ || Cu^{2+} + Cu
– +

$Ag^+ + e^- \rightarrow Ag$ E° = x
$Cu^{2+} + 2e^- \rightarrow Cu$, E° = y

E° cell is

a. x + 2y **b.** 2x + y
c. y – x **d.** y – 2x

35. Consider the following reaction at 1100°C

(I) $2C + O_2 \rightarrow 2CO$ ΔG° = –460 kJ mol^{-1}

(II) $2Zn + O_2 \rightarrow 2ZnO$

ΔG° = –360 kJ mol^{-1}

based on these, select correct alternate

a. zinc can be oxidized by CO
b. zinc oxide can be reduced by carbon
c. both are correct
d. none is correct

36. When $KMnO_4$ acts as an oxidizing agent and ultimately forms MnO_4^{2-}. MnO_2, Mn_2O_3 and Mn^{2+} then the number of electrons transferred in each case respectively is

a. 1, 5, 3, 7 **b.** 1, 3, 4, 5
c. 3, 5, 7, 1 **d.** 4, 3, 1, 5

37. On the basis of the information available from the reaction,

4/3 Al + O_2 → 2/3 Al_2O_3, ΔG = –827 kJ mol^{-1} of O_2.

The minimum e.m.f, required to carry out an electrolysis of Al_2O_3 is (F = 96500 C mol^{-1})

a. 6.42 V **b.** 8.56 V
c. 2.14 V **d.** 4.28 V

38. Same amount of electric current is passed through solutions of $AgNO_3$ and HCl. If 1.08 g of silver is obtained in the first case, the volume of hydrogen liberated at STP in the second case is

a. 224 ml **b.** 112 ml
c. 1120 ml **d.** 2240 ml

39. The e.m.f. of a Daniell cell at 298 K is E_1

$Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu$
(0.01 M) (1.0 M)

when the concentration of $ZnSO_4$ is 1.0 M and that of $CuSO_4$ is 0.01M, the e.m.f. changed to E_2. What is the relationship between E_1 and E_2?

a. $E_1 = E_2$ **b.** $E_2 = 0 \neq E_1$
c. $E_1 > E_2$ **d.** $E_1 < E_2$

40. A galvanic cell is constructed using the redox reaction

$\frac{1}{2} H_2 (g) + AgCl (s) \leftrightarrow H^+ (aq) + Cl^- (aq) + Ag (s)$. It is represented as

a. $Pt \mid H_2 (g) \mid HCl(soln) \parallel AgNO_3 (soln) \mid Ag$

b. $Ag \mid AgCl (s) \mid KCl (soln) \parallel HCl (soln), H_2 \mid Pt$

c. $Pt \mid H_2 (g) \mid HCl (soln) \parallel AgCl (s) \mid Ag$

d. $Pt \mid H_2 (g) \mid KCl (soln) \parallel AgCl (s) \mid Ag$

41. The standard electrode potential for the reaction $Zn + Cu^{2+} \leftrightarrow Cu + Zn^{2+}$ is 1.1 V. The electrode potential for the reaction, when 0.1 M Cu^{2+} and 0.1 M Zn^{2+} solution is used, will be

a. 1.1 V **b.** –0.11 V
c. 11.0 V **d.** + 0.011 V

42. For the redox reaction

$Zn (s) + Cu^{2+} (0.1 M) \rightarrow$
$Zn^{2+} (1M) + Cu (s)$

Taking place in a cell, E°cell is 1.10 volt. Ecell for the cell will be (2.303 RT/F = 0.0591)

a. 2.14 V **b.** 1.80 V
c. 1.07 V **d.** 0.82 V

43. For a cell reaction involving a two electron, the standard EMF of the cell is found to be 0.295V at 25°C. The equilibrium constant of the reaction at 25°C will be

a. 1×10^{-10} **b.** 29.5×10^{-2}
c. 10 **d.** 1×10^{10}

44. $Zn (s) + Cl_2 (1 atm) \rightarrow Zn^{2+} + 2Cl^-$

The E° of the cell is 2.12 V. To increase E

a. Cl^- concentration should be increased

b. Partial pressure of Cl_2 should be decreased

c. Zn^{2+} concentration should be increased

d. Zn^{2+} concentration should be decreased

45. $Cr_2O_7^{2-} + I^- \rightarrow I_2 + Cr^{3+}$

$E^\circ_{cell} = 0.79$ V, $E^\circ_{Cr2O72-} = 1.33$ V,

$E^\circ_{I2} = ?$

a. +0.18 V **b.** –0.18 V
c. 0.54 V **d.** –0.054 V

46. An electric current is passed through silver voltameter connected to a water voltameter. The cathode of the silver voltameter weighed 0.108 g more at the end of the electrolysis. The volume of oxygen evolved at STP is

a. 5.6 cm^3 **b.** 56 cm^3
c. 11.2 cm^3 **d.** 560 cm^3
e. 22.4 cm^3

47. Ionic mobility of Ag^+ is ($\lambda Ag^+ = 5 \times 10^{-4}\ ohm^{-1}\ cm^2\ eq^{-1}$)

a. 2.6×10^{-9} **b.** 5.2×10^{-9}
c. 1.54×10^{-9} **d.** 8.46×10^{-9}

48. The limiting molar conductivities Λ° for NaCl, KBr and KCl are 126, 152 and 150 S cm^2 mol^{-1} respectively. The Λ° for NaBr is

a. 278 S cm^2 mol^{-1}

b. 178 S cm^2 mol^{-1}

c. 128 S cm^2 mol^{-1}

d. 306 S cm^2 mol^{-1}

49. In a cell that utilizes the reaction

$Zn (s) + 2H^+ (aq) \rightarrow Zn^{2+} (aq) + H_2 (g)$

Addition of H_2SO_4 to cathode compartment, will

a. lower the E and shift equilibrium to the right

b. lower the E and shift the equilibrium to the left

c. increase the E and shift the equilibrium to the left

d. increase the E and shift the equilibrium to the right.

50. The $E_{M3+/M2+}$ values for Cr, Mn, Fe and Co are –0.41, +1.57, +0.77 and +1.97 V respectively. For which one of these metals the change in oxidation state form +2 to +3 is easiest?

a. Cr **b.** Mn
c. Fe **d.** Co

51. The hydrogen electrode is dipped in a solution of pH 3 at 25°C. The potential would be (the value of 2.303 RT / F is 0.059 V)

a. 0.177 V
b. 0.087 V
c. 0.059 V
d. –0.177 V.

52. Corrosion of iron is essentially an electrochemical phenomenon where the cell reactions are

a. Fe is oxidized to Fe^{2+} and dissolved oxygen in water is reduced to $^{\ominus}OH$

b. Fe is oxidized to Fe^{3+} and H_2O is reduced to O_2^{2-}

c. Fe is oxidized to Fe^{2+} and H_2O is reduced to O_2^{-}

d. Fe is oxidized to Fe^{2+} and H_2O is reduced to O_2.

53. Aluminium oxide may be electrolyzed at 1000°C to furnish aluminium metal (atomic mass = 27 amu; 1 faraday = 965000 coulombs). The cathode reaction is

$Al^{3+} + 3e^- \rightarrow Al^\circ$

To prepare 5.12 kg of aluminium metal by this method would require

a. 5.49×10^7 C of electricity

b. 1.83×10^7 C of electricity

c. 5.49×10^4 C of electricity

d. 5.49×10^{10} C of electricity

54. Electrolyte KCl KNO_3 HCl NaOAc NaCl

($S\ cm^2$ 149.9 145 426.2 91.0 126.5 mol^{-1})

Calculate using appropriate molar conductances of the electrolytes listed above at infinite dilution in H_2O at 25°C .

a. 517.2
b. 552.7
c. 390.7
d. 217.5

55. The chemical reaction,

$2AgCl\ (s) + H_2(g) \rightarrow 2HCl\ (aq) + 2Ag\ (s)$

taking place in a galvanic cell is represented by the notation

a. Pt (s) | H_2 (g), 1 bar | 1 M KCl (aq) | AgCl (s) | Ag (s)

b. Pt (s) | H_2 (g), 1 bar | 1 M KCl (aq) | 1 M Ag^+ (aq) | Ag (s)

c. Pt (s) | H_2 (g), 1 bar | 1 M KCl (aq) | AgCl (s) | Ag (s)

d. Pt (s) | H_2 (g), 1 bar | 1 M KCl (aq) | Ag (s) | AgCl (s)

56. The number of moles of $KMnO_4$ reduced by one mole of KI in alkaline medium is

a. 2
b. 1
c. 5
d. 6

57. A hypothetical electrochemical cell is shown below

$\overset{\ominus}{A}$ | A^+ (xM) || B^+ (yM) | $\overset{\oplus}{B}$

The emf measured is +0.20 V. the cell reaction is

a. the cell reaction cannot be predicted

b. $A + B^+ \rightarrow A^+ + B$

c. $A^+ + B \rightarrow A + B^+$

d. $A^+ + e^- \rightarrow A$; $B^+ + e^- \rightarrow B$

58. If $E^\circ Fe^{2+}/Fe = -0.441$ V and $E^\circ Fe^{3+}/Fe^{2+} = 0.771$ V, the standard EMF of the reaction

$Fe + 2Fe^{3+} \rightarrow 3Fe^{2+}$

will be

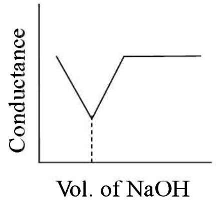
a. 1.212 V
b. 0.111 V
c. 0.330 V
d. 1.653 V

59. If equivalent conductance of 1 M benzoic acid is 12.8 $ohm^{-1}\ cm^2$ and if the conductance of benzoate ion and H^+ ion are 42 and 288.42 $ohm^{-1} cm^2$ respectively, its degree of dissociation is

a. 3.9 %
b. 0.039 %
c. 39 %
d. 0.34 %

60. Conductometric titration curve of an equimolar mixture of a HCl and HCN with NaOH(aq) can be given as

a.



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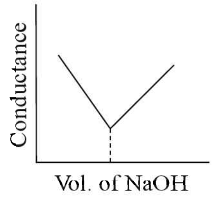
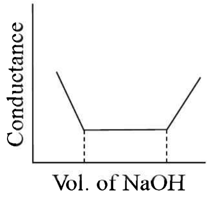
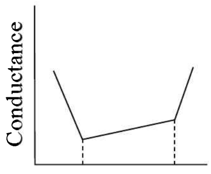


c.



d.



61. Two electrochemical cell

$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$ and $Fe \mid Fe^{2+} \parallel Cu^{2+} \mid Cu$ are connected in series. What will be the net e.m.f. of the cell at 25°C?

Given: $Zn^{2+} \mid Zn = -0.73$ V,

$Cu^{2+} \mid Cu = +0.34$ V

$Fe^{2+} \mid Fe = -0.41$ V

a. +1.85
b. –1.85 V
c. +0.83 V
d. –0.83 V

62. The reaction potential values of M, N and O are +2.46, –1.13 and –3.13 V respectively. Which of the following order is correct regarding their reducing property?

a. O > N > M
b. O > M > N
c. M > N > O
d. M > O > N

63. If the aqueous solutions of the following salts are electrolyzed for 1 hour with 10 ampere current, which solution will deposit the maximum mass of the metal at the cathode? The atomic weights are, Fe = 56, Zn = 65, Ag =108, Hf = 178 and W = 184

a. $ZnSO_4$
b. $FeCl_3$
c. WCl_6
d. $AgNO_3$

64. Given the standard reduction potentials $Zn^{2+} / Zn = -0.74$ V, $Cl_2 / Cl^- = 1.36$ V, $H^+ / ½ H_2 = 0$ V and $Fe^{2+} / Fe^{3+} =$ V. The order of increasing strength as reducing agent is

a. Zn, H_2, Fe^{2+}, Cl^-
b. H_2, Zn, Fe^{2+}, Cl^-
c. Cl^-, Fe^{2+}, H_2, Zn
d. Cl^-, Fe^{2+}, Zn, H_2

65. Given the data at 25°C

$Ag + I^- \rightarrow AgI + e^-$; E° = 0.152 V

$Ag \rightarrow Ag^+ + e^-$; E° = –0.800 V

What is the value of log Ksp for AgI?

(2.303 RT/F = 0.059 V)

a. –8.12
b. +8.612
c. –37.83
d. –16.13

66. One mole of acidified $K_2Cr_2O_7$ on reaction with excess KI will liberate …… moles of I_2

a. 1
b. 2
c. 3
d. 5
e. 7

67. The products formed when an aqueous solution of NaBr is electrolyzed in a cell having inert electrodes are

a. Na and Br_2
b. Na and O_2
c. H_2, Br_2 and NaOH
d. H_2 and O_2

68. The charge required for the reduction of 1 mol of MnO_4^- to MnO_2 is

a. 1 F
b. 3 F
c. 5 F
d. 6 F

69. What current is to be passed for 0.25 s for deposition of a certain weight of metal which is equal to its electrochemical equivalent?

a. 2 A
b. 4 A
c. 100 A
d. 200 A

70. If the molar conductance values of Ca^{2+} and Cl^- at infinite dilution are respectively, 118.88×10^{-4} m² mho mol⁻¹ and 77.33×10^{-4} m² mho mol⁻¹, then that of $CaCl_2$ is (in m² mho mol⁻¹)

a. 153.56×10^{-4}
b. 273.54×10^{-4}
c. 183.24×10^{-4}
d. 196.84×10^{-4}

71. Ag (s) | Ag^+ (aq) (0.01 M) || Ag^+ (aq) (0.1 M) | Ag (s), E°Ag (s) / Ag^+ (aq) = 0.80 Volt

a. $E_{cell} = 0.80$ V

b. $E_{cell} = 0.0296$ V

c. $E_{cell} = 0.0591$ V

d. Cell cannot function as anode and cathode are of the same material

72. Find the equivalent weight of $Cr_2O_7^{2-}$ in the following reaction:

$$Cr_2O_7^{2-} \xrightarrow{H^+} Cr^{3+}$$

a. Molecular weight / 2

b. Molecular weight / 3

c. Molecular weight / 4

d. Molecular weight / 6

73. $KMnO_4$ is a strong oxidizing agent in acid medium. To provide acid medium H_2SO_4 is used instead of HCl. This is because

a. Only H_2SO_4 is completely ionized.
b. Rate is faster in the presence of H_2SO_4
c. H_2SO_4 is a dibasic acid
d. HCl is oxidized by $KMnO_4$ to Cl_2
e. H_2SO_4 is a stronger acid than HCl.

74. $Zn^{2+} \rightarrow Zn(s)$; $E^\circ = -0.76$ V

$Cu^{2+} \rightarrow Cu(s)$; $E^\circ = -0.34$ V

Which of the following is spontaneous?

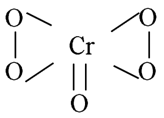
a. $Zn^{2+} + Cu \rightarrow Zn + Cu^{2+}$
b. $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$
c. $Zn^{2+} + Cu^{2+} \rightarrow Zn + Cu$
d. None of the above

75. The standard e.m.f. of a galvanic cell involving cell reaction with n = 2 is found to be 0.295 V at 25°C. The equilibrium constant of the reaction would be

(Given F = 96500 C mol^{-1}; R = 8.314 JK^{-1} mol^{-1})

a. 2.0×10^{11} **b.** 4.0×10^{12}
c. 1.0×10^{2} **d.** 1.0×10^{10}

76. Oxidation state of chromium in



a. + 9 **b.** + 6
c. + 1 **d.** – 4

77. The standard potential of the half cell reaction Zn^{2+} (aq) + $2e^- \rightarrow Zn$ (s) is –0.7628 V at 25°C

The standard potential for the reaction,

$2Zn^{2+} + 4e^- \rightarrow 2Zn$ (s) is

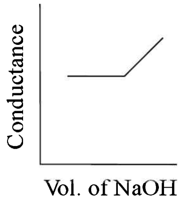
a. +0.7628 V **b.** –0.7628 V
c. –0.3814 V **d.** 0.3814 V

78. A dilute solution of H_2SO_4 was electrolyzed by passing a current of 2 amp. The time required for formation of 0.5 mole of oxygen is

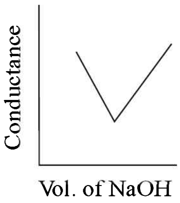
a. 13.4 hours **b.** 26.8 hours
c. 2.68 hours **d.** 53.4 hours

79. CH_3COOH canbe neutralized by NaOH. Conductometric titration curve can be given as

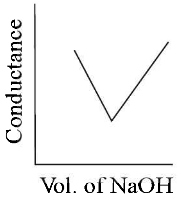
a.



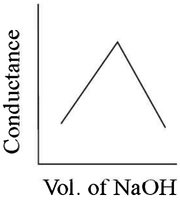
b.



c.



d.



80. Ksp of $BaSO_4$ is 1×10^{-10} . If the ionic conductances of Ba^{++} and SO_4^{--}ions are 64 and 80 ohm^{-1} cm^2 mol^{-1} respectively, then its specific conductance is

a. 1.44×10^{-8} ohm^{-1} cm^{-1}
b. 144×10^{-8} ohm^{-1} cm^{-1}
c. 1.44×10^{8} ohm^{-1} cm^{-1}
d. 144×10^{8} ohm^{-1} cm^{-1}

Brainteasers Objective Type Questions (Single choice only)

81. The e.m.f of the following three galvanic cells:

(1) Zn | Zn^{2+} (1 M) || Cu^{2+} (1 M) | Cu
(2) Zn | Zn^{2+} (0.1 M) || Cu^{2+} (1 M) | Cu
(3) Zn | Zn^{2+} (1 M) || Cu^{2+} (0.1 M) | Cu

are represented by E_1, E_2 and E_3. Which of the following statement is true?

a. $E_2 > E_1 > E_3$ **b.** $E_3 > E_2 > E_1$
c. $E_1 > E_2 > E_3$ **d.** $E_3 > E_1 > E_2$

82. When an electric current is passed through acidulated, water 112 mL of hydrogen gas at NTP collects at the cathode in 965 seconds. The current passes, in ampere is

a. 0.1 **b.** 0.5
c. 1.0 **d.** 2.0

83. The charge required to deposit 40.5 g of Al (atomic mass = 27.0 g) from the fused $Al_2(SO_4)_3$ is

a. 0.434×10^5 C **b.** 4.34×10^5 C
c. 3.34×10^5 C **d.** 43.4×10^5 C

84. The hydrogen electrode is dipped in a solution of pH = 3.0 at 25°C. The potential of hydrogen electrode would be

a. –0.177 V **b.** 0.177 V
c. 1.77 V **d.** 0.277 V

85. Three faraday of electricity is passed through aqueous solutions of $AgNO_3$, $NiSO_4$ and $CrCl_3$ kept in three vessels using inert electrodes. The ratio in mol in which the metals Ag, Ni and Cr will be deposited is

a. 1 : 2 : 3 **b.** 2 : 3 : 6
c. 6 : 3 : 2 **d.** 3 : 2 : 6

86. Calculate the weight of copper that will be deposited at the cathode in the electrolysis of a 0.2 M solution of copper sulphate when quantity of electricity equal to the required to liberate 2.24 L of hydrogen at STP from a 0.1 M aqueous sulphuric acid, is passed (atomic mass of Cu = 63.5)

a. 6.35 g **b.** 3.17 g
c. 12.71 g **d.** 63.5 g

87. The same amount of electricity was passed through two separate electrolytic cells containing solutions of nickel nitrate and chromium nitrate respectively. If 0.3 g of nickel was deposited in the first cell, the amount of chromium deposited is (atomic weight of Ni = 59, Cr = 52)

a. 0.130 g **b.** 0.236 g
c. 0.176 g **d.** 1.76 g

88. Given that: $E^\circ (Zn^{2+} / Zn) = -0.763$ V and

$E^\circ (Cd^{2+} / Cd) = -0.403$ V, the emf of the following cell:

$Zn \mid Zn^{2+} (a = 0.04) \parallel Cd^{2+} (a = 0.2) \mid Cd$

is given by

a. $E = +0.36 + [0.059 / 2] [\log (0.2/0.004)]$
b. $E = -0.36 + [0.059 / 2] [\log (0.2/0.004)]$
c. $E = +0.36 + [0.059 / 2] [\log (0.004/0.2)]$
d. $E = -0.36 + [0.059 / 2] [\log (0.004/0.2)]$

89. If the pressure of hydrogen gas is increased from 1 atm to 100 atm, keeping the hydrogen ion concentration constant at 1 M, the voltage of the hydrogen half cell at 25°C will be

a. –0.059 V **b.** +0.059 V
c. 5.09 V **d.** 0.259 V

90. When a current of 1.5 ampere is passed through acidulated water for two hours, then volume of hydrogen (H_2) at NTP produced will be

a. 1.5 litre **b.** 0.5 litre
c. 1.25 litre **d.** 2.5 litre

91. For the following cell with hydrogen electrodes at two different pressures p_1 and p_2

$$\underset{p_1}{Pt (H_2)} \mid \underset{1M}{H^+ (aq)} \mid \underset{p_2}{Pt (H_2)}$$

EMF is given by

a. $RT/F \log_e p_1 / p_2$
b. $RT/2F \log_e p_1 / p_2$
c. $RT/F \log_e p_2 / p_1$
d. $RT/2F \log_e p_2 / p_1$

92. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100 Ω. The conductivity of this solution is 1.29 S m^{-1}. Resistance of the same cell when filled with 0.2 M of the same solution is 520 Ω. The molar conductivity of 0.02 M solution of the electrolyte will be

a. 124×10^{-4} S m^2 mol^{-1}
b. 1240×10^{-4} S m^2 mol^{-1}
c. 1.24×10^{-4} S m^2 mol^{-1}
d. 12.4×10^{-4} S m^2 mol^{-1}

93. Which of the following reactions is most suitable for a fuel cell?

a. $2CO (g) + O_2 (g) \rightarrow 2CO_2 (g)$
b. $MnO_2 (s) + Li (s) \rightarrow LiMnO_2 (s)$
c. $HgO (l) + Zn (s) \rightarrow ZnO (s) + Hg (l)$
d. $Pb(s) + PbO_2 (s) + 2H^+ (aq) + HSO_4^- (aq) \rightarrow PbSO_4 (s) + 2H_2O (l)$

94. The volume of H_2 gas at NTP obtained by passing 4 amperes through acidified H_2O for 30 minutes is

a. 0.187 L **b.** 0.836 L
c. 0.0836 L **d.** 0.0536 L

95. $aK_2Cr_2O_7 + bKCl + cH_2SO_4 \rightarrow xCrO_2Cl_2 + yKHSO_4 + zH_2O$

The above equation balances when

a. a = 1, b = 6, c = 4 and x = 6, y = 2, z = 3

b. a = 2, b = 4, c = 6 and x = 2, y = 6, z = 3

c. a = 1, b = 4, c = 6 and x = 2, y = 6, z = 3

d. a = 4, b = 2, c = 6 and x = 6, y = 2, z = 3

e. a = 6, b = 4, c = 2 and x = 6, y = 3, z = 2

96. The standard emf of the cell

Cd (s) | $CdCl_2$ (0.1 M) || AgCl (s) | Ag (s) in which the cell reaction is

$$Cd\,(s) + 2AgCl\,(s) \rightarrow 2Ag\,(s) + Cd^{2+}\,(aq) + 2Cl^-\,(aq)$$

is 0.6915 V at 0°C and 0.6753 V at 25°C,

The enthalpy change of the reaction at 25°C is

a. –346.8 kJ
b. –176.0 kJ
c. –167.6 kJ
d. +127.6 kJ

97. 4.5 g of aluminium (at. mass 27 amu) is deposited at cathode from Al^{3+} solution by a certain quantity of electric charge. The volume of hydrogen produced at STP from H^+ ions is solution by the same quantity of electric charge will be

a. 44.8 L
b. 22.4 L
c. 11.2 L
d. 5.6 L.

98. If Zn^{2+} / Zn electrode is diluted 100 times, then the change in emf is

a. Decrease of 29.5 mV
b. Increase of 29.5 mV
c. Decrease of 59 mV
d. Increase of 59 mV

99. Two electrochemical cells,

Zn | Zn^{2+} || Cu^{2+} | Cu and

Fe | Fe^{2+} || Cu^{2+} | Cu

are connected in series. What will be the net e.m.f. of the cell at 25°C?

Given: Zn^{2+} | Zn = –0.76 V,

Cu^{2+} | Cu = +0.34 V,

Fe^{2+} | Fe = –0.41 V

a. –1.85 V
b. –0.83 V
c. +0.83 V
d. +1.85 V

100. In the reaction,

$$As_2S_5 + xHNO_3 \rightarrow 5H_2SO_4 + yNO_2 + 2H_3AsO_4 + 12H_2O,$$

The values of x and y are

a. 30, 30
b. 40, 40
c. 10, 10
d. 20, 20

101. Given that E° = +0.897 V,

Pb (s) | Pb^{2+} (0.040 M) || Fe^{3+} (0.20 M), Fe^{2+} (0.010 M) | Pt (s)

Calculate E at 25°.

a. +1.139 V
b. +1.015 V
c. +0.669 V
d. +0.926 V

102. The equilibrium constant of the reaction:

$$Cu\,(s) + 2Ag^+\,(aq) \rightarrow Cu^{2+}\,(aq) + 2Ag\,(s);$$

E° = 0.46 V at 298 K is

a. 2.4×10^{10}
b. 2.0×10^{10}
c. 4.0×10^{10}
d. 4.0×10^{15}

103. The standard oxidation potentials of Zn, Cu, Ag and Ni electrodes are +0.76, –0.34, –0.80 and +0.25 V respectively. Which of the following reaction will provide maximum voltage?

a. $Zn + 2Ag^+\,(aq) \rightarrow Zn^{2+}\,(aq) + 2Ag$

b. $Cu + 2Ag^+\,(aq) \rightarrow Cu^{2+}\,(aq) + 2Ag$

c. $Zn + 2H^+\,(aq) \rightarrow Zn^{2+}\,(aq) + H_2$

d. $Zn + Cu^{2+}\,(aq) \rightarrow Zn^{2+}\,(aq) + Cu$

104. The reduction potential of a half cell consisting of a Pt electrode immersed in 1.2 M Fe^{2+} and 0.012 M Fe^{3+} solution at 25°C is (E°Fe^{3+} / Fe^{2+} = 0.770)

a. –0.326 V
b. 0.652 V
c. 0.326 V
d. –0.652 V

105. The standard potentials of OCl^- / Cl^- and Cl^-/ ½ Cl_2 are 0.94 V and 1.36 V respectively. The E° value of OCl^- / ½ Cl_2 will be

a. –0.42 V
b. 2.3 V
c. 0.4 2 V
d. 0.V

106. The cell Zn | Zn^{2+} (1 M) || Cu^{2+} (1 M) | Cu (E°_{cell} = 1.10 V), was allowed to be completely discharged at 298 K. The relative concentration of Zn^{2+} to Cu^{2+} ($[Zn^{2+}]$ / $[Cu^{2+}]$) is

a. 37.3
b. $10^{37.3}$
c. 9.65×10^4
d. antilog (24.08)

107. In an experiment 0.04 F was passed through 400 ml of a 1 M solution of NaCl. What would b the pH of the solution after the electrolysis?

a. 8
b. 10
c. 12
d. 13

108. The resistance of N/10 solution is found to be 2.5×10^3 ohms. The equivalent conductance of the solution is (cell constant = 1.25 cm^{-1})

a. 1.25 $ohm^{-1}\,cm^2\,equiv^{-1}$.

b. 5.0 $ohm^{-1}\,cm^2\,equiv^{-1}$.

c. 2.5 ohm^{-1} cm^{-2} $equiv^{-1}$.

d. 2.5 ohm^{-1} cm^{2} $equiv^{-1}$.

e. 5.5 ohm^{-1} cm^{-2} $equiv^{-1}$.

109. How long (in hours) must a current of 5.0 amperes be maintained to electroplate 60 g of calcium from molten $CaCl_2$?

a. 16 hours
b. 11 hours
c. 8.6 hours
d. 26 hours

110. An alloy of Pb-Ag weighing 1.08 g was dissolved in dilute HNO_3 and the volume made to 100 ml. A silver electrode was dipped in the solution and the EMF of the cell set up

Pt (s), H_2 (g) | H^+ (1M) || Ag^+ (aq) | Ag (s)

was 0.62 V. If $E°_{cell}$ = 0.80 V. What is the percentage of Ag in the alloy? [At 25°C, RT/F = 0.06]

a. 1 %
b. 10 %
c. 25 %
d. 50 %
e. 75 %

111. Based on the following information,

F_2 (g) + $2e^-$ → $2F^-$ (aq)   E° = +2.87 V

Mg^{2+} (aq) + $2e^-$ → 2Mg (s) E° = –2.37 V

Which of the following chemical species is the strongest reducing agent?

a. F^- (aq)
b. F_2 (g)
c. Mg (s)
d. Mg^{2+} (aq)

112. E° Cr^{3+}/Cr^{2+} = –0.41 V The amount of chlorine evolved, when 2A of current is passed for 30 minutes in an aqueous solution of NaCl will be

a. 1.32 g
b. 3.54 g
c. 12.5 g
d. 8.56 g

113. The oxidation states of sulphur in the anions SO_3^{2-}, $S_2O_4^{2-}$ and $S_2O_6^{2-}$ follow the order:

a. $SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$

b. $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$

c. $S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$

d. $S_2O_6^{2-} < S_2O_4^{2-} < SO_3^{2-}$

114. In the balanced chemical reaction,

$IO_3^- + aI^- + bH^+ \rightarrow cH_2O + dI_2$
a, b, c, and d respectively corresponds to:

a. 4, 5, 6, 3
b. 3, 6, 5, 3
c. 5, 6, 2, 3
d. 5, 6, 3, 3

115. When a quantity of electricity is passed through $CuSO_4$ solution, 0.16 g of copper gets deposited. If the same quantity of electricity is passed through acidulated water, then the volume of H_2 liberated at STP will be (at. wt. of Cu = 64)

a. 4.0 cm^3
b. 56 cm^3
c. 604 cm^3
d. 8.0 cm^3

116. For decolourization of one mole of $KMnO_4$ the moles of H_2O_2 reqiured is

a. 1/2
b. 3/2
c. 5/2
d. 7/ 2

117. The standard reduction potentials of Fe/Fe^{2+} and Fe^{2+} / Fe^{3+} are –0.44 V and 0.77 V respectively. The reduction potential of Fe/Fe^{3+} couple is

a. 0.11 V
b. 0.037 V
c. –0.11 V
d. –0.037 V

118. $2Hg \rightarrow Hg_2^{2+}$, E° = +0.855 V
$Hg \rightarrow Hg^{2+}$, E° = +0.799 V
Equilibrium constant for the reaction

$Hg + Hg^{2+} \rightarrow Hg_2^{2+}$ at 27°C is

a. 79
b. 89
c. 69
d. 82.9

119. On the basis of the following E° values, the strongest oxidizing agent is:

$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-}$, E° = –0.35 V

$Fe^{2+} \rightarrow Fe^{3+} + e^-$, E° = –0.77 V

a. Fe^{3+}
b. $[Fe(CN)_6]^{3-}$
c. $[Fe(CN)_6]^{4-}$
d. Fe^{2+}

120. Consider the following standard reduction potentials,

Al^{3+} (aq) + $3e^-$ → Al (s)   E° = –1.66 V

I_2 (s) + $2e^-$ → $2I^-$ (aq)   E° = +0.54 V

Under standard conditions,

a. I^- (aq) is a stronger oxidizing agent than Al (s) and I_2 (s) is a stronger reducing agent than Al^{3+} (aq).

b. Al (s) is a stronger oxidizing agent than I^- (aq), and Al^{3+} (aq) is a stronger reducing agent than I_2 (s).

c. I_2 (s) is a stronger oxidizing agent than Al^{3+} (aq), and Al (s) is a stronger reducing agent than I^- (aq).

d. Al^{3+} (aq) is a stronger oxidizing agent than I_2 (s), and I^- (aq) is a stronger reducing agent than Al (s).

121. In which of the following the oxidation number of oxygen has been arranged in increasing order?

a. $OF_2 < O_3 < KO_2 < BaO_2$

b. $BaO_2 < KO_2 < O_3 < OF_2$

c. $OF_2 < KO_2 < BaO_2 < O_3$

d. $KO_2 < OF_2 < O_3 < BaO_2$

e. $BaO_2 < O_3 < OF_2 < KO_2$

122. If three Faradays of electricity is passed through the solutions of $AgNO_3$, $CuSO_4$ and $AuCl_3$, the molar ratio of the cations deposited at the cathodes will be

a. 1 : 2 : 3 **b.** 6 : 3 : 2
c. 6 : 1 : 3 **d.** 2 : 3 : 1

123. The hydrogen electrode is dipped in a solution of pH = 3 at 25°C. The potential of the cell would be (value of 2.303 RT/F is 0.059 V)

a. +1.77 V **b.** + 0.177 V
c. – 0.87 V **d.** –0.177 V

124. Which of these correctly Ecell as a functions of concentrations for the cell (for different values of M and M′)

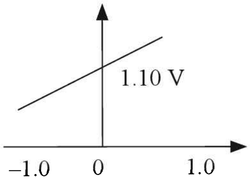
$Zn(s) + Cu^{+2}(M) \rightarrow Zn^{+2}(M') + Cu(s)$

$E^{o}_{cell} = 1.10$ V

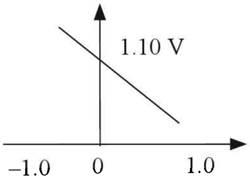
X– axis : $1 \log 10 \dfrac{[Zn^{+2}]}{[Cu^{+2}]}$,

Y – axis: $_{Ecell}$

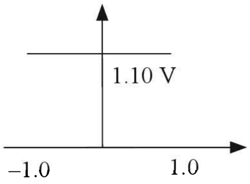
a.



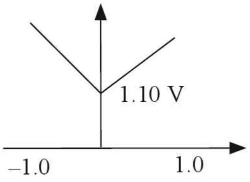
b.



c.



d.



125. What is the relationship between the standard cell potentials E°, for the following two galvanic cell reactions?

(I) $2Ag^{+}(aq) + Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2Ag(s)$

(II) $Ag\ (s) + \frac{1}{2} Sn^{4+}\ (aq) \rightarrow \frac{1}{2} Sn^{2+}\ (aq) + Ag^{+}\ (aq)$

a. E° (I) = 2E° (II)

b. E° (I) = E° (II)

c. E° (I) = –2E° (II)

d. E° (I) = –E° (II)

126. The standard reduction potentials of Cu^{2+} / Cu and Cu^{2+}/Cu^{+} are 0.337 V and 0.153 V respectively. The standard electrode potential of Cu^{+}/Cu half cell is

a. 0.507 V **b.** 0.421 V
c. 0.184 V **d.** 0.0501 V

127. For a galvanic cell that uses the following two half reactions,

$Cr_2O_7^{2-}\ (aq) + 14\ H^{+}\ (aq) + 6e^{-} \rightarrow 2Cr^{3+}\ (aq) + 7H_2O\ (l)$

$Pb\ (s) \rightarrow Pb^{2+}\ (aq) + 2e^{-}$

How many moles of Pb (s) are oxidized by one mole of $Cr_2O_7^{2-}$?

a. 6 **b.** 4
c. 3 **d.** 2

128. How many moles of electrons, are transferred in the following reduction-oxidation reaction?

$2MnO_4^{-}\ (aq) + 16H^{+}\ (aq) + 10Cl^{-}\ (aq) \rightarrow 2Mn^{2+}\ (aq) + 5Cl_2\ (g) + 8H_2O\ (l)$?

a. 2 **b.** 5
c. 10 **d.** 12

129. Given:

$Ag^{+}\ (aq) + e^{-} \rightarrow Ag\ (s)$ E° = +0.799 V

$AgI\ (s) + e^{-} \rightarrow Ag\ (s) + I^{-}\ (aq)$ E° = –0.152 V

$Ni^{2+}\ (aq) + 2e^{-} \rightarrow Ni\ (s)$ E° = –0.267 V

Which of the following reactions should be spontaneous under standard conditions?

(I) $2AgI(s) + Ni(s) \rightarrow 2Ag(s) + 2I^-(aq) + Ni^{2+}(aq)$

(II) $Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$

a. I is spontaneous and II is non spontaneous

b. Both I and II are spontaneous

c. Both I and II are non spontaneous

d. I is non-spontaneous and II is spontaneous

130. The cell reaction for a lead storage battery is

$$Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2Pb(SO_4)(s) + 2H_2O(l)$$

$$E^\circ = +1.92\ V$$

To provide a potential of about 12 V, one could

a. Connect six cells in series.

b. Adjust the pH to 12.

c. Adjust the pH to 1.

d. Greatly increase the surface area of the Pb (s) and PbO_2 (s).

131. If $E^\circ_{MnO4–/Mn2+}$ = 1.51 V and E° MnO_2 / Mn^{2+} = 1.23 V, the $E^\circ_{MnO4–/MnO2}$ is

a. +1.69 V **b.** –1.69 V

c. –3.38 V **d.** +0.845 V

132. For the reactions

(i) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $E^\circ = 1.51\ V$

(ii) $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$ $E^\circ = 1.23\ V$,

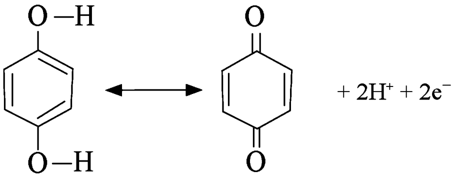
Then for the reaction

(iii) $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$ E° is

a. 2.45 V **b.** 0.85 V

c. 1.70 V **d.** –1.70V

133. For the half cell



At pH = 2, electrode potential is

a. 1.36 V **b.** 0.71

c. 1.42 V **d.** –1.48 V

134. The cell reaction for a lead storage battery is

$$Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2Pb(SO_4)(s) + 2H_2O(l)$$

$$E^\circ = +1.92\ V$$

To provide a potential of about 12 V, one could

a. Connect six cells in series.

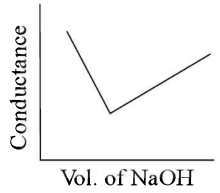
b. Adjust the pH to 12.

c. Adjust the pH to 1.

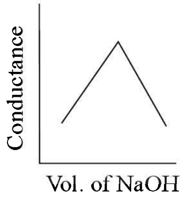
d. Greatly increase the surface area of the Pb (s) and PbO_2 (s).

135. When HNO_3(aq) is titrated with NaOH (aq) conductometrically, the graphical representation of this titration can be shown as

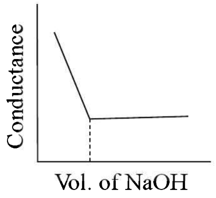
a.



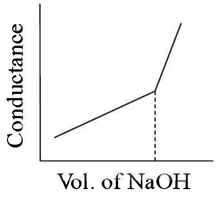
b.



c.



d.



Multiple Correct Answer Type Questions

136. Which of the following reaction is/are not possible at anode?

a. $F_2 + 2e^- \rightarrow 2F^-$

b. $2H^+ + ½ O_2 + 2e^- \rightarrow H_2O$

c. $2Cr_2^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14 H^+ + 6e^-$

d. $Fe^{2+} \rightarrow Fe^{3+} + e^-$

137. Which of the following statements are incorrect?

a. Specific conductance increases with dilution

b. Equivalent conductance decreases with dilution

c. The conductance of all electrolytes increase with temperature

d. Conductance becomes maximum at infinite dilution.

138. Electrolysis of water gives 11.2 L of hydrogen at STP at the cathode. The oxygen evolved at the anode under similar conditions is

a. 5.6 L **b.** 11.2 L

c. 0.25 mol **d.** 8 g

139. Which of the following statements are correct concerning redox properties?

a. A metal M for which E° for the half reaction $M^{n+} + ne \rightleftharpoons M$ is very negative will be a good reducing agent.

b The oxidizing power of halogens decreases from chlorine to iodine.

c The reducing power of hydrogen halides increases from hydrogen chloride to hydrogen iodide.

d Potassium is a better reductant than lithium.

140. Which of the following statements, about the advantage of roasting of sulphide ore before reduction is/are true?

a. Carbon and hydrogen are suitable reducing agents for metal sulphides.

b. The $\Delta_f G°$ of the sulphide is greater than those for CS_2 and H_2S.

c. The $\Delta_f G°$ is negative for roasting of sulphide ore to oxide.

d. Roasting of the sulphide to the oxide is thermodynamically feasible.

141. Which of the following is/are not redox reaction?

a. $Zn + 2AgCN \rightarrow 2Ag + Zn(CN)_2$

b. $Mg(OH)_2 + 2NH_4Cl \rightarrow MgCl_2 + 2NH_4OH$

c. $NaCl + KNO_3 \rightarrow NaNO_3 + KCl$

d. $CaC_2O_4 + 2HCl \rightarrow CaCl_2 + H_2C_2O_4$

142. Given that:

$Ni^{2+}/Ni = 0.25$ V, $Cu^{2+} / Cu = 0.34$ V,

$Ag^+/Ag = 0.80$ V and $Zn^{2+} / Zn = –0.76$ V

Which of the following reactions under standard condition can take place in the specified direction?

a. $Cu (s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag (aq)$

b. $Ni^{2+} (aq) + Cu (s) \rightarrow Ni (s) + Cu^{2+} (aq)$

c. $Zn (s) + 2H^+ (aq) \rightarrow Zn^{2+} (aq) + 3H_2 (g)$

d. $Cu (s) + 2H^+ (aq) \rightarrow Cu^{2+} (aq) + H_2 (g)$

143. Which of the following statement is/are not true for an electrochemical cell?

a. H_2 is anode and Cu is cathode

b. H_2 is cathode and Cu is anode

c. reductions occurs at H_2 electrode

d. oxidation occurs at Cu electrode

144. Which of the following statements concerning the rusting of iron is true?

a. The metal is reduced

b. The oxidation site can occur at a different place on the metal surface than the reduction site.

c. Salt increases the rate of corrosion by providing ions to carry the current.

d. The rusting of iron requires both oxygen and water.

145. Regarding the requisites of an electrolyte to be used in a salt bridge, which of the following statements is/are correct?

a. Low solubility of the electrolyte in water

b. High solubility of the electrolyte in water

c. Equal transport numbers of the cation and the anion of the electrolyte.

d. Large difference in the transport numbers.

146. Which of the reaction/s is/are feasible?

a. $2KI + Br_2 \rightarrow 2KBr + I_2$

b. $2KBr + I_2 \rightarrow 2KI + Br_2$

c. $2KBr + Cl_2 \rightarrow 2KCl + Br_2$

d. $2H_2O + 2F_2 \rightarrow 4HF + O_2$

147. By passage of 1 F of electricity:

a. 9 g of Al is deposited.

b. 5.6 L of O_2 gas evolved at anode.

c. 0.5 mol of Cu is deposited.

d. 0.5 mol of Ca is deposited.

148. Excess of KI reacts with $CuSO_4$ solution and then $Na_2S_2O_3$ solution is added to it. Which of the statements is/are correct for this reaction?

a. Cu_2I_2 is formed

b. CuI_2 is formed

c. $Na_2S_2O_3$ is oxidized

d. evolved I_2 is reduced

149. Which of the following statements is/are not true for the electrochemical Daniel cell?

a. Current flows from zinc electrode to copper electrode

b. Electrons flow from copper electrode to zinc electrode

c. Cations move toward zinc electrode

d. Cations move toward copper electrode

150. Which of the following statement is/ are true?

a. A fuel cell is a galvanic cell

b. One of the reactants in a fuel cell is a traditional fuel.

c. The cell reactants in a fuel cell are continuously supplied from an external source.

d. Modern fuel cells can be easily regenerated using household current.

151. Conceder Electrode potential data given below and select the statements which is/are not correct?

$Fe^{3+} (aq) + e^- \rightarrow Fe^{2+} (aq); E^\circ = +0.77$ V

$Al^{3+} (aq) + 3e^- \rightarrow Al (s); E^\circ = -1.66$ V

$Br_2 (aq) + 2e^- \rightarrow Br^- (aq); E^\circ = +1.08$ V

a. Fe^{2+} is stronger reducing agent than Br^-

b. Fe^{2+} is stronger reducing agent than Al

c. Al is stronger reducing agent than Fe^{2+}

d. Br^- is stronger reducing agent than Al

152. The standard reduction potentials of Zn and Ag in water are $Zn^{2+} + 2e^- \leftrightarrow Zn$; ($E^\circ = -0.76$ V) and $Ag^+ + e^- \leftrightarrow Ag$; ($E^\circ = +0.80$ V) at 298 K. Which of the following reaction is/are not feasible?

a. $Zn^{2+} (aq) + Ag^+ (aq) \rightarrow Zn (s) + Ag (s)$

b. $Zn^{2+} (aq) + 2Ag (s) \rightarrow 2Ag^+ (aq) + Zn (s)$

c. $Zn (s) + Ag (s) \rightarrow Zn^{2+} (aq) + Ag^+ (aq)$

d. $Zn (s) + 2Ag^+ (aq) \rightarrow Zn^{2+} (aq) + 2Ag (s)$

153. Which one of the following condition/s will not increase the voltage of the cell represented by the equation

$Cu (s) + 2Ag^+ (aq) \leftrightarrow Cu^{2+} (aq) + 2Ag (s)$?

a. increase in the dimension of Cu electrode

b. increase in the dimension of Ag electrode

c. increase in the concentration of Cu^{2+} ions

d. increase in the concentration of Ag^+ ions

154. Lead storage battery contains

a. Electrolyte as 38 % H_2SO_4

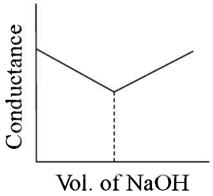
b. Pb rod as cathode

c. Pb rod as anode

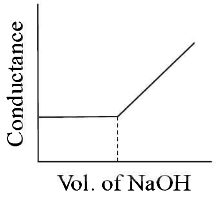
d. Pb plates coated with PbO_2 act as cathode

155. Which of these plots can not be obtained for a conductometric titration of a strong acid against a weak base?

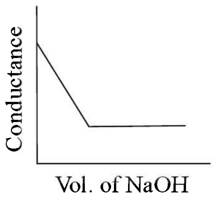
a.



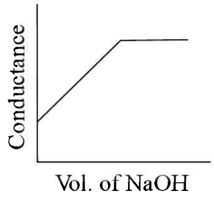
b.



c.



d.



156. Which is/are true for standard electrode potentials?

a. E° for oxidation is the negative of E° for reduction.

b. Cell constituents are in their standard states.

c. The potential for the standard hydrogen electrode is chosen to be +1.00 V.

d. The half reactions are written as reductions.

157. For a galvanic cell at equilibrium, which of the following is/are not true?

a. Ecell = 0 **b.** $\Delta H = 0$
c. Keq = 1 **d.** Ecell $\neq$ 0

158. The passage of electricity through certain electrolyte results in the liberation of H_2 gas at the cathode. The electrolyte could be:

a. $CuCl_2$ (aq) **b.** NaCl (aq)
c. $CaCl_2$ (aq) **d.** $AgNO_3$ (aq)

159. For the galvanic cell Pt(s) | Sn^{2+} (aq), Sn^{4+} (aq) || Pb^{2+} (aq) | Pb (s), what is/are not the function of the Pt (s)?

a. Pt is the anode and does not appear in the overall cell reaction.

b. Pt is the cathode and is a product in the overall cell reaction.

c. Pt is the anode and is a reactant in the overall cell reaction.

d. Pt is the cathode and does not appear in the overall cell reaction.

160. For the reduction of NO_3^- ion in an aqueous solution, E° is +0.96 V. Values of E° for some metal ions are given below.

[IIT 2009]

$V^{2+}(aq) + 2e^- \rightarrow V$ E° = –1.19 V

$Fe^{3+}(aq) + 3e^- \rightarrow Fe$ E° = –0.04 V

$Au^{3+}(aq) + 3e^- \rightarrow Au$ E° = +1.40 V

$Hg^{2+}(aq) + 2e^- \rightarrow Hg$ E° = +0.86 V

The pair of metals that is/are oxidized by NO_3^- in aqueous solution is/are

a. V and Hg **b.** Hg and Fe
c. Fe and Au **d.** Fe and V

Linked-Comprehension Type Questions

Comprehension 1

Given the following data:

Fe^{2+} (aq) + 2Ag (s) → Fe(s) + Ag^+(aq)

$Ag^+ + e^- \rightarrow Ag$ $E^\circ_{red} = -0.44$ V

Answer the following questions with respect to the reaction

Fe^{2+} (aq) + 2Ag(s) → Fe(s) + $2Ag^+$(aq)

161. What is E° for the reaction?

a. 12.4 **b.** –1.24
c. 6.2 **d.** –62.0

162. If $[Fe^{2+}]$ = 0.100M and $[Ag^+]$ = 0.0100 M,

what is the magnitude E at 25°C?

a. 1.15V **b.** 11.5V
c. –1.15 V **d.** –11.5V

163. For the reaction that is spontaneous, what is the maximum amount of work that can be performed?

a. 3.3×10^{-2} kwh
b. 6.6×10^{-2} kwh
c. 12.2×10^{-2} kwh
d. 1.22×10^{-2} kwh

Comprehension 2

Use the following data at 25°C for the questions given below

$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ E° = –0.28 V

$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ E° = –2.37 V

164. What is the slandered cell potential for a votaic cell constructed using the two half reaction.

a. –2.65 V **b.** –2.09 V
c. 0 **d.** 2.09 V

165. What is the cell potential if [Mg^{2+} = 0.50 M and [Ni^{2+}] = 1.0 M?

a. 1.95 V
b. 2.00 V
c. 2.10 V
d. 2.08 V

166. What is K for the equilibrium at 25 °C?

a. 4×10^{-70}
b. 4×10^{70}
c. 2×10^{-35}
d. 2×10^{70}

Comprehension 3

The emf ,E, is related to the change in Gibbs free energy, ΔG: $\Delta G = -nFE$, where is the number of electrons transferred during the redox process and F is a unit called the Faraday. The faraday is the amount of charge on 1 mol of electrons: 1F = 96,500 C/mol. Because E is related to ΔG, the sign of E indicates whether a redox process is spontaneous: $E > 0$ indicates a spontaneous process, and $E < 0$ indicates a non-spontaneous one.

167. The standard electrode potential for the following reaction is +1.33 V. What is the potential at pH = 2.0?

$$Cr_2O_7^{2-}(aq, 1M) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq, 1M) + 7H_2O(l)$$

a. +2.184 V
b. +0.5022V
c. +1.008 V
d. +1.0542 V

168. $Ag^+ (aq) + e^- \rightarrow Ag (s)$ E° = +0.800 V

$AgBr (s) + e^- \rightarrow Ag (s) + Br^- (aq)$ E° = +0.071 V

$Br_2 (l) + 2e^- \rightarrow 2Br^- (aq)$ E° = +1.066 V

Use some of the above data to calculate Ksp at 25°C for AgBr.

a. 6.7×10^{-12}
b. 2.8×10^{-14}
c. 3.7×10^{-19}
d. 4.9×10^{-13}

169. The E° at 298 K for the following reaction at the indicated concentrations is 1.5 V. Find the ΔG in kJ at 298 K.

$$Cr(s) + 3Ag^+(aq, 0.1 M) \rightarrow Ag(s) + Cr^{3+}(aq, 0.1 M)$$

a. –422.83 kJ
b. –212
c. –295
d. –140.94

170. Given the cell:

$Cd(s) \mid Cd(OH)_2(s) \mid NaOH(aq, 0.01 M) \mid H_2(g, 1 bar \mid Pt (s))$

with E_{cell} = 0.0V. If $E^\circ_{Cd^{2+}|Cd}$ = –0.39 V, then K_{sp} of $Cd(OH)_2$ is:

a. 10^{-15}
b. 10^{-13}
c. 10^{13}
d. 10^{15}

Comprehension 4

Redox reaction involve oxidation and reduction simultaneously. Redox are classified into four categories combination, decomposition, displacement, disproportionation reaction. The redox reaction have a great application in the study of various electrode processes, cells and in stoishiometric calculations etc.

171. Which of the following are disproportionation reactions?

(1) $UO^{2+} + Cr_2O_7^{2-} + H^+ \rightarrow UO_2^{2+} + Cr^{3+} + H_2O$

(2) $X_2 + OH^- \rightarrow XO^- + X^- + H_2O$

(3) $HO_2^- + Br^- + H_2O \rightarrow OH^- + Br_2$

(4) $C_6H_5CHO + OH^- \rightarrow C_6H_5COO^- + C_6H_5CH_2OH$

a. 1 and 2
b. 2 and 3
c. 3 and 4
d. 2 and 4

172. Consider the following standard oxidation potentials (at 25°C).

Ag | Ag^+: –0.799 V; Hg | Hg^{2+}: –0.789 V ; Mg | Mg^{2+}: +2.37 V; Mn | Mn^{2+}: +1.18 V ;

Sn | Sn^{2+} : 0.136 V.

Which of the following statements is/are incorrect under standard conditions?

(i) Sn can displace Mg and Ag from their solutions.
(ii) Ag can displace Hg and Mg from their solutions.
(iii) Mn can displace Sn, Hg and Ag from their solutions.
(iv) Mn can displace Sn, Mg and Hg from their solutions.

a. (i), (ii),(iii)
b. (ii), (iii), (iv)
c. (i), (ii), (iv)
d. (i), (ii), (iii), (iv)

173. In the redox reaction,

$MnO_4^{\ominus} + I_2 + H^+ \rightarrow Mn^{2+} + IO_3^{\ominus} + H_2O$,

$MnO_4^{\ominus}$ and I_2 would react in the molar ratio of:

a. 3 : 1
b. 1 : 3
c. 2 : 1
d. 1 : 2

174. P, Q, R and S are four metals. P can displace R from its salt solution, but Q and R cannot displace S. Q can displace hydrogen (H) for a dilute solution of a mineral acid, but R cannot. The reduction potentials of P, Q, R, S and H (hydrogen) are in the order

a. H > P> R > S > Q

b. P > S > Q > H > R

c. P > Q > R > S > H

d. R > H > Q > S > P

Comprehension 5

Tollen's reagent is used for the detection of aldehydes when a solution of $AgNO_3$ is added to glucose with NH_4OH then gluconic acid is formed.

$Ag^+ + e^- \rightarrow Ag$; E°red = 0.8 V

$C_6H_{12}O_6 + H_2O \rightarrow$ Gluconic acid $(C_6H_{12}O_7)$ $+ 2H^+ + 2e^-$

E°red = –0.05 V

$Ag(NH_3)_2^+ + e^- \rightarrow Ag\ (s) + 2NH_3$

E°red = 0.337 V

[Use 2.303 × RT/F = 0.0592 and F / RT = 38.92 at 298 K]

$$2Ag^+ + C_6H_{12}O_6 + H_2O \rightarrow 2Ag\ (s) + C_6H_{12}O_7 + 2H^+$$

175. Find K of this reaction.

a. 66.13 **b.** 58.38

c. 28.30 **d.** 46.29

[IIT 2006]

176. When ammonia is added to the solution, pH is raised to 11. Which half cell reaction is affected by pH and by how much?

a. Eoxd will increase by a factor of 0.65 from E°oxd.

b. Eoxd will decrease by a factor of 0.65 from E°oxd.

c. Ered will increase by a factor of 0.65 from E°red.

d. Ered will decrease by a factor of 0.65 from E°red.

[IIT 2006]

177. Ammonia is always is added in this reaction. Which of the following must be incorrect?

a. NH_3 combines with Ag^+ to form a complex

b. $Ag(NH_3)_2^+$ is a stronger oxidizing reagent than Ag^+.

c. In absence of NH_3 silver salt of gluconic acid is formed

d. NH_3 has affected the standard reduction potential of glucose/gluconic acid electrode.

[IIT 2006]

Comprehension 6

Redox reactions play a pivotal role in chemistry and biology. The values of standard redox potential (E°) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example of Daniel cell in which zinc goes into solution and copper gets deposited. Given below are a set of half cell reactions (acidic medium) along with their E° (V with respect to normal hydrogen electrode) values. Using this data obtained the correct explanations.

$I_2 + 2e^- \rightarrow 2I^-$ E° = 0.54

$Cl_2 + 2e^- \rightarrow 2Cl^-$ E° = 1.36

$Mn^{3+} + e^- \rightarrow Mn^{2+}$ E° = 1.50

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ E° = 0.77

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ E° = 1.23

178. Among the following, identify the correct statement.

a. Chloride ion is oxidized by O_2

b. Fe^{2+} is oxidized by iodine

c. Iodide ion is oxidized by chlorine

d. Mn^{2+} is oxidized by chlorine

[IIT 2007]

179. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because

a. O_2 oxidizes Mn^{2+} to Mn^{3+}

b. O_2 oxidizes both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}

c. Fe^{3+} oxidizes H_2O to O_2

d. Mn^{3+} oxidizes H_2O to O_2

[IIT 2007]

180. Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and H_2SO_4 in presence of air gives a Prussian blue precipitate. The blue colour is due to the formation of

a. $Fe_4[Fe(CN)_6]_3$ **b.** $Fe_3[Fe(CN)_6]_2$

c. $Fe_4[Fe(CN)_6]_2$ **d.** $Fe_3[Fe(CN)_6]_3$

[IIT 2007]

Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given. Mark

- **a.** if A and R both are correct and R is the correct explanation of A;
- **b.** if A and R both are correct but R is not the correct explanation of A;
- **c.** A is true but R is false;
- **d.** A is false but R is true,
- **e.** A and R both are false.

181. **(A):** In brown ring complex, $[Fe(H_2O)_5NO]\ SO_4$, the oxidation number of iron is +1.

(R): Due to charge transfer the one unpaired electron of NO shifts to Fe^{2+}, thereby Fe^{2+} converts into Fe^{+}.

182. **(A):** If standard reduction potential for the reaction

$Ag^+ + e^- \rightarrow Ag$ is 0.80 volts

then for the reaction

$3Ag^+ + 3e^- \rightarrow 3\ Ag$

it will be 2.4 volts

(R): If concentration is increased, reduction electrode potential is increased.

183. **(A):** 1 faraday of electricity is passed through acidified H_2O, volume of O_2 liberated at STP will be 5.6 L.

(R): Equivalent weight of oxygen is 16.

184. **(A):** The voltage of mercury cell remains constant for longer period of time.

(R): It is because net cell reaction does not involve any ion.

185. **(A):** The correct order of equivalent conductance at infinite dilution is KCl > NaCl > LiCl

(R): KCl is stronger electrolyte than NaCl which is stronger than LiCl.

186. **(A):** The tendency of an atom to reach a stable electronic arrangement may be satisfied by the transfer of electrons from one atom to another.

(R): Loss and gain of electrons constitute reduction and oxidation.

187. **(A):** In acidic medium equivalent weight of $K_2Cr_2O_7$ equals to 294 same as that of molecular weight.

(R): In acidic medium $K_2Cr_2O_7$ does not observe any change.

188. **(A):** For a weak electrolyte, the plot of molar conductivity (Λm) against $\sqrt{c}$ (c is concentration in mol lit^{-1}) is nearly linear.

(R): The molar conductivity at infinite dilution (Λm) for an electrolyte can be considered equal to the sum of the limiting molar conductivities of the individual ions.

189. **(A):** Cell constant is the E.M.F. of a cell.

(R): Cell constant is determined by using saturated KCl solution

190. **(A):** When acidified zinc sulphates solution is electrolyzed between zinc electrodes, it is zinc that is deposited at the cathode and hydrogen evolution does not take place.

(R): The electrode potential of zinc is more negative than hydrogen as the over-voltage for hydrogen evolution on zinc is quite large.

191. **(A):** For three half –cell reactions involving different number of electrons. $E_3 = E_1 + E_2$

(R): $\Delta G_3 = \Delta G_1 + \Delta G_2$

192. **(A):** The mobility of sodium ion is lower than that of potassium ion.

(R): The ionic mobilities depend upon the effective radius of the ion.

193. **(A):** At the end of electrolysis using platinum electrodes, an aqueous solution of $CuSO_4$ turns colourless.

(R): $CuSO_4$ changes stoichiometric $Cu(OH)_2$ during electrolysis.

194. **(A):** 1 faraday of electricity deposits 1 g equivalent of Ag or Cu or Al.

(R): 1 mol electrons are required to reduce 1 mol of Ag^+ or Cu^{2+} or Al^{3+} ion.

195. **(A):** When an aqueous solution of $NaNO_3$ is electrolysed, sodium is liberated at the cathode.

(R): Na^+ ions are discharged at cathode and NO_3^- at the anode.

196. **(A):** When acidified zinc sulphate solution is electrolyzed between zinc electrodes. It is zinc that is deposited at the cathode and hydrogen evolution does not take place

(R): The electrode potential of zinc is more negative than hydrogen as the overvoltage for hydrogen evolution on zinc is quite large.

197. **(A):** At the end of electrolysis using platinum electrodes, an aqueous solution of copper sulphate turn colourless.

(R): Copper in copper sulphate is converted to copper hydroxide during the electrolysis.

198. **(A):** Poggendroff compensation method is used for the measurement of emf of voltaic cells

(R): This method has the advantage of giving the emf an open circuit when it produces no current and this of determining emf of cells under reversible condition.

199. **(A):** Equivalent conductance increases with dilution for an electrolyte solution while its specific conductance decreases.

(R): The number of ions in one litre of electrolyte increases with dilution.

200. **(A):** Any cell having E°cell = 5.91.

Volt, will have equilibrium constant 10^3 at 298 K.

(R): As at 298 K, Keq

= 10 (E°cell /0.0591).

Matrix-Match Type Questions

201. Match the following:

Column I	**Column II**
A. Λ_m(p) 1/k × l/a	(p) 1/k × l/a
B. k	(q) $\Lambda^v / \Lambda^\infty$
C. α	(r) $\frac{k \times 1000}{N}$
D. Λ_E	(s) $\frac{k \times 1000}{m}$
	(t) increase with dilution

202. Match the following:

Column I	**Column II**
A. H_2SO_5	(p) +6 oxidation state
B. CrO_5	(q) peroxy linkage
C. $K_2Cr_2O_7$	(r) Oxidant
D. H_2O_2	(s) Bleaching action

203. Match the following:

Column I	**Column II**
A. Electrode reversible with respect to cation	(p) Pt/Fe^{2+}, Fe^{3+}
B. Electrode reversible with respect to anion	(q) Pt, H_2 (1 atm)/H^+ (a = 1)
C. Redox electrode	(r) Ag/AgCl (s), HCl (aq)
D. Reference electrode	(s) Ag/$AgNO_3$
	(t) E° is zero

204. Match the following:

Column I	**Column II**
A. Zn | Zn^{2+} || Cu^{2+} | Cu	(p) chemical cell with transference
B. H_2 (g P_{H_2}) | HCl a., AgCl (s), Ag	(q) chemical cell without transference
C. H_2 (g, P_{H_2}) | H^+ (a_1) |H^+ (a_2)| H_2 (g, P_{H_2})	(r) concentration cell with transference
D. H_2 (g, P_1) | H^+ a. | H_2 (g, P_2)	(s) concentration cell without transference

205. Match the following:

Column I	**Column II**
A. A gas in contact with an inert electrode	(p) electrode potential
B. the potential difference in volts between the two electrodes	(q) O_2 at anode metal and the solution of metal ion
C. Li metal has the lowest standard electrode	(r) H_2 (g)/Pt potential
D. electrolysis of aq. Na_2SO_4 using Pt electrodes	(s) strongest reducing agent
	(t) –3.06Volt

206. Match the following:

Column I	**Column II**
A. Dry cell	(p) Primary cell
B. Mercury cell	(q) Secondary cell
C. Lead storage Battery	(r) Electro chemical cell
D. Ni-Cd cell	(s) 12 volt
	(t) 1.35 volt

207. Match the following:

Column I	**Column II**
A. electrolysis of aq. NaOH	(p) reduction of H^+ and oxidation of OH^-
B. electrolysis of $CuCl_2$ with Cu electrode	(q) Cu at cathode and O_2 at anode

C. electrolysis of H_2O	(r) H_2 at cathode and O_2 at anode
D. electrolysis of aq. $CuSO_4$ decreases	(s) weight of cathode increases and weight of anode

208. Match the following:

Column I	**Column II**
A. anode	(p) E°cathode-E°anode
B. conductance	(q) mass of product deposited by 1 coulomb of electricity
C. electrochemical equivalent	(r) $(\text{resistance})^{-1}$
D. E°cell	(s) involves oxidation
	(t) molecular weight of ion

209. Match the following:

Column I	**Column II**
A. electrolytic cell	(p) Nernst equation
B. Ecell = $\frac{0.059}{n}\log\frac{\text{Cathode}}{\text{Canode}}$	(q) 96500 coulombs
C. connect two half cells	(r) EMF of cell
D. 1 faraday	(s) salt bridge
	(t) device converting electrical energy into chemical energy

210. Match the following:

Column I (Reactions)	**Column II (Nature of reactions/type)**
A. $O_2^- \rightarrow O_2 + O_2^{2-}$	(p) redox reaction
B. $CrO_4^{2-} + H^+ \rightarrow$	(q) one of the products has trigonal planar structure
C. $MnO_4^- + NO_2^- + H^+ \rightarrow$	(r) dimeric bridged tetrahedral metal ion
D. $NO_3^- + H_2SO_4 + Fe^{2+} \rightarrow$	(s) disproportionation

The IIT-JEE Corner

211. A standard hydrogen electrode has zero electrode potential because

a. hydrogen is easiest to oxidize

b. this electrode potential is assumed to be zero

c. hydrogen atom has only one electron

d. hydrogen is the lightest element

[IIT 1997]

212. The standard reduction potentials of Cu^{2+}/Cu and Cu^{2+}/Cu^+ are 0.337 V and 0.153 V respectively. The standard electrode potential of Cu^+/Cu half cell is

a. 0.184 V **b.** 0.827 V

c. 0.521 V **d.** 0.490 V

[IIT 1997]

213. The standard reduction potential values of three metallic cations X, Y, and Z are 0.52, –3.03 and –1.18 respectively. The order of reducing power of the corresponding metal is

a. Y > Z > X **b.** X > Y > Z

c. Z > Y > X **d.** Z > X > Y.

[IIT 1998]

214. A gas at 1 atm is bubbled through a solution containing a mixture of 1 M Y^- and 1 M Z^- at 25°C. If the reduction potential of Z > Y > X, then

a. Y will oxidise X and not Z

b. Y will oxidise Z and not X

c. Y will oxidise both X and Z

d. Y will reduce both X and Z

[IIT 1999]

215. The oxidation number of sulphur in S_8, S_2F_2, H_2S respectively, are

a. 0, +1 and –2 **b.** +2, +1 and –2

c. 0, +1 and +2 **d.** –2, +1 and –2.

[IIT 1999]

216. For the electrochemical cell, $M \mid M^+ \parallel X^- \mid X$, $E°_{M^+/M} = 0.44$ V and $E°_{X/X^-} = 0.33$ V.

From these data one can deduce that

a. $M + X \rightarrow M^+ + X^-$ is the spontaneous reaction

b. $M^+ + X^- \rightarrow M + X$ is spontaneous reaction

c. Ecell = 0.77 V

d. Ecell = –0.77 V

[IIT 2000]

217. Among the following, identify the species with an atom in +6 oxidation state:

a. MnO_4^- **b.** $Cr(CN)_6^{3-}$
c. NiF_6^{2-} **d.** CrO_2Cl_2

[IIT 2000]

218. Saturated solution of KNO_3 is used to make 'salt bridge' because:

a. velocity of K^+ is greater than that of NO_3^-.
b. velocity of NO_3^- is greater than that of K^+.
c. velocities of both K^+ and NO_3^- are nearly the same.
d. KNO_3 is highly soluble in water.

[IIT 2001]

219. The reaction,

$3ClO^- (aq) \rightarrow ClO_3 (aq) + 2Cl^- (aq)$
is an example of

a. oxidation reaction
b. reduction reaction
c. disproportionation reaction
d. decomposition reaction

[IIT 2001]

220. The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is:

a. LiCl > NaCl > KCl
b. KCl > NaCl > LiCl
c. NaCl > KCl > LiCl
d. LiCl > KCl > NaCl

[IIT 2001]

221. In the standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent weight of $K_2Cr_2O_7$ is:

a. (molecular weight) / 2
b. (molecular weight) / 6
c. (molecular weight) / 3
d. same as molecular weight

[IIT 2001]

222. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below:

$MnO_4^- (aq) + 8H^+ (aq) + 5e^- \rightarrow Mn^{+2} (aq) + 4H_2O (l) ; E° = 1.51 V$

$Cr_2O_7^{-2} (aq) + 14 H^+ (aq) + 6e^- \rightarrow 2Cr^{3+} (aq) + 7H_2O (l) ; E° = 1.38 V$

$Fe^{+3} (aq) + e^- \rightarrow Fe^{+2} ; E° = 0.77 V$

$Cl_2 (g) + 2e^- \rightarrow 2Cl^- (aq); E° = 1.40 V$

Identify the only incorrect statement regarding the quantitative estimation of aqueous $Fe(NO_3)_2$.

a. MnO_4^- can be used in aqueous HCl
b. $Cr_2O_7^{-2}$ can be used in aqueous HCl
c. MnO_4^- can be used in aqueous H_2SO_4
d. $Cr_2O_7^{-2}$ can be used in aqueous H_2SO_4

[IIT 2002]

223. In the electrolytic cell, flow of electrons is from:

a. cathode to anode in solution.
b. cathode to anode through external supply.
c. cathode to anode through internal supply.
d. anode to cathode through internal supply.

[IIT 2003]

224. The pair of the compounds in which both the metals are in the highest possible oxidation state is

a. $[Fe(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$
b. $[Co(CN)_6]^{3-}$, MnO_2
c. TiO_3, MnO_2
d. CrO_2Cl_2, MnO_4^-

[IIT 2004]

225. The emf of the cell

$Zn | Zn^{2+} (0.01 M) || Fe^{2+} (0.001 M) | Fe$ at 298 K is 0.2905 volt. Then the value of equilibrium constant for the cell reaction is

a. $e^{0.32/0.0295}$ **b.** $10^{0.32/0.0295}$
c. $10^{0.26/0.0295}$ **d.** $10^{0.32/0.0591}$

[IIT 2004]

226. The half-cell reaction for the corrosion

$2H^+ + ½ O_2 + 2e^- \rightarrow H_2O, E° = 1.23 V,$

$Fe^{2+} + 2e^- \rightarrow Fe (s) ; E° = –0.44 V$

Find the ΔG° (in kJ) for the overall reaction.

a. –76 **b.** –322
c. –161 **d.** –152

[IIT 2005]

227. We have taken a saturated solution of AgBr. Ksp of AgBr is 12×10^{14}. If 10^{-7} mole of $AgNO_3$ are added to 1 litre of this solution find conductivity (specific conductance) of this solution in terms of 10^{-7} S m^{-1} units.

Given $\lambda^{\circ}(Ag^{+}) = 6 \times 10^{-3}$ Sm^2 mol^{-1},

$\lambda^{\circ}(Br^{-}) = 8 \times 10^{-3}$ S m^2 mol^{-1},

$\lambda^{\circ}(NO_3^{-}) = 7 \times 10$ S m^2 mol^{-1}.

a. 55 **b.** 5.5
c. 110 **d.** 27

[IIT 2006]

228. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenyl amine as indicator. The number of moles of Mohr's salt required per mole of dichromate is:

a. 3 **b.** 4
c. 5 **d.** 6

[IIT 2007]

229. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 mA current. The time required to liberate 0.01 mole of H_2 gas at the cathode is (1 Faraday = 96500 C mol^{-1})

a. 9.65×10^4 s **b.** 19.3×10^4 s
c. 28.95×10^4 s **d.** 38.6×10^4 s

[IIT 2008]

ANSWERS

Straight Objective Type Questions

1. c	**2.** d	**3.** b	**4.** b	**5.** d	**6.** c	**7.** d	**8.** c	**9.** a	**10.** b
11. d	**12.** d	**13.** c	**14.** a	**15.** c	**16.** b	**17.** b	**18.** c	**19.** d	**20.** a
21. b	**22.** b	**23.** a	**24.** c	**25.** b	**26.** c	**27.** c	**28.** a	**29.** d	**30.** a
31. b	**32.** d	**33.** d	**34.** c	**35.** b	**36.** b	**37.** c	**38.** b	**39.** c	**40.** c
41. a	**42.** c	**43.** d	**44.** d	**45.** c	**46.** a	**47.** b	**48.** c	**49.** c	**50.** a
51. d	**52.** a	**53.** a	**54.** c	**55.** b	**56.** b	**57.** b	**58.** a	**59.** a	**60.** d
61. a	**62.** a	**63.** d	**64.** c	**65.** d	**66.** c	**67.** c	**68.** b	**69.** b	**70.** b
71. c	**72.** d	**73.** d	**74.** b	**75.** d	**76.** b	**77.** b	**78.** b	**79.** a	**80.** b

Brainteasers Objective Type Questions

81. a	**82.** c	**83.** b	**84.** a	**85.** c	**86.** a	**87.** c	**88.** c	**89.** a
90. c	**91.** b	**92.** a	**93.** a	**94.** b	**95.** c	**96.** c	**97.** d	**98.** c
99. d	**100.** b	**101.** b	**102.** d	**103.** a	**104.** b	**105.** a	**106.** b	**107.** d
108. b	**109.** a	**110.** a	**111.** c	**112.** a	**113.** b	**114.** d	**115.** b	**116.** c
117. d	**118.** a	**119.** a	**120.** c	**121.** b	**122.** b	**123.** d	**124.** b	**125.** d
126. a	**127.** c	**128.** c	**129.** b	**130.** a	**131.** a	**132.** c	**133.** c	**134.** a
135. a								

Multiple Correct Answer Type Questions

136. a, b, c	**137.** a, b	**138.** a, c, d	**139.** a, b, c	**140.** b, c, d	**141.** b, c, d
142. a, c	**143** b, c, d	**144.** b, c, d	**145.** b, c	**146.** a, c, d	**147.** a, b, c, d
148. a, c, d	**149.** a, b, c	**150.** a, b, c	**151.** b, d	**152.** a, b, c	**153** a, b, c
154. a, c, d	**155.** a, b, d	**156.** a, b, d	**157.** b, c, d	**158.** b, c	**159.** b, c, d
160. a, b, d					

Linked-Comprehension Type Questions

Comprehension 1

161. b **162.** c **163.** b

Comprehension 2

164. d **165.** c **166.** b

Comprehension 3

167. d **168.** d **169.** a **170.** a

Comprehension 4

171. d **172.** c **173.** c **174.** d

Comprehension 5

175. b **176.** a **177.** d

Comprehension 6

178. c **179.** d **180.** a

Assertion Reason Type Answers

181. a **182.** d **183.** c **184.** a

185. b **186.** c **187.** e **188.** d

189. d **190.** a **191.** d **192.** c

193. c **194.** c **195.** d **196.** a

197. c **198.** a **199.** c **200.** a

Matrix-Match Type Questions

201. A - (s, t), B - (p), C - (q), D - (r, t)

202. A - (p, q, r), B - (p, q, r), C - (p, r), D - (p, q, r, s)

203. A - (s), B - (r), C - (p), D - (q)

204. A - (p), B - (q), C - (r), D - (s)

205. A - (r), B - (p), C - (s), D - (q)

206. A - (p, r), B - (q, r, t), C - (q, r, s), D - (q, r)

207. A - (r), B - (s), C - (p), D - (q)

208. A - (s), B - (r), C - (q), D - (p)

209. A - (t), B - (r), C - (s), D - (q)

210. A - (p, s), B - (r), C - (p, q), D - (p)

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211. b **212.** c **213.** a **214.** a **215.** a **216.** b **217.** d **218.** c

219. c **220.** b **221.** b **222.** a **223.** c **224.** d **225.** b **226.** b

227. a **228.** d **229.** d

Hints and Explanations

1. More negative is the reduction potential, higher is the reducing property, that is, the power to give up electrons

2. The reduction potentials (as given) of the ions are in the order:

   $Ag^+ > Hg_2^{2+} > Cu^{2+} > Mg^{2+}$

   Mg^{2+} (aq) will not be reduced as its reduction potential is much lower than water (–0.83 V)

   Hence the sequence of deposition of the metals will be Ag, Hg, Cu.

3. Anodic reaction:

   $H_2 \rightarrow 2H^+ + 2e^-$

   Cathodic reaction:

   $AgCl + e^- \rightarrow Ag + Cl$

4. Here pH of 0.1 M HCl and 0.1 M CH_3COOH is not same i.e, different concentration so emf of this cell will not be zero.

5. Reactions during discharging of lead storage battery are:

   An anode

   $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

At cathode

$PbO_2 (s) + SO_4^{2-} (aq) + 4H^+ (aq) + 2e^-$

$\rightarrow PbSO_4 (s) + 2H_2O$

Net reaction

$Pb(s) + PbO_2 (s) + 4H^+ (aq) + 2SO_4^{2-} (aq)$

$\rightarrow 2PbSO_4 (s) + 2H_2O$

Thus H_2SO_4 is consumed in this reaction.

7. Water is reduced at the cathode and oxidized at the anode instead of Na^+ and SO_4^{2-}.

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$;

Anode: $H_2O \rightarrow 2H^+ + ½ O_2 + 2e^-$

8. The given values are oxidation potential. On Changing these to reduction potential values

EMF = E°c – E°a

$= E^o_{Fe^{2+}/Fe} - E^o_{Zn^{2+}/Zn}$

= –0.41 – (– 0.76)

= –0.41 + 0.76 = 0.35 V

10. Copper is more reactive than Ag, so it displaces silver from $AgNO_3$.

$Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$

11. E°cell = E°c – E°a

= –0.44 – (–0.14)

= –0.44 + 0.14

= –0.30 V

13. Mg and Al have lower reduction potential than water. So water is reduced more easily to give H_2 gas at the cathode.

14. $\frac{\text{Mass of hydrogen}}{\text{Mass of copper}}$

$= \frac{\text{Eq. mass of hydrogen}}{\text{Eq. mass of copper}}$

$\frac{0.504\text{ g}}{m_{Cu}} = \frac{1}{(63.5/2)}$

$m_{Cu} = \frac{0.504\text{ g} \times 63.5}{2} = 16.0\text{ g}$

16. Number of faraday $= \frac{It}{96500}$

$= \frac{80 \times 10^{-6} \times 100 \times 24 \times 60 \times 60}{96500}$

$= 7.16 \times 10^{-3}$

17. $\Lambda_{eq} = \frac{k}{c_{eq}} = \frac{0.0041\text{ mho cm}^{-1}}{0.01\text{ eq L}^{-1}}$

$= \frac{0.00419 \times 1000}{0.01}\text{ mho cm}^2\text{ eq}^{-1}$

(1 L = 1000 cm^2)

= 419 mho cm^2 eq^{-1}.

18. O_2PtF_6 can be written as $O_2^+[PtF_6]^-$. In this compound oxidation state of Pt is +6 and O_2 carries a charge of +1.

Let X = oxidation state of oxygen in

O_2^+ So 2X = +1

X = + ½

20. During the electrolysis of aq. Na_2SO_4, H_2 is evolved at the cathode as $E_{R.P.}$ of sodium(–2.71 V) is much lower than that of water (–0.83 V) while O_2 is evolved at the anode as $E^a_{R.P.}$ potential of SO_4^{2-} ion (–0.2 V) is much less than that of water (–1.23 V).

23. The equivalent conductance of $BaCl_2$ at infinite dilution.

$\lambda\infty$ of $BaCl_2$ = ½ $\lambda\infty$ of Ba^{++} + $\lambda\infty$ of Cl^-

$= \frac{127 + 76}{2} = 139.5\text{ ohm}^{-1}\text{ cm}^2$

25. emf of the cell (Ecell) = Ecathode – Eanode

= –0.76 – 0.41 = –1.17 V

26. ΔG° = –nF E°cell = –2 × 96500 × 1.1

= –212300 J = –212.3 kJ

27. Fe^{2+} / Fe E° = –0.44

Fe^{3+} / Fe^{2+} E° = 0.77

The metals having higher negative electrode potential can displaced metals having lower values of negative electron potential from their salt solutions.

29. 11.2 lit. of hydrogen is liberated by 96500 C (1 faraday) of charge.

So 0.112 litre of hydrogen is liberated by a charge of

$\frac{96500}{112} \times 0.112 = 965\text{ C}.$

30. When the concentration of Ag^+ ions increases, then voltage of the cell also increases due to an increase in the collisions of ions.

31. In electrolysis of NaCl when Pt electrode is taken then H_2 liberated at cathode while with Hg cathode it forms sodium amalgam because more voltage is required to reduce H^+ at Hg than Pt.

33. Oxidation no. of Fe in $[Fe(H_2O)_5 (NO)^+]^{2+}$

$= x + 0 + 1 = 2$

$x = 2 - 1 = +1$

35. $ZnO + C \longrightarrow Zn + CO$, $\Delta G^\circ = -ve$

So this is spontaneous.

36.

$$K\overset{+7}{Mn}O_4 + e^- \longrightarrow (\overset{+6}{Mn}O_4)^{-2}$$

$$K\overset{+7}{Mn}O_4 + 3e^- \longrightarrow \overset{+4}{Mn}O_2$$

$$K\overset{+7}{Mn}O_4 + 4e^- \longrightarrow ½\, \overset{+3}{Mn_2}O_3$$

$$K\overset{+7}{Mn}O_4 + 5e^- \longrightarrow \overset{+2}{Mn}$$

37. $\Delta G = -nEF$

For 1 mol of Al, n = 3

For 4/3 mol of Al, n = 3 × 4/3 = 4

According to the question,

$827 \times 1000 = 4 \times E \times 96500$

or $E = 2.14$ V

38. According to Faraday's second law of electrolysis,

$$\frac{W_{Ag}}{W_H} = \frac{E_{Ag}}{E_H}$$

$$WH = \frac{1.08 \times 1}{108} = 0.01 \text{ g}$$

Since 2 g of hydrogen at STP has a volume of 22.4 litres, therefore volume of 0.01 g of hydrogen at STP

$$= \frac{22.4}{2} \times 0.01 = 0.112 \text{ litre} = 112 \text{ ml}$$

39. Cell concentration is $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \text{ In } \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

greater the factor $[(Zn^{2+}) / (Cu^{2+})]$, less is the EMF. So $E_1 > E_2$.

40. The given cell is represented as:

Pt | H_2 (g) | HCl (soln) || AgCl (s) | Ag, as H_2 undergoes oxidation and AgCl (Ag^+) undergoes reduction in this representation.

41. $$E_{cell} = \frac{E^\circ_{cell}}{N} - 0.0591 \log \frac{Zn^{2+}}{Cu^{2+}}$$

$$= 1.1 - \frac{0.0591}{2} \log \frac{0.1}{0.1}$$

$= 1.1 - 0.02955 \log 1$

$= 1.1 - 0.02955 \times 0 = 1.1$ V

42. $$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log Q$$

$Cu + Zn \longrightarrow Zn + Cu$

0.1 M 1M

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{1}{0.1} = 10$$

$$Ecell = 1.10 - \frac{0.0591}{2} \log 10$$

$= 1.10 - 0.0295$

$= 1.0705$ V

43. $$E^\circ_{cell} = \frac{2.303\, RT}{nF} \log Keq$$

$$0.295 = \frac{0.0591}{2} \log Keq$$

$\log Keq = 10$

$Keq = 10^{10}$

44. $$\frac{\text{Wt. of Ag deposited}}{\text{Wt. of } O_2 \text{ produced}} = \frac{108}{8}$$

$$\frac{0.108}{\text{Wt. of } O_2} = \frac{108}{8}$$

So weight of O_2 produced $= 8 \times 10^{-3}$ g

$$= \frac{22400}{32} \times 8 \times 10^{-3} \text{ cm}^3 = 5.6 \text{ cm}^3$$

45. $$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \frac{\text{In } [Zn^{2+}][Cl^-]^2}{PCl_2}$$

46. In the given reaction, I^- has been oxidized to I_2 and $Cr_2O_7^{2-}$ ions have been reduced to Cr^{3+}.

$$E^\circ_{cell} = E^\circ_{Cr_2O_7^{2-}} - E^\circ_{I_2}$$

$$0.79 = 1.33 - E^\circ_{I_2}$$

$$E^\circ_{I_2} = 0.54 \text{ V}$$

47. $$\text{Ionic mobility} = \frac{\text{Ionic conductance}}{96500}$$

$$= \frac{5 \times 10^{-4}}{96500} = 5.18 \times 10^{-9} \text{ cm/sec.}$$

48. By Kohlrausch's law

Λ° NaBr $= \Lambda^\circ$ NaCl $+ \Lambda^\circ$KBr $- \Lambda^\circ$KCl

$= 126 + 152 - 150$

$= 128$ S cm^2 mol^{-1}

49. $Zn(s) + 2H^+ \rightarrow Zn^{2+}(aq) + H_2(g)$

Reaction quotient $Q = \dfrac{[Zn^{2+}]}{[H^+]^2}$

corresponding cell is

$Zn \mid Zn^{2+}(C_1) \parallel H^+(aq) \mid Pt(H_2)$

Anode cathode

$$E^\circ_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log K$$

$$= E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[H^+]^2}$$

$$= E^\circ_{cell} + \frac{0.0591}{2}\log\frac{[H^+]^2}{[Zn^{2+}]}$$

If H_2SO_4 is added to cathodic compartment, then Q decreases (due to increase in H^+). So equilibrium is displaced towards right and Ecell increases.

51. pH = 3, $[H^+] = 10^{-3}$

E red = E° red + 0.059 log [ion]

$E = 0 + 0.059 \log [10^{-3}]$

$E = +0.059(-3) = -0.177$ V.

52. $Fe \rightarrow Fe^{2+} + 2e$ (anode reaction)

$O_2 + 2H_2O + 4e \rightarrow$

$4OH^-$ (cathode reaction)

The overall reaction is

$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$.

$Fe(OH)_2$ may be dehydrated to iron oxide FeO, or further oxidized to $Fe(OH)_3$ and then dehydrated to iron rust, Fe_2O_3.

53. $Q = \dfrac{mFZ}{M}$

$= \dfrac{5120 \times 96500 \times 3}{27}$

$= 5.49 \times 10^7$ C of electricity

54. Λ^∞AcOH $= \Lambda^\infty$AcONa $+ \Lambda^\infty$HCl $- \Lambda^\infty$NaCl

$= 91.0 + 426.2 - 126.5$

$= 390.7$ S cm^2 mol^{-1}.

55. $2AgCl(s) + H_2(g) \rightarrow 2HCl(aq) + 2Ag(s)$

the activities of solids and liquids are taken as unity and at low concentrations, the activity of a solute is approximated to its molarity.

The cell reaction will be

$Pt(s) \mid H_2(g)$, 1 bar $\mid H^+(aq)$ 1 M $\mid AgCl(aq)$ 1 M $\mid Ag(s)$

56. $$\overset{+7}{KMnO_4} \xrightarrow{OH^-} \overset{+6}{K_2MnO_4}$$

Change in oxidation number of Mn in basic medium is 1. Hence mole of KI is equal to mole of $KMnO_4$ that is, 1 mole.

57. Ecell = +ve thus redox changes are

$A \rightarrow A^+ + e$ LHS shows oxidation

$B^+ + e \rightarrow B$ RHS shows reduction

$A + B^+ \rightarrow A^+ + B$

58. $E^\circ_{Fe^{2+}/Fe} = -0.441$ V

$E^\circ_{Fe^{3+}/Fe^{2+}} = 0.771$ V

If $E^\circ_{cell} = E^\circ_{OPFe/Fe^{2+}} + E^\circ_{RPFe^{3+}/Fe^{2+}}$

$= +0.441 + 0.771 = 1.212$ V

59. $\Lambda^\circ(C_6H_5COOH) = \lambda^\circ(C_6H_5COO^-) + \lambda^\circ(H^+)$

$= 42 + 288.42 = 330.42$

$$\alpha = \frac{\Lambda^{\underline{C}}_{\underline{m}}}{\Lambda^\circ_m} = \frac{12.8}{330.42} = 0.039 = 3.9\ \%$$

65. $E^\circ\, I^- / AgI / Ag = EAg^+ / Ag + \dfrac{0.0591}{1}\log KspAgI$

$-0.152 = +0.8 + \dfrac{0.0591}{1}\log KspAgI$

$\log KspAgI = -16.13$

66. $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow$

$2Cr^{3+} + 7H_2O + 3I_2$

Thus 3 moles of I_2 per mole of $K_2Cr_2O_7$ are produced.

67. $NaBr \rightleftharpoons Na^+ + Br^-$

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

$Na^+ + OH^- \rightarrow NaOH$ (at cathode)

$Br^- - e^- \rightarrow Br$

$Br + Br \rightarrow Br_2$ (at anode)

68. $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

Charge required for the reduction of 1 mol of MnO_4^- to MnO_2 = 3F (as charge = nF).

69. Electrochemical equivalent is the weight deposited by 1 coulomb.

$Q = I \times t$

$1 = I \times 0.25$

So $I = 4$ A.

70. $\Lambda^\circ_m (CaCl_2) = \lambda^\circ_m (Ca^{2+}) + 2\lambda^\circ_m (Cl^-)$

$= 118.88 \times 10^{-4} + 2\,(77.33 \times 10^{-4})$

$= 273.54 \times 10^{-4}$ m² mho mol⁻¹

71. It is a concentration cell

$$E_{cell} = \frac{0.0591}{n} \log_{10} \frac{C_2\,(RHS)}{C_1\,(LHS)}$$

$$= \frac{0.0591}{1} \log_{10} \frac{0.1}{0.01} = 0.0591\ V$$

72. Reduction of $Cr_2O_7^{2-}$ to Cr^{3+} is a $6e^-$ change,

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Thus, equivalent weigh of $Cr_2O_7^{2-}$

= Mol. weight/6.

74. Electrode potential of cell must be +ve for spontaneous reaction.

$Zn^{2+} \rightarrow Zn \quad E^0 =– 0.76\ V$

$Cu^{2+} \rightarrow Cu \quad E^0 = – 0.34\ V$

Redox reaction is

$Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation)

$Cu^{2+} + 2e^- \rightarrow Cu$ (reduction)

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

75. $E^\circ = \dfrac{0.0591}{n} \log_{10} K$

here, n = 2, E° == 0.295

$\log_{10} K = \dfrac{2 \times 0.295}{0.0591}$ or $K = 10^{10}$

76. It comprises of the following things.

$Cr^{x+} + O_2^{2-} + O_2^{2-} + O^{2-} = CrO_5$

Peroxide Oxide

So, x is + 6

77. The potential is not affected if the reaction is multiplied by any integer. It is an intensive property.

78. Electrolysis: $H_2O \rightarrow H_2 + ½\,O_2$

1 mole of water on decomposition gives two equivalents of oxygen.

Quantity of electricity required

= 2 × 96500 coulombs.

$$\text{Time required} = \frac{2 \times 96500}{2} = 96500 \text{ sec}$$

$$= \frac{96500}{60 \times 60} = 26.8 \text{ hours}$$

Brainteasers Objective Type Questions

81. $Ecell = E^\circ cell - \dfrac{2.303\ RT}{nF} \log_{10} \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

$$E_1 = E^\circ cell - \frac{2.303\ RT}{2F} \log_{10} \frac{1}{1} = E^\circ cell$$

$$E_2 = E^\circ cell - \frac{2.303\ RT}{2F} \log_{10} \frac{0.1}{1.0}$$

$$E_3 = E^\circ cell - \frac{2.303\ RT}{2F} \log_{10} \frac{1}{0.1}$$

Hence $E_2 > E_1 > E_3$

82. As 22400 mL of hydrogen at STP (or NTP) = 2 g

So 112 mL of hydrogen at STP

$$= \frac{2\ g \times 112\ mL}{22400\ mL} = 10^{-2}\ g$$

$2H^+ + 2e^- \rightarrow H_2$

2F 1 mol

= 2 × 96500 C = 2g

2 g hydrogen is deposited by = 2 × 96500 C 10^{-2} g hydrogen will be deposited by

$$= \frac{2 \times 96500 \times 10^{-2}\ g}{2\ g} = 965\ C$$

Charge (Q) = I .t

$$I = \frac{Q}{t} = \frac{965\ C}{965\ s} = 1\ Cs^{-1} = 1\ A$$

83. $Al^{3+} + 3e^- \rightarrow Al$

3F 1 mol = 27.0 g

= 3 × 96500 C

The required charge

$$= \frac{40.5\text{ g} \times 3\text{ mol} \times 96500\text{ C mol}^{-1}}{27.0\text{ g}}$$

$= 4.34 \times 10^5$ C

84. pH = 3.0 or $[H^+] = 10^{-3}$ M

$2H^+ + 2e^- \rightarrow H_2\,(g)$

$E_{H^+/H_2} = E^\circ_{H^+/H_2} - \frac{0.059}{2}$

$\log_{10} \frac{1}{[H^+]^2}$

$= 0.0\text{ V} - \frac{0.059}{2} \log_{10} \frac{1}{(10^{-3})^2}$

$= 0.0\text{ V} - \frac{0.059}{2} \log_{10} (10^3)^2$

$= \frac{-0.059}{2} \times 6 = -0.177$ V

85. (i) $Ag^+\,(aq) + e^- \rightarrow Ag\,(s)$

1 mol = 1 F 1 mol

3 F 3 mol

(ii) $Ni^{2+}\,(aq) + 2e^- \rightarrow Ni\,(s)$

2 mol = 2F 1 mol

3 F 3/2 mol

(iii) $Cr^{3+}\,(aq) + 3e^- \rightarrow Cr\,(s)$

3 mol = 3F 1 mol

The required ratio of moles of Ag, Ni and Cr is: 3 mol Ag : 3/2 mol Ni: 1 mol Cr

that is, 6 mol Ag : 3 mol Ni : 2 mol Cr (6 : 3 : 2)

86. At STP mass of 22.4 L H_2 = 2 g

Mass of 2.24 L H_2 at STP = 0.2 g

$$\frac{\text{Mass of copper deposited}}{\text{Mass of hydrogen}} = \frac{\text{Eq. mass of copper}}{\text{Eq. mass of hydrogen}}.$$

$$\frac{m_{Cu}}{0.2\text{ g}} = \frac{63.5/2}{1}$$

$$m_{Cu} = \frac{63.5\text{ g} \times 0.2}{2} = 6.35\text{ g}.$$

87. $\frac{m_{Ni}}{m_{Cr}} = \frac{\text{Eq. mass of Ni}}{\text{Eq. mass of Cr}}$

For Ni^{2+} and Cr^{3+}, we have

$$\frac{0.3\text{ g}}{m_{Cr}} = \frac{59/2}{52/3}$$

$$m_{Cr} = 0.3\text{ g} \times \frac{(52/3)}{(59/2)} = 0.176\text{ g}$$

88. Since $E^\circ Cd^{2+}/Cd > E^\circ Zn^{2+}/Zn$, therefore, Zn electrode acts as anode and Cd electrode as cathode.

At anode:

$Zn\,(s) \rightarrow Zn^{2+}\,(aq) + 2e^-$

At cathode:

$Cd^{2+} + 2e^- \rightarrow Cd\,(s)$

$Zn\,(s) + Cd^{2+}\,(aq) \rightarrow Zn^{2+}\,(aq) + Cd\,(s)$

$Q = [Zn^{2+}] / [Cd^{2+}] = 0.004 / 0.2$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= -0.403\text{ V} - (-0.763\text{ V}) = 0.36$ V

$E_{cell} = 0.36\text{ V} - \frac{0.059}{2}\text{ V} \log_{10} \frac{0.004}{0.2}$

89. $2H^+\,(1\text{ M}) + 2\,e^- \rightarrow H_2\,(g, 100\text{ atm})$

$Q = \frac{[H_2\,(g)]}{[H^+]^2} = \frac{100}{(1)^2} = 100$

$E_{H^+/H_2} = E_{H^+/H_2} - \frac{0.059}{2}\text{ V} \log_{10} Q$

(at 25°C)

$= 0.0\text{ V} - \frac{0.059}{2}\text{ V} \log_{10} 100 = -0.059$ V

90. $Q = I.t = 1.5 \times 7200 = 10800$ C.

Atomic wt. of hydrogen is 1 and its valency in water is 1.

Therefore equivalent wt. of hydrogen

$= \frac{\text{atomic wt.}}{\text{valency}} = \frac{1}{1} = 1$

A charge of 96500 can produce 1 g of hydrogen

Therefore amount of hydrogen produced by a charge of 10800

$C = \frac{10800}{96500} = 0.112$ g

Since 2 g of hydrogen molecule at NTP has a volume of 22.4 litres, therefore volume of 0.112 g of hydrogen at NTP is:

$\frac{22.4}{2} \times 0.112 = 1.25$ litre.

91. L.H.S half cell:

$H_2\,(g) \rightarrow 2H^+\,(1M) + 2e^-$

p_1

R.H.S half cell:

$$2H^+ (1M) + 2e^- \rightarrow \underset{p_2}{H_2 (g)}$$

$$\underset{p_1}{H_2 (g)} \rightarrow \underset{p_2}{H_2 (g)}$$

E°cell = 0.00 V, $K = \underset{p_1}{p_2}$, n = 2

$$Ecell = E°cell - \frac{RT}{nF} \log_e K = 0 - RT \log_e \frac{p_2}{p_1}$$

$$Ecell = \frac{RT}{2F} \log_e \frac{p_1}{p_2}$$

92. c = 0.1 M, R = 100 ohm, k = 1.29 ohm^{-1} m^{-1} 1/a = k . R = 1.29 × 100 = 129 m^{-1} c = 0.02 M, R = 520

$$k = \frac{1}{R} \times \frac{1}{a} = \frac{1}{320} \times 129$$

= 0.248 ohm^{-1} m^{-1}

k decreases with dilution,

c = 0.02 and not 0.2

$$\Lambda = k \text{ x } \frac{1}{M \text{ (in m / L)}}$$

$$= k \text{ x } \frac{1}{M \times 10^3 \text{ (m/m}^3\text{)}}$$

$$= \frac{0.248}{0.02 \times 10^3} = 12.4 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$$

= 124 × 10^{-4} S m^2 mol^{-1}

94. Quantity of electricity passed

= (4 A) × (30 × 30 s) = 7200 C

$H_2O \rightarrow H_2 + ½ O_2$

that is, $2H^+ + 2e^- \rightarrow H_2$

As 2 × 96500 C liberate H_2 = 22.4 L at STP

So 7200 C will liberate

$$= \frac{22.4}{2 \times 96500} \text{ x } 7200 \text{ L}$$

= 0.836 L.

95. $K_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2KHSO_4 + 2CrO_3 + H_2O$

$[2KCl + H_2SO_4 \rightarrow 2KHSO_4 + 2HCl] \times 2$

$[CrO_3 + 2HCl \rightarrow CrO_2Cl_2 + H_2O] \times 2$

$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \rightarrow 2CrO_2Cl_2 + 6KHSO_4 + 3H_2O$

96. $\Delta G = -n FE_{cell}$

= –2 × 96500 × 0.6753 (at 25°C)

= 130333 J

$\Delta S = n F (\partial E / \partial T)_P$

$$(\partial E / \partial T)_P = \frac{E_2 - E_1}{T_2 - T_1}$$

$$= \frac{0.6753 - 0.6915}{298 - 273} = -6.48 \times 10^{-4}$$

So $\Delta S = 2 \times 96500 \times (-6.48 \times 10^{-4})$

= –125.064 JK^{-1} mol^{-1}

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

On substituting the values, we have

ΔH = –167.6 kJ

97. 1 faraday charge liberates 1 eq. of substance.

Eq wt. of Al = 27 / 3 = 9

$$\text{Number of eq. of Al} = \frac{\text{wt. of Al}}{\text{Eq. wt.}}$$

$$= \frac{4.5}{9} = 0.5$$

Number of faraday required = 0.5

Number of eq. of H_2 produce = 0.5 eq.

Volume occupied by 1 eq. of H_2

$$= \frac{22.4}{2} = 11.2$$

volume occupied by 0.5 = 11.2 × 0.5

= 5.6 litre of STP

98. $$E_{cell} = E°_{cell} - \frac{0.0591}{2} \log_{10} \frac{1}{[Zn^{2+}]}$$

$$= E°_{cell} + 0.02955 \log_{10} C$$

$$E'_{cell} = E°_{cell} + 0.02955 \log_{10} \frac{C}{100}$$

$$= E°_{cell} + 0.02955 \log_{10} C + 0.02955 (-2)$$

So E_{cell} will decrease by 0.02955 × 2 V

= 0.059 V = 59 mV.

99. EMF for the cell, Zn | Zn^{2+} || Cu^{2+} | Cu

= 0.34 – (–0.76) = 1.10 V.

EMF for the cell, Fe | Fe^{2+} || Cu^{2+} | Cu

= 0.34 – (–0.41) = 0.75 V

As the two cells are connected in series, therefore then net EMF of the two cells

$= 1.10 + 0.75 = 1.85$ V

100. The balanced equation is,

$As_2S_5 + 40HNO_3 \rightarrow 5H_2SO_4 + 40\ NO_2 + 2H_3AsO_4 + 12H_2O$,

Thus, the value of x and y are 40 and 40.

102. For a cell reaction in equilibrium at 298 K.

$$E^\circ_{cell} = \frac{0.0591}{n} \times \log_{10} K_C$$

$$0.46 = \frac{0.0591}{2} \times \log_{10} K_C$$

$$\log_{10} K_C = \frac{2 \times 0.46}{0.0591} = 15.57$$

$$K_C = 3.7 \times 10^{15} = 4 \times 10^{15}$$

103. The reduction potential of Zn, Cu, Ag and Ni (obtained by reversing the sign of oxidation potentials) are –0.76, +0.34, +0.80 and –0.25 respectively.

The maximum EMF of the cell is obtained when the electrode potential of the anode is minimum and that of the cathode is maximum, that is, Zn and Ag respectively.

$$EMF = E^\circ_{cathode} - E^\circ_{anode}$$

$= +0.80 - (-0.76) = +1.56$ V.

104. $E = 0.77 - \dfrac{0.0591}{1} \log_{10} \dfrac{[Fe^{2+}]}{[Fe^{3+}]}$

$$= 0.77 - 0.059 \log_{10} \frac{1.2}{0.012}$$

$= 0.77 - 0.118 = 0.652$ V

105. (i) $H_2O + OCl^- + 2e^- \rightarrow Cl^- + 2OH^-$

$E^\circ = 0.94$ V

(ii) $\frac{1}{2} Cl_2 + e^- \rightarrow Cl^-$;

$E^\circ = 1.36$ V

On subtracting equation (ii) from equation (i), we get

$H_2O + e^- + OCl^- \rightarrow 2OH^- + \frac{1}{2} Cl_2$

$E^\circ = 0.94 - 1.36 = -0.42$ V.

106. $E_{cell} = E^\circ_{cell} - \dfrac{0.0591}{n} \log_{10} Q$

Here $Q = \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

For complete discharge $E_{cell} = 0$.

So $E^\circ_{cell} = \dfrac{0.0591}{2} \log_{10} \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

$$\frac{[Zn^{2+}]}{[Cu^{2+}]} = 10^{37.3}$$

107. $NaCl + H_2O$ Electrolysis

$NaOH + \frac{1}{2} H_2 + \frac{1}{2} Cl_2$

At anode At cathode

400 ml of 1 M NaCl solution contains NaCl

$= \dfrac{1}{1000}$ x 400 mol = 0.4 mol

$$\text{As } Na^+ + e^- \longrightarrow Na \xrightarrow{H_2O} \underline{\quad}$$

$NaOH + \frac{1}{2} H_2$

As 1 F produces 1 mol of NaOH

So 0.04 F produces NaOH = 0.04 mol

Thus, 400 ml of the solution now contain 0.04 mol of NaOH.

Molar concentration of NaOH solution

$$= \frac{0.04}{400} \times 1000 = 0.1 \text{ M}$$

$[OH^-] = 0.1$ M

$[H^+] = 10^{-13}$ M

So pH = 13.

108. $k = G \times G^* = \dfrac{1}{R} \times G^*$

$= \dfrac{1}{2.5 \times 10^3\ \Omega}$ x 1.25 cm^{-1}

$= 5 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$

$$\Lambda eq = \frac{1000\ K}{Normality}.$$

$$= \frac{1000 \times 5 \times 10^{-4}}{0.1\ N}$$

$= 5.0\ \Omega^{-1}\ cm^2\ eq^{-1}$

109. $Ca^{2+} + 2e^- \rightarrow Ca$

As 1 mol i.e. 40 g Ca is deposited by 2 F, i.e. 2 × 96500 C

So 60 g Ca will be deposited by

$$= \frac{2 \times 96500}{40} \times 60 \text{ C} = 289500 \text{ C}$$

As $Q = I \times t$

$$t = \frac{289500}{5}\ s = 57900\ s$$

$$= \frac{57900}{60 \times 60}\ hrs = 16\ hours$$

110. The cell reaction is

$$H_2 + 2Ag^+ \rightarrow 2H^+ + 2Ag$$

$$E_{cell} = E^\circ_{cell} - \frac{2.303\ RT}{2F} \log_{10} \frac{1}{[Ag^+]^2}$$

$$0.62 = 0.80 + 0.06 \log_{10} [Ag^+]$$

$$\log_{10} [Ag^+] = \frac{-0.18}{0.06} = -3$$

$$[Ag^+] = \text{antilog}\ (-3) = 1.0 \times 10^{-3}\ M$$

$$= (1.0 \times 10^{-3}) \times 108\ g\ L^{-1}$$

$$= 0.108\ g\ L^{-1}$$

Amount of Ag present in 100 ml solution

$$= 0.0108\ g$$

$$\text{So \% of Ag} = \frac{0.0108}{108} \times 100 = 1\ \%$$

112. $Q = I.t = 2 \times 1800 = 3600$ C.

Atomic wt. of chlorine is 35.5 and its valency in NaCl is 1.

Therefore equivalent weight of chlorine

$$\frac{\text{Atomic wt.}}{\text{Valency}} = \frac{35.5}{1} = 35.5$$

96500 of charge evolves 35.5 g of chlorine

Therefore amount of chlorine evolved by a charge of 3600

$$C = \frac{35.5}{96500} \text{ x } 3600 = 1.32\ g$$

113. $S_2O_6^{2-} = +5$

So increasing order of oxidation state of 'S' is

$$S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$$

114. As the balanced equation is

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3H_2O + 3I_2$$

So for it a = 5, b = 6, c = 3 and d = 3

115. $\frac{\text{Wt. of Cu deposited}}{\text{Wt. of } H_2 \text{ produced}}$

$$= \frac{\text{eq. wt. of Cu}}{\text{eq. et. of H}} = \frac{64/2}{1}$$

$$\frac{0.16}{\text{wt. of } H_2} = \frac{32}{1}$$

wt. of $H_2 = 0.16 / 32 = 5 \times 10^{-3}$ g

volume of H_2 liberated at STP

$$= \frac{22400}{2} \times 5 \times 10^{-3}\ cc = 56\ cc$$

116. $2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

$$5H_2O_2 + 5[O] \rightarrow 5H_2O + 5O_2$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

As 5 moles of H_2O_2 are required to reduce 2 moles of $KMnO_4$.

So 5/2 moles of H_2O_2 are required per mole of $KMnO_4$.

117. $Fe^{2+} + 2e^- \rightarrow Fe \quad E^\circ = -0.44\ V$ .....(1)

$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E^\circ = 0.77\ V$ .....(2)

Adding equations (1) and (2)

$Fe^{3+} + 3e^- \rightarrow Fe$ ....(3)

$$E_1^\circ + E_2^\circ = -0.88 + 0.77 = -0.11\ V$$

$$n = 3$$

$$E_3^\circ = \frac{-0.11}{3} = -0.037\ V$$

118. E° for the given reaction

$$= 0.855 - 0.799 = 0.056\ V$$

$$E^\circ_{cell} = \frac{0.0591}{2} \log_{10} K_C$$

$$\log_{10} K_C = \frac{0.056 \times 2}{0.059} = 1.8983$$

$$K_C = \text{Antilog } 1.8983 = 79.12 \approx 79$$

119. $[Fe(CN)_6]^{3-} \rightarrow [Fe(CN)_6]^{4-}$, $E^\circ = +0.35$ V

$Fe^{3+} \rightarrow Fe^{2+}$, $E^\circ = +0.77$ V

Higher the positive reduction potential, stronger is the oxidizing agent. Oxidising agent oxidizes other compounds and gets itself reduced easily.

121. Oxidation number of oxygen in OF_2

$\Rightarrow x + (-2) = 0 \Rightarrow x = +2$

Oxidation number of oxygen in KO_2

$\Rightarrow (+1) + 2x = 0 \Rightarrow x = -1/2$

Oxidation number of oxygen in BaO_2

$\Rightarrow (+2) + 2x = 0 \Rightarrow x = -1$

As, Correct order is

$BaO_2 < KO_2 < O_3 < OF_2$

122. $Ag^+ + e^- \rightarrow Ag$,

$Cu^{2+} + 2e^- \rightarrow Cu$

$Au^{3+} + 3e^- \rightarrow Au$,

3F will deposit 3 moles of Ag, 3/2 moles of Cu and 1 mole of Au.

So Molar ratio = 3 : 3/2 : 1 = 6 : 3 : 2

123. $H^+ + e^- \rightarrow \frac{1}{2} H_2$,

$$E = E^\circ - \frac{0.0591}{n} \log_{10} \frac{1}{[H^+]}$$

$$= 0 - \frac{0.0591}{1} \text{pH}$$

$$= -0.0591 \times 3 = -0.177 \text{ V}$$

126. $Cu^{2+} + 2e^- \rightarrow Cu\ (s)$, $E^\circ = 0.33 = -0.66$ F

$Cu^{2+} + e^- \rightarrow Cu^+$, $E^\circ = 0.153 = 0.153$ V

$Cu^+ + e^- \rightarrow Cu\ (s)$

$-\Delta G^\circ_3 = \Delta G_2 + \Delta G_1$

$= +0.153 \text{ F} - 0.66 \text{ F} = 0.507$

131. $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$\Delta G^\circ = -5 \times 1.51$ F

$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$

$\Delta G^\circ = -2 \times 1.23$ F

$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$

$\Delta G^\circ = (-7.55 \text{ F} + 2.46 \text{ F}) = -5.09$ F

$$E^\circ MnO_4^- / MnO_2 = \frac{-5.09 \text{ F}}{-3\text{F}} = +1.696 \text{ V.}$$

133. $E = E^\circ - 0.059 \log[H^+]^2$

$$= 1.30 - \frac{0.059}{2} \log(10^{-2})^2$$

$$= 1.30 + \frac{0.236}{2} = 1.418 \text{ V}$$

Multiple Correct Answer Type Questions

136. As only Oxidation takes place at anode and Cr^{3+} is not oxidized to $Cr_2O_7^{2-}$ under given condition.

137. As specific conductance decreases with dilution, whereas the equivalent conductance increases with dilution and conductance of all electrolytes increase with temperature as the ions move faster at higher temperature .

140. As ΔG°_f for most of the sulphides are more than those of CS_2 and H_2S so carbon and hydrogen can not reduced metal sulphides into metal.

141. Zn Oxidation $\xrightarrow{Zn^{2+} + 2e^-}$

$Ag^+ + e^- \xrightarrow{\text{Reduction}} Ag$

142. In an electrochemical cell, oxidation takes place at the anode and reduction takes place at the cathode.

Therefore H_2 is anode and Cu is cathode.

146. $2KBr + I_2 \rightarrow 2KI + Br_2$

As this reaction is not possible because Br^- ion is not oxidized in Br_2 with I_2 due to higher electrode potential of I_2 than bromine.

148. $CuSO_4 + 2KI \rightarrow CuI_2 + K_2SO_4$

$2CuI_2 \rightarrow Cu_2I_2 + I_2$

so CuI_2 is not formed.

149. In Daniel cell the cell reaction is,

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

So Cu^{2+} ions (cations) move towards Cu electrode (cathode) and get accumulated as Cu metal.

152. Standard emf of the cell (E°cell)

= E°cathode – E°anode

= 0.80 – (–0.76) = 1.56 V.

as emf is +ve, therefore the cell reaction

$Zn\ (s) + 2Ag^+\ (aq) \rightarrow Zn^{2+}\ (aq) + 2Ag\ (s)$ is feasible.

153. As reduction occurs at Ag electrode, so increase in the concentration of Ag^+ or decreases in concentration of Cu^{2+} will increases the voltage.

157. As For a galvanic cell under equilibrium condition,

$E_{cell} = 0.$

Comprehensions

161. $Fe^{2+} + 2e^- \rightarrow Fe \qquad E^\circ_{red} = -0.44V$

$\underline{2(Ag \rightarrow Ag^+ + e^-) \qquad E^\circ_{red} = -0.80V}$

$Fe^{2+} + 2Ag \rightarrow 2Ag^+ + Fe \quad E^\circ = -1.24\ V$

162. E for the reaction is calculated using the Nernst equation:

$$E = E^\circ - \left(\frac{0.0592\ V}{2}\right) \log \frac{[Ag^+]^2}{[Fe^{2+}]}$$

$$= -1.24\ V - (-0.0296\ V) \log \frac{(0.0100)^2}{(0.100)}$$

$$= -1.24\ V - (-0.887\ V) = -1.15\ V$$

163. The reaction that is spontaneous is

$2Ag^+ + Fe \rightarrow Fe^{2+} + 2Ag$ with $E = 1.24$ V.

$$W_{max} = -nFE = -(2\ mole^-)$$

$$\left(\frac{96.500\ C}{1\ mole}\right)(1.24\ V)\ \frac{1J}{/1C - V}$$

$$= -2.39 \times 10^5\ J$$

or in kwh ,

$$(2.39 \times 10^5\ J)\left(\frac{1\ kwh}{3.6 \times 10^6 J}\right)$$

$$= 6.6 \times 10^{-2}\ kwh$$

164. The half- reaction with the most negative standard potential becomes the oxidation half-reaction.

$$E^\circ = E^\circ_{(cathode)} - E^\circ_{(anode)} = -0.28\ V - (-0.237\ V)$$

$= 2.09$ V.

The overall reaction is

$Mg(s) + Ni^{2+}(aq) \rightarrow Mg^{2+}(aq) + Ni(s)$.

165. The Nernst equation is used to solve for thecell potential. Note that two moles of electrons are transferred in the reaction.

$$E = \frac{2.09\ V}{2} - 0.5092\ V \log \frac{0.50}{1.0}$$

$$= 2.10\ V$$

166. $\log K = \dfrac{nE^\circ}{0.0592} = \dfrac{(2.09)}{0.0592} = 70.6$

$K = 10^{70.6} = 4 \times 10^{70}$

167. $E_{Cr_2O_7^{2-}|Cr^{3+}} = E^\circ_{Cr_2O_7^{2-}|Cr^{3+}} - \dfrac{0.0591}{6}$

$$\times \left(\frac{\log [Cr^{3+}]^2}{[Cr_2O_7^{2-}]} \times \frac{1}{[H^+]^{14}}\right)$$

$$E_{Cr_2O_7^{2-}|Cr^{3+}} = 1.33 - \frac{0.0591}{6} \log \frac{1}{(0.01)^{14}}$$

On solving we get $E_{Cr_2O_7^{2-}/Cr^{+3}} = 1.0542$ V

169. As $\Delta G = \Delta G^\circ + RT\ In\ Q$

$\Delta G^\circ = -nFE^\circ cell$

So $\Delta G = -nFE^\circ + 2.303\ RT \log \dfrac{[Cr^{3+}]}{[Ag^+]^3}$

On solving

$\Delta G = -422838.3$ J or -422.83 kJ

170. $E^\circ cell = 0.06\ (3 - 4) = -0.06\ V$

$Ecell = E_{H^+|H_2} - E_{OH^-|Cd(OH)2|Cd}$

$= E_{H^+|H^2} - E_{cd^{2+}|Cd}$

i.e. $Ecell = E^\circ - \dfrac{0.06}{2} \log \dfrac{[Cd^{2+}]}{[H^+]^2}$

As Ecell= 0,

So $E^\circ cell = 0.03 \log \times \dfrac{[Cd^{2+}]\,[OH^-]^2}{K^2_w}$

$$\log \frac{K_{sp}}{K^2_w} = \frac{0.39}{0.03} = 13$$

On taking antilog

$Ksp = 10^{13} \times (10^{-14})^2 = 10^{-15}$

171. In $Cl_2 + OH^- \rightarrow ClO^- + Cl^- + H_2O$, the oxidation number of Cl increases from 0 to +1 and decreases from 0 to –1.

In $C_6H_5CHO + OH^- \rightarrow$

$C_6H_5COO^- + C_6H_5CH_2OH$,

C_6H_5CHO is oxidized to $C_6H_5COO^-$ and at the same time reduced to $C_6H_5CH_2OH$ (Cannizaro reaction).

173. $MnO_4^- + I_2 \rightarrow Mn^{2+} + 2IO_3^- + \ldots.$

O.N. of Mn : decrease = 5

O.N. of I : increase = 5 for one I atom and 10 for two I atoms

Molar ratio, $MnO_4^- : I_2 = 2 : 1$

175. $E^\circ cell = \dfrac{RT}{nF}\ In\ K$

$$(0.8 - 0.05) = \frac{1}{2} \times \frac{0.0592}{2.303}\ In\ K$$

$$In\ K = \frac{(0.8 - 0.05) \times 2 \times 2.303}{0.0592} = 58.38$$

176. On increasing concentration of NH_3 the concentration of H^+ ion decreases, Therefore Ered increases.

178. Reduction potential of I_2 is less than Cl_2.

179. Reaction of Mn^{3+} with H_2O is spontaneous.

187. A and R both are false.

$$Cr_2O_7^{2-} + 14\,H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

(in acidic medium)

so equivalent weight $= \dfrac{\text{mol. wt.}}{6}$

$= \dfrac{294}{6} = 49.0$

188. For a strong electrolyte the plot of molar conductivity (Λm) against $\sqrt{c}$ is nearly linear.

197. During electrolysis, $CuSO_4$ converted into Cu^{++}

$$CuSO_4 \leftrightarrow Cu^{++} + SO_4^{--}$$

The IIT-JEE Corner

212. (i) $Cu^{2+} + 2e^- \rightarrow Cu$;

as $\Delta G°_1 = -nFE° = -2F \times 0.337$

for the process (ii)

$Cu^{2+} + e^- \rightarrow Cu^+$;

$\Delta G°_2 = -1F \times 0.153$

now subtract eq. (ii) from (i)

$Cu^+ + e^- \rightarrow Cu$; $\Delta G°_3 = \Delta G°_1 - \Delta G°_2$

$= -0.674\ F - (-0.153\ F)$

$= -0.674\ F + 0.153\ F$

$= -0.521\ F$

Now $-nFE°_{Cu^{2+}/Cu} = -0.521\ F$

$E°Cu^{2+} / Cu = -0.521\ V$.

213. Lower the reduction potential, stronger is the reducing agent.

214. Higher the reduction potential, better the oxidizing agent. Since the R.P. of Y is greater.

than X but less than Z, hence, Y will oxidize X but not Z.

215. $\overset{(0)}{S_8}$ elemental state

$\overset{x}{S_2}\,\overset{-1}{F_2}$

$2x - 2 = 0$

$2x = 2$ so $x = 1$

$\overset{+1}{H_2}\,\overset{x}{S}$

$x + 2 = 0$

$x = -2$

216. $M^+ + e^- \rightarrow M$; $E° = +\,0.44\ V$

$X + e^- \rightarrow X^-$; $E° = +\,0.33\ V$

Now in case of **b.**

$E°_{mf} = E°c - E°a$

$= E°\ M^+ / M - E°\ X / X^-$

$= 0.44 - 0.33 = 0.11\ V$

Thus $M^+ + X^- \rightarrow M + X$ is a spontaneous reaction.

217.

(A) $[\overset{+7}{Mn}\,O_4]^-$ (B) $[Cr^{3+}\,(CN)_6]^{3-}$

(C) $[\overset{+4}{Ni}\,F_6]^{-2}$ (D) $\overset{+6}{Cr}\,O_2\,Cl_2$

218. Ionic mobilities (or transport numbers) of $K^+NO_3^-$ are nearly same.

219.

$$3[\overset{+1}{Cl}\,O]^{-1} \rightarrow \overset{+6}{Cl}O_3 + 2Cl^{-1}$$

This is an example of disproportionation reaction.

220. Since the ionic character decreases in the order KCl > NaCl > LiCl

221. $Cr_2O_7^{-2} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Since $K_2Cr_2O_7$ accepts 6 electrons for its reduction to Cr^{3+} ions.

Eq. wt. $= \dfrac{\text{Mol. wt.}}{6}$

222. When MnO_4^- is used in aqueous HCl, MnO_2 reacts with Fe^{+2} as well as with HCl as explained below:

$$MnO_4^- + 5Fe^{+2} + 8H^+ \rightarrow 5Fe^{+3} + 4H_2O + Mn^{2+}$$

$E°cell = 1.51 - 0.77 = 0.74 > 0$

$$2MnO_4^- + 16\,H^+ + 10Cl^- \rightarrow 2Mn^{+2} + 8H_2O + 5Cl_2$$

$E°cell = 1.51 - 0.77 = 0.74 > 0$

As such MnO_4^- cannot be used for the quantitative estimation of aqueous $Fe(NO_3)_2$. Thus option A is not correct. Similarly, we can show that $Cr_2O_7^{2-}$ will react with Fe^{2+} but not with HCl.

$Cr_2O_7^{-2} + 6Fe^{+2} + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O + 3Cl_2$

$E°cell = 1.38 - 0.77 = 0.61\ V > 0$

$Cr_2O_7^{-2} + 6Cl^- + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O + 3Cl_2$

$E°cell = 1.38 - 1.40 = -0.02\ V < 0$

Thus, the second reaction is not possible. Thus $Cr_2O_7^{-2}$ in aqueous HCl can be used for the quantitative estimation of aqueous $Fe(NO_3)_2$.

Option (C) and (D) are correct.

223. In an electrolytic cell, electrons do not flow themselves. It is the migration of ions towards oppositely charged electrodes that indirectly constitutes the flow of electrons from cathode to anode through internal supply.

224. The maximum O.S. of Cr is +6 in CrO_2Cl_2 and that of Mn is +7 in MnO_4^-.

225. $Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$ (n = 2)

$$E = E° - \frac{0.0591}{n} \log Kc$$

$$0.0295 = E° - \frac{0.0591}{2} \log \frac{0.01}{0.001}$$

$E° = 0.2905 + 0.0295 = 0.32$ volt

$$E° = \frac{0.0591}{n} \log Keq$$

$$0.32 = \frac{0.0591}{2} \log Keq = 0.02945 \log Keq$$

$Keq = 10^{0.32/0.0295}$

226. $Fe(s) \rightarrow Fe^{2+} + 2e^-;\quad \Delta G°_1$

$$\frac{2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2O(l) \quad \Delta G°_2}{Fe(s) + 2H^+ + \frac{1}{2}O_2 \rightarrow Fe^{2+} + H_2O \quad \Delta G°_3}$$

$\Delta G°_2 + \Delta G°_1 = \Delta G°_3$

$\Delta G°_3 = (-2F \times 0.44) + (-2F \times 1.23)$

$= -(2 \times 96500 \times 0.44 + 2 \times 96500 \times 1.23)$

$= -322310\ J = -322\ kJ.$

227. The solubility of AgBr in presence of 10^{-7} molar $AgNO_3$ is 3×10^{-7} M.

Therefore $[Br^-] = 3 \times 10^{-4}\ m^3$,

$[Ag^+] = 4 \times 10^{-4}\ m^3$ and $[NO_3^-] = 10^{-4}\ m^3$

Therefore $Ktotal = KBr^- + KAg^+ + KNO_3^- = 55\ Sm^{-1}$

228. $Cr_2O_7^{2-} + Fe^{2+} \rightarrow Fe^{3+} + Cr^{3+}$

n factor of $Cr_2O_7^{2-} = 6$

n factor of $Fe^{2+} = 1$

So to reduce one mole of dichromate 6 moles of Fe^{2+} are required

229. $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

For 0.01 mole H_2 0.02 mole of e^-s are consumed

Charge required $= 0.02 \times 96500\ C = i \times t$

$$\text{Time required} = \frac{0.02 \times 96500}{10 \times 10^{-3}}$$

$= 19.3 \times 10^4$ sec

Numericals For Practice

1. Given the following standard potentials at 25°C:

$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$ $\quad E° = -0.403V$

$CdS(s) + 2e^- \rightarrow Cd(s) + 2S^{2-}(aq)$ $\quad E° = -1.21V$

Calculate K_{sp} for CdS

a. 1×10^{-25} **b.** 1×10^{-27}
c. 1×10^{27} **d.** 1×10^{-29}

2. $ClO_3^- \xrightarrow{0.54\ V} ClO^- \xrightarrow{0.45\ V}$

$\frac{1}{2}Cl_2 \xrightarrow{1.07\ V} Cl^-$

If E° for the conversion of ClO^- to Cl^- is 0.71 and that of ClO_3^- to Cl^- is X find the value of X?

a. 0.3 **b.** 0.5507
c. 0.6 **d.** 0.06

3. Given $E°_{Cr^{3+}/Cr} = -0.72$ V, $E°_{Fe^{2+}/Fe} = -0.42$ V. The potential for the cell

Cr | Cr^{3+} (0. 1 M) || Fe^{2+} (0.01 M) | Fe is

a. 0.26 V
b. 0.399 V
c. –0.339 V
d. –0.26 V

4. An electric current of 1 A is passed through acidulated water for 160 minutes and 50 seconds. What is the volume of the oxygen liberated at the anode (as reduced to NTP)?

a. 2.24 litre
b. 22.4 litre
c. 1.12 litre
d. 11.2 litre

5. $E^\circ_{Cu^{2+}/Cu^{+}} = 0.153$ V; $E^\circ_{Cu^{2+}/Cu} = 0.337$ V. $E^\circ_{Cu^{+}/Cu}$ is

a. 0.495 V
b. 0.521 V
c. 0.186 V
d. 0.369 V

6. A voltaic cell is constructed that is based on the following reaction:

Sn^{2+} (aq) + Pb(s) ⟶ Sn(s) + Pb^{2+}(aq)

If the concentration of Sn^{2+} in the cathode compartment is 1.00 M and the cell generates an emf of +0.22 V, what is the concentration of Pb^{2+} in the anode compartment?

a. 2×10^{-8} M
b. 2×10^{8}
c. 2×10^{-6} M
d. 2×10^{-6}

7. If in the above problem the anode compartment contains $[SO_4^{2-}]$ = 1.00 M in equilibrium with $PbSO_4$ (s), what is the K_{sp} of $PbSO_4$?

a. 3.4×10^{-8}
b. 1.7×10^{8}
c. 3.4×10^{8}
d. 1.7×10^{-8}

8. A graph is plotted between E_{cell} of quinhydrone half cell and pH of solution. Intercept is 0.698 V. At what pH, E_{cell} will become 0.491 V?

a. 1.75
b. 3.5
c. 4.5
d. 11.5

9. Given that K = 3.76×10^{14} for the reaction $2Fe^{3+}$(aq) + Cu(s) ⟶$2Fe^{2+}$ (aq) + Cu^{2+}(aq)

at 25°C, which of the following corresponds to Eo for the reaction?

a. –0.43 V
b. –0.22 V
c. 0.43 V
d. 0.22 V

10. Calculate the cell EMF in mV for Pt | H_2 (1 atm) | HCl (0.01 M) | AgCl (s) | Ag (s) at 298 K If ΔG°_f values are at 25°C –109.56 kJ/mol for AgCl (s) and –130.79 kJ/mol for ($H^+ + Cl^-$) (aq)

a. 228 mV
b. 45.6 mV
c. 654 mV
d. 456 mV

11. Using standard cell potentials, calculate ΔG° for the reaction 5AgI(s) + Mn^{2+}(aq) + $4H_2O$(l) ⟶ 5Ag(s) + $5I^-$(aq) + MnO_4^-(aq) + $8H^+$(aq)

a. 160 kJ
b. 801 kJ
c. –160 kJ
d. –801 kJ

12. What is the electrode potential at 25°C for the reaction Cd(s) + $2H^+$ (aq) ⟶ Cd^{2+}(aq) + H_2(g) when the concentrations are:

Cd^{2+}(aq) = 0.100 M; P_{H2} = 2.00 atm; and H^+ = 0.200 M?

a. 0.283 V
b. 0.365
c. 0.382
d. 0.424 V

13. At 298 K a cell reaction exhibits a standard emf of +0.17 V. The equilibrium constant for the cell reaction is 5.5×10^5. What is the value of n for the cell reaction?

a. 4
b. 2
c. 6
d. 1

14. How long does it take to plate on to a surface 1.00 g of chromium metal using a current of 3.00 amperes? (1F = 96,500 coulombs) give this half-reaction

a. 3.71×10^3s
b. 1.36×10^3 s
c. 6.17×10^2 s
d. 3.71×10^{-3} s

15. The mass of copper deposited from a solution of Cu_2S by passing a current of 2.5 ampere for 6 minute is

a. 0.6 g
b. 0.7 g
c. 0.5 g
d. 0.9 g

16. In the electrolysis of aqueous NaCl, how many liters of Cl_2(g) (at STP) are generated by a current of 16.8 A for a period of 90.0 min?

a. 21.0 L Cl_2
b. 10.5 L Cl_2
c. 5.2 L Cl_2
d. 20.5 L C12

17. The reduction potential of a hydrogen electrode at pH = 10, at 298 K is

a. –0.591 V
b. zero
c. + 0.591 V
d. –0.0591 V

18. How many atoms of calcium will be deposited from a solution of $CaCl_2$ by a current of 25 milliamperes flowing for 60 s?

a. 4.7×10^{17}
b. 4.7×10^{18}
c. 4.7×10^{9}
d. 4.7×10^{12}

19. The standard potential for the reduction of AgSCN(s) is + 0.0895 V:

AgSCN(s) e^-⟶ Ag (s) + SCN^- (aq)

Using this value and the electrode potential foe $Ag^+(aq)$, calculate the K_{sp} for AgSCN.

a. 1×10^{12} **b.** 2×10^{-12}
c. 1×10^{-12} **d.** 2×10^{12}

20. At 25°C, electrode potential of Mg^{2+}/Mg electrode in which concentration of Mg^{2+} ions is 0.1 M ($E^\circ_{Mg^{2+}/Mg} = -2.36$ V)

a. –2.36 V **b.** –2.39 V
c. –4.75 V **d.** – 3.95 V

21. Find the oxidizing power of (1 M, MnO_4^-/Mn^{2+}, 1M) couple decreased if the H^+ concentration is decreased from 1M to 10^{-4} M at 25°C?

a. 0.38 V **b.** –0.38V
c. –0.19 **d.** –0.76

22. A cell reaction is given by $A + B^{2+} (aq) \rightarrow C + D^{2+} (aq)$. If its equilibrium constant (Kc) is 100, what is the value of E°cell at 25°C?

a. 0.0591 **b.** 0.1283
c. 0.0356 **d.** 0.2366

23. Consider the following E° values

$E_{(Fe^{3+}/Fe^{2+})} = +0.77$ V
$E_{(Sn^{2+}/Sn)} = -0.14$ V

Under standard conditions the potential for the reaction

$Sn(s) + 2Fe^{3+} (aq) \rightarrow 2Fe^{2+} (aq) + Sn^{2+} (aq)$ is

a. 1.68 V **b.** 0.91 V
c. 0.63 V **d.** 1.46 V

24. A voltaic cell utilizes the following reaction and operates at 20°C:

$2Fe^{3+}(aq) + H_2(g) \rightarrow 2Fe^{2+}(aq) + 2H^+(aq)$

What is the emf of this cell under standard conditions?

a. 1.572 V **b.** 0.771 V
c. 0.385 V **d.** 0.762V

25. In the above problem : What is the emf for this cell when $[Fe^{3+}] = 0.50$ M, $P_{H_2} = 0.25$ atm, $[Fe^{2+}] = 0.010$ M, and the pH in both compartments is 4.00

a. 2.182 V **b.** 10.91 V
c. 1.091 V **d.** 21.82V

26. In a half-cell containing $[Tl^{3+}] = 0.2$ M and $[Tl^+] = 0.02$ M, the cell potential is –1.2495 V for the reaction $Tl^+ \rightarrow Tl^{3+} + 2e^-$. The standard reduction potential of the Tl^+ / Tl^{3+} couple at 25°C is

a. 1.22 V **b.** 1.44 V
c. 0.61 V **d.** 2.44 V

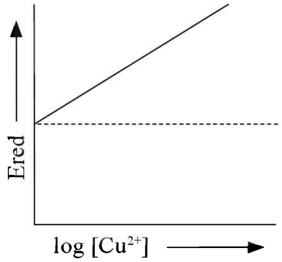
27. For the following cell Pb | $PbCl_2(s)$ | $PbCl_2$(soln.) | AgCl(s) | Ag the potential at 298 K is 0.490 V and the variation of emf with temperature is given by $E = a - (1.86 \times 10^{-4}\ V\ K^{-1})(T - 25\ K)$ Calculate ΔG.

a. 47.28 Kcal **b.** –94.57 K.cal.
c. –47.28 Kcal **d.** 94.57 K.cal

28. The standard emf of a cell, involving one electron change is found to be 0.591 V at 25°C. The equilibrium constant of the reaction is (F = 96500 C mol^{-1}, R = 8.314 $JK^{-1}\ mol^{-1}$)

a. 1.0×10^{30} **b.** 1.0×10^1
c. 1.0×10^5 **d.** 1.0×10^{10}

29. $Cu^{2+} + 2e \rightarrow Cu$; log $[Cu^{2+}]$ vs E_{red} graph is given below OA = 0.34 V then electrode potential of the half cell of Cu | Cu^{2+} (0.1 M) will be :



a. $-0.34 + \frac{0.0591}{2}$ V
b. $0.34 + \frac{0.0591}{2}$ V
c. 0.34 V
d. –0.34 V

30. Electrolysis of a solution of HSO_4^- ions produces $S_2O_8^{2-}$. Assuming 75 % current efficiency, what current must be employed to achieve a production rate of 1 mole of $S_2O_8^{2-}$ per hour?

a. 7.14 amp **b.** 35.75 amp
c. 71.5 amp **d.** 142.85 amp

31. The emf of a cell corresponding to the reaction

$Zn(s) + 2H^+ (aq) \rightarrow Zn^{2+} + H_2(g)$
(0.1 M) (1 atm)

is 0.28 V at 25°C and $E^\circ_{Zn/Zn^{2+}} = 0.76$ V find the pH of the solution at H electrode.

a. 8.635 **b.** 5.365
c. 6.365 **d.** 4.617

32. From the following standard electrode potentials at 25°C

$Cu^{2+} + 2e = Cu$; E° = +0.34V
$Cu^{2+} + e = Cu^+$; E° = +0.15 V

Calculate equilibrium constant of the reaction $Cu + Cu^{2+} \rightarrow 2Cu^+$.

a. 3.72×10^{-5} **b.** 3.72×10^{7}

c. 3.72 × 10–7 **d.** 3.72×10^{5}

33. Calculate the equilibrium constant at 298 K for the disproportionation of 3 mole of aqueous HNO_2 to yield NO and NO_3^- ions. The E° for reduction of HNO_2 to NO is 0.98 V and E° for reduction of NO_3^- to HNO_2 is 0.95 V

a. 53.49 **b.** 40.53

c. 49.53 **d.** 42.53

34. The specific conductance of 0.01 M solution of acidic acid was found to be 0.0162 S m–1 at 25°C. Calculate the degree of dissociation of the acid. Molar conductance of acetic acid at infinite dilution is 390.6×10^{-4} $Sm^2\ mol^{-1}$ at 25°C

a. 2.6% **b.** 9.4%

c. 3.7 % **d.** 4.7 %

ANSWER KYES

Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.
1.	a	2.	c	3.	a	4.	c	5.	b
6.	a	7.	d	8.	b	9.	c	10.	d
11.	b	12.	c	13.	b	14.	a	15.	c
16.	b	17.	a	18.	b	19.	c	20.	b
21.	b	22.	a	23.	b	24.	b	25.	c
26.	a	27.	b	28.	d	29	a	30.	c
31.	a	32.	c	33.	c	34.	d		

Hints and Explanations

1. The two half- reactions can be arranged into an oxidation and reduction half – reaction which when added together from the solubility equilibrium:

$Cd(s) \rightarrow Cd^{2+}(aq) + 2e^-$ $E° = –0.403$ V

$CdS(s) + 2e^- \rightarrow Cd(s) + 2S^{2-}(aq)$ $E° = -1.21$ V

$CdS \rightleftharpoons Cd^{2+}(aq) + S^{2-}(aq)$

$E = -1.21V - (-0.423\ V)$

$= -0.81$ V

K_{sp} is the equilibrium constant and it is related to the standard potential as follow:

$$\log K = \frac{nE°}{0.0592\ V} = \frac{2(-0.81\ V)}{0.0592\ V}$$

$= -27$

taking the anitlog give $K = 1 \times 10^{-27}$

3. As $E°_{(Cr^{3+}/Cr)} = -0.72$ V and $E°_{(Fe^{2+}/Fe)} = -0.42V$

$2Cr + 3Fe^{2+} \rightarrow 3Fe + 2Cr^{3+}$

$$E_{Cell} = E°_{cell} - \frac{0.0591}{6}\log_{10/}\frac{(Cr^{3+})^2}{(Fe^{2+})^3}$$

$$= (-0.42 + 0.72) - \frac{0.0591}{6}\log_{10}\frac{(0.1)^2}{(0.01)^3}$$

$$= 0.30 - \frac{0.0591}{6}\log_{10}\frac{(0.1)^2}{(0.01)^3}.$$

$$= 0.30 - \frac{0.0591}{6}\log_{10}\frac{10^{-2}}{10^{-6}}$$

$$= 0.30 - \frac{0.0591}{6}\log_{10} 10^4$$

On solving, we get

$E_{cell} = 0.2606$ V.

4. t = 160 min 50 sec = 9650 sec, $I = 1$ A

volume of O_2 (released) = ?

$$\text{Acidulated Water} \rightarrow \underset{(\text{anode})}{O_2\uparrow}$$

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

At cathode: $H^+ + e^- \rightarrow H$

$2H \rightarrow H_2\uparrow$

At anode: $2OH^- \rightarrow H_2O + [O] + 2e^-$

$O + O \rightarrow O_2\uparrow$

According to Faraday's law

Volume of gas evolved at NTP = $V = \dfrac{ItV_e}{96500}$

Here V_e = equivalent volume = volume of gas evolved at NTP by 1 Faraday charge.

$$V_e = \frac{22.4}{32} \times 16 = 11.2\text{ L}$$

$$V = \frac{1 \times 9650 \times 11.2}{96500} = 1.12\text{ L.}$$

5. $Cu^+ \rightarrow Cu^{2+} + e^-$; $E°_I = -0.153$ V

$Cu^{2+} + 2e^- \rightarrow Cu$; $E°_{II} = +0.337$ V

Adding $Cu^+ + e^- \rightarrow Cu$; $E° = ?$

$$E° = \frac{n_1E_1 + n_2E_2}{n} = \frac{1 \times (-0.153) + 2(0.337)}{1}$$

= 0.521 V

6. $E° = -0.136\text{ V} - (-0.126\text{ V})$

$= -0.010$ V ; n = 2

$$0.22 = -0.010 - \frac{0.0592}{2}\log\frac{[Pb^{2+}]}{[Sn^{2+}]}$$

$$= -0.010 - \frac{0.0592}{2}\log\frac{[Pb^{2+}]}{1.00}$$

$$\log[Pb^{2+}] = \frac{-0.23\,(2)}{0.0592} = -7.770$$

$= -7.8$;

$[Pb^{2+}] = 1.7 \times 10^{-8}$

$= 2 \times 10^{-8}$ M

7. For $PbSO_4$ (s),

$K_{sp} = [Pb^{2+}][SO_4^{-2}]$

$= (1.0)(1.7 \times 10^{-8})$

$= 1.7 \times 10^{-8}$

8. $Q + 2H^+ + 2e^- \rightleftharpoons QH_2$

$$E_{cell} = E°_{cell} - \frac{0.0591}{2}\log_{10}\frac{1}{[H^+]^2}$$

$E_{cell} = E°_{cell} - 0.0591$ pH

Intercept = $E°_{cell}$ = 0.698V

$$pH = 0.698 - \frac{0.491}{0.0591} = 3.5$$

9. E° = (0.0592 V) log K/n

= (0.0592 V/2) log (3.76×10^{14})

= 0.43 V.

13. $E° = \dfrac{0.0592}{n}$ V log K;

$$n = \frac{0.0592\text{ V}}{E°}\log K$$

$$n = \frac{0.0592\text{ V}}{0.17\text{ V}}\log 5.5 \times 10^5;$$

n = 2

15. Charge passed = I.t = 2.5 × 360 = 900 C

Valency of copper in Cu_2S is 1

So equivalent wt. of copper

$$= \frac{\text{atomic wt.}}{\text{valency}} = \frac{63.5}{1} = 63.5$$

96500 coulomb of charge deposit 63.5 g of copper

therefore 900 C of charge will deposit

$$\frac{63.5}{96500} \text{ x } 900 = 0.5 \text{ g of copper}$$

17. Consider the cell,

Pt, H_2 (g) | H^+ (1.0 M) || H^+ (1×10^{-10} M) | H_2, Pt

It is a concentration cell

$E_{cell} = 0.0591 \log c_2 / c_1$

$= 0.0591 \log 1 \times 10^{-10}$

$= -0.591$ V

18. $Q = I.t = 25 \times 10^{-3} \times 60 = 1.5$ C

When 96500 C of charge is passed, the no. of electrons that will flow through the solution $= 6.023 \times 10^{23}$

Therefore number of electrons that will flow when 1.5 C of charge is passed

$$= \frac{6.023 \times 10}{96500} \times 1.5 = 9.4 \times 10^{18}$$

For depositing one calcium atom, number of electrons required = 2

So no. of atoms of calcium required to deposit 9.36 × 10^{18} electrons is

$$\frac{1}{2} \times (9.4 \times 10^{18}) = 4.7 \times 10^{18}$$

19. $AgSCN\,(s) + e^- \rightarrow Ag(s) + SCN^-(aq)$

$$E^\circ_{red} = 0.0895\text{ V}$$

$$\begin{array}{ll} Ag(s) \rightarrow Ag^+(aq) + e^- & E_{red} = 0.799\text{V} \\ \hline AgSCN(s) \rightarrow Ag^+(aq) + SCN^-(aq) & \end{array}$$

$E^\circ = 0.0895 - 0.799 = -0710\text{V}$

$E^\circ = \dfrac{0.0592}{n} \log K_{sp} = \dfrac{(-0.710)(1)}{0.0592}$

$= -11.993 = -12.0$

$K_{sp} = 10^{-11.993}$

$= 1.02 \times 10^{-12}$

$= 1 \times 10^{-12}$

20. According to Nernst equation, the electrode potential of Mg^{2+}/Mg electrode

$(E) = E^\circ + \dfrac{0.0591}{n} \log [Mg^{2+}]$

$= -2.36 + \dfrac{0.0591}{2} \log (0.1)$

$= -2.36 + 0.02955\,(-1) = -2.39\text{ V}$

21. The half cell reaction is,

$MnO^-_4 + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$

$E_{MnO4^-}/Mn^{2+} = E^\circ_{MnO4^-} / Mn^{2+}$

$+ \dfrac{0.059}{5} \log 10 \dfrac{[MnO_4^-]\,[H^+]^8}{[Mn^{2+}]}$

Or

$E_{RP} = E^\circ_{RP} + 0.0118 \log 10 \dfrac{1 \times 1}{1}$

$E_{RP} = E^\circ_{RP}$

If $H^+ = 10^{-4}$

Then $E_{RP} = E^\circ_{RP} + 0.0118 \log 10 \dfrac{1 \times (10^{-4})^8}{1}$

$E_{RP} = E^\circ_{RP} - 0.38\text{ V}$

i.e., the couple MnO^-_4/Mn^{2+} shows a decrease in its E_{RP} by 0.38 volt or an increase in its E_{OP} by 0.38 V and thus less oxidizing power.

22. $\text{Ecell} = \text{E°cell} - \dfrac{0.0591}{n} \log \text{Kc}$

since Ecell at equilibrium is 0, therefore 0

$= \text{E°cell} - \dfrac{0.0591}{n} \log \text{Kc}$

$\text{E°cell} = \dfrac{0.0591}{n} \log \text{Kc}$

$0.591 = \dfrac{0.0591}{1} \log \text{Kc}$

on solving

$\text{Kc} = 1.0 \times 10^{10}$

23. $Sn(s) + 2Fe^{3+}\,(aq) \rightarrow$

$$2Fe^{2+}\,(aq) + Sn^{2+}\,(aq)$$

$E^\circ_{(cell)} = E^\circ_{(ox)} + E^\circ_{(red)}$

$= E^\circ_{Sn/Sn^{2+}} + E^\circ_{(Fe^{3+}/Fe^{2+})}$

Given

$E^\circ\,Sn^{2+} / Sn = -0.14\text{ V}$

$E^\circ\,Sn / Sn^{2+} = +0.14\text{ V}$

$E^\circ\,Fe^{3+} / Fe^{2+} = 0.77\text{ V}$

$E^\circ\text{cell} = 0.14 + 0.77 = 0.91\text{ V}$

24. $2[Fe^{3+}(aq) + 1\,e^- \rightarrow Fe^{2+}(aq)$

$$E^\circ_{red} = 0.771\text{ V}$$

$$\begin{array}{l} H_2(g) \rightarrow 2H^+(aq) + 2e^- \quad E_{red} = 0.000\text{V} \\ \hline 2Fe^{3+}(aq) + H_2(g) \rightarrow 2Fe^{2+}(aq) + 2H^+(aq) \end{array}$$

$E^\circ = 0.771 - 0.000$

$= 0.771\text{V}$

25. $E = E^\circ - \dfrac{0.0592}{n} \log \dfrac{[Fe^{2+}]^2\,[H^+]^2\,;}{[Fe^{3+}]^2\,P_{H2}}$

$[H^+] = 10^{-pH} = 1.0 \times 10^{-4},\ n = 2$

$E = E^\circ - \dfrac{0.0592}{2} \log \dfrac{(0.010)^2\,(1.0 \times 10^{-4})^2}{(0.50)^2\,(0.25)}$

$= 0.771 - \dfrac{0.0592}{2} \log (1.6 \times 10^{-11})$

$E = 0.771 - \dfrac{0.0592\,(-10.80)}{2}$

$= 0.771 + 0.320 = 1.091\text{ V}$

26. For the oxidation reaction, $Tl^+ \rightarrow Tl^{3+} + 2e^-$

$E = E^\circ - \dfrac{RT}{nF} \log_{10} \dfrac{[\text{Oxi.}]}{[\text{Red.}]}$

$= -1.2495 = E^\circ - \frac{0.059}{2}\log_{10}\frac{0.2}{0.02}$.

$E^\circ = 1.220$ V

27. For the given cell, the Electrode Reduction reaction can be given as

right: $2AgCl(s) + 2e^- = 2Ag(s) + 2Cl^-(aq)$ ……(i)

Left: $PbCl_2(s) + 2e^- = Pb(s) + 2Cl^-(aq)$ ……(ii)

Subtracting Eq. (ii) from Eq. (i), we get

$2AgCl(s) + Pb(s) = 2Ag(s) + PbCl_2(s)$

Now since $E = a - (1.86 \times 10^{-4}\ V\ K^{-1})$ $(T - 25\ K)$ Therefore

$\left(\frac{\partial E}{\partial T}\right) = -1.86 \times 10^{-14}\ V\ k^{-1}$

Now using the relation

$\Delta G = -nFE$

$= -2(96500\ C\ mol^{-1})\ (0.490\ V)$

$= -94570\ C\ mol^{-1}$

$= -94.57$ K.cal.

28. Relation between Keq and Ecell is

$E^\circ cell = \frac{2.303\ RT}{nF}\log Eeq$

$E^\circ cell = \frac{0.0591}{n}\log Eeq$

$0.591 = \frac{0.0591}{1}\log Eeq$

$\log Eeq = 10$

$Eeq = 1 \times 10^{10}$

29. $E_{Cu/Cu}{}^{2+} = E^\circ{}_{Cu/Cu}{}^{2+} - \frac{0.059}{2}\log[Cu^{2+}]$

If $\log[Cu^{2+}] = 0$,

i.e. , $[Cu^{2+}] = 1$

then $E_{Cu/Cu}{}^{2+} = EoCu/Cu^{2+}$

or intercept OA $= E^\circ{}_{Cu}{}^{2+}{}_{/Cu} = 0.34$

Now $E_{Cu/Cu}{}^{2+} = -0.34 - \frac{0.059}{2}\log 0.1$

$= -0.34 + \frac{0.059}{2}$

32. (i) $Cu = 2Cu^{2+} + 2e$;

$E^\circ = -0.34$;

$\Delta G^\circ = -2(-0.34)F = 0.68\ F$

(ii) $2Cu^{2+} + 2e = 2Cu^+$; $E^\circ = +0.15$;

$\Delta G^\circ = -(0.15)\ F = -0.30F$

On adding (i) and (ii), we get

$Cu + Cu^{2+} = 2Cu+$; $\Delta G^\circ = +0.38F$

As $-\Delta G^\circ = 2.303\ RT \log_{Keq}$

So $-0.38\ F = 2.303\ RT \log K_{eq}$

$-0.38 = 0.0591 \log K_{eq}$

$\log K_{eq} = -6.429 = 7.571$

So on taking Antilog we get

$Keq = 3.72 \times 10^{-7}$

33. $N^{3+} \rightarrow N^{5+} + 2e$; $E^\circ = -0.94$ V

$2N^{3+} + 2e \rightarrow 2N^{2+}$ $E^\circ = 0.99V$

$3N^{3+} \rightarrow 2N^{2+} + N^{5+}$

As $E^\circ{}_{cell} = E^\circ{}_{OP} + E^\circ{}_{RP}$

HNO_2/NO_3^- HNO_2/NO

So $E^\circ cell = -0.95 + 0.98 = 0.05$

As $E^\circ cell = \frac{0.059}{2}\log Kc$

So $0.05 = \frac{0.059}{2}\log Kc$

On solving Kc = 49.53

34. $k = 0.0162\ S\ m^{-1}$; $c = 0.01\ mol\ dm^{-3}$

$= 10\ mol\ m^{-3}$

$\Lambda m = \frac{k}{c} = \frac{0.0162\ S\ m^{-1}}{10\ mol\ m^{-3}}$

$= 16.2 \times 10^{-4}\ S\ m^2 mol^{-1}$

$\Lambda^\circ m = 390.6 \times 10^{-4}\ S\ m^2\ mol^{-1}$ (given)

$\alpha = \frac{\Lambda m}{\Lambda^\circ m} = \frac{16.2 \times 10^{-4}\ S\ m^2\ mol^{-1}}{390.6 \times 10^{-4}\ S\ m^2\ mol^{-1}}$

$= 0.047 = 4.7\%$

CHAPTER 7

Chemical Kinetics

Chapter Contents

Rates of chemical reactions; Order of reactions; Rate constant; First order reactions; Temperature dependence of rate constant (Arrhenius equation) and Various levels of multiple-choice questions.

CHEMICAL KINETICS

Chemical kinetics (‘kinesis’ meaning movement) is the study of rate and mechanism of a reaction and factors effecting it like temperature, pressure catalyst, radiations etc.

- On the basis of rate, reactions are characterized as slow, moderate and very fast types.
- Very fast reactions take 10^{-14}–10^{-16} for their completion and they are not studied under kinetics, these are studied by flash photolysis and spectrographic methods.example,– Ionic reactions

  $NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$

  $HCl + KOH \rightarrow KCl + H_2O$
- Very slow reactions like rusting of iron or blackening of white lead, formation of water at room temperature and burning of coal are also not studied under kinetics.
- Moderate reactions like molecular reactions (most of the organic reactions) are studied under kinetics example, (i) Hydrolysis of sugar or ester (ii) Decomposition of N_2O_5, H_2O_2, NH_4NO_2 etc.

Rate of Reaction

It is defined as “The rate of change of concentration of a reactant or a product per unit time” that is it is nothing but it is the per unit mole of rate of decomposition of any reactant or formation of product.

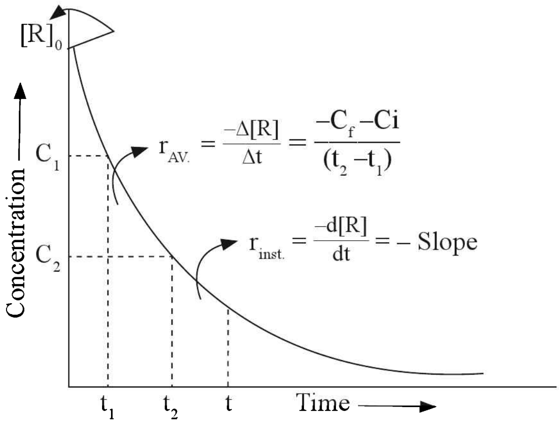
$$\text{Rate of reaction (r)} = \frac{C_1 - C_2}{t_2 - t_1}$$

As rate of reaction varies greatly with time, so generally, average reaction rate and instantaneous reaction rates are used. Average rate ways to is the rate at some particular instant of time and is equal to the time rate of change of the active mass of any of the reactants or any of the products.

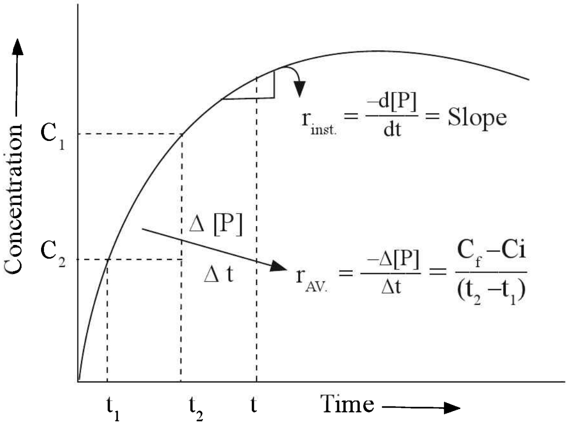
example For a reaction $A \rightarrow P$

$$\text{Rate of disappearance of A} = -\frac{\Delta[A]}{\Delta T}$$

$$\text{Rate of appearance of P} = -\frac{\Delta\,[P]}{\Delta T}$$



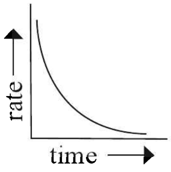
[Reactant]
(a)



[Product]
(b)

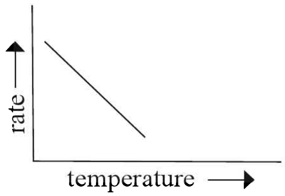
Features of Rate of Reaction

- It is always a positive quantity.
- It is proportional to the active masses of the reactant.
- It is measured by measuring active mass or molar concentration of a reactant or a product as a function of time.
- Rate of reaction for reactants decreases with time as concentration of reactant decreases.



Example., $2NO_2 + F_2 \rightarrow 2NO_2F$

Here rate of reaction is measured by decrease in concentration of F_2.



REMEMBER

$2NO + O_2 \rightarrow 2NO_2$

The only reaction with negative temperature coefficient.

Units of Rate of Reaction

mol L^{-1} time^{-1} or atm time^{-1}. (gaseous substance).

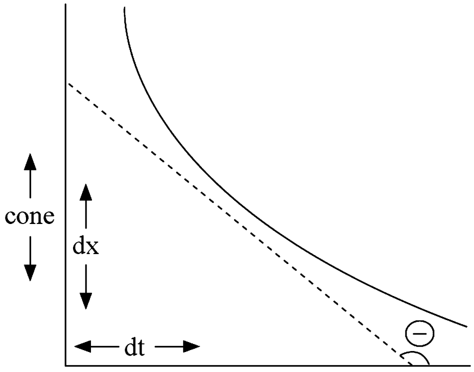
Instantaneous Rate of Reaction

As average reaction rate fails to predict rate at a particular moment of time so we use instantaneous rate which is equal to small change in concentration (dx) during a small interval of time (dt). It is given as dx/dt.

$$R_{\text{instant}} = \frac{dc}{\Delta t}$$

$\Delta t \rightarrow 0$

limit



Instanteneous Reaction Rate

- $dx/dt = \tan\theta$ = slope of curve
- It can be written for any of the reactant or the product in terms of stoichiometric coefficients (V_j) which is negative for reactants and positive for products as follows:

$$\frac{dx}{dt} = \frac{1}{V_j}\frac{d(J)}{dt}$$

$aA + bB \rightarrow cC + dD$

$$\text{Rate w.r.t. } [A] = -\frac{d\,[A]}{dt} \times \frac{1}{a}$$

$$\text{Rate w.r.t. } [B] = -\frac{d\,[B]}{dt} \times \frac{1}{b}$$

$$\text{Rate w.r.t. } [C] = -\frac{d\,[C]}{dt} \times \frac{1}{c}$$

$$\text{Rate w.r.t. } [D] = -\frac{d\,[D]}{dt} \times \frac{1}{d}$$

- For the reactants, negative sign indicates decrease of concentration and for products positive sign indicates increase in concentration.
- For a reversible reaction at dynamic equilibrium, net reaction rate is always zero as

  $(dx/dt)_f = (dx/dt)_B$

  Example,– $N_2 + 3H_2 \leftrightarrow 2NH_3$

  For N_2: $\frac{dx}{dt} = \frac{-dN_2}{dt}$

  for H_2: $\frac{-dx}{dt} = \frac{-dH_2}{dt}$

  for NH_3: $\frac{dx}{dt} = \frac{dNH_3}{dt}$

  Example, $H_2O_2 + 2H^+ + 3I^- \rightarrow I_3^- + 2H_2O$

  $$\frac{dH_2O_2}{dt} = \frac{-1}{2}\frac{dH^+}{dt} = \frac{-1}{3}\frac{dI^-}{dt} = \frac{dI^-}{dt} = \frac{dI_3^-}{dt} = \frac{1}{2}\frac{dH_2O}{dt}$$

  Example, $\underset{aq}{BrO_3^-} = \underset{aq}{5Br^-} + \underset{aq}{6H^+} \rightarrow \underset{aq}{3Br_2} + \underset{l}{3H_2O}$

  $$\frac{-dBrO_3}{dt} = \frac{-1}{5}\frac{dBr^-}{dt} = \frac{-1}{6}\frac{dH^+}{dt} = \frac{1}{3}\frac{dBr_2}{dt} = \frac{1}{3}\frac{dH_2}{dt}$$

Illustrations

1. Write the expression for the rate of following gaseous reaction:

   $2N_2O_5\,(g) \leftrightarrow 4NO_2\,(g) + O_2\,(g)$

   which takes place in a closed vessel. If the concentration of NO_2 increases by 1.6×10^{-4} mol litre^{-1} in 4 second, find the rate of reaction and rate of change of concentration of N_2O_5.

Solution $2N_2O_5\,(g) \leftrightarrow 4NO_2\,(g) + O_2\,(g)$

Rate of reaction (r)

$$= -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

$$\text{Rate of reaction} = \frac{1}{4} \times \frac{1.6 \times 10^{-4}}{4}$$

$= 1.0 \times 10^{-3}$ mol L^{-1} s^{-1}

$$\text{Change in conc. of } N_2O_5 = \frac{1}{2} \times \frac{1.6 \times 10^{-3}}{4}$$

$= 2.0 \times 10^{-3}$

2. When $[N_2O_5] = 0.22$ M, the rate of decomposition of N_2O_5 is 1.3×10^{-4} mol L^{-1} s^{-1}. What is the value of k for this first order reaction?

Solution $r = k\,[N_2O_5]$

$$k = \frac{r}{[N_2O_5]}$$

$$= \frac{1.3 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}}{0.22\ \text{M}}$$

$= 5.91 \times 10^{-4}$ s^{-1}

3. Show by using rate law, how much rate of the reaction

   $2N + 2O_2 \rightarrow 2NO_2$

   will change if the volume of the reaction vessel is reduced to one-third of its value.

Solution $r_1 = k\,[NO]^2\,[O_2]$ ……… (i)

When volume is reduced to one-third, the concentration of each reactant increases by three times.

$r_2 = k\,[3NO]^2\,[3O_2]$ …… (ii)

On dividing equation (ii) by equation (i), we get,

$$\frac{r_2}{r_1} = \frac{k\,[3NO]^2\,[3O_2]}{k\,[NO]^2\,[O_2]} = 27$$

$r_2 = 27\,r_1$

So the reaction is increased by 27 times.

4. The reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$, is forming NO_2 at the rate of 0.0076 mole/lit/sec at some time:

   (a) What is the rate of change of $[O_2]$ at this time?

(b) What is the rate of change of $[N_2O_5]$ at this time?

(c) What is the rate of reaction at this time?

Solution $\text{Rate} = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = +\frac{1}{4}\frac{d[NO_2]}{dt}$

$$= +\frac{d[O_2]}{dt}$$

Here $\frac{d[NO_2]}{dt} = 0.0076$ mole/lit/sec

(a) Rate of appearance of O_2

$= \frac{1}{4} \times$ rate of appearance of NO_2

$$\frac{d[O_2]}{dt} = \frac{1}{4} \times \frac{d[NO_2]}{dt}$$

$= \frac{1}{4} \times 0.0076$

$= 0.0019$ mole/lit/sec

(b) Rate of disappearance of N_2O_5

$= \frac{1}{2} \times$ rate of appearance of NO_2

$$-\frac{d[N_2O_5]}{dt} = \frac{1}{2} \times \frac{d[NO_2]}{dt}$$

$$\frac{d[N_2O_5]}{dt} = -\frac{1}{2} \times 0.0076$$

$= -0.0038$ mole/lit/sec

(c) Rate of reaction $= \frac{1}{4} \times \frac{d[NO_2]}{dt}$

$= \frac{1}{4} \times 0.0076 = 0.0019$ mol/lit/sec

5. The reaction $2A + B + C \rightarrow D + E$ is found to be of first order in A. Second order in B and zero order in C.

(i) Give the rate law for the reaction in the form of differential equation.

(ii) What is the effect in rate of increasing concentration of A, B and C two times?

Solution (i) The rate law for the reaction is given by

$$\frac{dx}{dt} = k[A][B]^2[C]^0$$

$$\frac{dx}{dt} = k[A][B]^2$$

(ii) On increasing the concentration of A, B and C two times then,

$$\frac{dx}{dt} = k[2A][2B]^2[2C]^0$$

$$\frac{dx}{dt} = k[2A][2B]^2$$

$= 8k[A][B]^2$

Therefore, rate increases by 8 times

6. Dinitro pentoxide decomposes as follows:

$N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$

Given

$d[N_2O_5]/dt = k_1[N_2O_5]$

$d[NO_2]/dt = k_2[N_2O_5]$

$d[O_2]/dt = k_3[N_2O_5]$

What is the relation between k_1, k_2 and k_3?

Solution $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$

Rate w.r.t. N_2O_5 or NO_2 or O_2 may be expressed as follows in the form of relation

$$-\frac{d[N_2O_5]}{dt} = +\frac{1}{2}\frac{d[NO_2]}{dt} = +2\frac{d[O_2]}{dt}$$

On substituting the given values in the question

$k_1[N_2O_5] = k_2/2\,[N_2O_5] = 2k_3[N_2O_5]$

$2k_1 = k_2 = 4k_3$

Reaction Rate or Velocity Constant

To explain it, let us consider this reaction:

$nA \rightarrow \text{Product}$

$$-\frac{dx}{dt} \propto [A]^n$$

$$or \quad -\frac{dx}{dt} = K[A]^n$$

According to Rate Law equation,

If $[A]^n = 1$ than

$-\frac{dx}{dt} = K$ (At a particular temperature)

K = Rate constant or specific reaction rate

Hence at unity concentration rate of a reaction is equal to rate constant.

- **K Temperature** (that is rate constant increases with increase of temperature)
- Rate constant also depends upon presence of catalyst and nature of reactant.
- Rate constant does not depend upon concentration pressure and volume.
- Unit of rate constant is $(\text{mole/litre})^{1-n}$ time^{-1} or litre^{n-1} mol^{1-n} time^{-1} (Here n = order of reaction).

Factors Effecting Rate of Reaction and Rate Constant

Physical State of Reactants

Rate also changes with physical state.

$$\xrightarrow[\text{Decreasing order of rate of reaction}]{\text{Gaseous state > liquid states > solid states}}$$

Temperature

Rate of reaction increases with the increase of temperature as it increases the number of effective collisions. It is observed that for every 10°C rise in temperature –dx/dt or rates becomes double to triple as the number of molecules with every greater than activation energy becomes two – three times.

$$\text{Temp. Coefficient } (\mu) = \frac{\text{K at t°C + 10°C}}{\text{K at t°C}}$$

The value of temperature coefficient lies in between 2–3.

In case we increase temperature by more than 10°C the above relation can be given as:

$$\frac{K_{T_2}}{K_{T_1}} = (\mu)^{\Delta T/10}$$

[Here $\Delta T = T_2 - T_1$]

$$\log_{10} \frac{K_{T_2}}{K_{T_1}} = \frac{\Delta T}{10} \log_{10} \mu$$

$$\frac{K_{T_2}}{K_{T_1}} = \text{Antilog } [\frac{\Delta T}{10} \log_{10} \mu]$$

Concentration

Rate increases with the increase of concentration as due to more number of reactants there are more collisions.

Rate of reaction (dx/dt) α Concentration

Pressure

For gaseous reactants rate varies with pressure just like concentration.

$$\frac{dx}{dt} \,\alpha \text{ Pressure (as } P \,\alpha\, C \text{)}$$

Surface Area

Greater the surface area, faster is the rate of reaction due to more number of active sites.

Rate (dx/dt) α Surface area

Nature of Reactant and Product

- For ionic reactants reaction rate is fast as activation energy is zero for them.
  example,
  $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$
- Molecules have slow reaction rate due to need of more activation energy. Example,
  $2CO + O_2 \rightarrow 2CO_2$

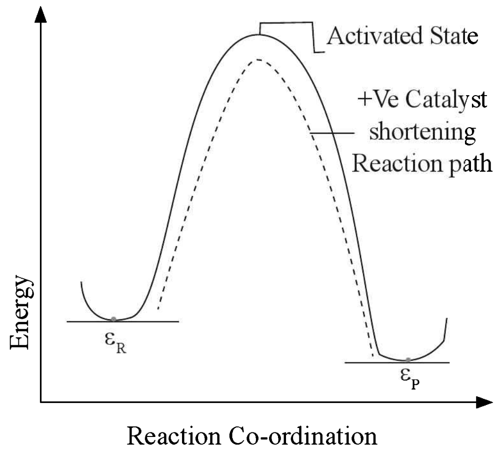
Radiation

Rate of photochemical reactions depends upon intensity of light radiations.

$$\frac{dx}{dt} \,\alpha \text{ Intensity of radiation}$$

Positive Catalyst

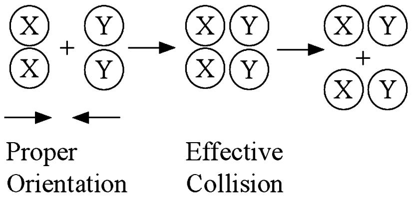
It increases the rate of a reaction by decreasing the activation energy by accepting a new alternative smaller path for the reaction. It is reverse in case of negative catalyst to that of positive catalyst. Catalysts are more effective in 'Solid powdered form' due to larger surface area, that is, more active sites.

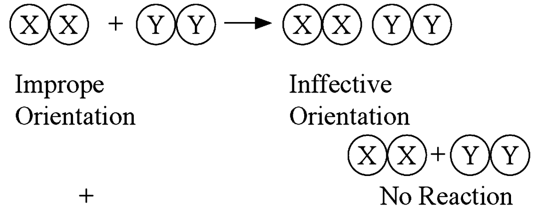


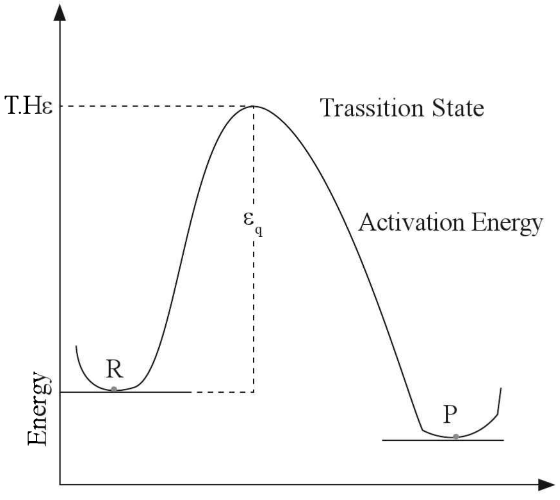
COLLISION THEORY

A reaction takes place as the reacting molecules undergo collisions with one another that is a chemical reaction is the result of effective collisions.

For effective collisions: (a) Colliding molecules must have sufficient potential energy. (b) Collision should be with proper orientation.







Reaction Co-ordination

The minimum energy needed to convert a reactant into product is called Threshhold energy. (T.H.E)

or

It is the minimum amount of energy possessed by reacting molecules in order to have effective collisions for the formation of product.

Threshhold energy = Potential energy of reactant + Ea

- Rate of reaction according to this theory is given as

  Rate = f. P. Z

  Here f is fraction of molecules with potential energy greater than thresh hold energy or collision crossing over the energy barrier having energy ≈ or > Ea.

  $f = e^{-Ea/RT}$

  P is the orientation factor.

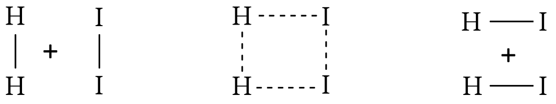
  Z is the collision frequency which is proportional to $U_{r.m.s}$ and temperature dependent.

- Transition state or activated state theory or absolute rate theory was developed by Henry Erying.

  A + BC → ABC → AB + C

  ABC: Activated Complex; AB + C: Product

example.,



ACTIVATION ENERGY

It is the minimum amount of additional external energy needed to convert a reactant into product or to make potential energy of the reactant equals to threshold energy. It is denoted by Ea.

Ea = Threshold energy – Potential energy of reactants

Or

Average kinetic energy of reactants

$$\text{Rate of Reaction} \propto \frac{1}{Ea}$$

Hence lower the activation energy faster is the rate of the reaction.

Determination of Activation Energy

- Larger the value of Ea of a reaction, smaller is k.
- Larger the value of Ea of a reaction, greater will be the influence of change in temperature on rate constant.

Arrehenius Equation

It is used to evaluate energy of activation and to show the effect of temperature on rate constant as follows

$$K = Ae^{-Ea/RT}$$

Or

$$\log_{10} K = \log_{10} A - \frac{Ea}{2.303\,RT} \quad \ldots\ldots\ldots(1)$$

- Here A is frequency or Arrhenius or pre exponential factor or maximum rate constant of the reaction. It signifies total number of collisions or frequency of binary collisions per unit volume per unit time.
- When Ea is zero or temperature is infinite

$$K = Ae^{o} = A$$

Here $e^{-Ea/RT}$ is known as Boltzmann factor showing fraction of molecules with E > Ea.

- At two different temperatures T_1 and T_2

$$Ea = \frac{2.303\,R\,T_1\,T_2}{T_2 - T_1} \log_{10} \frac{K_2}{K_1}$$

$$\log_{10} \frac{K_2}{K_1} = \frac{Ea}{2.303\,R} \frac{(T_2 - T_1)}{(T_1\,T_2)}$$

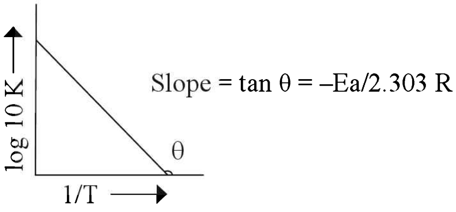
Here K_1 and K_2 are constant at temperature T_1 and T_2 K respectively.

Graph between $\log_{10}$ K and 1/T

When a graph is plotted between log K and 1/T a straight line with a negative slope is obtained. Here slope is equal to –Ea /2.303R that is Ea = –2.303 R × slope as

$$\log_{10} K = \log_{10} A - \frac{Ea}{2.303\,R}\left[\frac{1}{T}\right]$$

$$Y = C + MX$$



$$\Delta H = H_P - H_R$$

$$\Delta H = (Ea)_f - (Ea)_b$$

$$E_{TH} = H_R + (Ea)_f$$

or

$$E_{TH} = H_P + (Ea)_b$$

In Exothermic Reactions ΔH is negative.

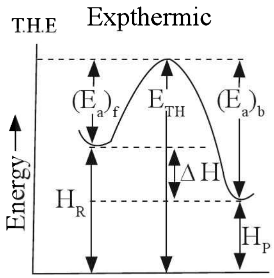
As potential energy of reactant > potential energy of product

Ea of backward reaction > Ea of forward reaction

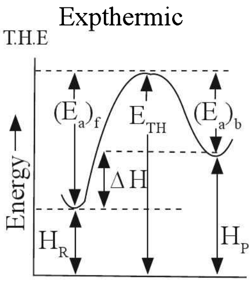
In Endothermic Reactions ΔH is positive.

As potential energy of reactant < potential energy of product

Ea of backward reaction < Ea of forward reaction



Reaction Co-ordination



Reaction Co-ordination

REMEMBER

- **Modified Arrhenius Equation**:

$$\frac{d\,InK}{dt} = \frac{E}{RT^2}$$

Illustrations

7. Find the activation energy of a reaction whose rate constant is tripled by a 10°C rise in temperature, in the activity of 27°C.

Solution $K_2/K_1 = 3$,

$$T_1 = 273 + 37 = 310\text{ K}$$

$$\log_{10} \frac{K_2}{K_1} = \frac{Ea}{2.303\,R} \frac{(T_2 - T_1)}{(T_1\,T_2)}$$

$$\log_{10}\ 3 = \frac{Ea}{2.303 \times 8.314} \frac{(310 - 300)}{(300 \times 310)}$$

$$Ea = 84.97\text{ kJ mol}^{-1}$$

8. For first order gaseous reaction log k when plotted against 1/T it give a straight line with a slope of –8000. Calculate the activation energy of the reaction.

Solution

$$k = Ae^{-Ea/RT}$$

$$\log k = \log A - \frac{Ea}{2.303\ R} \times \frac{1}{T}$$

When curve is plotted between log k and 1/T. A straight line is obtained and a slope of this curve

$$= -\frac{Ea}{2.303\ R}$$

$$\frac{Ea}{2.303\ R} = 8000$$

$$Ea = 8000 \times 2.303 \times 1.987 = 36608 \text{ calories}$$

$$= 36.6 \text{ Kcal.}$$

9. Given that the temperature coefficient k_{35}/k_{25} for the saponification of ethyl acetate by sodium hydroxide as 1.75. Calculate the activation energy in calories.

Solution

Suppose the rate constants at 35°C and 25°C are k_{35} and k_{25}.

As $k = Ae^{-\Delta Ea/RT}$

$$\frac{k_{35}}{k_{25}} = 1.75 = \frac{Ae^{-\Delta Ea/308 \times 1.987}}{Ae^{-\Delta E/-98 \times 1.987}}$$

On taking log, we get

$$\log_{10} 1.75 = \frac{\Delta E}{2.303 \times 1.987} \frac{(308 - 298)}{308 \times 298}$$

$$\Delta E = 2.303 \times 1.987 \times \frac{298 \times 308}{10} \times 0.2430$$

$$= 10210 \text{ cal mole}^{-1}$$

$$= 10.21 \text{ Kcal mole}^{-1}$$

10. In general, it is observed that the rate of a chemical reaction doubles with every 10° rise in temperature. If this generalization holds for a reaction in the temperature range 295 K to 305 K, what would be the value of activation energy for this reaction? ($R = 8.314\ J K^{-1} mol^{-1}$).

Solution

Given: $T_1 = 295$ K, $T_2 = 305$ K

$$Ea = 2.303\ R \frac{[T_1 T_2]}{T_2 - T_1} \frac{[\log k_2]}{k_1}$$

$$\log \frac{k_2}{k_1} = \log \frac{2k}{k} = \log 2 = 0.3010$$

$$\frac{T_1 T_2}{T_2 - T_1} = \frac{295 \times 305}{305 - 295} = 8997.5$$

$$Ea = 2.303 \times 8.314 \times 8997.5 \times 0.3010$$

$$= 51855.2 \text{ J/mol}$$

Molecularity

It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction or elementary reaction.

- It is a theoretical value.
- It is always a whole number.
- It does not determine rate of reaction.
- It does not depend upon external factors like temperature, pressure etc.
- Molecularity can not be more than three as there is nearly no chance for more than three molecules to undergo an effective collision at a time.
- In a multi-step reaction molecularity is determined separately in each step.
- The overall molecularity of a complex reaction is equal to the molecularity of the slowest step.
- If molecularity is one reaction is called unimolecular. Example,

  $PCl_5 \rightarrow PCl_3 + Cl_2$
- If molecularity is two reaction is called bimolecular. Example,

  $$\underset{}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$
- If molecularity is three reaction is called termolecular. Example,

  $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$

Rate Law and Order of Reaction

The rate of any reaction depends upon the concentration of the reactants in rate law equation that is rate law and rate of reaction depend upon the order of the reaction.

Let us consider this reaction

$xA + yB \rightarrow$ Product

Rate law equation for the reaction can be given as

$R \propto [A]^p [B]^q$

$R = K [A]^p [B]^q$

Order of reaction = p + q

Here p, q are experimental quantities which may or may not be equal to the respective stiochiometric coefficients (x, y).

Order of Reaction

Order of reaction is defined as number of reactants which determine rate of reaction.

Or

Number of reactants whose molar concentration changes during the chemical reaction.

Or

It is the sum of exponents raised on active masses of reactants in a rate law equation.

- It is an experimental value.
- It may be zero, negative or in fraction.
- It determines rate of reaction.
- Order of reaction depends upon temperature, pressure and concentration etc.
- Anything in excess is not counted in order of reaction. Example, In hydrolysis of ester and sugar water is in excess so it is neglected for order.
- Order of reaction is determined by the slowest step of the reaction.
- High order reactions are rare due to less chance of effective collisions between molecules.
- For an elementary reaction order of reaction must be equal to molecularity of the reaction

REMEMBER

Rate constant and order for various reacting species is an experimental finding and cannot be predicted directly from the stiochiometry of the balanced reaction.

Example,

$$2O_3 \rightleftharpoons 3O_2$$

Mechanism

Step I: $O_3 \xleftrightarrow{K_c} O_2 + [O]$ (fast)

Step II: $O_3 + [O] \xleftrightarrow{K} 2O_2$ (slow)

$$\text{Rate} = K\,[O_3]\,[O] \qquad \ldots\ldots\ldots(1)$$

$$K_C = \frac{[O_2]\,[O]}{[O_3]} \quad \text{or} \quad [O] = K_C \cdot \frac{[O_3]}{[O_2]} \qquad \ldots\ldots(2)$$

Hence

$$\text{Rate} = K\,[O_3]\,.\,K_C \cdot \frac{[O_3]}{[O_2]} = K'\,[O_3]^2\,[O_2]^{-1}$$

Order = 1

First Order Reaction

Here the reaction rate is determined by one concentration variable term only.

$$A \rightarrow \text{Products}$$

$$-\frac{dx}{dt} \propto [a]^1$$

$$dx/dt = K\,[a]$$

At after time ‘t’ the concentration is $(a - x)$ so

$$\frac{dx}{dt} \propto (a - x)$$

$$\frac{dx}{dt} = K\,(a - x)$$

On integrating

$$-In\,(a - x) = Kt + c$$

When $t = 0, x = 0$

$$c = -In\,a$$

$$-In\,(a - x) = Kt - In\,a$$

$$Kt = In\,a - In\,(a - x) = In\,\frac{a}{(a - x)}$$

$$K = \frac{2.303}{t}\log_{10}\frac{a}{(a - x)}$$

or

$$\boxed{t = \frac{2.303}{K}\log_{10}\frac{N_0}{N}}$$

Hence $N = N_0\,e^{-KT}$

or $A = A_0\,.\,e^{-KT}$

This is known as Wilhelmy’s equation which shows decrease in concentration with respect to time.

Here t = time period

K = rate constant

A_0 or N_0 = initial amount or activity

A or N = amount or activity after ‘t’ time.

Examples of First Order Reaction:

$$H_2O_2 \rightarrow H_2O + ½\,O_2$$

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

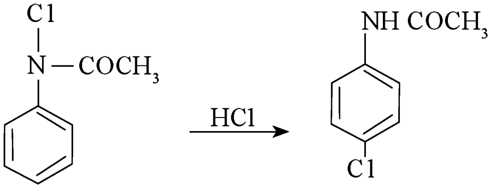
$2N_2O_5 \rightarrow 4NO_2 + O_2$

$SO_2Cl_2 \rightarrow SO_2 + Cl_2$

$C_6H_5N = NCl + H.OH \rightarrow C_6H_5OH + N_2 + HCl$

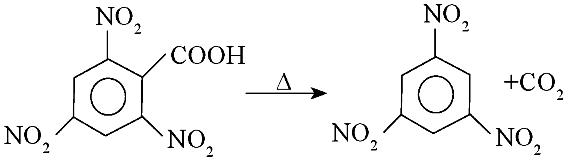
$(CH_3)_2\,CH = N = N\,CH\,(CH_3)_2 \xrightarrow{\Delta} N_2 + C_6H_{14}$

$$\begin{array}{l} COOH \\ | \\ COOH \end{array} \rightarrow CO + CO_2 + H_2O$$



N-chloro acetanilide

p-chloro acetanilide



All radioactive decays are first order example.,

$${}_{88}Ra^{226} \rightarrow {}_{86}Rn^{222} + {}_{2}\alpha^{4}$$

Features of First Order Reactions

- Unit of K is time^{-1}.
- K does not depend upon concentration unit Or change in concentration.
- $t_{1/2}$ does not depend upon initial concentration (a). It depends only upon rate constant.

If $t = t_{1/2}$ or t_{50}

$X = a/2$

Then t_{50} or $t_{1/2} = \dfrac{2.303}{K} \log_{10} \dfrac{a}{a - a/2}$

$$t_{1/2} = \frac{2.303}{K} \log_{10} 2 = \frac{2.303}{K} \times 0.3010$$

$$t_{1/2} = \frac{0.693}{K}$$

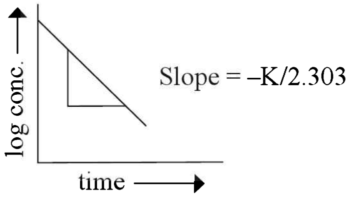
- If t_{75} or ¾ a value of 'X' is used

$t_{75} = 2 \times t_{50}$

- If $t_{87.5}$ is used

$t_{87.5} = 3 \times t_{50}$

- If a graph is plotted between time 't' and $\log_{10}$ (a or conc.), a straight line is obtained whose slope is equal to $\frac{-K}{2.303}$.



- Time taken for the completion of any fraction of reaction does not depend upon the initial concentration of the reactant and for 'n' fraction it is given as

$$t_{1/n} = \frac{2.303}{K} \log_{10} \frac{n}{n-1}$$

Pseudo–Unimolecular Reaction

Those reactions which are not truly of the first order but under certain conditions become reactions of the first order.

- Here molecularity is more than one but order of reaction is always first.

Example (1) Hydrolysis of ethyl acetate

	$CH_3COOC_2H_5 + H_2O$	$\rightarrow CH_3COOH$	$+ C_2H_5OH$
Initially	a	0	0
After 't' time	(a – x)	x	x
At ∞	0	a	a

For it rate constant K is given as

$$k = \frac{2.303}{t} \log_{10} \frac{V_0 - V_\infty}{V_t - V_\infty}$$

As $a = V_0 - V_\infty$ and $(a - x) = (V_t - V_\infty)$

Here V_∞ = volume at infinite

V_0 = initial volume

V_t = volume at t time

Case I: When V_0 is not given

$$K = \frac{2.303}{t} \log_{10} \frac{V_\infty}{V_\infty - V_t}$$

Case II: When V_∞ is not given

$$K = \frac{2.303}{t} \log_{10} \frac{V_0}{V_t}$$

Example, (2) Hydrolysis of sugar

$$\underset{}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

For it rate constant is given as

$$t = \frac{2.303}{K} \log_{10} \cdot \frac{r_\infty - r_0}{r_\infty - r_t}$$

Here r_0 = initial optical rotation

r_∞ = rotation at infinite dilution.

r_t = rotation at t time.

Illustrations

11. A first order reaction completes 50 per cent in 69.3 minute. How much time it will take for 90 per cent completion?

Solution $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.3} = 0.01$

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$0.01 = \frac{2.303}{t} \log_{10} \frac{100}{10}$$

$$t = \frac{2.303}{0.01} = 230.3 \text{ minute.}$$

12. A reaction obeying second order in A is 50 per cent complete after 450 minute. If $[A]_0$ = 1.35 M. Calculate the value of rate constant.

Solution t = 450 minute

a = 1.35 M

x = 0.675 M

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

$$k = \frac{1}{450} \times \frac{0.675}{1.35\,(0.675)}$$

$= 1.646 \times 10^{-3}$ mol^{-1} litre min^{-1}

13. A substance, A decomposes by a first order reaction. Starting initially with [A] = 2.00 M, after 200 min [A] = 0.250 M. Calculate for this reaction (i) $t_{1/2}$ and (ii) k.

Solution First order reaction,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$= \frac{2.303}{200} \log_{10} \frac{2.00}{0.25}$$

$$= \frac{2.303}{200} \log_{10} 8$$

$= 0.0104$ min^{-1}

For first order reaction,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0104}$$

= 66.63 min

14. Thermal decomposition of a compound is of first order. If 50 per cent of a sample of the compound is decomposed in 120 minutes, how long will it take for 90 per cent of the compound to decompose?

Solution $k = \frac{0.693}{t_{50\%}} = \frac{0.693}{120 \text{ min}}$

$$t = \frac{2.303}{k} \log_{10} \frac{a}{a-x}$$

$$t_{90\%} = \frac{2.303}{0.693 \backslash 120 \text{ min}} \log_{10} \frac{100}{100-90}$$

$$= \frac{2.303 \times 120 \text{ min}}{0.693} \log_{10} 10$$

$$= \frac{2.303 \times 120 \text{ min}}{0.693} \times 1 = 399 \text{ min}$$

15. Show that in case of a first order reaction, the time required for 99.9 per cent of the reaction to take place is ten times that required for half of the reaction.

Solution $t = \frac{2.303}{k} \log_{10} \frac{[A]_a}{[A]_t}$

$$= \frac{2.303}{k} \log_{10} \frac{a}{a-x}$$

$$= \frac{2.303}{k} \log_{10} \frac{1}{1-f}$$

Here f is the fraction of reaction completed in time, t.

$$t_{50\%} = \frac{2.303}{k} \log_{10} \frac{1}{1-0.5} = \frac{2.303}{k} \log_{10} 2 \quad \text{....(i)}$$

$$t_{99.9\%} = \frac{2.303}{k} \log_{10} \frac{1}{1-0.999}$$

$$= \frac{2.303}{k} \log_{10} \frac{1}{0.001}$$

$$= \frac{2.303}{k} \log_{10} \frac{1}{10^{-3}} = \frac{2.303}{k} \log_{10} 10^3 \quad \text{...(ii)}$$

On diving equation (ii) by (i), we get

$$\frac{t_{99.9\%}}{t_{50\%}} = \frac{2.303}{k} \times \frac{k}{2.303} \times \log \frac{10^3}{\log 2}$$

$$= \frac{3.000}{0.3010} = 9.967 = 10$$

16. What will be the initial rate of a reaction if its rate constant is 10^{-3} min^{-1} and the concentration of reactant is 0.2 mol dm^{-3}? How much of the reactant will be converted into products in 200 minutes?

Solution As K has unit min^{-1} so given reaction is of first order.

$$\text{Rate} = k\,[\ ]^1$$

$$\text{Rate} = 10^{-3} \times [0.2]^1 = 2 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$$

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$10^{-3} = \frac{2.303}{200} \log_{10} \frac{100}{(100-x)}$$

x = 18.12 %. D.t.

17. The half time of first order decomposition of nitramide is 2.1 hour at 15°C.

$NH_2NO_2\ (aq) \rightarrow N_2O\ (g) + H_2O\ (l)$

If 6.2 g of NH_2NO_2 is allowed to decompose, calculate:

(a) time taken for NH_2NO_2 is decompose 99 per cent

(b) Volume of dry N_2O produced at this point measured at STP.

Solution $t = \frac{2.303}{k} \log_{10} \frac{a}{a-x}$

If t = t/2, x = a/2

$$t_{1/2} = \frac{2.303}{k} \log_{10} \frac{a}{a - a/2} \quad \ldots\ldots (i)$$

If t = t $_{99\%}$, x = 99a/100

$$t_{99\%} = \frac{2.303}{k} \log_{10} \frac{a}{a - 99a/100} \ldots\ldots (ii)$$

From equation (i) and (ii)

$$t_{99\%} = \frac{\log_{10} 100}{\log_{10} 2} \times t_{1/2}$$

$$= \frac{2}{0.3010} \times 2.1 = 13.95 \text{ hour}$$

Mole of N_2O formed

$= \frac{99}{100} \times$ mole of NH_2NO_2 taken

$$= \frac{99}{100} \times \frac{6.2}{62} = 0.099$$

Thus, volume of N_2O formed at STP = 0.099 × 22.4

= 2.217 litre

18. A substance reacts according to first order kinetics and rate constant for the reaction is 1×10^{-2} sec^{-1}. If its initial concentration is 1 M.

(a) What is initial rate?

(b) What is rate after 1 minute?

Solution (a) Initial rate = $k\,[\ ]^1 = 1 \times 10^{-2} \times [1] = 1 \times 10^{-2}$

Rate = 1×10^{-2} mol litre^{-1} sec^{-1}

(b) $k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$

$$10^{-2} = \frac{2.303}{1 \times 60} \log_{10} \frac{1}{(1-x)}$$

$(1 - x) = 0.549$

Rate after 1 minute = k [] after 1 minute

= k [0.549] = 10^{-2} [0.549]

Rate after 1 minute = 5.49×10^{-3} mol litre^{-1} sec^{-1}

19. The reaction

$$SO_2Cl_2 \xrightarrow{K_1} SO_2 + Cl_2$$

is a first order reaction with $k_1 = 2.2 \times 10^{-5}$ sec^{-1} at 302°C. What percentage of SO_2Cl_2 will get decomposed in 90 minutes when the reaction is carried out at 302°C?

Solution $k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$

Here $k = 2.2 \times 10^{-5}$ sec^{-1}

t = 90 minutes = 90 × 60 = 5400 sec

So $2.2 \times 10^{-5} = \frac{2.303}{5400} \log_{10} \frac{a}{a-x}$

$$\log_{10} \frac{a}{a-x} = 0.0516$$

$$\frac{a}{a-x} = \text{antilog}\,(0.0516) = 1.127$$

$$a = 1.127\,a - 1.127\,x$$

$$0.127\,a = 1.127\,x$$

$$\frac{x}{a} = \frac{0.127}{1.127} = 0.113$$

$$= 11.3\%$$

Concentration replaced by other quantities in first order reactions

Reaction involving gases in a closed vessel or container

$$X\,(g) \rightarrow Y\,(g) + Z\,(g)$$

Case I: If the initial pressure of X (g) be P_0 and after time ‘t’, suppose its pressure be P,

then $P_0 \propto a$

$P \propto (a - x)$

$$K = \frac{2.303}{t}\log_{10}\frac{P_0}{P}$$

Case II: If the initial pressure of X (g) be P_0 and after time ‘t’ the total pressure of the reaction mixture is P_t, then

$P_0 \propto a$

$(a - x) \propto 2P_0 - P_t$

$$K = \frac{2.303}{t}\log_{10}\frac{P_0}{2P_0 - P_t}$$

Case III: If the total pressure at any time ‘t’ is given to be P_t and total pressure after a long period of time is P’.

$P_t \propto (a + x)$

$P' \propto 2a$

Also $P' - P_t \propto (a - x)$

$$K = \frac{2.303}{T}\log_{10}\frac{P'}{2(P' - P_t)}$$

Case IV: If the total pressure of product at any time ‘t’ is given to be P_t and total pressure of product after a long period is P’.

$$P_0 = \frac{P'}{2}$$

$$P_0 - x = \frac{1}{2}(P' - P_t)$$

$$K = \frac{2.303}{T}\log_{10}\frac{P'}{P' - P_t}$$

- For the decomposition of N_2O_5 and NH_4NO_2 and hydrolysis of benzene diazonium chloride the relation used is given as

$$K = \frac{2.303}{t}\log_{10}\frac{V_\infty}{V_\infty - V_t}$$

- For the decomposition of H_2O_2 the relation used is given as

$$K = \frac{2.303}{t}\log_{10}\frac{V_o}{V_t}$$

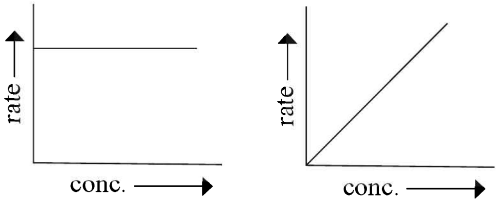
Methods for Determining Order of Reaction

Order of a reaction is determined mainly by:

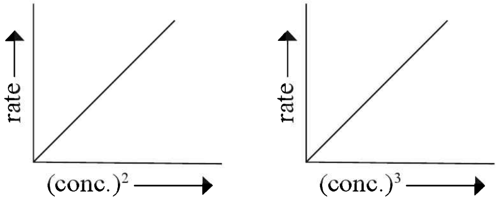
(i) ***Graphical methods*:** Here graps are ploted between rate and concentration to find the order of the reaction.

[Rate = $k(\text{concentration})^n$]

Plots of Rate vs Concentration



Zero Order　　Frist Order



Second Order　　Third Order

(ii) ***Van’t Hoff differential method***

As $dx/dt \propto C^n$

So $$\frac{-dC_1}{dt} = KC_1^n \quad \ldots(1)$$

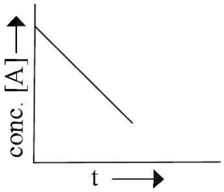
$$\frac{-dC_2}{dt} = KC_2^n \quad \ldots(2)$$

On taking log and subtracting both equation number (1) and (2), we get

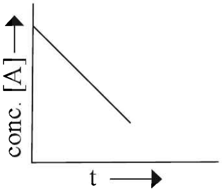
$$n = \frac{\log(-dC_1/dt) - \log(-dC_2/dt)}{\log C_1 - \log C_2}$$

Note: The values of $-dC_1/dt$ and $-dC_2/dt$ can be observed from 'C' vs 't' plots.

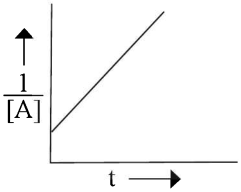
Plots from integrated rate equations: When the graphs are plotted between $1/(a-x)^{n-1}$ and time t a straight line will be formed which decides order of reaction as follows:



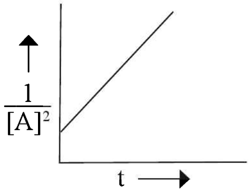
Zero Order



Frist Order



Second Order



Third Order

(iii) ***Half life method*:** It is used when the rate law involves only one concentration term.

$$t_{1/2} \propto (a)^{1-n}$$

or

$$t_{1/2} \propto 1/a^{n-1}$$

For two different concentrations

$$\frac{(t\,½)_1}{(t\,½)_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

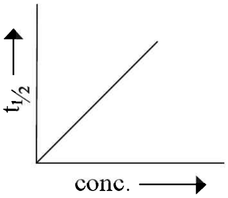
On taking logarithms on both sides

$$\log_{10}\frac{(t_{1/2})_1}{(t_{1/2})_2} = (n-1)\log_{10}(a_2/a_1)$$

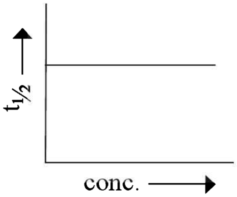
Hence

$$n = 1 + \frac{\log(t\,½)_1 - \log(t\,½)_2}{\log a_2 - \log a_1}$$

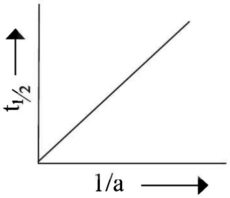
Here n is the order of reaction.



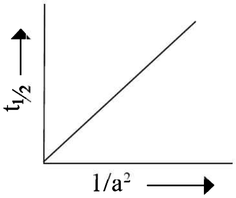
Zero Order



Frist Order



Second Order



Third Order

(iv) ***Hit and Trial Method (Integration method)*:** Here we put the values of a, x, t in kinetic equation of various orders and the equation that gives the most constant values of rate constant K for a series of time intervals gives the order of the reaction.

(v) ***Initial concentration method*:** Here first measure the initial rate of the reaction, that is the rate at the beginning of the reaction so that the known concentration of the different reactants have not changed noticeably.

Reaction	Order	Rete lowEquation	Expression	Unit of K
$A \rightarrow P$	Zero	Rate = $K[A]^o$ Rate = K	$K = \frac{1}{t}[A_o - A]$	Mol lit^{-1} $time^{-1}$
$A \rightarrow P$	First	Rate = $K[A]^1$	$K = \frac{2.303}{t}\log_{10}\frac{[A_o]}{[A]}$	$Time^{-1}$
$2A \rightarrow P$	Second	Rate = $K[A]^2$	$K = \frac{1}{t}\left(\frac{1}{A} - \frac{1}{A_o}\right)$	Lit mol^{-1} $tome^{-1}$
$A + B \rightarrow P$	Second	Rate = K [A] [B]	$K = \frac{2.303}{t(a-b)}\log\frac{b[A]}{a[B]}$	Lit^2 mol^{-2} $time^{-1}$
$3A \rightarrow P$	Third	Rate = $K[A]^3$	$K = \frac{1}{2t}\left(\frac{1}{(A)^2} - \frac{1}{(A_o)^2}\right)$	Mol^{-2} $time^{-1}$

Now change the initial concentration of only one of the reactants keeping the initial concentration of all the reactants same as before and determine the initial rate again. This data achieved gives the order with respect to this reactant. Now for another reactants repeat this process.

Illustrations

20. Rate of a reaction

A + B → C is given below as a function of differential concentrations of A and B.

Exp.	[A] Mol lit^{-1}	[B] Mol lit^{-1}	Rate Mol lit^{-1} time^{-1}
1	0.01	0.01	0.005
2	0.02	0.01	0.010
3	0.01	0.02	0.005

Determine order of reaction with respect to A and B and also calculate the half life of A in the reaction?

Solution Rate = $k [A]^x [B]^y$

$0.005 = k [0.01]^x [0.01]^y$ ……… (1)

$0.010 = k [0.02]^x [0.01]^y$ ………(2)

$0.005 = k [0.01]^x [0.02]^y$ ……… (3)

For x

Diving eq. (2) by (1)

$(2) = (2)^x$

$x = 1$

For y :

Dividing eq. (3) by (1)

$Y = 0$

Rate = $k [A]^1 [B]^0$

$0.005 = k [0.01]^1 [0.01]^0$

$$k = \frac{0.005}{0.01} = 0.5$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.5} = 1.386 \text{ time}$$

21. The data given below are for the reaction of NO and Cl_2 to form NOCl at 295 K.

[Cl_2]	[NO]	Initial rate (mol litre^{-1} sec^{-1})
0.05	0.05	1×10^{-3}
0.15	0.05	3×10^{-3}
0.05	0.15	9×10^{-3}

(a) What is the order w.r.t NO and Cl_2 in the reaction?

(b) Write the rate expression.

(c) Calculate the rate constant.

(d) Determine the reaction rate when concentration of Cl_2 and NO are 0.2 M and 0.4 M respectively.

Solution $2NO + Cl_2 \rightarrow 2NOCl$

Rate = $k [Cl_2]^m [NO]^n$ ……. (i)

Here m and n are order of reaction w.r.t Cl_2 and NO respectively.

According to given data:

$1 \times 10^{-3} = k [0.05]^m [0.05]^n$ ……. (ii)

$3 \times 10^{-3} = k [0.15]^m [0.05]^n$ ……. (iii)

$9 \times 10^{-3} = k [0.05]^m [0.15]^n$ ………(iv)

From equation (ii) and (iii),

$m = 1$

From equation (ii) and (iv),

$n = 2$

(a) Order w.r.t NO is 2 and w.r.t Cl_2 is 1

(b) Rate expression (r) = $k [Cl_2]^1 [NO]^2$

(c) Rate constant (k) = $\frac{r}{[Cl_2]^1 [NO]^2}$

$$= \frac{1 \times 10^{-3}}{[0.05]^1 [0.05]^2} = 8 \text{ litre}^2 \text{ mol}^{-2} \text{ sec}^{-1}$$

(d) $r = k [Cl_2]^1 [NO]^2$

$= 8 [0.2]^1 [0.4]^2$

$= 0.256$ mol litre^{-1} sec^{-1}

22. The following data are for the reaction

A + B → Products:

[A]	[B]	Initial rate (mol litre^{-1} sec^{-1})
0.1	0.1	4.0×10^{-4}
0.2	0.2	1.6×10^{-3}
0.5	0.1	1.0×10^{-2}
0.5	0.5	1.0×10^{-2}

(a) What is the order with respect to A and B for the reaction?

(b) Calculate the rate constant.

(c) Determine the reaction rate when the concentrations of A and B are 0.2 M and 0.35 M, respectively.

Solution

According to rate law equation

$R = k\,[A]^m\,[B]^n$

Rate law for four cases is as follows:

$4.0 \times 10^{-4} = k\,(0.1)^m\,(0.1)^n$ .... (i)

$1.6 \times 10^{-3} = k\,(0.2)^m\,(0.2)^n$ ....(ii)

$1.0 \times 10^{-2} = k\,(0.5)^m\,(0.1)^n$ ....(iii)

$1.0 \times 10^{-2} = k\,(0.5)^m\,(0.5)^n$ .... (iv)

(a) On dividing equation (iii) by (i), we get

$$\frac{1.0 \times 10^{-2}}{1.0 \times 10^{-2}} = \frac{k\,(0.5)^m\,(0.1)^n}{k\,(0.5)^m\,(0.5)^n}$$

$1 = (1/5)^n$

$n = 0$

So the order of reaction with respect to B is zero.

On dividing equation (i) by (iii), we get

$$\frac{4.0 \times 10^{-4}}{1.0 \times 10^{-2}} = \frac{k\,(0.1)^m\,(0.1)^n}{k\,(0.5)^m\,(0.1)^n}$$

$4 \times 10^{-2} = (1/5)^m$

$(0.2)^m = 0.04$

$(0.2)^m = (0.2)^2$

$m = 2$

So the order of reaction with respect to A is two.

(b) On substituting the values of m and n in equation (ii), we get

1.6×10^{-3} mol lit^{-1} sec^{-1} = k $(0.2\ \mathrm{M})^2\,(0.2\ \mathrm{M})^0$

1.6×10^{-3} mol lit^{-1} sec^{-1} = 0.04 M^2 k

$$k = \frac{1.6 \times 10^{-3}\ \text{mol lit}^{-1}\ \text{sec}^{-1}}{0.04\ \text{M}^2}$$

$= 4.0 \times 10^{-2}$ mol^{-1} lit sec^{-1}

(c) $R = k[A]^2\,[B]^0$

$R = 4 \times 10^{-2} \times (0.2)^2\,(0.35)^0$

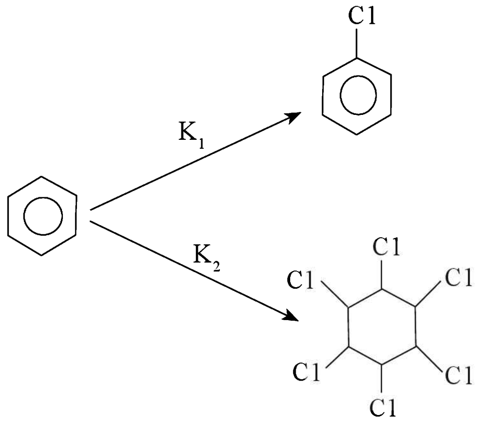
$= 4 \times 10^{-2} \times 0.04 = 1.6 \times 10^{-3}$ mol lit^{-1} sec^{-1}

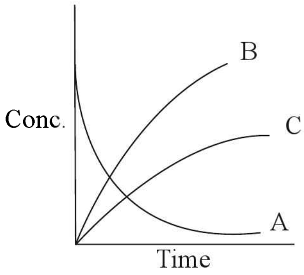
Enhance Your Knowledge

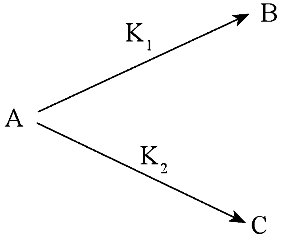
Elementary and Complex Reactions

It is interesting to know that a balanced chemical equation never shows us a true picture of how the reaction is taking place as very rarely a reaction gets competed in one step only.

- The reaction which occurs in one step only is known as an elementary reaction and when a sequence of such reactions (mechanism) provides us the desired products these reactions are known as complex reactions.
- Such reactions may be consecutive, reverse and side reactions.
  Example, In the complete combustion of an alkane the final products are always CO_2, and water, however during this reaction a series of many elementary reactions take place during which alcohol, aldehyde and acid are formed.
- **Rate law equation for reactions involving parallel and side reactions.**
  Parallel Reactions: In such a reaction, the reactant decomposes or reacts in more than one ways.
  Example,







$$R_1 = K_1\,[A] = \frac{d\,[B]}{dt}$$

$$R_2 = K_2\,[A] = \frac{d\,[C]}{dt}$$

$$R_1 + R_2 = \frac{-d\,[A]}{dt} = (K_1 + K_2)\,[A]$$

If $K_{Av.} = K_1 + K_2$ and $R_{Av.} = R_1 + R_2$

Then $R_{v.} = K_{Av.}\,[A]$

Ratio of concentration of B and C can be calculated as follows:

$$\frac{[B]}{[C]} = \frac{K_1}{K_2}$$

Rate constant of parallel reaction can be find out as follows:

$$K = K_1 + K_2 = \frac{2.303}{T}\log_{10}\frac{[A_0]}{[A]}$$

Here A_0 = Initial concentration of A

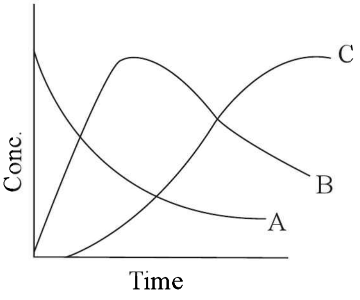
A = Amount of A left after time t

Fraction yield of B and C can be find out as follows:

- Fraction yield of B = $K_1/(K_1 + K_2)$ or $K_{av.}$
- Fraction yield of C = $K_2/(K_1 + K_2)$ or K_{av}

Consecutive or Successive reaction

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$



Here rate of disappearance of A = $K_1 + K_2\,[A]$

$$[A]_t = [A]_0\,e^{-K1\,T}$$

$$[B]_t = \frac{K_1[A]_0}{K_2 - K_1}\,[e^{-K1\,T} - e^{-K2\,T}]$$

Time at which [B] becomes maximum can be find out by using the relation

$$t_{max.} = \frac{2.303}{(K_2 - K_1)}\log_{10}\frac{K_2}{K_1}$$

$$[B]_{max} = \frac{K_1}{K_2 - K_1}\,[A_0]\,(K_2/K_1)^{K_1/K_1 - K_2}$$

$$-\,(K_2/K_1)[^{K_2/K_1 - K_2}]$$

Or

$$[B]_{max} = \frac{[A_0]}{(K_2 - K_1)}\,[K_2\,(1 - e^{-K_1\,t}) - K_1\,(1 - e^{-K_2\,t})]$$

Illustrations

23. Bicyclohexane was found to undergo two parallel first order rearrangements. At 730 K, the first order rate constant for the formation of cyclohexane was measured as $1.28 \times 10^{-4}\ s^{-1}$, and for the formation of methyl cyclopentene the rate constant was $3.6 \times 10^{-5}\ s^{-1}$. What is the percentage distribution of the rearrangement products?

Solution

$$\begin{tikzcd} & \text{Cyclohexene} \\ \text{Bicyclohexane} \arrow[ur, "K_1"] \arrow[dr, "K_2"'] & \\ & \text{Methyl cyclopentene} \end{tikzcd}$$

$$\text{Percentage of cyclohexene} = \frac{k_1}{k_1 + k_2} \times 100$$

$$= \frac{1.28 \times 10^{-4}}{1.28 \times 10^{-4} + 3.6 \times 10^{-5}} \times 100$$

$$= \frac{1.28}{1.64} \times 100$$

= 78 percent

Hence percentage of methylcyclopentene = 22 per cent.

Reversible or opposing reaction

	P	K_1 K_2	Q
Initially	a		0
After ‘t’ time	$(a - x)$		x
Conc. at eq.	$(a - x_c)$		x_c

On putting and solving, we get

$$(K_1 + K_2) = \frac{2.303}{t} \log_{10} \frac{X_C}{X_C - X}.$$

Zero Order Reaction

In such reactions rate of reaction is independent of concentration of the reactants.

$$\frac{-dx}{dt} \propto [\text{concentration}]^0$$

that is, $dx/dt = K$

On integration we get

$x = Kt + C$

If $t = 0$, $c = 0$ then

$x = Kt$

$K = x/t$

- Unit of K is mol L^{-1} time^{-1}

  Example,– Photochemical reactions

  $H_2 + Cl_2 \xrightarrow{hv} 2HCl$

  (Studied over water surface)

  $N_2O \rightarrow N_2 + \frac{1}{2} O_2$ (Studied over Pt surface)

  $2NH_3 \xrightarrow{(Mo)} N_2 + 3H_2$

  $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$

  $2HI \rightarrow H_2 + I_2$ (Studied over Gold surface)

Features of Zero Order Reaction:

- The concentration of the reactant decreases linearly with time.

  $[A]_t = [A]_0 - kt$

- Rate = K (at all concentrations)
- $t_{1/2} \propto a$ (initial concentration)

Photo Chemical Reactions

Those reactions which take place only in the presence of light are called photochemical reactions. Example, Photosynthesis and formation of HCl

- For such reactions ΔG° (standard Gibb’s free energy change) can be positive also.

  Example, In the synthesis of carbohydrate and HCl formation.

- Red light has lowest energy. Photochemical reactions which can be initiated by red light can be initiated

- Such reactions are not effected by temperature however effected by intensity of light radiations.

Photosensitizer: It is a substance which when added to a reaction mixture helps to start the photochemical reaction but itself does not undergo any chemical change. Example, Chlorophyll in photosynthesis and Hg vapours in dissociation of H_2.

Non Photoactive $\xrightarrow{\text{By photosensitizer}}$ Photo-active

Luminiscence: It is the Emission of cold light without action of heat.

Chemiluminiscence: It is the conversion of chemical energy in to cold light energy.

Example, In glow worm, the glow is due to oxidation of luciferin protein. (Bioluminiscence).

Flourescence: Here emission of light stops when radiation is cut off at once that is glow is as long as radiation occurs Example, CaF_2

Phosphorescence: Here emission of light occurs for some time even after light radiation is cut off. Example, ZnS

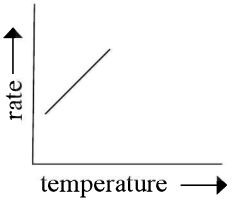
Rhuantum efficiency:

$$\Phi = \frac{\text{Number of molecules reacting in a given time}}{\text{no. of quanta absorbed at the same time}}$$

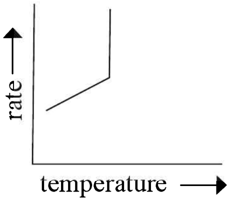
Example,

- for HCl Φ is high (As both steps are exothermic) but for HBr Φ is low (as second step is endothermic).
- **Vision:** Here retina undergoes geometrical isomerisation by absorbing a photon of light.

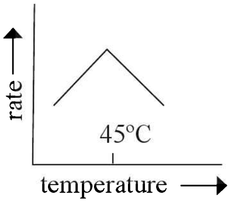
VARIOUS PLOTS



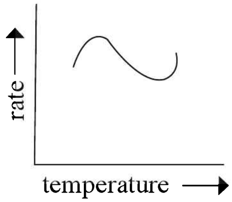
Normal reactions



Explosive reactions



Biological reactions



Oxidation reactions

Solved Problems from the IITs

1. In the Arrhenius equation for a certain reaction, the values of A and Ea (energy of activation) are 4×10^{13} sec^{-1} and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half life period be 10 minute?

[IIT 1990]

Solution According to Arrhenius equation,

$$k = Ae^{-Ea/RT}$$

$$\log_e k = \log_e A - \frac{Ea}{RT}.$$

$$2.303 \log_{10} K = 2.303 \log_{10} A - \frac{Ea}{RT}.$$

For a first order reaction

$$t_{1/2} = \frac{0.693}{k}$$

$$\text{So} \quad k = \frac{0.693}{600} \text{ sec}^{-1}$$

$(t_{1/2} = 10 \text{ min} = 600 \text{ sec})$

$$= 1.1 \times 10^{-3} \text{ sec}^{-1}$$

$$\log(1.1 \times 10^{-3}) = \log(4 \times 10^{13}) - \frac{98.6 \times 10^3}{2.303 \times 8.314 \times T}$$

$$T = 310.95 \text{ K}.$$

2. The decomposition of N_2O_5 according to equation $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ is a first order reaction. After 30 minutes from start of the decomposition in a closed vessel, total pressure developed is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of reaction.

[IIT 1991]

Solution $2N_2O_5 \rightarrow 4NO_2 + O_2$

As on decomposition of 2 moles of N_2O_5, 4 moles of NO_2 and 1 mole of O_2 are produced so total pressure after completion corresponds to 5 moles and initial pressure of 2 moles.

Initial pressure of N_2O_5,

$$P_0 = \frac{2}{5} \times 584.5 = 233.8 \text{ mm Hg}$$

After 30 minutes,

the total pressure = 284.5 mm Hg

$$\begin{array}{lccc} 2N_2O_5 & \rightarrow & 4NO_2 & + \quad O_2 \\ P_0 - 2P & & 4P & P \end{array}$$

$$P_0 + 3P = 284.5$$

$3P = 284.5 - 233.8 = 50.7$ mm Hg

$P = \frac{50.7}{3} = 16.9$ mm Hg

Pressure of N_2O_5 after 30 minutes

$= 233.8 - (2 \times 16.9)$

$= 200$ mm Hg

$k = \frac{2.303}{30} \log_{10} \frac{233.8}{200}$

$= 5.2 \times 10^{-3}\ \text{min}^{-1}$

3. The gas phase decomposition of dimethyl ether follows first order kinetics

$CH_3OCH_3\ (g) \rightarrow CH_4\ (g) + H_2\ (g) + CO\ (g)$

The reaction is carried out in a constant volume container at 500°C and has a half life of 14.5 minutes. Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure after 12 minutes? Assume ideal gas behaviour.

[IIT 1993]

Solution $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.5} = 0.047793\ \text{min}^{-1}$

Let the pressure of dimethyl ether 12 minutes be 'P' atm.

According to first order equation

$k = \frac{2.303}{t} \log_{10} \frac{P_0}{P}$

$\log_{10} \frac{0.4}{P} = \frac{0.047793 \times 12}{2.303} = 0.2490$

$\frac{0.4}{P} = 1.7743$

$P = \frac{0.4}{1.7743} = 0.2254$ atm

Decrease in pressure

$X = 0.4 - 0.2254 = 0.1746$ atm

$$\begin{array}{cccc} CH_3OCH_3\ (g) \rightarrow & CH_4\ (g) + & H_2\ (g) + & CO\ (g) \\ P_0 - X & X & X & X \end{array}$$

Total pressure $= P_0 + 2X$

$= 0.4 + 2 \times 0.1746$

$= 0.7492$ atm

4. From the following data from the reaction between A and B.

[A] mol L^{-1}	[B] mol L^{-1}	Initial rate mol $\text{litre}^{-1}\ \text{sec}^{-1}$ 300K	320K
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	–
1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	–

Calculate

(i) The order of reaction with respect to A and B.

(ii) The rate constant at 300 K.

(iii) The energy of activation.

(iv) The pre-exponential factor.

[IIT 1994]

Solution Rate $= k\ [A]^x\ [B]^y$

From experiment (1)

$5.0 \times 10^{-4} = k\ [2.5 \times 10^{-4}]^x\ [3.0 \times 10^{-5}]^y$ ...(i)

From experiment (2)

$4.0 \times 10^{-3} = k\ [5.0 \times 10^{-4}]^x\ [6.0 \times 10^{-5}]^y$ .... (ii)

Dividing equation (ii) by (i), we get

$\frac{4.0 \times 10^{-3}}{5.0 \times 10^{-4}} = 2^x \cdot 2^y = 8$

From experiment (3)

$1.6 \times 10^{-2} = k\ [1.0 \times 10^{-3}]^x\ [6.0 \times 10^{-5}]^y$ .....(iii)

Dividing equation (iii) by (ii), we get

$\frac{1.6 \times 10^{-2}}{4.0 \times 10^{-3}} = 2^x = 4$

$x = 2$ and $y = 1$

Thus order with respect to A is second and order with respect to B is first.

(ii) Rate $= k\ [A]^2\ [B]$

From experiment (1)

$5 \times 10^{-4} = k\ [2.5 \times 10^{-4}]^2\ [3.0 \times 10^{-5}]$

$k = \frac{5 \times 10^{-4}}{[2.5 \times 10^{-4}]^2\ [3.0 \times 10^{-5}]}$

$= 2.67 \times 10^8\ L^2\ \text{mol}^{-2}\ s^{-1}$

(iii) According to Arrhenius equation

$$\log_{10}\frac{2.0\times10^{-3}}{5.0\times10^{-4}}=\frac{Ea}{2.303\times8.314}\times\frac{20}{300\times320}$$

$$Ea=\frac{2.303\times8.314\times300\times320}{20}\times\log_{10}4$$

$= 55.333$ kJ mol^{-1}

(iv) $\log_{10}k=\log_{10}A-\frac{Ea}{2.303\,RT}$

$$\log_{10}\frac{A}{k}=\frac{55.333}{2.303\times8.314\times300}=9.633$$

$\frac{A}{k}=4.29\times10^{9}$

$A=4.29\times10^{9}\times2.67\times10^{8}$

$=1.145\times10^{18}$

5. t 380°C, the half life period for the first order decomposition of H_2O_2 is 360 minute. The energy of activation of the reaction is 200 kJ mole^{-1}. Calculate the time required for 75 per cent decomposition at 450°C.

[IIT 1995]

$$K_1 \text{ at } 653\text{ K}=\frac{0.693}{t_{1/2}}=\frac{0.693}{360}$$

$=1.925\times10^{-3}$ min^{-1}

$$\log_{10}\frac{K_2}{K_1}=\frac{Ea}{2.303\,R}\frac{(T_2-T_1)}{(T_1\,T_2)}$$

$$\log\frac{K_2}{1.925\times10^{-3}}$$

$$=\frac{200\times10^{3}}{2.303\times8.314}\frac{[723-653]}{[653\times723]}$$

$K_2=0.068$ min^{-1}

$$t=\frac{2.303}{K_2}\log_{10}\frac{a}{a-x}$$

$$=\frac{2.303}{0.068}\log_{10}\frac{100}{25}=20.39\text{ minute}$$

6. The time required for 10 per cent completion of a first order reaction at 298 K is equal to that required for its 25 per cent completion at 308 K. If the pre-exponential factor for the reaction is 3.56×10^{9} sec^{-1}, calculate its rate constant at 318 K and also the energy of activation.

[IIT 1997]

Solution $k=\frac{2.303}{t}\log_{10}\frac{a}{a-x}$

At 298 K

$x = 10$, $a = 100$

$$k_{298}=\frac{2.303}{t_1}\log_{10}\frac{100}{90}\quad\text{.... (i)}$$

At 308 K,

$a = 100$, $\times = 25$, $(a-x) = 75$

$$k_{308}=\frac{2.303}{t_2}\log_{10}\frac{100}{75}\quad\text{... (ii)}$$

On dividing equation (ii) by (i)

$t_1=t_2$

so $\frac{k_{308}}{k_{298}}=2.73$

$$\log_{10}\frac{k_{398}}{k_{298}}=\frac{E}{2.303\,R}(1/T_1-1/T_2)$$

$$\log_{10}2.73=\frac{E}{2.303\times8.314}\left(\left(\frac{1}{308}-\frac{1}{298}\right)\right)$$

$E = 76.622$ kJ mol^{-1}

Similarly we can solve for k_{318} which is equal to 9.22×10^{-4} s^{-1}

7. The rate constant of a reaction is 1.5×10^{7} s^{-1} at 50°C and 4.5×10^{7} s^{-1} at 100°C. Calculate the Arrhenius parameter A and Ea.

[IIT 1998]

Solution $\log_{10}\frac{k_2}{k_1}=\frac{Ea}{2.303\,R}\left(\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right)$

$$\log_{10}\frac{4.5\times10^{7}}{1.5\times10^{7}}$$

$$=\frac{Ea}{2.303\times8.314}\left(\frac{1}{323}-\frac{1}{373}\right)$$

$Ea=2.2\times10^{4}$ J mol^{-1}

$$\log_{10}k=\log_{10}A-\frac{Ea}{2.303\,RT}$$

$\log_{10}(1.5\times10^{7})$

$$=\log_{10}A-\frac{2.2\times10^{4}}{2.303\times8.314\times323}$$

$A=5.42\times10^{10}$ s^{-1}

8. The rate constant for an isomerisation reaction, A → B is $4.5 \times 10^{-3}\ \text{min}^{-1}$. If the initial concentration of A is 1 M, calculate the rate of reaction after one hour.

[IIT 1999]

Solution The dimension of the rate constant of the reaction (min^{-1}) indicates that it is first order reaction.

$$K = \frac{2.303}{t} \log_{10} \frac{1}{1-x}$$

$$4.5 \times 10^{-3} = \frac{2.303}{1 \times 60} \log_{10} \frac{1}{1-x}$$

On solving, we get

$x = 0.237$

After one hour

$[B] = 0.237$ M

So $[A] = 1 - 0.237 = 0.763$ M

Rate after 1 hour $= K\,[A]^n$

$= 4.5 \times 10^{-3} \times 0.763$

$= 3.43 \times 10^{-3}$ M/min

9. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol^{-1}.

[IIT 2000]

Solution According to Arrhenius equation

$$K = Ae^{-Ea/RT}$$

Let k_{500} and k_{400} be the rate constants at temperatures 500 K and 400 K (in presence of catalyst) respectively. E_{500} and E_{400} be the activation energies at temperatures 500 K and 400 K respectively.

$$K_{500} = Ae^{-E\,500/R \times 500} \quad \text{....(i)}$$

$$K_{400} = Ae^{-E\,400/R \times 400} \quad \text{....(ii)}$$

Given $k_{500} = k_{400}$ (same rates in presence and absence of a catalyst)

On comparing equation (i) with (ii)

$$\frac{E_{500}}{R \times 500} = \frac{E_{400}}{R \times 400}$$

or $\dfrac{E_{500}}{5} = \dfrac{E_{400}}{4}$

$$E_{500} = \frac{E_{400}}{4} \times 5 \quad \text{.... (iii)}$$

given $E_{500} = E_{400} + 20$

On substituting the values in equation (iii)

$E_{400} + 20 = E_{400} \times 1.25$

$E_{400} = \dfrac{20}{0.25} = 80\ \text{kJ mol}^{-1}$

so $E_{500} = 80 + 20 = 100\ \text{kJ mol}^{-1}$

10. For the given reaction,

A + B → Products

following data were obtained:

	$[A_0]$	$[B_0]$	R_0 mol lit^{-1} sec^{-1}
1.	0.1M	0.2M	0.05
2.	0.2M	0.2M	0.10
3.	0.1M	0.1M	0.05

(i) Write the rate law expression.

(ii) Find the rate constant.

[IIT 2004]

Solution Let order with respect to A and B are α and β respectively. Rate law expression may be given as

$$\text{Rate} = k\,[A]^{\alpha}\,[B]^{\beta}$$

$$0.05 = k\ [0.1]^{\alpha}\,[0.2]^{\beta} \quad \text{..... (i)}$$

$$0.10 = k\ [0.2]^{\alpha}\,[0.2]^{\beta} \quad \text{...... (ii)}$$

$$0.05 = k\,[0.1]^{\alpha}\,[0.1]^{\beta} \quad \text{.......(iii)}$$

On dividing equation (i) by (ii), we obtain

$1/2 = [1/2]^{\alpha}$

that is, $\alpha = 1$

On dividing equation (i) by (iii), we obtain

$1 = [2]^{\beta}$

that is, $\beta = 0$

$\text{Rate} = k\,[A]^1\,[B]^0$

On putting the value of α and β in eq. (i)

$0.05 = k\,[0.1]^1\,[0.2]^0$

$k = 0.5\ \text{sec}^{-1}$

11. A constant temperature and volume X decomposes as,

$2X\,(g) \rightarrow 3Y\,(g) + 2Z\,(g)$

P_X is the partial pressure of X.

Observation No.	Time (min)	P_x (in mm Hg)
1	0	800
2	100	400
3	200	200

(i) What is the order of the reaction with respect to X?

(ii) Find the rate constant.

(iii) Find the time for 75 per cent completion of the reaction.

(iv) Find the total pressure when pressure of X is 700 mm Hg.

[IIT 2005]

Solution (i) From the given data it is clear that that half life of the reaction is constant that is 100 min so it is a first order reaction.

(ii) $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{100}$

$= 6.93 \times 10^{-3}\ \text{min}^{-1}$

(iii) $t_{75\%}$ that is, $t_{3/4} = 2 \times t_{1/2}$

$= 2 \times 100 = 200\ \text{min}$

(iv)

	$2X\,(g)$	$\rightarrow$ $3Y\,(g)$	$+$ $2Z\,(g)$
$t = 0$	800	0	0
dt	$800 - 2X$	$3X$	$2X$

Total pressure = $800 - 2X + 3X + 2X$

$= 800 + 3X$

$800 - 2X = 700$

$X = 50$

Total pressure $= 800 + 3 \times 50$

$= 950$ mm Hg

MULTIPLE-CHOICE QUESTIONS

Straight Objective Type Questions (Single Choice only)

1. The rate constant of a reaction depends on
   - **a.** Extent of reaction
   - **b.** Time of reaction
   - **c.** Temperature
   - **d.** Initial concentration of the reactants

2. A plot of $1/[BrO^-]$ vs time is linear for the reaction:

   $3BrO^- (aq) \rightarrow BrO_3^- (aq) + 2Br^- (aq)$

   What is the order of the reaction with respect to the hypobromite ion, BrO^-?
   - **a.** One
   - **b.** Two
   - **c.** Three
   - **d.** Four

3. The specific rate constant of a first order reaction depends on the
   - **a.** temperature
   - **b.** time
   - **c.** concentration of the reactant
   - **d.** concentration of the product

4. For a zeroth-order reaction: C → products, $-\Delta[C]/\Delta t = k$, which of the following graphs would be expected to give a straight line?
   - **a.** $[C]^2$ vs t
   - **b.** [C] vs t
   - **c.** In [C] vs t
   - **d.** 1/[C] vs t

5. For the zeroth-order reaction: A → products, what will happen to the rate of reaction if the concentration A is doubled?
   - **a.** The rate will be doubled
   - **b.** The rate will be halved
   - **c.** The rate will remain the same
   - **d.** The rate will be quadrupled

6. $3A \rightarrow 2B$, rate of reaction $+d(B)$ is equal to dt
   - **a.** $-\frac{3}{2}\frac{d[A]}{dt}$
   - **b.** $-\frac{2}{3}\frac{d[A]}{dt}$
   - **c.** $-\frac{1}{3}\frac{d[A]}{dt}$
   - **d.** $+2\frac{d[A]}{dt}$

7. The elementary reaction:

   $2HI \rightarrow H_2 + I_2$, is an example of a _____ reaction.
   - **a.** Tetramolecular
   - **b.** Termolecular
   - **c.** Bimolecular
   - **d.** Unimolecular

8. Activation energy of a chemical reaction can be determined by
   - **a.** evaluating rate constant at standard temperature
   - **b.** evaluating velocities of reaction at two different temperatures
   - **c.** evaluating rate constants at two different temperatures
   - **d.** changing concentration of reactants

9. The elementary reaction representing the formation of ozone:

   $O_2 (g) + O (g) + M (g) \rightarrow O_3 (g) + M^* (g)$

   is an example of ______ reaction.
   - **a.** Tetramolecular
   - **b.** Termolecular
   - **c.** Bimolecular
   - **d.** Unimolecular

10. Catalyst is a substance which
    - **a.** supplies energy to the reaction
    - **b.** increases the equilibrium concentration of the product
    - **c.** changes the equilibrium constant of the reaction
    - **d.** shortens the time to each equilibrium

11. Which statement below regarding the half-life of a second order reaction is true?
    - **a.** The length of the half life remains unchanged throughout the course of the reaction.
    - **b.** Each half life is four times as long as the preceding one.
    - **c.** Each half life is half as long as the preceding one.
    - **d.** Each half life is twice as long as the preceding one.

12. Graph between $\log_{10} k$ and (1/T) is linear of slope S. Hence Ea is
    - **a.** R × S
    - **b.** S/R
    - **c.** R/S
    - **d.** 2.303 RS

13. For a first order reaction, the half life period is independent of

a. initial concentration
b. cube root of initial concentration
c. first power of final concentration
d. square root of final concentration

14. The rate of a certain hypothetical reaction A + B + C → Products is given by

$$r = -\frac{d[A]}{dt} = k\,[A]^{1/2}\,[B]^{1/3}\,[C]^{1/4}$$

The order of the reaction is

a. 13/12 **b.** 13/14
c. 12/13 **d.** 13/11

15. $3A \rightarrow B + C$

It would be a zero order reaction when:

a. the rate of reaction is proportional to square of concentration of A
b. the rate of reaction remains same at any concentration of A
c. the rate remains unchanged at any concentration of B and C
d. the rate of reaction doubles if concentration of B is increased to double

16. What will be initial rate of a reaction if its constant is 10^{-3} min^{-1} and the concentration of reactant is 0.2 mol dm^{-3}?

a. 0.02 mol dm^{-3} min^{-1}
b. 0.002 mol dm^{-3} min^{-1}
c. 0.0002 mol dm^{-3} min^{-1}
d. 2 mol dm^{-3} min^{-1}

17. For an endothermic reaction, where ΔH represents the enthalpy of the reaction in kJ/mole. The minimum value for the energy of activation will be

a. less than ΔH
b. zero
c. more than ΔH
d. equal to ΔH

18. The rate of a gaseous reaction is given by the expression k[A][B]. If the volume of the reaction vessel is suddenly reduced to 1/4th of the initial volume, the reaction rate relating to original rate will be

a. 8 **b.** 16
c. 1/8 **d.** 1/10

19. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are 3.0×10^{-4} s^{-1}, 104.4 kJ mol^{-1} and 6×10^{14} s^{-1} respectively. The value of the rate constant as $T \rightarrow \infty$ is

a. 2.0×10^{18} s^{-1} **b.** 6.0×10^{14} s^{-1}
c. infinity **d.** 3.6×10^{30} s^{-1}

20. In the following reaction, how is the rate of appearance of the underlined product related to the rate of disappearance of the underlined reactant?

$BrO_3^-\,(aq) + 5Br^-\,(aq) + 6H^+\,(aq) \rightarrow 3Br_2(l)\ 3H_2O\,(l)$

a. $\frac{d[Br_2]}{dt} = -\frac{5}{3}\,\frac{d\,[Br^-]}{dt}$

b. $\frac{d[Br_2]}{dt} = -\,\frac{d\,[Br^-]}{dt}$

c. $\frac{d[Br_2]}{dt} = -\,\frac{d\,[Br^-]}{dt}$

d. $\frac{d[Br_2]}{dt} = -\frac{3}{5}\,\frac{d\,[Br^-]}{dt}$

21. The rate constant of a first order reaction, A → products, is 60×10^{-4} s^{-1}. Its rate at [A] = 0.01 mol l^{-1} would be

a. 60×10^{-6} mol l^{-1} min^{-1}
b. 36×10^{-4} mol l^{-1} min^{-1}
c. 60×10^{-2} mol l^{-1} min^{-1}
d. 36×10^{-1} mol l^{-1} min^{-1}

22. For the reaction,

$2A + B \rightarrow 3C + D$

Which of the following does not express the reaction rate?

a. $\frac{d[D]}{dt}$ **b.** $-\frac{d[A]}{2\,dt}$

c. $-\frac{d[C]}{3\,dt}$ **d.** $-\frac{d\,[B]}{dt}$

23. The rate of a first order reaction is 1.5×10^{-2} mol L^{-1} min^{-1} at 0.5 M concentration of the reactant. The half-life of the reaction is

a. 0.383 hour **b.** 23.1 min
c. 8.73 min **d.** 7.53 min

24. The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation, $k = A.e^{-E^*/RT}$. Activation energy (E^*) of the reaction can be calculated by ploting

a. log k vs T^{-1} **b.** log k vs $\frac{1}{\log T}$

c. k vs T **d.** k vs $\frac{1}{\log T}$

25. For the reaction,

$2N_2O_5 \rightarrow 4NO_2 + O_2$, rate and rate constant are 1.02×10^{-4} and 3.4×10^{-5} sec^{-1} respectively then concentration of N_2O_5 at that time will be

a. 1.732 **b.** 3
c. 3.4×10^{5} **d.** 1.02×10^{-4}

26. The experimental data for the reaction

$2A + B_2 \rightarrow 2AB$ is

Exp.	[A]	$[B_2]$	Rate(Ms^{-1})
1	0.50 M	0.50 M	1.6×10^{-4}
2	0.50 M	1.00 M	3.2×10^{-4}
3	1.00 M	1.00 M	3.2×10^{-4}

the rate equation for the above data is

a. rate = $k[B_2]$

b. rate = $k[B_2]^2$

c. rate = $k[A]^2 [B]^2$

d. rate = $k[A]^2[B]$

27. If the rate of the reaction is equal to the rate constant, the order of the reaction is

a. 3 **b.** 0

c. 1 **d.** 2

28. The reaction A → B follows first order kinetics. The time taken for 0.8 mole of A to produce 0.6 mole of B is 1 hour. What is the time taken for conversion of 0.9 mole of A to produce 0.675 mole of B?

a. 2 hours **b.** 1 hour

c. 0.5 hour **d.** 0.25 hour

29. In a first order reaction A → B if k is rate constant and initial concentration of the reactant A is 0.5 M then the half life is

a. 0.693/0.5 k **b.** log 2/k

c. log 2/k √0.5 **d.** In 2/k

30. Molecular hydrogen can be made from methane gas by the reaction below. How is the rate of disappearance of CH_4 related to the rate of appearance of H_2?

$$\frac{\Delta [CH_4] = ?}{\Delta t}$$

$CH_4\ (g) + H_2O\ (l) \rightarrow CO\ (g) + 3h\ ()$

a. $+3\frac{\Delta [H_2]}{\Delta t}$

b. $+\frac{\Delta [H_2]}{\Delta t}$

c. $+\frac{1\Delta [H_2]}{3\ \Delta t}$

d. None of these

31. Methanol can be produced by the following reaction:

$CO\ (g) + 2H_2\ (g) \rightarrow CH_3OH\ (g)$

How is the rate of disappearance of hydrogen gas related to the rate of appearance of methanol?

$$-\frac{\Delta [H_2]}{\Delta t} = ?$$

a. $+\frac{2\ \Delta [CH_3OH]}{\Delta t}$

b. $+\frac{1\Delta [CH_3OH]}{2\ \Delta t}$

c. $+\frac{\Delta [H_4]}{\Delta t}$

d. None of these

32. Hydroquinone, HOC_4H_4OH, can be formed by the reaction with acetylene below:

$$3HC \equiv CH + 3CO + 3H_2O \rightarrow 2HOC_4H_4OH + CO_2$$

How is the rate of disappearance of acetylene ($HC \equiv CH$) related to the appearance of hydroquinone (Hq)?

$$-\frac{\Delta [HC \equiv CH]}{\Delta t} = ?$$

a. $+\frac{2\ \Delta [Hq]}{3\ \Delta t}$

b. $+\frac{3\ \Delta [Hq]}{2\ \Delta t}$

c. $+\frac{\Delta [Hq]}{\Delta t}$

d. $+\frac{1\ \Delta [Hq]}{2\ \Delta t}$

33. The reaction that occurs in a Breathalyzer, a device used to determine the alcohol level in a person's blood stream, is given below. If the rate of appearance of $Cr_2(SO_4)_3$ is 1.24 mol/min at a particular moment, what is the rate of disappearance of C_2H_6O at the moment?

$$2K_2Cr_2O_7 + 8H_2SO_4 + 3C_2H_6O \rightarrow 2Cr_2(SO_4)_3 + 2K_2SO_4 + 11H_2O$$

a. 1.86 mol/min

b. 2.75 mol/min

c. 3.86 mol/min

d. 0.86 mol/min

34. The decomposition of dinitrogen pentoxide is described by the chemical equation

$2N_2O_5\ (g) \rightarrow 4NO_2\ (g) + O_2\ (g)$

If the rate of disappearance of N_2O_5 is equal to 1.40 mol/min at a particular moment, what is the rate of appearance of NO_2 at the moment?

a. 1.80 mol/min
b. 3.40 mol/min
c. 0.800 mol/min
d. 2.80 mol/min

35. The decomposition of dinitrogen pentoxide is described by the chemical equation

$2N_2O_5\,(g) \rightarrow 4NO_2\,(g) + O_2\,(g)$

If the rate of appearance of NO_2 is equal to 0.560 mol/min at a particular moment, what is the rate of appearance of O_2 at that moment?

a. 2.70 mol/min
b. 3.40 mol/min
c. 0.140 mol/min
d. 1.14 mol/min

36. The decomposition of dinitrogen pentoxide is described by the chemical equation

$2N_2O_5\,(g) \rightarrow 4NO_2\,(g) + O_2\,(g)$

If the rate of appearance of O_2 is equal to 2.40 mol/min at a particular moment, what is the rate of disappearance of N_2O_5 at that moment?

a. 3.48 mol/min
b. 4.80 mol/min
c. 2.40 mol/min
d. 1.80 mol/min

37. Which statement is true for the general rate law:

Rate = $k\,[A]^m\,[B]^n$?

a. The exponents in the rate law must be positive integers.
b. The values for the exponents must be determined by experiment.
c. It can be written from the stoichiometry of the overall reaction.
d. The overall order of the reaction is equal to 'm' times 'n'.

38. For a reaction that follows the general rate law, Rate = $k\,[A]\,[B]^2$, what will happen to the rate of reaction if the concentration of A is increased by a factor of 3.00? The rate will

a. Increase by a factor of 6.00.
b. Decrease by a factor of 1/6.00.
c. Decrease by a factor of 1/3.00.
d. Increase by a factor of 3.00.

39. For a reaction that follows the general rate law, Rate = $k\,[A]\,[B]^2$, what will happen to the rate of reaction if the concentration of B is increased by a factor of 2.00? The rate will

a. Increase by a factor of 4.00.
b. Increase by a factor of 2.00.
c. Decrease by a factor of 1/4.00.
d. Decrease by a factor of 1/2.00.

40. The reaction between chlorine and nitric oxide to form nitrosyl chloride is shown below. If the reaction rate doubles when the concentration of Cl_2 is doubled and the rate quadruples when the concentration of NO is doubled, by what factor will the rate increase if both concentrations, NO and Cl_2 are doubled?

$Cl_2\,(g) + 2NO\,(g) \rightarrow 2NOCl\,(g)$

a. 4 **b.** 8
c. 12 **d.** 16

41. The hydrolysis of tert-butyl chloride is given in the reaction below:

$(CH_3)_3CCl\,(aq) + H_2O\,(l) \rightarrow (CH_3)_3COH\,(aq) + H^+\,(aq) + Cl^-\,(aq)$

If the rate law is: Rate = $k\,[(CH_3)_3CCl]$, what is the order of the reaction with respect to water?

a. First **b.** Second
c. Third **d.** Zero

42. Given the following hypothetical reaction:

$2E\,(g) + F\,(g) + G\,(g) \rightarrow$ Products.

If the rate law is: Rate = $k\,[E]^2\,[F]^{-1}$, what is the order of reaction with respect to E?

a. First **b.** Second
c. Third **d.** Fourth

43. Given the following hypothetical reaction:

$2E\,(g) + F\,(g) + G\,(g) \rightarrow$ Products.

If the rate law is: Rate = $k\,[E]^2\,[F]^{-1}$, What is the overall order of reaction?

a. First **b.** Second
c. Third **d.** Zero

44. The decomposition of ammonia to nitrogen and hydrogen on a tungsten filament at 800°C is independent of the concentration of ammonia at high pressures of ammonia. What is the order of the reaction with respect to ammonia?

a. First **b.** Second
c. Third **d.** Zero

45. Cerium (IV) ion reacts with thallium (I) ion in a one-step reaction shown below:

$2Ce^{4+}\,(aq) + Tl^{+}\,(aq) \rightarrow 2Ce^{3+}\,(aq) + Tl^{3+}\,(aq)$

If the rate law is: Rate = k $[Ce^{4+}]^2$ $[Tl^{+}]$, What is the overall order of the reaction?

a. Zero **b.** First
c. Second **d.** Third

46. Iodide and hypochlorite ion react in aqueous solution according to the reaction below:

$I^- + OCl^- \rightarrow OI^- + Cl^-$

If the concentration of OH^- in the solution is doubled, the rate of the reaction is halved. What is the order of the reaction with respect to OH^-?

a. +2 **b.** +1
c. –2 **d.** –1

47. Chlorine reacts with chloroform according to the reaction given below:

$Cl_2 + CHCl_3 \rightarrow CCl_4 + HCl$

When the initial concentration of Cl_2 is doubled the reaction rate increases by a factor of 1.41. What is the order of the reaction with respect to Cl_2?

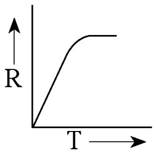
a. ½ **b.** – ½
c. –1 **d.** 2

48. If the units for rate are M s^{-1}, what are the units for the rate constant (k), if the overall order of the reaction is three?

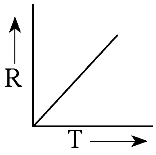
a. $M^{-1}\ s^{-1}$ **b.** $M^{-2}\ s^{-1}$
c. s^{-1} **d.** $M^2\ s^{-1}$

49. Which curve corresponds to the temperature dependence of the rate R of a simple one-step reaction?

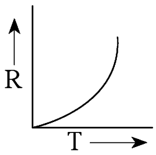
a.



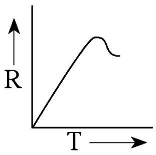
b.



c.



d.



50. For a particular first order reaction, it takes 48 minutes for the concentration of the reactant to decrease to 25% of its initial value. What is the value for rate constant (in s^{-1}) for the reaction?

a. $2.4 \times 10^{-4}\ s^{-1}$
b. $1.8 \times 10^{-3}\ s^{-1}$
c. $3.18 \times 10^{-4}\ s^{-1}$
d. $4.8 \times 10^{-4}\ s^{-1}$

51. The first order reaction,

$SO_2Cl_2 \rightarrow SO_2 + Cl_2$, has a rate constant equal to $2.20 \times 10^{-5}\ s^{-1}$ at 593 K. What percentage of the initial amount of SO_2Cl_2 will remain after 2.00 hours?

a. 45.8 %
b. 85.4 %
c. 15.4 %
d. 75.6 %

52. The first order reaction,

$2N_2O$ (g) → $2N_2$ (g) + O_2 (g), has a rate constant equal to 0.76 s^{-1} at 1000 K. How long will it take for the concentration of N_2O to decrease to 42 % of its initial concentration?

a. 3.1 s
b. 0.18 s
c. 1.1 s
d. 2.4 s

53. The isomerization reaction,

$CH_3NC \rightarrow CH_3CN$, is first order and the rate constant is equal to 0.46 s^{-1} at 600 K. What is the concentration of CH_3NC after 0.20 minutes if the initial concentration is 0.10 M?

a. 14.0×10^{-4} M
b. 4.0×10^{-4} M
c. 2.4×10^{-4} M
d. 6.4×10^{-4} M

54. The following reaction is first order:

$C_2H_6 \rightarrow 2CH_3$. If the rate constant is equal to $5.5 \times 10^{-4}\ s^{-1}$ at 1000 K, how long will it take for 0.35 mol of C_2H_6 in a 1.00 L container to decrease to 0.10 mol in the same container?

a. 38 min
b. 26 min
c. 19 min
d. 68 min

55. The decomposition of cyclopropane, was observed at 500°C and its concentration was monitored as a function of time. The data set is given below. What is the order of the reaction with respect to cyclopropane?

Time (hour)	[Cyclopropane], M
0	1.00×10^{-2}

2	1.38×10^{-3}
4	1.91×10^{-4}
6	2.63×10^{-5}

a. First **b.** Second

c. Third **d.** Zero

56. The rate constant (k) for a first order reaction is equal to 4.2×10^{-4} s^{-1}. What is the half life for the reaction?

a. 3.7×10^{3} s

b. 7.1×10^{3} s

c. 2.71×10^{3} s

d. 1.7×10^{3} s

57. Acetaldehyde decomposes at 750 K:

$CH_3CHO \rightarrow CO + CH_4$. The reaction is first order in acetaldehyde and the half life of the reaction is found to be 530 seconds. What is the rate constant for the reaction at this temperature?

a. 3.7×10^{-3} s^{-1}

b. 3.13×10^{3} s^{-1}

c. 1.3×10^{-3} s^{-1}

d. 2.3×10^{-3} s^{-1}

58. The first order reaction,

$SO_2Cl_2 \rightarrow SO_2 + Cl_2$, has a half life of 8.75 hours at 593 K. How long will it take for the concentration of SO_2Cl_2 to fall to 12.5% of its initial value?

a. 6.24 hours

b. 26.2 hours

c. 16.2 hours

d. 22.6 hours

59. For the first order reaction,

$2N_2O\ (g) \rightarrow 2N_2\ (g) + O_2\ (g)$, what is the concentration of N_2O after 3 half-lives if 0.15 mol of N_2O is initially placed into in a 1.00 litre reaction vessel?

a. 9.1×10^{-2} M

b. 0.9×10^{-2} M

c. 2.68×10^{-2} M

d. 1.9×10^{-2} M

60. Carbon-14, which is present in all living tissue, radioactively decays via a first order process. A one-gram sample of wood taken from a living tree gives a rate for carbon-14 decay of 13.6 counts per. If the half-life for carbon-14 is 5720 years. How old is a wood sample that gives a rate for carbon-14 decay of 3.9 counts per minute?

a. 1.0×10^{4} years

b. 2.1×10^{3} years

c. 5.4×10^{3} years

d. 3.0×10^{4} years

61. Fluorine-18 is an isotope used in Positron Emission Tomography (PET) to scan the brain. If a researcher has 1.50 μg of ^{18}F, how long before it decays to 1.0 ng? The half-life of ^{18}F is 109.8 minutes.

a. 2.9×10^{-2} hours

b. 91 hours

c. 39 hours

d. 19 hours

62. The second order reaction,

$2Mn(CO)_5 \rightarrow Mn_2(CO)_{10}$ has a rate constant equal to 3.0×10^{9} M^{-1} s^{-1} at 25°C. If the initial concentration of $Mn(CO)_5$ is 1.0×10^{-5} M, how long will it take for 90 % of the reactant to disappear?

a. 3.0×10^{-4} s

b. 3.9×10^{-6} s

c. 3.0×10^{4} s

d. 4.3×10^{-3} s

63. The reaction: $2HI \rightarrow H_2 + I_2$, is second order and the rate constant at 800 K is 9.70×10^{-2} M^{-1} s^{-1}. How long will it take for 8.00×10^{-2} mol/litre of HI to decrease to one-fourth of its initial concentration?

a. 587 s

b. 387 s

c. 148 s

d. 687 s

64. For the hypothetical second order reaction:

A → Products, the general rate law is: Rate = k $[A]^2$. How long is the third half life of the reaction if $[A]_0$ is 0.080 M and the first half life is 22 minutes.

a. 48 min

b. 66 min

c. 88 min

d. 78 min

65. A mechanism for a naturally occurring reaction that destroys ozone is:

Step I:

$O_3\ (g) + HO\ (g) \rightarrow HO_2\ (g) + O_2$

Step II:

$HO_2\ (g) + O\ (g) \rightarrow HO\ (g) + O_2\ (g)$

Which species is an intermediate?

a. O **b.** O_3

c. HO **d.** HO_2

66. The decomposition of ozone in the stratosphere can occur by the following two-step mechanism:

Step I:

$Br + O_3 \rightarrow BrO + O_2$

Step II:

$BrO + O \rightarrow Br + O_2$

Which species is an intermediate in this mechanism?

a. BrO **b.** Br
c. O_3 **d.** O

67. A mechanism for a naturally occurring reaction that destroys ozone is

Step I:

$O_3 (g) + HO (g) \rightarrow HO_2 (g) + O_2 (g)$

Step II:

$HO_2 (g) + O (g) \rightarrow HO (g) + O_2 (g)$

What is the molecularity of the overall reaction?

a. Bimolecular
b. Unimolecular
c. None of these because molecularity only refers to elementary steps
d. None of these because molecularity is the difference of the exponents in the rate law

68. A three-step mechanism has been suggested for the formation of carbonyl chloride:

Step I: $Cl_2 \rightarrow 2Cl$
Step II: $Cl + CO \rightarrow COCl$
Step III: $COCl + Cl_2 \rightarrow COCl_2 + Cl$

Which species is an intermediate in the mechanism?

a. $COCl_2$
b. COCl
c. Cl
d. CO

69. A gas molecule at 298 K and 1 atm pressure undergoes a collision with another gas molecule approximately every ____ seconds.

a. 10^{-3}
b. 10^{-6}
c. 10^{-9}
d. 10^{-12}

70. What fraction of collisions will have sufficient energy to react for gas whose activation energy is 68 kJ/mol at 25°C?

a. 2.4×10^{-6}
b. 6.2×10^{-12}
c. 1.2×10^{4}
d. 1.2×10^{-12}

71. When the temperature of a gas whose activation energy is 55 kJ/mol is increased from 300 K to 320 K, the fraction of collisions with sufficient energy to react

a. Increases by a factor of 4.
b. Increases by a factor of 2
c. Decrease by a factor of 4
d. Decrease by a factor of 2.

72. A common rule of thumb in organic chemistry is that increasing the temperature of a reaction at room temperature by 10°C doubles the rate. Calculate Ea for a reaction that follows this rule of thumb. Assume room temperature is 25°C.

a. 0.597
b. 15.2
c. 52.9
d. 45.9

73. Consider a bimolecular reaction in the gas phase. Which one of the following changes in conditions will not cause an increase in the rate of the reaction?

a. Increase the volume at constant temperature.
b. Increase the temperature at constant volume
c. Add a catalyst
d. All of the above will increase the rate of reaction

74. The reaction for the decomposition of dinitrogen monoxide gas to form an oxygen radical is: $N_2O (g) \rightarrow N_2 (g) + O (g)$. If the activation energy is 250 kJ/mol and the frequency factor is 8.0×10^{11} s^{-1}, what is the rate constant for the first order reaction at 1000 K?

a. 7.0×10^{-2} s^{-1}
b. 3.7×10^{-2} s^{-1}
c. 0.71×10^{-3} s^{-1}
d. 9.7×10^{-6} s^{-1}

75. The aquation of tris-(1,10-phenanthroline) iron (II) in acid solution takes place according to the equation:

$$Fe(phen)_3^{2} + 3H_3O^+ + 3H_2O \rightarrow Fe(H_2O)_6^{2+} + 3\,(phen)H^+$$

If the activation energy is 126 kJ/mol and frequency factor is 8.62×10^{17} s^{-1}, at what temperature is the rate constant equal to 3.63×10^{-3} s^{-1} for the first order reaction?

a. 0°C

b. 50°C

c. 45°C

d. 90°C

76. The equation tris(1, 10-phenanthroline) iron(II) in acid solution takes place according to the equation:

$$Fe(phen)_3^{2+} + 3H_3O^+ + 3H_2O \rightarrow Fe(H_2O)_6^{2+} + 3\,(Phen)H^+$$

If the activation energy (Ea) is 126 kJ/mol and the rate constant at 30°C is 9.8×10^{-3} min^{-1}, what is the frequency factor (A)?

a. 9.5×10^{18} min^{-1}

b. 2.5×10^{19} min^{-1}

c. 55×10^{19} min^{-1}

d. 5.0×10^{19} min^{-1}

77. The first order isomerization reaction:

Cyclopropane → Propene, has a rate constant of 1.10×10^{-4} s^{-1} at 470°C and 5.70×10^{-4} s^{-1} at 500°C. What is the activation energy (Ea) for the reaction?

a. 340 kJ/mol

b. 260 kJ/mol

c. 160 kJ/mol

d. 620 kJ/mol

78. The first order isomerisation reaction:

Cyclopropane → propene, has a rate constant of 1.10×10^{-4} s^{-1} at 470°C and an activation energy of 264 kJ/mol. What is the temperature of the reaction when the rate constant is equal to 4.36×10^{-3} s^{-1}?

a. 240°C

b. 150°C

c. 540°C

d. 450°C

79. A mechanism for a naturally occurring reaction that destroys ozone is:

Step I: $O_3\,(g) + HO\,(g) \rightarrow HO_2\,(g) + O_2\,(g)$

Step II: $HO_2\,(g) + O\,(g) \rightarrow HO\,(g) + O_2\,(g)$

Which species is a catalyst?

a. O b. O_3

c. HO_2 d. HO

80. A mechanism for a naturally occurring reaction that destroys ozone is

Step I: $O_3\,(g) + HO\,(g) \rightarrow HO_2\,(g) + O_2\,(g)$

Step II: $HO_2\,(g) + O\,(g) \rightarrow HO\,(g) + O_2\,(g)$

Which species is a catalyst and what type of catalysis is occurring?

a. HO_2, heterogeneous

b. HO_2, homogeneous

c. HO, homogeneous

d. HO, heterogeneous

Brainteasers Objective Type Questions (Single choice only)

81. The decomposition of hydrogen peroxide is given by the following reaction:

$2H_2O_2\,(aq) \rightarrow 2H_2O\,(l) + O_2\,(g)$

In the presence of KI the reaction is thought to occur by the following mechanism:

Step I: $H_2O_2 + I^- \rightarrow H_2O + IO^-$

Step II: $IO^- + H_2O_2 \rightarrow H_2O + O_2 + I^-$

What is the role of I^- in this mechanism?

a. Intermediate

b. Transition state

c. Catalyst

d. Frequency factor

82. The following set of data was obtained by the method of initial rates for the reaction:

$$2HgCl_2\,(aq) + C_2O_4^{2-}\,(aq) \rightarrow 2Cl^-\,(aq) + 2CO_2\,(g) + Hg_2Cl_2\,(s)$$

What is the rate law for the reaction?

$[HgCl_2]$, M	$[C_2O_4^{2-}]$, M	Rate, M/s
0.10	0.10	1.3×10^{-7}
0.10	0.20	5.2×10^{-7}
0.20	0.20	1.0×10^{-6}

a. Rate = $k\,[HgCl_2]\,[C_2O_4^{2-}]^2$

b. Rate = $k\,[HgCl_2]^2\,[C_2O_4^{2-}]$

c. Rate = $k\,[HgCl_2]\,[C_2O_4^{2-}]^{2-}$

d. Rate = $k\,[HgCl_2]\,[C_2O_4^{2-}]^{-1}$

83. Which of the following statements are true about reaction mechanisms?

(I) A rate law can be written from the molecularity of the slowest elementary step.

(II) The final rate law can include intermediates.

(III) The rate of the reaction is dependent on the fastest step in the mechanism.

(IV) A mechanism can never be proven to be the correct pathway for a reaction.

a. I and II
b. I and IV
c. II and III
d. I, II and III

84. The data given below is for the reaction of NO and Cl_2 to form NOCl at 295 K

What is the rate law?

$[Cl_2]$	[NO]	Initial rate (mol l^{-1} s^{-1})
0.05	0.05	1×10^{-3}
0.15	0.05	3×10^{-3}
0.05	0.15	9×10^{-3}

a. $r = k\,[NO]\,[Cl_2]$
b. $r = k\,[Cl_2]^1\,[NO]^2$
c. $r = k\,[Cl_2]^2\,[NO]$
d. $r = k\,[Cl_2]^1$

85. The following set of data was obtained by the method of initial rates for the reaction:

$$2HgCl_2\,(aq) + C_2O_4^{2-}\,(aq) \rightarrow 2Cl^-\,(aq) + 2CO_2\,(g) + Hg_2Cl_2\,(s)$$

$[HgCl_2]$, M	$[C_2O_4^{2-}]$, M	Rate, M/s
0.10	0.10	1.3×10^{-7}
0.10	0.20	5.2×10^{-7}
0.20	0.20	1.0×10^{-6}

What is the value of the rate constant, k?

a. 1.6×10^{-4} 1/M².s
b. 1.3×10^{-4} 1/M².s
c. 1.4×10^{-7} 1/M².s
d. 1.3×10^{-6} 1/M².s

86. The equation of tris(1,10-phenanthroline) iron(II) in acid solution takes place according to the equation:

$$Fe(phen)_3^{2+} + 3H_3O^+ + 3H_2O \rightarrow Fe(H_2O)_6^{2+} + 3\,(phen)\,H^+.$$

If the activation energy (Ea) is 126 kJ/mol and the rate constant at 30°C is 9.8×10^{-3} min^{-1}, what is the rate constant at 50°C?

a. 2.2×10^{-1} min^{-1}
b. 3.4×10^{-2} min^{-1}
c. 0.23×10^{-1} min^{-1}
d. 1.2×10^{-1} min^{-1}

87. From the following data for the reaction between A and B

[A]	[B]	initial rate	(mol $l^{-1}s^{-1}$)
mol l^{-1}	mol	l^{-1} 300 K	320 K
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	–
1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	–

Calculate the rate of the equation.

a. $r = k\,[B]^1$
b. $r = k\,[A]^2$
c. $r = k\,[A]^2\,[B]^1$
d. $r = k\,[A]\,[B]$

88. The following set of data was obtained by the method of initial rates for the reaction:

$$(H_3C)_3CBr + OH^- \rightarrow (H_3C)_3COH + Br^-$$

What is the order of reaction with respect to ion, OH^-?

$[(H_3C)_3CBr]$, M	$[OH^-]$, M	Initial rate, M/s
0.25	0.25	1.1×10^{-4}
0.50	0.25	2.2×10^{-4}
0.50	0.50	2.2×10^{-4}

a. First
b. Second
c. Third
d. Zero

89. At 380°C, half life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75 % decomposition at 450°C if half life for decomposition of H_2O_2 is 10.17 min at 450°C.

a. 20.4 min
b. 408 min
c. 10.2 min
d. none

90. A three-step mechanism has been suggested for the formation of carbonyl chloride:

Step I: $Cl_2 \rightarrow 2Cl$ (fast, equilibrium)

Step II: $Cl + CO \rightarrow COCl$ (fast, equilibrium)

Step III: $COCl + Cl_2 \rightarrow COCl_2 + Cl$ (slow)

What is the molecularity of the rate-determining step?

- **a.** Termolecular
- **b.** Unimolecular
- **c.** Bimolecular
- **d.** None of these

91. The following set of data was obtained by the method of initial rates for the reaction:

$(H_3C)_3CBr + OH^- \rightarrow (H_3C)_3COH + Br^-$

What is the rate of the reaction?

$[(H_3C)_3CBr]$, M	$[OH^-]$, M	Initial rate, M/s
0.25	0.25	1.1×10^{-4}
0.50	0.25	2.2×10^{-4}
0.50	0.50	2.2×10^{-4}

- **a.** 4.4×10^{-4} s^{-1}
- **b.** 2.4×10^{-4} s^{-1}
- **c.** 14.0×10^{-4} s^{-1}
- **d.** 3.14×10^{-4} s^{-1}

92. For a first reaction A → B, the reaction rate at reactant concentration of 0.01 M is found to be 2.0×10^{-5} mol L^{-1} s^{-1}. The half life period of the reaction is

- **a.** 220 s **b.** 30 s
- **c.** 300 s **d.** 347 s

93. The following set of data was obtained by the method of initial rates for the reaction:

$BrO_3^- (aq) + 5Br^- (aq) + 6H^+ (aq) \rightarrow 3Br_2 (aq) + 3H_2O (l)$

Calculate the initial rate when BrO_3^- is 0.30 M, Br^- is 0.050 M and H^+ is 0.15 M.

$[BrO_3^-]$, M	$[Br^-]$, M	$[H^+]$, M	Rate, M/s
0.10	0.10	0.10	8.0×10^{-4}
0.20	0.10	0.10	1.6×10^{-3}
0.20	0.15	0.10	2.4×10^{-3}
0.10	0.10	0.25	5.0×10^{-3}

- **a.** 3.17×10^{-4} M/s
- **b.** 6.7×10^{-3} M/s
- **c.** 2.7×10^{-3} M/s
- **d.** 1.71×10^{-3} M/s

94. The reaction of hydrogen and iodine monochloride is given as:

$H_2 (g) + 2\,ICl (g) \rightarrow 2HCl (g) + I_2 (g)$

This reaction is of first order with respect to H_2 (g) and ICl (g), following mechanisms were proposed:

Mechanism (1):

$H_2 (g) + 2\,ICl (g) \rightarrow 2HCl (g) + I_2 (g)$

Mechanism (2):

$H_2 (g) + ICl (g) \rightarrow HCl (g) + HI_2 (g)$; slow

$HI (g) + ICl (g) \rightarrow HCl (g) + I_2 (g)$; fast

Which of the above mechanism(s) can be consistent with the given information about the reaction?

- **a.** 2 only
- **b.** Both 1 and 2
- **c.** Neither 1 nor 2
- **d.** 1 only

95. The following set of data was obtained by the method of initial rates for the reaction:

$S_2O_8^{2-} (aq) + 3I^- (aq) \rightarrow 2SO_4^{2-} (aq) + I_3^- (aq)$

What is the rate law for the reaction?

$[S_2O_8^{2-}]$, M	$[I^-]$, M	Initial rate, M s^{-1}
0.25	0.10	9.00×10^{-3}
0.10	0.10	3.60×10^{-3}
0.20	0.30	2.16×10^{-2}

- **a.** Rate = k $[S_2O_8^{2-}] [I^-]^2$
- **b.** Rate = k $[S_2O_8^{2-}]^2 [I^-]$
- **c.** Rate = k $[S_2O_8^{2-}] [I^-]$
- **d.** Rate = k $[S_2O_8^{2-}] [I^-]^5$

96. If 60% of a first order reaction was completed in 60 minutes, 50 % of the same reaction would be completed in approximately

- **a.** 50 minutes **b.** 45 minutes
- **c.** 60 minutes **d.** 40 minutes

(log 4 = 0.60, log 5 = 0.69)

97. Hydrogen peroxide decomposes to water and oxygen according to the reaction below:

$2H_2O_2 (aq) \rightarrow 2H_2O (l) + O_2 (g)$

In the presence of large excesses of I^- ion, the following set of data is obtained. What is the average rate of disappearance of H_2O_2 (aq) in M/s in the first 45.0 seconds of the reaction if 1.00 litre of H_2O_2 reacts at 25°C and 1.00 atm pressure?

Time, s	O_2 (g) collected, ml
0.0	0.0
45.0	2.00
90.0	4.00
135.0	6.00

a. 2.63×10^{-4} M/s
b. 6.33×10^{-6} M/s
c. 3.63×10^{-6} M/s
d. 1.36×10^{-3} M/s

98. The following set of data was obtained by the method of initial rates for the reaction:

$S_2O_8^{2-}$ (aq) + $3I^-$ (aq) $\rightarrow$ $2SO_4^{2-}$ (aq) + I_3^- (aq)

What is the initial rate when $S_2O_8^{2-}$ is 0.15 M and I^- is 0.15 M?

$[S_2O_8^{2-}]$, M	$[I^-]$, M	Initial rate, M s^{-1}
0.25	0.10	9.00×10^{-3}
0.10	0.10	3.60×10^{-3}
0.20	0.30	2.16×10^{-2}

a. 8.10×10^{-3} M s^{-1}
b. 2.80×10^{-4} M s^{-1}
c. 6.18×10^{-3} M s^{-1}
d. 18.1×10^{-3} M s^{-1}

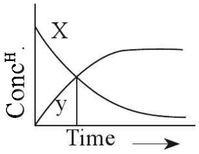
99. In aqueous solution, hypobromite ion (BrO^-), reacts to produce bromate ion (BrO_3^-), and bromide ion (Br^-), according to the following chemical equation.

$3BrO^-$ (aq) $\rightarrow$ BrO_3^- (aq) + $2Br^-$ (aq)

A plot of $1/[BrO^-]$ vs. time is linear and the slope is equal to 0.056 M^{-1} s^{-1}. If the initial concentration of BrO^- is 0.80 M, how long will it take one-half of the BrO^- ion to react?

a. 2.12 s
b. 22 s
c. 12 s
d. 3.22 s

100. The accompanying figure depicts the change in concentrations of species X and Y for the reaction X → Y, as a function of time. The point of intersection of the two curves represents



a. $t_{1/2}$ **b.** $t_{3/4}$
c. $t_{2/3}$ **d.** unpredictable

101. Consider the following statements:

(1) Rate of a process is directly proportional to its free energy change.

(2) The order of an elementary reaction step can be determined by examining the stoichiometry.

(3) The first order reaction describe exponential time coarse.

Of the statements

a. 1 and 2 are correct
b. 1 and 3 are correct
c. 2 and 3 are correct
d. 1, 2 and 3 are correct

102. Hydrogen iodide decomposes at 800 K via a second order process to produce hydrogen and iodine according to the following chemical equation.

2HI (g) $\rightarrow$ H_2 (g) + I_2 (g)

At 800 K it takes 142 seconds for the initial concentration of HI to decrease from 6.75×10^{-2} M to 3.50×10^{-2} M. What is the rate constant for the reaction at this temperature?

a. 6.69×10^{-3} M^{-1} s^{-1}
b. 7.96×10^{-2} M^{-1} s^{-1}
c. 19.6×10^{-3} M^{-1} s^{-1}
d. 9.69×10^{-2} M^{-1} s^{-1}

103. A complex reaction, 2A + B → C takes place in two steps as follows:

$$A + B \xrightarrow{k_1} 2C, \; A + 2B \xrightarrow{k_2} C$$

If $K_1 << K_2$, order of reaction is

a. Zero order **b.** One
c. Two **d.** Three

104. When the concentration of A is doubled, the rate for the reaction: 2A + B → 2C quadruples. When the concentration of B is doubled the rate remains the same. Which mechanism below is consistent with the experimental observations?

a. Step I: 2A ⇌ D (fast equilibrium)
Step II: B + D → E (slow)
Step III: E → 2C (fast)

b. Step I: A + B ⇌ D (fast equilibrium)
Step II: A + D → 2C (slow)

c. Step I: A + B → D (slow)
Step II: A + D ⇌ 2C (fast equilibrium)

d. Step I: 2A → D (slow)
Step II: B + D → E (fast)
Step III: E → 2C (fast)

105. Which of the following are the examples of pseudo-unimolecular reactions?

(1) Acid catalysed hydrolysis of an ester

(2) Inversion of can sugar

(3) Decomposition of ozone

(4) Decomposition of N_2O_5

Select the correct answers using the codes given below

a. 1 and 2 **b.** 1 and 3
c. 2, 3 and 4 **d.** 1, 2 and 4

106. For a reaction $2NH_3 \rightarrow N_2 + 3H_2$

It is observed that

$$\frac{-d[NH_3]}{dt} = K_1 (NH_3),$$

$$\frac{d[N_2]}{dt} = K_2 (NH_3),$$

$$\frac{d[H_2]}{dt} = K_3 (NH_3),$$

What is the relation between K_1, K_2 and K_3?

a. $K_1 = K_2 = K_3$
b. $3K_1 = 6K_2 = 2K_3$
c. $6K_1 = 3K_2 = 2K_3$
d. $2K_1 = 3K_2 = 6K_3$

107. The rate equation for a chemical reaction is

Rate of reaction = k [X] [Y]

Consider the following statements in this regard

(1) The order of reaction is one

(2) The molecularity of reaction is two

(3) The rate constant depends upon temperature

Of these statements:

a. 1 and 3 are correct
b. 1 and 2 are correct
c. 2 and 3 are correct
d. 1, 2 and 3 are correct

108. Which of the following statements are correct?

(1) Order of a reaction can be known from experimental results and not from the stoichiometry of reaction.

(2) Molecularity a reaction refers to (i) each of the elementary steps in (an overall mechanism of) a complex reaction or (ii) a single step reaction

(3) Overall molecularity of a reaction may be determined in a manner similar to overall order of reaction

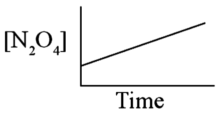
(4) Overall order of a reaction $A^m + B^n \rightarrow AB_x$ is m + n.

Select the correct answer using the following codes:

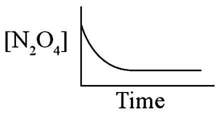
a. 2 and 3 **b.** 1, 3 and 4
c. 2, 3 and 4 **d.** 1, 2 and 3

109. Which of these graphs best describes the rate at which N_2O_4 decomposes to NO_2 if the reaction is of first-order?

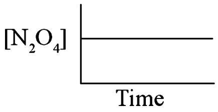
a.



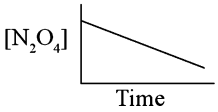
b.



c.



d.



110. The following data pertains to the reaction between A and B

S. No.	[A] mol L^{-1}	[B] mol L^{-1}	Rate Mol L^{-1} t^{-1}
1	1×10^{-2}	2×10^{-2}	2×10^{-4}
2	2×10^{-2}	2×10^{-2}	4×10^{-4}
3	2×10^{-2}	4×10^{-2}	8×10^{-4}

Which of the following inferences are drawn from the above data?

(1) Rate constant of the reaction is 10^{-4}

(2) Rate law of the reaction is k [A][B]

(3) Rate of reaction increases four times by doubling the concentration of each reactant.

Select the correct answer the codes given below:

a. 1 and 3 **b.** 2 and 3
c. 1 and 2 **d.** 1, 2 and 3

111. Which of the following statements are correct about half life period?

(1) time required for 99.9% completion of a reaction is 100 times the half life period.

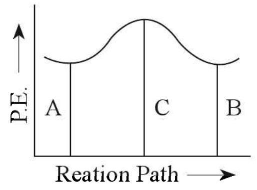
(2) time required for 75% completion of a 1st order reaction is double the half life of the reaction.

(3) average life = 1.44 times the half life for 1st order reaction

(4) it is proportional to initial concentration for zeroth order

a. 1, 2 and 3 **b.** 2, 3 and 4
c. 2 and 3 **d.** 3 and 4

112. With respect to the figure given below which of the following statement is correct



a. ΔE for the forward reaction is C – B
b. ΔE for the forward reaction is B – A
c. E (for reverse reaction) = C – A
d. $E_{\text{(Forward)}} > E_{\text{(Backward)}}$

113. The rate constant for the reaction,

$2N_2O_5 \rightarrow 4NO_2 + O_2$

is 3.0×10^{-4} s^{-1}. If start made with 1.0 mol L^{-1} of N_2O_5, calculate the rate of formation of NO_2 at the moment of the reaction when concentration of O_2 is 0.1 mol L^{-1}.

a. 1.2×10^{-4} mol L^{-1} s^{-1}
b. 3.6×10^{-4} mol L^{-1} s^{-1}
c. 9.6×10^{-4} mol L^{-1} s^{-1}
d. 4.8×10^{-4} mol L^{-1} s^{-1}

114. A gaseous compound decomposes on heating as per the following equation:

A(g) → B (g) + 2C (g). After 5 minutes and 20 seconds, the pressure increases by 96 mm Hg. If the rate constant for this first order reaction is 5.2×10^{-4} s^{-1}, the initial pressure of A is

a. 480 mm **b.** 376 mm
c. 696 mm **d.** 313 mm

115. The basic theory of Arrhenius equation is that

(1) Activation energy and pre exponential factors are always temperature independent

(2) The number of effective collisions is proportional to the number of molecule above a certain threshold energy.

(3) As the temperature increases, the number of molecules with energies exceeding the threshold energy increases.

(4) The rate constant in a function of temperature

a. 2, 3 and 4 **b.** 1, 2 and 3
c. 2 and 3 **d.** 1 and 3

116. For the two gaseous reactions, following data are given

$A \rightarrow B;\ k_1 = 10^{10}\, e^{-20000/T}$

$C \rightarrow D;\ k_2 = 10^{12}\, e^{-24606 \backslash T}$

The temperature at which k_1 becomes equal to k_2 is

a. 468 K **b.** 1000 K
c. 800 K **d.** 1200 K
e. 300 K

117. The bromination of acetone that occurs in acid solution is represented by this equation.

$CH_3COCH_3\,(aq) + Br_2\,(aq) \rightarrow$
$CH_3COCH_2Br\,(aq) + H^+\,(aq) + Br^-\,(aq)$

These kinetic data were obtained from given reaction concentrations.

Initial concentrations, (M)

$[CH_3COCH_3]$	$[Br_2]$	$[H^+]$
0.30	0.05	0.05
0.30	0.10	0.05
0.30	0.10	0.10
0.40	0.05	0.20

Initial rate, disappearance of Br_2, Ms^{-1}

5.7×10^{-5}
5.7×10^{-5}
1.2×10^{-4}
3.1×10^{-4}

Based on these data, the rate equation is:

a. Rate = k $[CH_3COCH_3]\,[Br_2][H^+]^2$
b. Rate = k $[CH_3COCH_3]\,[Br_2][H^+]$
c. Rate = k $[CH_3COCH_3]\,[H^+]$
d. Rate = k $[CH_3COCH_3]\,[Br_2]$

118. If the volume of the vessel in which the reaction $2NO + O_2 \rightarrow 2NO_2$ is occurring is diminished to 1/3 rd of its initial volume. The rate of the reaction will be increased by

a. 5 times **b.** 8 times
c. 27 times **d.** 35 times

119. When the reactants are A, B and C at one mole per litre each the rate equation is, rate = k $[A]^X\,[B]^{1/Y}\,[C]^{X/Y}$. The order of the reaction is

a. $X + \frac{(1+X)}{Y}$ **b.** $X - Y + \frac{X}{Y}$

c. $X + Y + \frac{X}{Y}$ **d.** $2(X + Y)$

120. For the mechanism,

$$A + B \underset{k_2}{\overset{k_1}{\longrightarrow}} C;\ C \xrightarrow{k_3} D;$$

The equilibrium step is fast.

The reaction rate, d/dt [D] is

a. $k_1 k_2 k_3 [A][B]$

b. $\frac{k_1 k_3}{k_2}[A]\,[B]$

c. $\frac{k_1 k_3 [A]\,[B]}{k_2 + k_3}$

d. $\frac{k_2 k_3}{k_1}[A]\,[B]$

Multiple Correct Answer Type Questions

121. For the reaction

$P + Q \rightarrow 2R + S$. Which of the following statement is/are correct?

a. Rate of disappearance of P = rate of appearance of S

b. Rate of disappearance of P = rate of disappearance of Q

c. Rate of disappearance of Q = 2 × rate of appearance of R

d. Rate of disappearance of Q = ½ × rate of appearance of R

122. In Arrhenius equation: $k = Ae^{-Ea/RT}$

a. The exponential factor has the units of reciprocal of temperature.

b. The pre-exponential factor has the units of rate of the reaction.

c. The pre-exponential factor has the units of rate constant of the reaction.

d. The exponential factor is a dimensionless quantity.

123. In a hypothetical reaction A → B, the activation energy for the forward and backward reaction are 15 and 9 kJ mol^{-1} respectively. The potential energy of X is 10 kJ mol^{-1}

a. Heat of reaction is 6 kJ.

b. The threshold energy of the reaction is 25 kJ

c. The potential energy of B is 16 kJ

d. Heat of reaction is 9 kJ.

124. Which of the following is/are correctly matched?

a. $\frac{k_{20} + T^\circ C}{kT^\circ C} = \frac{1}{4}$; Endothermic reaction

b. $\frac{k_{20} + T^\circ C}{kT^\circ C} = 4$; Exothermic reaction

c. $\frac{k_{10} + T^\circ C}{kT^\circ C} = 2$; Endothermic reaction

d. $\frac{k_{10} + T^\circ C}{kT^\circ C} = \frac{1}{2}$; Exothermic reaction

125. For a first order reaction

a. Plot between 't' and $\log_{10}(a - X)$ will be a parabola.

b. $dx/dt = k(a - x)$

c. $K = \frac{2.303}{t}\log_{10}\frac{a}{a - X}$.

d. $t_2 - t_1 = \frac{2.303}{k}\log_{10}\frac{a - X_1}{a - X_2}$

126. Which of the following statement is/are correct regarding a catalyst?

a. Decreases the activation energy.

b. Increases the average kinetic energy of reacting molecules.

c. Increases the frequency of collision of reacting.

d. Alters the reaction mechanism.

127. For a first order reaction, which is/are correct here?

a. The time taken for the completion of 75 % reaction is twice the $t_{1/2}$ of the reaction

b. The degree of dissociation is equal to $1 - e^{-kt}$.

c. A plot of reciprocal concentration of the reactant versus time gives a straight line

d. The pre-exponential factor in the Arrhenius equation has the dimension of time, T^{-1}.

128. Which of the following statement(s) is/are incorrect?

a. A plot of P versus 1/V is linear at constant temperature.

b. A plot of P versus 1/T is linear at constant volume.

c. A plot of log K_P versus 1/T is linear

d. A plot of log [x] versus time is linear for zero order reaction.

129. Which of the following are not the permitted values of molecularity?

a. 0

b. 2

c. 5

d. 1

130. Which of the following reaction is/are of the first order?

a. The acidic hydrolysis of ester.

b. The inversion of cane-sugar in the presence of an acid.

c. The decomposition of ammonium nitrate in an aqueous solution.

d. Formation of NH_3 by Haber's Process.

131. In which of the following ways does an activated complex differ from an ordinary molecule?

a. ΔH°_f is probably positive.

b. It is quite unstable and has no independent existence

c. The system has no vibrational character

d. The system has a greater vibrational character

132. Which of the following is/are experimentally determined?

a. Rate law

b. Order

c. Molecularity

d. Rate constant

133. For a reaction X → Y, the rate law is

$R = k[X]^2$, which of the following statements are correct?

a. K remains constant in the reaction at all temperatures.

b. The unit of rate constant Litre $mole^{-1}$ s^{-1}.

c. The reaction follows first order kinetics.

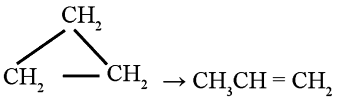
d. The $t_{1/2}$ of the reaction depends upon initial concentration of reactant.

134. Which of the following is/are examples of unimolecular reactions?

a. $2NO + Cl_2 \rightarrow 2NOCl$

b. $O_3 \rightarrow O_2 + O$

c.



d. $NO + O_3 \rightarrow NO_2 + O_2$

135. Two reactions X → Products and Y → products have rate constant k_X and k_Y at temperature T and activation energies E_X and E_Y respectively. If $k_X > k_Y$ and $E_X < E_Y$ and assuming that for both the reaction is same, then

a. At lower temperature $k_Y > k_X$

b. At higher temperature k_X will be greater than k_Y

c. At lower temperature k_X and k_Y will be close to each other in magnitude

d. At temperature rises, k_X and k_Y will be close to each other in magnitude

136. The calculation of the Arrhenius factor is based on the

a. Idea that the reactant species must come together, leading to the formation of the transition state which then transforms into the products

b. Idea that, for a reaction to take place, the reactant species must come together

c. Calculation of the order of thereaction

d. Calculation of the molecularity of the reaction

137. For producing the effective collisions, the colliding molecules must possess

a. Energy equal to activation energy

b. Energy equal to or greater than threshold energy

c. Proper orientation

d. Energy greater than threshold energy

138. In Arrhenius equation, $k = A \exp(-Ea/RT)$. A may be regarded as the rate constant at

a. Very high temperature

b. Very low temperature

c. High activation energy

d. Zero activation energy

139. The basic theory behind Arrhenius's equation is that

a. The activation energy and pre-exponential factor are always temperature-independent

b. The rate constant is a function of temperature

c. The number of effective collisions is proportional to the number of molecules above a certain threshold energy

d. As the temperature increases, so does the number of molecules with energies exceeding the threshold energy.

140. For a first order reaction, which of the following are not correct?

a. $t_{7/8} = 2\,t_{3/4}$

b. $t_{3/4} = 2\,t_{1/2}$

c. $t_{15/16} = 4\,t_{1/2}$

d. $t_{15/16} = 3\,t_{3/4}$

141. In the formation of sulphur trioxide by the contact process,

$2SO_2 + O_2 \rightleftharpoons 2SO_3$, the rate of reaction can be measured as $-d(SO_2) = 6.0 \times 10^{-4}\ \text{mol}\ L^{-1}\frac{s^{-1}}{dt}$.

Here the incorrect statements are

a. The rate of reaction expressed in terms of O_2 will be 4.0×10^{-4} mole L^{-1} s^{-1}

b. The rate of reaction expressed in terms of O_2 will be 6.0×10^{-6} mole L^{-1} s^{-1}

c. The rate of reaction expressed in terms of SO_3 will be 6.0×10^{-4} mol $L^{-1}s^{-1}$.

d. The rate of reaction expressed in terms of O_2 will be 3.0×10^{-4} mole L^{-1} s^{-1}

142. Which of the following expressions is/are not correct?

a. $\log k = \log A - \frac{Ea}{2.303\ RT}$.

b. $\text{In}\ A = \text{In}\ k + \frac{Ea}{RT}$.

c. $k\ Ae^{-RT/Ea}$

d. $\text{In}\ k = \text{In}\ A + Ea/RT$

143. Which of the following are examples of pseudo-unimolecular reactions?

a. $CH_3COCH_3 + H_2O \xrightarrow{OH^-} CH_3COOH + CH_3OH$

b. $C_2H_5COCl + H_2O \rightarrow C_2H_5COOH + HCl$

c. $CH_3COOCH_3 + H_2O \xrightarrow{OH^+} CH_3COOH + CH_3OH$

d. $C_{12}H_{22}O_{11} + H_2O \xrightarrow{OH^+} C_6H_{12}O_6 + C_6H_{12}O_6$

144. In hypothetical reaction

$X_2 + Y_2 \rightarrow 2XY$

Follows the mechanism as given below

$X_2 \rightleftharpoons X + X$ (fast reaction)

$X + Y_2 \rightarrow XY + Y$ (slow reaction)

$X + Y \rightarrow XY$ (fast reaction)

Here the correct statement is/are

a. Order of reaction is 3/2.

b. Molecularity is 2.

c. $R = k\ [X]\ [Y_2]$

d. Both molecularity and order = 3

145. Which of the following graphs for a first order reaction ($A \rightarrow$ Products) would be straight line?

a. Rate vs time

b. Rate vs [A]

c. Rate vs log [A]

d. log [A] vs time

146. The rate law for the reaction

$RCl + NaOH \rightarrow ROH + NaCl$

is given by Rate = k(RCl). The rate of the reaction is

a. Halved by reducing the concentration of RCl by one half.

b. Increased by increasing the temperature of the reaction.

c. Remains same by change in temperature.

d. Doubled by doubling the concentration of NaOH.

147. What happens when the temperature of a reaction system is increased by 10°C?

a. The effective number of collisions between the molecules possessing certain threshold energy increases atleast by 100%.

b. The total number of collisions between reacting molecules increases atleast by 100%

c. The activation energy of the reaction is increased

d. The total number of collisions between reacting molecules increases merely by 1-2%.

148. Which of the following statement about the Arrhenius equation is/are correct?

a. On raising temperature, rate constant of the reaction of greater activation energy increases less rapidly than that of the reaction of smaller activation energy.

b. The term $e^{-Ea/RT}$ represents the fraction of the molecules having energy in excess of threshold value.

c. The pre-exponential factor becomes equal to the rate constant of the reaction at extremely high temperature.

d. When the activation energy of the reaction is zero, the rate becomes independent of temperature

149. In Arrhenius equation: $K = Ae^{-Ea/RT}$

a. The pre-exponential factor has the units of rate constant of the reaction

b. The exponential factor is a dimensionless quantity

c. The exponential factor has the units of reciprocal of temperatures

d. The pre-exponential factor has the units of rate of the reaction

150. Two reactions A → Products and B → Products have rate constants k_A and k_B at temperature T and activation energies E_A and E_B respectively. If $k_A > k_B$ and $E_A < E_B$ and assuming that A for both the reactions is same, then:

a. At lower temperature k_A and k_B will be close to each other in magnitude

b. At lower temperature $k_B > k_A$

c. At higher temperature k_A will be greater than k_B

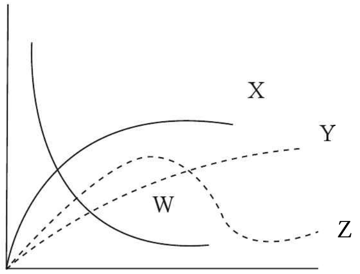
d. As temperature rises, k_A and k_B will be close to each other in magnitude

Linked-Comprehension Type Questions

Comprehension 1

The mathematical representation of a reaction is given by rate law which is experimentally determined. order of a reaction w.r.t. any reactant is the power of it's concentration shown by the rate law equation. Rate constant represents the proportionality factor in rate law equation. Both order of reaction and rate constant are determined from rate law equation. Molecularity is defined only for an elementary reaction. Molecularity can be 1, 2, 3 while order can be 0 to 3 or in fraction also.

151. For the reaction $P + Q \rightleftharpoons R + S$. The variation of the concentration of the products is given by the curve



152. The rate constant (k) for a reaction 2x + y → product was observed to be 2.64×10^{-6} litre $mol^{-1}\ S^{-1}$ after 20 sec, 2.78×10^{-6} litre mol^{-1} after 35 sec and 2.54×10^{-6} litre $mol^{-1}\ S^{-1}$ after 50 second. The order of the reaction is

a. Zero
b. I^{st}
c. II^{nd} order
d. III^{rd} order

153. 2 P + 3 Q + R → product

If for this reaction Rate (R) = K $[P]^{-1/2}$ $[Q]^1$ $[R]^{1/2}$

The order of this reaction is

a. Zero
b. Ist
c. IInd
d. 3/2

Comprehension 2

For a reaction shown as

$m_1 A + m_2 B \rightarrow n_1 C + n_2 D$

The rate of reaction in terms of stoichiometric coefficients of reactants and products can be given as

$$\frac{dx}{dt} = \frac{-1\ d\,(A)}{m_1\ dt} = \frac{-1\ d(B)}{m_2 dt} = \frac{1\ d(C)}{n_1\ dt} = \frac{1\ d\,(D)}{n_2\ dt}$$

154. Observe the reaction given below

$A + 2B \rightarrow 3C$
g g g

If the rate of this reaction $-\frac{dA}{dt}$ is 2×10^{-3} mol lit^{-1} min^{-1} than the value of $\frac{dB}{dt}$ and $\frac{dC}{dt}$ will be respectively

a. 1×10^{-3}, $2/3 \times 10^{-3}$

b. 4×10^{-3}, 6×10^{-3}

c. 6×10^{-3}, 4×10^{-3}

d. $2/3 \times 10^{-3}$, 1×10^{-3}

155. For the reaction $2NH_3 \rightarrow N_2 + 3H_2$ it is found that $-\frac{dNH_3}{dt} = K_1\,(NH_3)$

$\frac{dN_2}{dt} = K_2\,[NH_3]$,

$\frac{dH_2}{dt} = K_3\,[NH_3]$

the correct relation between K_1, K_2 and K_3 can be given as ?

a. $3K_1 = 2K_2 = 6K_3$

b. $6K_1 = 3K_2 = 2K_3$

c. $K_1 = K_2 = K_3$

d. $2K_1 = 3K_2 = 6K_3$

156. For the reaction W + X →Y +Z , the rate (dx/dt) when plotted against time 't' gives a straight line parallel to time axis. The order and rate for this reaction are

a. O, K
b. 1, K+1
b. II, K+1
d. K, K+1

157. For this reaction $X^- + OH^- \rightarrow X^- + XO^-$ in an aqueons medium,the rate of the reaction is given as

$$\frac{(d(XO^-)}{dt} = K\,\frac{[X^-][XO^-]}{[OH^-]}$$

The overall order for this reaction is

a. Zero
b. 1
c. –1
d. ½

Comprehension 3

Arrhenius equation describes the effect of temperature on rate constant as0 K=Ae–Ea/RT

Here Ea represents activation energy, A represents frequency factor. The equation clearly indicates that an increase of temperature or lowering of Ea leads to increase in rate of reaction. According to collision theory steric factor ‘P’ is equally important and contributes to effective collisions. Now the modified form of Arrhenius equation is given as $K= PZ_{AB}\, e^{-Ea/RT}$

158. The activation energy for a simple chemical reaction $X \rightarrow Y$ is Ea for forward direction. The value of Ea for backword direction may be

a. –Ea **b.** 2Ea

c. > or < Ea **d.** Zero

159. For the following reaction at a particular temperature which takes place as-follows

$2N_2O_5 \rightarrow 4NO_2 + O_2$

$2NO_2 + ½\ O2 \rightarrow N_2O_5$

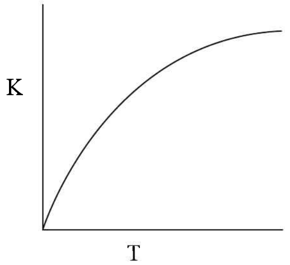
The value of activation energies are $E_1$and E_2 respectively then

a. $E_1>E_2$ **b.** $E_1=2E_2$

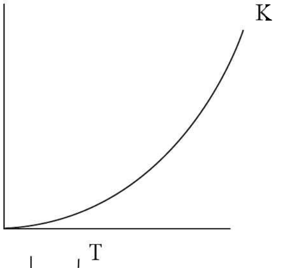
c. $2E_1=E_2$ **d.** $E_1<E_2$

160. Which of the given graph represents the variation of rate constant (K) verses temperature(T)?

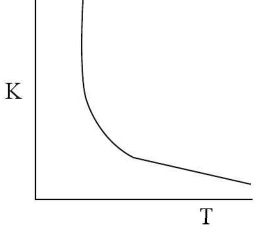
a.



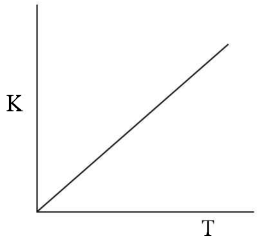
b.



c.



d.



Comprehension 4

In a hypothetical reaction given below

$2XY_2\,(aq) + 2Z^-\,(aq) \rightarrow$

(Excess)

$2XY_2^-\,(aq) + Z_2\,(aq)$

XY_2 oxidizes Z^- ion in aqueous solution to Z_2 and gets reduced to XY_2^-.

The order of the reaction with respect to XY_2 as concentration of Z^- is essentially constant.

Rate = k $[XY_2]^m$

Given below the time and concentration of XY_2 taken

Time (s)	(XY_2) M
0.00	4.75×10^{-4}
1.00	4.30×10^{-4}
2.00	3.83×10^{-4}

161. The order with respect to XY_2 is

a. 0 **b.** 1

c. 2 **d.** 3

162. The rate constant for this reaction is

a. 0.02 **b.** 0.01

c. 0.2 **d.** 0.1

163. The half life of the reaction (in seconds) is

a. 2.39 **b.** 13.35

c. 6.93 **d.** 1 9.63

Assertion-Reason Type Questions

In the following question two statements Assertion (A) and Reason (R) are given Mark.

a. If A and R both are correct and R is the correct explanation of A;

b. If A and R both are correct but R is not the correct explanation of A;

c. A is true but R is false;

d. A is false but R is true,

e. A and R both are false.

164. **(A)**: Order of reaction is an experimental property and irrespective of the fact whether the reaction is elementary or complicated, it is the sum of the powers of the concentration terms appearing in the rate law that is, experimentally observed rate law.

(R): Order of reaction may change with change in experimental conditions.

165. **(A)**: Hydrolysis of methyl acetate in aqueous solution is a pseudo first order reaction.

(R): In this reaction concentration of H_2O remains nearly constant during the course of the reaction.

166. **(A)**: A catalyst does not alter the heat of reaction.

(R): Catalyst increases the rate of reaction.

167. **(A)**: In first order reaction $t_{1/2}$ is independent of initial concentration.

(R): The unit of K is $time^{-1}$.

168. **(A)**: If order with respect to species involved in any reaction is not equals to the stoichiometric coefficient of that species in the reaction then reaction must be an elementary reaction.

(R): In an elementary reaction the order with respect to species involved is equal to the stoichiometric coefficients.

169. **(A)**: If temperature does not affect the rate of reaction, Ea = 0

(R): Lesser the activation energy, slower will be the reaction.

170. **(A)**: The rate constant increases exponentially with the increase in temperature.

(R): With the rise in temperature, the average kinetic energy of the molecules increases.

171. **(A)**: Arrhenius equation explains the temperature dependence of rate of a chemical reaction.

(R): Plots of log K vs 1/T are linear and the energy of activation is obtained from such plots.

172. **(A)**: $2FeCl_3 + SnCl_2 \rightarrow FeCl_2 + SnCl_4$ is a 3rd order reaction

(R): The rate constant for third order reaction has unit $L^2\ mol^{-2}\ s^{-1}$.

173. **(A)**: $NO_2 + CO \rightarrow CO_2 + NO$

Rate = k $[NO_2]^2$

The rate is independent of concentration of CO.

(R): The rate does not depend upon [CO] because it is involved in fast step.

174. **(A)**: In order for molecules to interact, they must approach each other so closely to colloid with each other

(R): Rearrangement of chemical bonds occur during collision. They must collide each other and rearrangement of chemical bonds occur during collision)

175. **(A)**: The rate of a reaction normally increases by a factor of 2 or 3 for every 10^{oC} rise in temperature.

(R): Increase in temperature increases the number of collisions.

176. **(A)**: A catalyst enhances the rate of reaction.

(R) : The energy of activation of the reaction is lowered in presence of a catalyst.

177. **(A)**: In rate laws, the exponents for concentration do not necessarily match the stoichiometric coefficients.

(R): It is the mechanism and not the balanced chemical equation for the overall change that governs the reaction rate.

178. **(A)**: In rate laws, unlike in the expression for equilibrium constants, the exponents for concentrations do not necessarily match stoichiometric coefficients.

(R): It is the mechanism and not the balanced chemical equation for the overall change the governs the reaction rate.

Reaction rate is experimentally quantity and not necessary depends on stoichiometric coefficients

179. **(A)**: Order can be different from molecularity of a reaction.

(R): Slow step is the rate determining step and may involve lesser number of reactants.

180. **(A)**: For the hydrogen halogen photochemical reaction, the quantum yield for the formation of HBr, is lower than that of HCl.

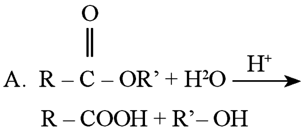
(R): $Br + H_2 \rightarrow HBr + H$ has higher activation energy than $Cl + H_2 \rightarrow HCl + H$

Matrix-Match Type Questions

181. Match the following:

List I	**List II**
A. Half life of zero order reaction	(p) a/2k
B. Half life of first order reaction	(q) 0.693/k
C. Temperature coefficient	(r) 1/ka
D. Half life of second order reaction	(s) 2 – 3

182. Match the following:

List I	**List II**
A.  $R-\overset{\overset{O}{\|}}{C}-OR' + H^2O \xrightarrow{H^+} R-COOH + R'-OH$	(p) Zero order
B. $H^2 + Cl^2 \xrightarrow{hv} 2HCl$	(q) First order
C. $R-Cl + O-H \rightarrow R-OH + Cl^-$	(r) Second order
D. $C_{12}H_{22}O_{11} + H.OH \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$	(s) Pseudo unimolecular

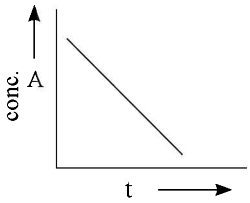
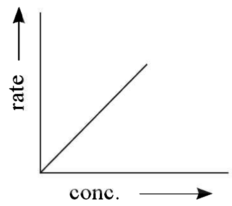
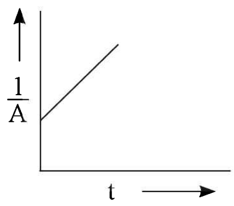
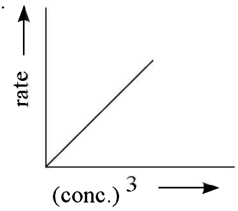
183. Match the following:

List I	**List II**
A. Temperature coefficient	(p) Zero
B. Order	(q) Between 2 – 3
C. Ea for ionic reactants	(r) First
D. Radioactive disintegration	(s) > 3

184. Match the following:

List I	**List II**
1. zero order reaction	(p) mole-^{1} Lt sec-^{1}
2. first order reaction	(q) mole-^{2} Lt2 sec-^{1}
3. second order reaction	(r) mole Lt-^{1} sec-^{1}
4. third order reaction	(s) sec-^{1}

185. Match the following:

List I	**List II**
A. 	(p) 1
B. 	(q) 2
C. 	(r) 3
D. 	(s) 0

186. Match the following:

List I (Reactions)	**List II**
A. $2N_2O_5\,(g) \rightarrow 4NO_2\,(g) + O_{2(g)}$	(p) Titration of a liquid of reaction mixture with alkali
B. $CH_3COOC_2H_5\,(aq) + H_2O \xrightarrow{[H^+]} CH_3COOH\,(aq) + C_2H_5OH\,(aq)$	(q) Measurement of pressure of reaction mixture at constant V and T
C. $C_6H_5N = N - Cl\,(aq) \rightarrow C_6H_5Cl(l) + N_2(g)$	(r) Measurement of optical activity
D. $C_{12}H_{22}O_{11}\,(aq) + H_2O \xrightarrow{[H^+]} C_6H_{12}O_6\,(aq) + C_6H_{12}O_6\,(aq)$ Glucose Fructose	(s) Measurement of volume of gas at constant P and T.

187. Match the following:

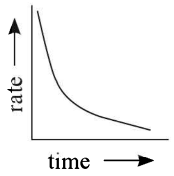
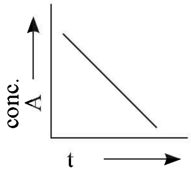
(Here a = Initial concentration of the reactant, p = Initial pressure of the reactant)

List I	**List II**
A. t ½ = constant	(p) Zero order
B. t ½ α a	(q) First order
C. t ½ α 1/a	(r) Second order
D. t ½ α p^{-1}	(s) Pseudo first order

188. Match the following:

List I	**List II**
A $NH_4NO_2 \rightarrow N_2 + 2H_2O$	(p) Zero order
B. $H_2 + Cl_2 \rightarrow 2HCl$	(q) Ist order
C. $C_{12}H_{22}O_{11}$ (aq) + $H_2O \rightarrow$ $C_6H_{12}O_6$ (aq) + $C_6H_{12}O_6$ (aq)	(r) Pseudo Ist order
D. $2HI \rightarrow H_2 + I_2$	(s) Photo chemical reaction

189. Match the following:

List I	**List II**
A. $2NH_3 \rightarrow N_2 + 3H_2$	(p) t1/2 = X min as a constant temperature any time of the reaction.
B. $2N_2O_5 \rightarrow 4NO_2 + O_2$	(q) 
C. $CH_3COOC_2H_5 + H_2O \rightarrow$ $CH_3COOH + C_2H_5OH$	(r) 
D. $C_6H_5COOC_2H_5 \rightarrow$ + NaOH $\rightarrow C_6H_5COONa$ + C_2H_5OH	(s) $K = Ae^{-}$ Ea/RT

190. Match the following:

For the reaction

$X + Y \rightarrow Z$

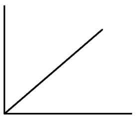
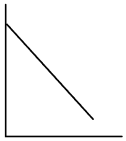
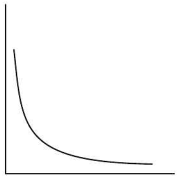
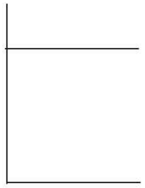
If the graps given in list I may be of these types

(i) Concⁿ vs time (x - axis)

(ii) t ½ vs Initial concn (a) (x- axis)

(iii) Rate (–dx) vs time (x- axis)

(iv) $\left(\frac{Co - Ct}{C_t}\right)^{dt}$ vs time (x- axis)

List I	**List II**
A. 	(p) Zero order
B. 	(q) I^{st} order
C. 	(r) II^{nd} order
D. 	(s) Pseudo unimolecular

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191. The rate law has the form; Rate = $k[A][B]^{3/2}$, can the reaction be an elementary process?

a. yes

b. no

c. may be yes or no

d. can not be predicted

[IIT 1997]

192. The rate constant of a reaction is given by In k (sec^{-1}) = 14.34 – (1.25 × 10^4)/T

What will be the energy of activation?

a. 24.83 kcal mol^{-1}

b. 49.66 kcal mol^{-1}

c. 12.42 kcal/mol

d. none

[IIT 1997]

193. For a first order reaction,

a. The degree of dissociation is equal to $(1 - e^{-kt})$

b. The pre-exponential factor in the Arrhenius equation has the dimensions of time T^{-1}.

c. The time taken for the completion of 75 % reaction is thrice the t ½ of the reaction.

d. both (a) and (b)

[IIT 1998]

194. The rate law for the reaction

$RCl + NaOH (aq) \rightarrow ROH + NaCl$
is given by

Rate = k[RCl]. The rate of the reaction will be

a. Doubled on doubling the concentration of sodium hydroxide

b. Halved on reducing the concentration of alkyl halide to one half

c. Decreased on increasing the temperature of reaction

d. Unaffected by increasing the temperature of the reaction.

[IIT 1998]

195. In the above equation, what is the value of Arrhenius factor?

a. 3×10^6 **b.** 6.3×10^9

c. 5.42×10^{13} **d.** 5.42×10^{10}

[IIT 1998]

196. The rate constant of a reaction is $1.5 \times 10^7\ s^{-1}$ at 50°C and $4.5 \times 10^7\ s^{-1}$ at 100°C. What is the value of activation energy?

a. 2.2×10^3 J mol^{-1}

b. 2300 J mol^{-1}

c. 2.2×10^4 J mol^{-1}

d. 220 J mol^{-1}

[IIT 1998]

197. The rate constant for an isomerization reaction A → B, is 4.5×10^{-3} min^{-1}. If the initial concentration of A is 1 M. Calculate the rate of reaction after 1 hour.

a. 0.34354 M min^{-1}

b. 0.034354 M min^{-1}

c. 0.0034354 M min^{-1}

d. 0.0003454 M min^{-1}

[IIT 1999]

198. The rate constant for the reaction,

$2N_2O_5 \rightarrow 4NO_2 + O_2$

is $3.0 \times 10^{-5}\ s^{-1}$. If the rate is 2.40×10^{-5} mol litre^{-1} s^{-1}, then the concentration of N_2O_5 (in mol litre^{-1}) is

a. 1.4 **b.** 1.2

c. 0.04 **d.** 0.8

[IIT 2000]

199. If 'I' is the intensity of absorbed light and 'C' is the concentration of AB for the photochemical process

$AB + h\nu \rightarrow AB^*$, the rate of formation of AB^* is directly proportional to

a. C **b.** I

c. I^2 **d.** C.I.

[IIT 2001]

200. Consider the chemical reaction,

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

The rate of this reaction can be expressed in terms of time derivatives of concentration of N_2 (g), H_2 (g) or NH_3 (g). Identify the correct relationship amongst the rate expressions.

a. rate = $-d[N_2]/dt = -1/3\ d[H_2]/dt = ½\ d[NH_3]/dt$

b. rate = $-d[N_2]/dt = -3\ d[H_2]/dt = 2\ d[NH_3]/dt$

c. rate = $-d[N_2]/dt = -1/3\ d[H_2]/dt = 2d[NH_3]/dt$

d. rate = $-d[N_2]/dt = -d[H_2]/dt = d[NH_3]/dt$

[IIT 2002]

201. In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^4 sec. The rate constant of reaction in sec^{-1} is

a. 2×10^4 **b.** 3.45×10^{-5}

c. 1.386×10^{-4} **d.** 2×10^{-4}

[IIT 2003]

202. In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^4 sec. The rate constant of reaction in sec^{-1} is

a. 2×10^4 **b.** 3.45×10^{-5}

c. 1.386×10^{-4} **d.** 2×10^{-4}

[IIT 2003]

203. The reaction X → product follows first order kinetics. In 40 minutes, the concentration of X changes from 0.1 M to 0.025 M, then the rate of reaction when concentration of X is 0.01 M is

a. 3.47×10^{-5} M/min

b. 1.73×10^{-4} M/min

c. 1.73×10^{-5} M/min

d. 3.47×10^{-4} M/min

[IIT 2004]

204. Which of the following is incorrect about order of reaction?

a. it is calculated experimentally

b. it is sum of powers of concentration in rate law expression

c. the order of reaction cannot be fractional

d. there is not necessarily a connection between order and stoichiometry of a reaction.

[IIT 2005]

205. Consider a reaction aG + bH → Products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is

a. 0　　**b.** 1

c. 2　　**d.** 3

[IIT 2007]

206. For a first order reaction A → P, the temperature (T) dependent rate constant (k) was found to follow the equation

$\log k = -(2000)\ i/T + 6.0$. The pre-exponential factor A and the activation energy Ea, respectively, are

a. $1.0 \times 10^6\ s^{-1}$ and 9.2 kJ mol^{-1}

b. 6.0 s^{-1} and 16.6 kJ mol^{-1}

c. $1.0 \times 10^6\ s^{-1}$ and 16.6 kJ mol^{-1}

d. $1.0 \times 10^6\ s^{-1}$ and 38.3 kJ mol^{-1}

[IIT 2009]

ANSWERS

Straight Objective Type Questions

1. c	**2.** b	**3** a	**4.** b	**5.** c	**6.** b	**7.** c	**8.** c
9. b	**10.** d	**11.** d	**12.** d	**13.** a	**14.** a	**15.** b	**16.** c
17. c	**18.** b	**19.** b	**20.** d	**21.** a	**22.** c	**23.** b	**24.** a
25. b	**26.** a	**27.** c	**28.** b	**29.** b	**30.** c	**31.** a	**32.** b
33. a	**34.** d	**35.** c	**36.** b	**37.** b	**38.** d	**39.** a	**40.** b
41. d	**42.** b	**43.** a	**44.** d	**45.** d	**46.** d	**47.** a	**48.** b
49. c	**50.** d	**51.** b	**52.** c	**53.** b	**54.** a	**55.** a	**56.** d
57. c	**58.** b	**59.** d	**60.** a	**61.** d	**62.** a	**63.** b	**64.** c
65. d	**66.** a	**67.** c	**68.** b	**69.** c	**70.** d	**71.** a	**72.** c
73. a	**74.** a	**75.** b	**76.** d	**77.** b	**78.** c	**79.** d	**80.** c

Brainteasers Objective Type Questions

81. c	**82.** a	**83.** b	**84.** b	**85.** b	**86.** a	**87.** c	**88.** d
89. a	**90.** c	**91.** a	**92.** d	**93.** c	**94.** a	**95.** c	**96.** b
97. c	**98.** a	**99.** b	**100.** a	**101.** b	**102.** d	**103.** c	**104.** d
105. a	**106.** b	**107.** c	**108.** d	**109.** d	**110.** b	**111.** b	**112.** b
113. c	**114.** d	**115.** a	**116.** b	**117.** c	**118.** c	**119.** a	**120.** b

Multiple Correct Answer Type Questions

121. a, b	**122.** a, d	**123.** a, b, d	**124.** c, d	**125.** b, c	**126.** c, d	**127.** b, c, d
128. a, d	**129.** a, b, d	**130.** b, d	**131.** a, c	**132.** a, b, c	**133.** b, d	**134.** a, b, d
135. b, d	**136.** b, c	**137.** b, d	**138.** a, b	**139.** b, c	**140.** a, d	**141.** b, c, d
142. a, d	**143.** a, b	**144.** c, d	**145.** b, c, d	**146.** a, b	**147.** b, d	**148.** b, c, d
149. a, b	**150.** c, d					

Matrix-Match Type Questions

181. a-(p), b-(q), c-(s), d-(r) **182.** a-(q,s), b-(p), c-(r), d-(q, s)

183. a-(q), b-(p, r, s), c-(p), d-(r) **184.** a-(r), b-(s), c-(p), d-(q)

185. a-(s), b-(p), c-(q), d-(r) **186.** a-(q), b-(p), c-(s), d-(r)

187. a-(q, s), b-(p), c-(p, r), d-(p, r) **188.** a (q), b (p, s) , c (q, r) d (p)

189. a (r), b (p, q, s), c (p, q, s), d (p, q) **190.** a (p, r), b (p , c (q, s) , d (p, q, s)

Assertion Reason Type Questions

164. b **165.** a **166.** b **167.** a **168.** d **169.** c **170.** b **171.** b

172. b **173.** a **174.** a **175.** b **176.** a **177.** a **178.** a **179.** a **180.** a

Linked-Comprehension Type Questions

Comprehension 1

151. b **152.** c **153.** b

Comprehension 2

154. b **155.** b **156.** A **157.** A

Comprehension 3

158. c **159.** b **160.** b

Comprehension 4

161. b **162.** d **163.** c

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191. b **192.** a **193.** d **194.** b

195. d **196.** c **197.** c **198.** d

199. b **200.** a **201.** c **202.** c

203. d **204.** c **205.** d **206.** d

Hints and Explanations

1. It is a characteristics constant of a particular reaction at a given temperature. It does not depend upon initial concentration of the reactants, time of reaction and extent of reaction.

3. k depends upon temperature.

6. $\text{Rate} = -\frac{1}{3}\frac{d(A)}{dt} = \frac{1}{2}\frac{d(B)}{dt}$

$= -\frac{2}{3}\frac{d(A)}{dt}$

10. Catalyst lowers the activation energy barrier and thus it shortens the time to reach equilibrium.

14. $\text{Order} = \frac{1}{2} + 1/3 + \frac{1}{4} = \frac{6+4+3}{12}$

$= 13/12$

16. From the units of rate constant (10^{-3} min^{-1}) it is found that it is a first order reaction.

$r = k\,[\text{conc.}]$

$= 10^{-3} \times 0.2$

$= 0.0002 \text{ mol dm}^{-3} \text{ min}^{-1}$

17. For an endothermic reaction, Ea will be more than ΔH while for an exothermic reaction, Ea will be less than ΔH.

18. When the volume is reduced to ¼ th, concentration becomes four times. Since it is a second order reaction, so rate become 16 times.

19. $k = Ae^{-Ea/RT}$ (Arrhenius equation)

when $T \to \infty$

$k = A\,e^0$, or $k = A$

Thus $k = 6 \times 10^{14}\ \text{s}^{-1}$

21. $r = k\,[A] = 60 \times 10^{-4} \times 0.01$

$$= 60 \times 10^{-4} \times \frac{1}{10^2}$$

$$= 60 \times 10^{-6} \text{ mol l}^{-1} \text{ min}^{-1}$$

22. The rate of reaction is given as

$$-\frac{d[A]}{2\,dt} = -\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = \frac{d[D]}{dt}$$

25. Rate = k $[N_2O_5]^1$

$[N_2O_5]^1$ = Rate/k

$$= \frac{1.02 \times 10^{-4}}{3.4 \times 10^{-5}} = 3$$

29. For a first order kinetics,

$$k = \frac{2.303}{t}\log_{10}\frac{a}{a-x}\,.$$

$$\text{At } t_{1/2},\ k = \frac{2.303}{t_{12}}\log_{10}\frac{a}{a - a/2}\,.$$

$$t_{1/2} = \frac{2.303}{k}\log_{10} 2 = \frac{\mathrm{In}\,2}{k}$$

84. From expt 2 and 3 it is clear that when (A) is doubled keeping (B) constant, rate becomes four times, thus r α $[A]^2$

Now rate equation is $r = k\,[A]^2\,[B]^n$.

From expt. 1 and 2

$$5 \times 10^{-4} = k\,[2.5 \times 10^{-4}]^2\,[3 \times 10^{-5}]^n \quad \ldots\ldots\ldots\ldots\ldots (1)$$

$$4 \times 10^{-3} = k\,[5 \times 10^{-4}]^2\,[6 \times 10^{-5}]^n \quad \ldots\ldots\ldots\ldots\ldots (2)$$

divide 2 and 1

$$\frac{4 \times 10^{-3}}{5 \times 10^{-4}} = \frac{k\,[5 \times 10^{-4}]^2\,[6 \times 10^{-5}]^n}{k\,[2.5 \times 10^{-4}]^2\,[3 \times 10^{-5}]^n}$$

$8 = 2^2.\ 2^n$

$2^n = 8/4 = 2^1$

$n = 1$

$r = k\,[A]^2\,[B]^1$

89. At 450°C,

$$k = \frac{0.693}{t\,½} = \frac{0.693}{10.17 \text{ min}}$$

$= 0.0681 \text{ min}^{-1}$

Now for 75 % decomposition

$x = 75\ \%$ of $a = 0.75\ a$

$$t = \frac{2.303}{k}\log\frac{a}{a-x}$$

$$= \frac{2.303}{0.0681 \text{ min}^{-1}}\log\frac{a}{a - 0.75a}$$

$$= \frac{2.303}{0.0681 \text{ min}^{-1}}\log\frac{1}{0.25}$$

$= 20.39$ min

92. Rate = k[A] (It is a first order reaction)

$$k = \frac{r}{[A]} = \frac{2.0 \times 10^{-5}\text{ Ms}^{-1}}{0.01\text{ M}}$$

$$= \frac{2 \times 10^{-5}\text{ s}^{-1}}{10^{-2}} = 2 \times 10^{-3}\text{ s}^{-1}$$

$$t\,½ = \frac{0.693}{k} = \frac{0.\,693}{2 \times 10^{-3}}\text{ s}$$

$= 346.5$ s $= 347$ s

94. As it is the slowest step so it is rate determining step.

$r = K\,[H_2\,(g)]\,[\,ICl\,(g)]$

96. For a first order reaction,

$$k = \frac{2.303}{t}\ \log_{10}\frac{a}{a-x}\,.$$

$$k = \frac{2.303}{60}\ \log_{10}\frac{100}{40} = \frac{2.303}{60}\text{x}\log_{10} 2.5$$

$= 0.0153$

$$t_{1/2} = \frac{2.303}{k}\ \log_{10}\frac{100}{50} = \frac{2.303}{0.0153} \times \log_{10} 2$$

$= 45.31$ min.

101. The order of an elementary reaction is determined experimentally and therefore statement two is not correct.

105. Pseudo unimolecular reactions are in presence of one or more reactants in excess. Usually such reactions are conducted in solvents, which are themselves one of the reactants.

107. Statement (1) is not correct because sum of powers raised to concentration terms in the rate law denotes the order of reaction, which is 1 + 1 = 2 and not equal to unity.

108. The stoichiometric coefficients of reaction has no relation to the order of reaction.

110. According to the rate law

Rate = k [A] [B]

From first experiment we have

$2 \times 10^{-4} = k\,(1 \times 10^{-2})\,(2 \times 10^{-2})$

$k = 2$

The rate law:Rate = k [A][B] shows that rate of reaction becomes four times the original rate, when the concentration of each reactant is doubled.

113. As mol L^{-1} of N_2O_5 reacted $= 2 \times 0.1 = 0.2$

So $[N_2O_5]$ left $= 1.0 - 0.2 = 0.8$ mol L^{-1}

Rate of reaction $= k \times [N_2O_5]$

$= 3.0 \times 10^{-4} \times 0.8 = 2.4 \times 10^{-4}$ mol L^{-1} s^{-1}.

Rate of formation of $NO_2 = 4 \times 2.4 \times 10^{-4}$

$= 9.6 \times 10^{-4}$ mol L^{-1} s^{-1}.

114. $A\ (g) \rightarrow B\ (g) + 2C\ (g)$

At 320 seconds, x moles of A decomposes giving x moles of B and 2x moles of C.

Total number of moles = $a - x + x + 2x$

$= a + 2x$

So number of moles has increased by 2x.

$2x = 96$ mm

$x = 48$ mm.

For a first order reaction,

$$5.2 \times 10^{-4} = \frac{2.303}{320} \log_{10} \frac{a}{a - 48} \ .$$

Solving, $\log \frac{a}{a-48} = 0.07225$

Solving,

$a = 313$ mm.

116. $A \rightarrow B;\ k_1 = 10^{10}\ e^{-20000/T}$

$C \rightarrow D;\ k_2 = 10^{12}\ e^{-24606 \backslash T}$

When $k_1 = k_2$

$10^{10}\ e^{-20000}/T = 10^{12}\ e^{-24606/}T$

$e^{-4606}/T = 100$

$$\frac{4606}{T} = 2.303 \log 100$$

$$\frac{4606}{T} = 2.303 \times 2$$

As , $T = \frac{4606}{2.303 \times 2} = 1000$ K

117. According to the given data, when concentration of Br_2 is doubled, the initial rate of disappearance of Br_2 remains unaffected. So order of reaction with respect to Br_2 is zero. The rate law for the reaction will be:

$k[CH_3COCH_3]\ [H^+]$

118. For a given reaction –

$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$

Rate of reaction = $k\ [NO]^2\ [O_2]$

Rate of reaction directly proportional to concentration of the compound or inversely proportional to the volume of the vessel.

that is, $C\ \alpha\ \frac{n}{V}$

If volume of vessel is reduced by 1/3rd of its initial value, then concentration of compound is increased by 3 times and consequently the rate of reaction by 27 times.

119. When the reactants are A, B and C at one mole per litre each the rate equation is, rate = $k\ [A]^X\ [B]^{1/Y}\ [C]^{X/Y}$. The order of the reaction is

(A) $X + \frac{(1 + X)}{Y}$ (B) $X - Y + \frac{X}{Y}$

(C) $X + Y + \frac{X}{Y}$ (D) $2(X + Y)$

rate = $k\ [A]^X\ [B]^{1/Y}\ [C]^{X/Y}$

$$\text{order} = X + \frac{1}{Y} + \frac{X}{Y}$$

$$= X + \frac{(1 + X)}{Y}$$

120. $\frac{[C]}{[A][B]} = \frac{k_1}{k_2}$ (equilibrium constant)

So $[C] = \frac{k_1\ [A][B]}{k_2}$ .... (1)

$\frac{d[D]}{dt} = k_3[C]$ .... (2)

From (1) and (2)

$$\frac{d[D]}{dt} = \frac{k_3 \cdot k_1}{k_2} [A][B]$$

174. They must collide each other and rearrangement of chemical bonds occur during collision.

178. Reaction rate is experimentally quantity and not necessarily depends on stoichiometric coefficients.

192. Compare with the equation

$$\text{In } k = \text{In } A - \frac{Ea}{RT}$$

Thus, $\frac{Ea}{R} = 1.25 \times 10^4$

and $Ea = R \times 1.25 \times 10^4$

$$Ea = \frac{1.98}{1000} \times 1.25 \times 10^4$$

$Ea = 24.75$ Kcal mol^{-1}

194. It is a pseudo first order reaction. Since $r\ \infty$ (RCl), so rate is halved when the conc. of alkyl halide is halved.

195. $\log k = \log A - \frac{Ea}{2.303\ RT}$

$$\log 1.5 \times 10^7 = \log A - \frac{22011}{2.303 \times 8.314}$$

$7 + \log 1.5 = \log A - 3.5591$

$\log A - \log 1.5 = 10.5591$

$$\log \frac{A}{1.5\ s^{-1}} = 10.5591$$

A =Antilog(10.5591)=3.615x 10^{10}

$1.5\ s^{-1}$

Now, $A = 3.615 \times 10^{10} \times 1.5$

$= 5.4225 \times 10^{10} s^{-1}$

196. $k_1 = 1.5 \times 10^7\ s^{-1}, k_2 = 4.5 \times 10^7\ s^{-1}$

$T_1 = 50 + 273 = 323\ K,$

$T_2 = 100 + 273 = 373\ K$

$$\log \frac{k_2}{k_2} = \frac{Ea}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log \frac{4.5 \times 10^7}{1.5 \times 10^7} = \frac{Ea}{2.303 \times 8.31}$$

$$\left(4 \frac{373 - 323}{373 \times 323}\right)$$

$$\log 3 = \frac{Ea \times 50}{19.147 \times 373 \times 323}$$

$$\text{or } 0.4771 = \frac{Ea \times 50}{19.147 \times 373 \times 323}$$

on solving, Ea = 22.11 J/mole

$\approx 2.2 \times 10^4$ J/mole

197. $a = 1\ M, t = 60\ min, k = 4.5 \times 10^{-3}\ min^{-1}$

$a - x = ?$

$$k = \frac{2.303}{t} \log \frac{a}{a - x}\ .$$

$$\log \frac{a}{a - x} = \frac{kt}{2.303} = \frac{4.5 \times 10^{-3} \times 60}{2.303}$$

$$\text{or } \log \frac{a}{a - x} = 0.1172$$

$$\frac{a}{a - x} = \text{Antilog } (0.1172) = 1.31$$

$$\frac{1}{a - x} = 1.31$$

$$a - x = \frac{1}{1.31} = 0.7633$$

After one hour, conc. of A is $(a - x) = 0.7633$

Rate of reaction after 1 hour = k (conc.)

$= 4.5 \times 10^{-3} \times 0.7633$

$= 3.43 \times 10^{-3}\ M\ min^{-1}$

198. $r = k\ [N_2O_5]^1$

$$[N_2O_5] = \frac{r}{k} = \frac{2.40 \times 10^{-5}}{3 \times 10^{-5}} = 0.8$$

199. The rate of formation of AB^* is directly proportional to the intensity of incident light (I).

200. $$\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt}$$

$$= +\frac{1}{2}\frac{d[NH_3]}{dt}$$

201. $$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$= \frac{2.303}{2 \times 10^4\ s^{-1}} \log \frac{800}{50}$$

$= 1.386 \times 10^{-4}\ s^{-1}.$

202. $$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$= \frac{2.303}{2 \times 10^4\ s^{-1}} \log \frac{800}{50}$$

$= 1.386 \times 10^{-4}\ s^{-1}.$

203. $$k = \frac{2.303}{t} \log \frac{C_0}{C_t} = \frac{2.303}{40\ min}$$

$$\log \frac{0.1\ M}{0.025\ M}\ .$$

$$= \frac{2.303}{40} \log 4 = \frac{2.303 \times 0.6021}{40}\ min^{-1}$$

$$\text{Rate} = k[A] = \frac{2.303 \times 0.6021}{40}\ min^{-1}$$

$\times\ 0.01\ M$

$= 3.47 \times 10^{-4}\ M/min$

205. $aG + bH \rightarrow \text{Product}$

rate $\alpha\ [G]^a\ [H]^b$

$a = 1, b = 2$

The overall order of reaction = 1 + 2 = 3

206. Here

$$\log K = 6 - \frac{2000}{T}$$

$$\text{As, } \log K = \frac{\log A - Ea}{2303\ RT}$$

So, $A = 10^6\ sec^{-1}$ and Ea = 38.3 kJ/m

Numericals For Practice

1. In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is

   a. 30 minutes
   b. 60 minutes
   c. 7.5 minutes
   d. 15 minutes

2. For the reaction aA → xP when [A] = 2.2 mM the rate was found to be 2.4 mM s^{-1}. On reducing concentration of A to half, the rate changes to 0.6 m M s^{-1}. The order of reaction with respect to A is

   a. 1.5
   b. 2.0
   c. 2.5
   d. 3.0

3. The following data are obtained from the decomposition of a gaseous compound

Initial pressure , atm	1.6	0.8	0.4
Time for 50% reac., min	80	113	160

The order of the reaction is

a. 0.5
b. 1.0
c. 1.5
d. 2.0

4. What will be initial rate of a reaction if its constant is 10^{-3} min^{-1} and the concentration of reactant is 0.2 mol dm^{-3}?

a. 0.02 mol dm^{-3} min^{-1}
b. 0.002 mol dm^{-3} min^{-1}
c. 0.0002 mol dm^{-3} min^{-1}
d. 2 mol dm^{-3} min^{-1}

5. In a zero order reaction, 47.5% of the reactant remains at the end of 2.5 hours. The amount of reactant consumed in one hour is

a. 10.5 %
b. 32.0 %
c. 52.6 %
d. 21.0 %

6. The data given below is for the reaction of NO and Cl_2 to form NOCl at 295 K

$[Cl_2]$	[NO]	Initial rate (mol l^{-1} s^{-1})
0.05	0.05	1×10^{-3}
0.15	0.05	3×10^{-3}
0.05	0.15	9×10^{-3}

What is the rate law?

a. $r = k\,[NO]\,[Cl_2]$
b. $r = k\,[Cl_2]^1\,[NO]^2$
c. $r = k\,[Cl_2]^2\,[NO]$
d. $r = k\,[Cl_2]^1$

7. A gaseous compound decomposes on heating as per the following equation:

$A(g) \rightarrow B(g) + 2C(g)$. After 5 minutes and 20 seconds, the pressure increases by 96 mm Hg. If the rate constant for this first order reaction is 5.2×10^{-4} s^{-1}, the initial pressure of A is

a. 480 mm
b. 376 mm
c. 696 mm
d. 313 mm

8. For a reaction, $A \rightarrow B + C$, it was found that at the end of 10 minutes from the start. The total optical rotation of the system was 50° and when the reaction is complete it was 100°. Assume that only B and C are optically active and dextro rotatory, the rate constant of this first order reaction would be

a. 6.9 min^{-1}
b. 0.069 min^{-1}
c. 0.69 min^{-1}
d. 6.9×10^{-2} min^{-1}

9. For the elementary reaction, $2NO + H_2 \rightarrow N_2O + H_2O$, the half life time is 19.2 sec at 820°C when partial pressure of NO and H_2 are 60 mm of Hg and 10 mm of Hg respectively. The value of half-life time at the same temperature when partial pressure of NO and H_2 are 600 mm of Hg and 20 mm of Hg respectively would be

a. 10.9 sec
b. 19.2 sec
c. 119 sec
d. 90.2 sec

10. At 380°C, half life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75 % decomposition at 450°C if half life for decomposition of H_2O_2 is 10.17 min at 450°C.

a. 20.4 min
b. 408 min
c. 10.2 min
d. none

11. Two reactions one of first order and other of second order have same values of rate constants ($k_1 = k_2$) when concentrations are expressed in mole dm^{-3}. If the concentrations are expressed in mole ml^{-1} the relation between their rate constant k_1' and k_2' will be

a. $k_1' = 10\,k_2'$
b. $k_1' = k_2'$
c. $k_1' \times 10^3 = k_2'$
d. $k_2' \times 10^3 = k_1'$

12. The rate constant of a first order reaction, $A \rightarrow$ products, is 60×10^{-4} s^{-1}. Its rate at [A] = 0.01 mol l^{-1} would be

a. 60×10^{-6} mol l^{-1} min^{-1}
b. 36×10^{-4} mol l^{-1} min^{-1}
c. 60×10^{-2} mol l^{-1} min^{-1}
d. 36×10^{-1} mol l^{-1} min^{-1}

13. At a given instant there are 25 % undecayed radioactive nuclei in a sample. After 10 seconds the number of undecayed nuclei reduces to 12.5%. The time in which the number of undecayed nuclei will further reduce to 6.25 % of the reduced number is

a. 20 sec
b. 40 sec
c. 30 sec
d. 10 sec

14. The activation energies of two reactions are 18 kJ mol^{-1} and 4.0 kJ mol^{-1} respectively. Assuming the pre-exponential factor to be the same for both reactions, the ratio of their rate constants at 27°C is

a. 3.66×10^{-3}
b. 3.612×10^{-10}
c. 6.312×10^{-8}
d. 3.612×10^{-8}

15. The activation energy of a reaction is zero. The rate constant (k) of the reaction at 280 K of the reaction at 280 K is 1.6×10^{-6} s^{-1}. The value of the velocity constant for this reaction at 300 K is

a. Zero
b. 1.6×10^{-6} s^{-1}
c. 3.2×10^{-6} s^{-1}
d. 1.6×10^{-5} s^{-1}

16. From the following data for the reaction between A and B

[A]	[B]	initial rate	(mol $l^{-1}s^{-1}$)
mol l^{-1}	mol l^{-1}	300 K	320 K
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	–
1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	–

Calculate the rate equation.

a. $r = k [B]^1$ **b.** $r = k [A]^2$
c. $r = k [A]^2 [B]^1$ **d.** $r = k [A] [B]$

17. For the reaction, $C_2H_4 + H_2 \rightarrow C_2H_6$, $\Delta E^\circ = -30$ kcal. If the reaction is reversible and if the activation energy for the forward reaction is 28.0 kcal and its drops to 10.5 kcal in the presence of a catalyst, the activation energies for the uncatalysed and catalysed reverse reaction are respectively (in kcal)

a. 58, 40.5 **b.** –58, –40.5
c. 40.5, 58 **d.** 58.0, –58.0

18. For the thermal rearrangement of vinyl allyl ether $= 5 \times 10^{11} \exp(-128000/RT)$, where k is in s^{-1} and activation energy in J mol^{-1}. The enthalpy of activation in kJ mol^{-1} is

a. 224.3 **b.** 142.3
c. 12.43 **d.** 124.3

19. The decomposition of N_2O_5 in chloroform was followed by measuring the volume of O_2 gas evolved: $2N_2O_5 \rightarrow 2N_2O_4 + O_2$ (g). The maximum volume of O_2 gas obtainable was 100 cm^3. In 500 minutes, 90 cm^3 of O_2 were evolved. The first order rate constant of the reaction, in $minute^{-1}$, is

a. $\frac{100}{10 \times 500}$ **b.** $\frac{2.303}{500} \log \frac{90}{100}$.

c. $\frac{2.303}{500}$ **d.** $\frac{2.303}{500} \log \frac{100}{90}$

20. For the reaction $Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$, the initial concentration of I^- was 0.20 mol lit^{-1} and the concentration after 20 min was 0.18 mol lit^{-1}. Then the rate of formation of I_2 in mol lit^{-1} min^{-1} would be

a. 5×10^{-4} **b.** 2×10^{-3}
c. 5×10^{-3} **d.** 1×10^{-3}

21. The rate of the reaction $A + 2B \rightarrow 3C$ gets increased by 72 times when the concentration of A is tripled and that of B is doubled. The order of the reaction with respect to A and B are ….. and …… respectively

a. 2, 2 **b.** 1, 2
c. 2, 3 **d.** 3, 2

22. The isomerization of cyclopropane to propene is of first order with $k = 8.25 \times 10^{-4}$ s^{-1} at 500°C. If cyclopropane is enclosed in a heated tube at 500°C, the minimum time needed to yield at least 10% propene in resultant gas sample will be

a. 172.4 s **b.** 270.2 s
c. 127.7 s **d.** 321.5 s

23. Radium has atomic weight 226 and half life of 1600 years. The number of disintegration produced per second from one gram are:

a. 1.7×10^9 **b.** 3.6×10^8
c. 3.7×10^{10} **d.** 4.6×10^{10}

24. If 60% of a first order reaction was completed in 60 minutes, 50 % of the same reaction would be completed in approximately

a. 50 minutes **b.** 45 minutes
c. 60 minutes **d.** 40 minutes
(log 4 = 0.60, log 5 = 0.69)

25. The activation energy of a reaction is 94.14 kJ/mole and the value of rate constant at 313 K is 1.8×10^{-5} s^{-1}. Calculate frequency factor A.

(Given Ea/2.303 RT = 15.7082, $\log_{10} 18 = 0.2553$)

a. 9.19×10^{10} collision/sec
b. 91.9×10^{10} collision/sec
c. 198.5×10^{11} collision/sec
d. 1.984×10^{10} collision /sec

26. On introducing a catalyst at 500 K, the rate of a first order reaction increases by 1.718 times. The activation energy in presence of a catalyst is 4.15 kJ mol^{-1}. The slope of the plot of In k (in sec^{-1}) vs 1/T (T is in K) in the absence of the catalyst is

a. –1000 **b.** –100
c. +100 **d.** –10

27. One mole of N_2O_4 gas at 300 K is kept in a closed container at 1 atm. It is heated to 600 K when 20 % by mass of N_2O_4 decomposes to NO_2 (g). The resultant pressure in the container would be

a. 1.0 atm **b.** 1.2 atm
c. 2.4 atm **d.** 2.0 atm

28. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are 3.0×10^{-4} s^{-1}, 104.4 kJ mol^{-1} and 6×10^{14} s^{-1} respectively. The value of the rate constant as $T \rightarrow \infty$ is

a. 2.0×10^{18} s^{-1} **b.** 6.0×10^{14} s^{-1}
c. infinity **d.** 3.6×10^{30} s^{-1}

29. The rate of a certain hypothetical reaction
$A + B + C \rightarrow$ Products
is given by

$$r = -\frac{d[A]}{dt} = k\,[A]^{1/2}\,[B]^{1/3}\,[C]^{1/4}$$

The order of the reaction is

a. 13/12 **b.** 13/14

c. 12/13 **d.** 13/11

30. A reaction P → Q is completed 25% in 25 min, 50 % completed in 25 min if [P] is halved, 25 % completed in 50 min if [P] is doubled. The order of reaction is

a. Zero **b.** 1

c. 2 **d.** 3

ANSWER KEYS

Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.
1.	a	2.	b	3.	c	4.	c	5.	d
6.	b	7.	d	8.	b	9.	b	10.	a
11.	d	12.	a	13.	b	14.	a	15.	b
16.	c	17.	a	18.	d	19.	c	20.	a
21.	c	22.	c	23.	c	24.	b	25.	b
26.	a	27.	c	28.	b	29.	b	30.	a

Hints and Explanations

1. Order 1

Concentration changes from 0.8 M to 0.4 M in (50 %) 15 minutes this half life is = 15 minutes = T_{50}

A change from 0.1 M to 0.025 M is 75 % and for first order reaction

$T_{75} = 2 \times T_{50} =$ $2 \times 15 = 30$ minutes

$T_{50} = 15$ minutes

$$k = \frac{2.303 \log 2}{T_{50}} = \frac{2.303 \log 2}{15}$$

$\alpha = 0.1$ M

$(\alpha - x) = 0.025$ M

for first order :

$$k = \frac{2.303}{t} \log \left(\frac{\alpha}{\alpha - x}\right)$$

$$\frac{2.303 \log 2}{15} = \frac{2.303}{t} \log \frac{0.1}{0.025}$$

$$= \frac{2.303}{t} \log 4$$

$$\frac{2.303 \log 2}{15} = \frac{2 \times 2.303 \log 2}{t}$$

t = 30 minutes.

2. $\alpha A \rightarrow xP$

Rate of reaction = $[A]^a$

Order of reaction = α.

$[A]_1 = 2.2$ mM, $r_1 = 2.4$ m M s^{-1} ……..(i)

$[A]_2 = \frac{2.2}{2}$ mM, $r_2 = 0.6$ mM s^{-1} or $\frac{2.4}{4}$

on reducing the concentration of A to half, the rate of reaction is decreased by four times.

Rate of reaction = $[A]^2$

Order of reaction = 2

3. $$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{80}{113} = (p_2/p_1)^{n-1}$$

Here p_2, p_1 are the initial pressures

$80/113 = (0.8/1.6)^{n-1}$

Taking logarithms,

$\log 0.7 = (n - 1) \log 0.5$

on solving,

$n = 1.5$

4. From the units of rate constant (10^{-3}min^{-1}) it is found that it is a first order reaction.

$r = k\,[\text{conc.}]$

$= 10^{-3} \times 0.2$

$= 0.0002 \text{ mol dm}^{-3} \text{ min}^{-1}$

5. In a zero order reaction, the rate remains constant.

Rate of reaction, $-\frac{d[c]}{dt} = \frac{52.5}{2.5}$

$= 21$ moles lit^{-1} hour^{-1}

In our hour, the amount of reactant consumed = 21 %.

6. From expt 2 and 3 it is clear that when (A) is doubled keeping (B) constant, rate becomes four times, thus $r \propto [A]^2$

Now rate equation is $r = k\,[A]^2\,[B]^n$

From expt. 1 and 2

$5 \times 10^{-4} = k\,[2.5 \times 10^{-4}]^2\,[3 \times 10^{-5}]^n$ ……………. (1)

$4 \times 10^{-3} = k\,[5 \times 10^{-4}]^2\,[6 \times 10^{-5}]^n$ …………….(2)

divide 2 and 1

$$\frac{4 \times 10^{-3}}{5 \times 10^{-4}} = \frac{k\,[5 \times 10^{-4}]^2\,[6 \times 10^{-5}]^n}{k\,[2.5 \times 10^{-4}]^2\,[3 \times 10^{-5}]^n}$$

$8 = 2^2 . 2^n$

$2^n = 8/4 = 2^{110}$

$n = 1$

$r = k\,[A]^2\,[B]^1$

7. $A\,(g) \rightarrow B\,(g) + 2C\,(g)$

At 320 seconds, x moles of A decomposes giving x moles of B and 2x moles of C.

Total number of moles = $a - x + x + 2x$

$= a + 2x$

So number of moles has increased by 2x

$2x = 96$ mm

$x = 48$ mm.

For a first order reaction,

$$5.2 \times 10^{-4} = \frac{2.303}{320} \log_{10} \frac{a}{a - 48}$$

Solving, $\log \frac{a}{a - 48} = 0.07225$

Solving,

$a = 313$ mm.

8. For a first order reaction

	A	→	B	+	C
At t = 0	a		0		0
At t = t	a – X		X		X
At t = ∞	0		a		a

Suppose $r_1°$ and $r_2°$ are the specific rotations for B and C.

$r_1 = X\,(r_1° + r_2°) = 50$

So $\frac{X = 50}{r_1° + r_2°}$

$r_\infty = a\,(r_1° + r_2°) = 100$

$a = \frac{100}{r_1° + r_2°}$.

$$k = \frac{2.303}{10} \log_{10} \frac{100}{50} = 0.069 \text{ min}^{-1}$$

10. At 450°C,

$$k = \frac{0.693}{t\,½} = \frac{0.693}{10.17 \text{ min}}$$

$= 0.0681 \text{ min}^{-1}$

Now for 75 % decomposition

$x = 75\ \%$ of $a = 0.75\,a$

$$t = \frac{2.303}{k} \log \frac{a}{k\,a - x}$$

$$= \frac{2.303}{0.0681 \text{ min}^{-1}} \log \frac{a}{a - 0.75a}$$

$$= \frac{2.303}{0.0681 \text{ min}^{-1}} \log \frac{1}{0.25}$$

$= 20.39$ min

11. As $k \propto [a]^{1-n}$

For a first order reaction

$k_1 \propto [a]^{1-1}$

$k_1 \propto 1$

As k is constant and independent of unit of a, so $k_1 = k'_1$

For second order reaction,

$k_2 \propto 1/a$

$$k_2 \propto \frac{1}{a \text{ mole dm}^{-3}} \qquad = \frac{1}{a \times 10^{-3} \text{ mole ml}^{-1}}$$

$$k'_2 \propto \frac{1}{a \text{ mole ml}^{-1}}$$

So $k_2 = k'_2 \times 10^3 = k'_1$

12. $r = k\,[A] = 60 \times 10^{-4} \times 0.01$

$= 60 \times 10^{-4} \times \frac{1}{10^2}$

$= 60 \times 10^{-6}$ mol l^{-1} min^{-1}

13. Suppose the number of radioactive nuclei is N_0 at t = 0,

The number of radioactive nuclei at a given instant 't' is $N_0/4$.

After t = 10 sec, the number of undecayed nuclei reduces to 12.5% of N_0 that is, becomes half of the $N_0/4$. It means $t_{1/2}$ is 10 sec.

$$\frac{0.693}{10} = \frac{2.303}{t} \log_{10} \frac{N_0}{N_0 \times 6.25/100}$$

$$\frac{0.693}{10} = \frac{2.303}{t} \log \frac{100}{6.25}$$

$$t = \frac{2.303 \times 10}{0.693} \log_{10} 16 = 40 \text{ sec}$$

14. $\ln k_1 = \ln A - 18/RT.$

$\ln k_2 = \ln A - 4/RT$

$\ln k_1 - \ln k_2 = -18/RT + 4/RT$

$= \frac{1}{RT}(4 - 18)$

$= -\frac{14 \text{ kJ}}{RT}$

$$\log_{10} \frac{k_1}{k_2} = -\frac{14 \times 10^3}{2.303 \times 8.314 \times 300}$$

so $k_1/k_2 = 3.656 \times 10^{-3}$

15. According to

$k = Ae^{-Ea/RT}$

$Ea = 0$

$k = Ae^{o} = A$

So the value of k at 280 K = the value of k at 300 K $= 1.6 \times 10^{-6}$ s^{-1}

17. $\Delta E^{o} = E_{a\,(f)} - E_{a\,(r)}$

This holds good for uncatalysed and catalysed reactions

ΔE^{o} is the same for both these reactions.

For the uncatalysed reaction, –30 kcal

$= 28.0$ kcal $- E_{a\,(r)}.$

So $E_{a\,(r)} = 58.0$ kcal

For the catalysed reaction, –30 kcal

$= 10.5$ kcal $- E_{a\,(r)}$

So $E_{a\,(r)} = 40.5$ kcal

18. $k = 5 \times 10^{11} \times \exp(-128000/RT)$

$= A.\exp(-Ea/RT)$

$Ea = 128000$ J mol^{-1}

For gaseous reaction

$\Delta H = Ea + (\Delta n - 1)RT,$

Here Δn is change in the number of molecules, when the activated complex is formed.

Here $\Delta n = 0$ (unimolecular reaction).

So $\Delta H = 128000 - 8.314 \times 448$ J mol^{-1}

$= (128000 - 3725)$ J mol^{-1}

$= 124275$ J mol^{-1}

$= 124.3$ kJ mol^{-1}

19. $2N_2O_5 \rightarrow 2N_2O_4 + O_2\,(g)$

(solution) (solution)

The maximum volume of O_2 gas obtainable is directly proportional to the initial concentration of N_2O_5

that is 100 cm^3 α $[N_2O_5]_0$.

90 cm^3 of O_2 evolved is α N_2O_5 decomposed

So (100 – 90) that is, 10 cm^3 is α N_2O_5 remaining that is 10 cm^3 α $[N_2O_5]_t$

The first order rate constant

$$k = \frac{2.303}{500 \text{ min}} \log \frac{[N_2O_5]_0}{[N_2O_5]_t}$$

$$= \frac{2.303}{500 \text{ min}} \log \frac{100}{10} = \frac{2.303 \text{ min}^{-1}}{500}$$

20. Rate of disappearance of I^{-1},

$$\frac{-d[I^-]}{dt} = \frac{(0.20 - 0.18) \text{ mol L}^{-1}}{20 \text{ min}}$$

$= 10^{-3}$ mol L^{-1} min^{-1}

Rate of reaction $= -\frac{1}{2}\frac{d[I^-]}{2\,dt}$

$= +\frac{d\,[I_2]}{dt}$

So rate of formation of I_2,

$$\frac{d[I_2]}{dt} = -\frac{1}{2}\frac{d[I^-]}{dt} = \frac{10^{-3}}{2}$$

$= 5 \times 10^{-4}$ mol L^{-1} min^{-1}

21. $r = k\,[A]^a\,[B]^b$ …..(1)

$72\,r = k\,[3A]^a\,[2B]^b$ ….(2)

On diving equation (2) by equation (1), we get

$72 = 3^a 2^b$

Test by substituting the given values of a and b

When a = 2, b = 3, we get

$3^a 2^b = 3^2 \times 2^3 = 9 \times 8 = 72.$

22. $t = 2.303 \log_{10} 100 = 127.7$ sec

$8.25 \times 10^{-4}\ 90$

23. $\lambda = \dfrac{2.303}{1600 \times 365 \times 24 \times 86400}$

$\times \dfrac{1 \times 6.023 \times 10^{23}}{226}$

$= 3.7 \times 10^{10}$

24. For a first order reaction,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a - x} .$$

$$k = \frac{2.303}{60} \log_{10} \frac{100}{40} = \frac{2.303}{60} x\log_{10} 2.5$$

$= 0.0153$

$$t_{1/2} = \frac{2.303}{k} \log_{10} \frac{100}{50} = \frac{2.303}{0.0153} \times \log_{10} 2$$

$= 45.31$ min.

25. As $k = Ae^{-Ea/RT}$

$In\ k = In\ A - \dfrac{Ea}{RT}$.

$\log_{10} k = \log_{10} A - \dfrac{Ea}{2.303\ RT}$

$\log_{10} A = \log_{10} k + \dfrac{Ea}{2.303\ RT}$

$\log_{10} A = \log_{10} (1.8 \times 10^{-5}) + 15.7082$

$\log_{10} A = 0.2553 - 5 + 15.7082$

$= 10.9635$

A = Antilog (10.9635)

$A = 91.94 \times 10^{10}$ collision/sec.

26. Suppose k and k' are the rate constants of the uncatalysed and catalysed reactions and Ea and E'a are their corresponding activation energies.

$k = Ae^{-Ea/RT}$

$k' = Ae^{-E'a/RT}$

As $E'a = 4.15$ kJ mol^{-1}

So $\dfrac{k'}{k} = e^{(Ea - E'a)/RT}$

As $k' = (1 + 1.718)\ k = 2.718\ k = e \times k$

So $e = e^{(Ea - E'a)/RT}$

$Ea - E'a = RT$

$Ea = E'a + RT = 4.15 + 8.3 \times 500 \times 10^{-3}$

$= 8.3$ kJ mol^{-1}

$In k = In A - \dfrac{Ea}{R} \times \dfrac{1}{T}$.

Slope $= -\dfrac{Ea}{R} = -\dfrac{8.3 \times 10^3}{8.3} = -1000$

27. $N_2O_4 \rightarrow 2NO_2$

Initial moles 1

Moles after disso. $1 - 0.2 = 0.8$ 0.4

Total moles after dissociation

$= 0.8 + 0.4 = 1.2$

Initial temperature = 300 K

As $P_1 V = n_1 RT_1$

$1 \times V = 1 \times R \times 300$ ....(1)

Temperature after dissociation = 600 K

$P_2 V_2 = n_2 RT_2$

$P_2 \times V = 1.2 \times R \times 600$ ...(2)

On dividing equation (2) by (1), we get

$P_2 = \dfrac{1.2 \times 600}{300} = 2.4$ atm

28. $k = Ae^{-Ea/RT}$ (Arrhenius equation)

when $T \rightarrow \infty$

$k = A\ e^0$, or $k = A$

Thus $k = 6 \times 10^{14}$ s^{-1}

29. Order $= \frac{1}{2} + 1/3 + \frac{1}{4} = \dfrac{6 + 4 + 3}{12}$

$= 13/12$

30. According to hit and trial method, if reaction is of zero order,

$k = \dfrac{1}{t}\ \{[A]_0 - [A]\}$

Case I.

$k = \dfrac{1}{25} \times \dfrac{25}{100} = 10^{-2}$

Case II.

$k = \dfrac{1}{25} \times \dfrac{1}{2}\ \{[A]_0 - [A]\}$

$= \dfrac{1}{25} \times \dfrac{1}{2} \times \dfrac{50}{100} = 10^{-2}$

Case III.

$k = \dfrac{1}{50} \times 2\ \{[A]_0 - [A]\}$

$= \dfrac{1}{50} \times 2 \times \dfrac{25}{100} = 10^{-2}$

As k is constant So the give reaction is of zero order.