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Unit 4 — Equilibrium | Redox Reactions

EQUILIBRIUM

Equilibrium state of a system is the state, in which system has no tendency for a change without external stimulation and so there is no net change occurs with time. Equilibrium is attained when the rates of the two opposing processes become equal.
There are two types of equilibrium :

- **Physical equilibrium :** If the opposing processes involve only physical changes, the equilibrium is called physical equilibrium.
- **Chemical equilibrium :** If the opposing processes involve chemical changes, the equilibrium is called chemical equilibrium.

Physical Equilibrium	Types of Equilibrium	Chemical Equilibrium
Solid-liquid equilibrium (Melting of ice) $$H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$$ ice water	Solid-vapour equilibrium (Sublimation equilibrium) $$I_{2(s)} \rightleftharpoons I_{2(Vapour)}$$	A reaction in which not only the reactants react to form the products under certain conditions but also products react to form reactants under the same condition, is called a reversible reaction.
Solid-solution equilibrium (Dissolution of sugar in water) $$Sugar_{(Solid)} \rightleftharpoons Sugar_{(in\ solution)}$$	Gas-solution equilibrium (Dissolution of a gas in a liquid under pressure in a closed cell.) $$CO_{2(g)} \rightleftharpoons CO_{2(in\ solution)}$$	A reaction which cannot take place in the reverse direction, *i.e.*, the products formed do not react to give back the reactants under the same conditions, is called an irreversible reaction.
Liquid-vapour equilibrium (Evaporation of water in a closed vessel) $$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$	It is governed by Henry's law which states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.	
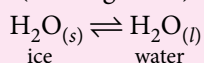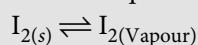
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GENERAL CHARACTERISTICS OF EQUILIBRIA INVOLVING PHYSICAL PROCESSES

Some important characteristics of physical equilibria are as follows :
- At equilibrium, some observable property of the system becomes constant.
- Equilibria involving gases can be attained only in closed vessels. This is because if the vessel is opened, the gas will escape and there will be no equilibrium.
- Equilibrium is dynamic in nature but stable.

- At equilibrium, the concentrations of the reactants and products become constant at constant temperature.
  $$e.g., \text{CO}_{2(g)} \rightleftharpoons \text{CO}_{2(aq)}; \quad \frac{[\text{CO}_{2(aq)}]}{[\text{CO}_{2(g)}]} = K$$
  where, K is equilibrium constant.
- The magnitude of the equilibrium constant represents the extent to which the process proceeds before equilibrium is attained. For example, greater value of the K greater will be the dissolution of $\text{CO}_{2(g)}$ in water.

General Characteristics of Chemical Equilibrium

- At equilibrium, the concentration of each of the reactants and the products becomes constant.
  This may be represented graphically for a general reversible reaction, $A + B \rightleftharpoons C + D$, as shown in figure.
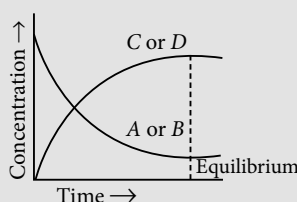
- Chemical equilibrium can be attained from either direction, *i.e.*, from the direction of the reactants as well as from the direction of the products.

- At equilibrium, the rate of forward reaction becomes equal to the rate of backward reaction and hence, the equilibrium is dynamic in nature.

- A chemical equilibrium can be established only if none of the products is allowed to escape out or separate out as a solid.

Law of Mass Action

The rate at which a substance reacts is proportional to the product of the active masses of the reactants, each raised to the power equal to its stoichiometric coefficient as represented in the balanced chemical equation.

Law of Chemical Equilibrium

Equilibrium Law

At a given temperature, the product of concentrations of the products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value which is called equilibrium constant. For a reaction, $aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Relation between K_p vs K_c
$$K_p = K_c (RT)^{\Delta n_g}$$

where, K_p = Equilibrium constant when all the reactants and products are in gaseous state.
Δn_g = Moles of gaseous products – moles of gaseous reactants.

IMPORTANT FEATURES OF EQUILIBRIUM CONSTANT

- Expression for equilibrium constant is applicable only when concentrations of the reactants and products have attained constant value at equilibrium state.

- The value of equilibrium constant is independent of initial concentrations of the reactants and products.
- Equilibrium constant is temperature dependent, having one unique value for a particular balanced reaction at a given temperature.

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Chemical equation	Equilibrium constant
$aA + bB \rightleftharpoons cC + dD$	K_c
$cC + dD \rightleftharpoons aA + bB$	$K_c' = (1/K_c)$
$naA + nbB \rightleftharpoons ncC + ndD$	$K_c'' = (K_c^n)$

APPLICATIONS OF EQUILIBRIUM CONSTANTS

- Predicting the extent of reaction

Negligible K_c

K_c

Extremely Large K_c

Reaction hardly proceeds $\quad 10^{-3} \quad\quad 1 \quad\quad 10^3$

Both reactants and products are present at equilibrium

Reaction proceeds almost to completion
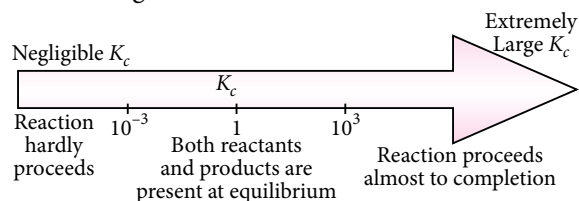
- Predicting the direction of reaction

$Q < K$ Reaction will shift in forward direction.	$Q = K$ Reaction in equilibrium	$Q > K$ Reaction will shift in backward direction.

- Relation between K_c and standard Gibbs free energy.

$$\Delta_r G^\circ = -RT \ln K_c$$

LE CHATELIER'S PRINCIPLE

- A change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or counteract the effect of the change.

Factors Affecting the Equilibrium

- Effect of change of concentration
  - ➢ With increase in concentration of any reactant at equilibrium, the equilibrium shifts to forward direction.

- Effect of change of pressure
  - ➢ Low pressure favours those reactions which are accompanied by increase in total number of moles.
  - ➢ High pressure favours those reactions which are accompanied with decrease in total number of moles.
  - ➢ Pressure has no effect on an equilibrium reaction which proceeds with no change in total number of moles.

- Effect of change of temperature
  - ➢ K_c for an exothermic reaction decreases as the temperature increases.
  - ➢ K_c for an endothermic reaction increases as the temperature increases.

- Effect of adding inert gas on equilibrium
  - ➢ At constant volume, when $(n_p = n_r)_{gaseous}$, there is no effect.
  - ➢ At constant pressure, when $(n_p \neq n_r)_{gaseous}$, effect is observed.
    When an inert gas is added, it wil increase the volume of the system. Therefore, equilibrium will shift in a direction in which there is increase in number of moles of gases.

- Effect of catalyst
  - ➢ Catalyst does not affect equilibrium constant.

Ionic Equilibrium

In weak electrolytes, equilibrium is established between ions and unionised molecules. Such an equilibrium is called ionic equilibrium,
$$AB_{(s)} + aq \rightleftharpoons A^+_{(aq)} + B^-_{(aq)}$$

The substances which dissociate almost completely into ions in aqueous solution, are called strong electrolytes. They are very good conductor of electricity, *e.g.*, NaOH, NaCl, HCl, etc.

The substances which dissociate to a small extent in aqueous solution are called weak electrolytes. They conduct electricity to a small extent, *e.g.,* NH_4OH, CH_3COOH, etc.

ACIDS, BASES AND SALTS

Arrhenius Concept of Acids and Bases

- Acid is a substance that dissociates in water to give hydrogen ions ($H^+_{(aq)}$).
- Base is a substance that produces hydroxyl ions ($OH^-_{(aq)}$) in water.
- Arrhenius concept explained neutralisation, salt hydrolysis, strength of acids and bases, etc.
- It also did not explain substances like NH_3, CaO are known to be basic but do not contain any hydroxyl groups and substances like CO_2, SO_2 are known to be acidic but do not contain any hydrogen. This limitation is, however overcome if water is supposed to play an important role.

$$NH_{3(g)} + H_2O \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$
$$CO_2 + H_2O \rightleftharpoons CO^{2-}_{3(aq)} + 2H^+_{(aq)}$$
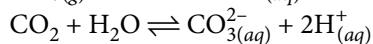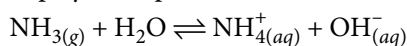
- Inability of explaining the reaction between an acid and base in absence of water.

$$NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$$
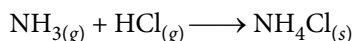
Bronsted-Lowry Concept of Acids and Bases

- Acid is a substance that is capable of donating a hydrogen ion.
- Base is a substance that is capable of accepting a hydrogen ion.

$$\underset{\text{Base}}{NH_{3(aq)}} + \underset{\text{Acid}}{H_2O_{(l)}} \rightleftharpoons \underset{\substack{\text{Conjugate}\\\text{acid}}}{NH^+_{4(aq)}} + \underset{\substack{\text{Conjugate}\\\text{base}}}{OH^-_{(aq)}}$$

(Adds proton / Loses proton)
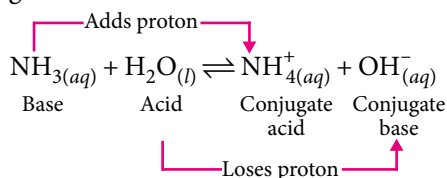
- The acid-base pair that differs only by one proton is called a conjugate acid-base pair.
- A strong Bronsted acid has a weak conjugate base and vice-versa.
- It cannot explain the reactions between acidic oxides like CO_2, SO_2 etc. and the basic oxides like CaO, BaO, etc. which take place even in the absence of the solvent.

$$CaO + SO_3 \longrightarrow CaSO_4$$

- Substances like BF_3, $AlCl_3$, etc. do not have any hydrogen but are known to behave as acids.

Lewis Concept of Acids and Bases

- An acid is a species which accepts an electron pair.
- A base is a species which donates an electron pair.
  e.g., $BF_3 + :NH_3 \longrightarrow BF_3 : NH_3$
- Electron deficient species like $AlCl_3$, BF_3, etc. can act as Lewis acids while species like H_2O, NH_3, OH^-, etc. which can donate a pair of electrons, can act as Lewis bases.

Formation of Salts

When acids and bases are mixed in right proportion, they react with each other to form salts.

Salts

Simple salts

Normal salt
$NaCl$, KCl, KNO_3 etc.

Acidic salts
$NaHSO_4$, $KHCO_3$, NaH_2PO_4, etc.

Basic salts
$Mg(OH)Cl$, $Pb(OH)NO_3$, $Fe(OH)_2Cl$, etc.

Double salts
Alums, Mohr's salt, etc.

Complex salts
$K_4[Fe(CN)_6]$, $Na[Ag(CN)_2]$, etc.

Mixed salts
$Ca(OCl)Cl$, $MgNH_4PO_4$, $NaKSO_4$, etc.
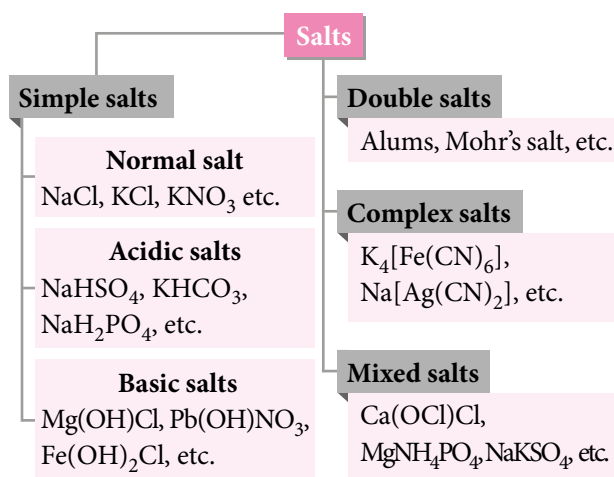
Relative Strength of Acids & Bases

- $$\frac{\text{Strength of acid } (HA)_1}{\text{Strength of acid } (HA)_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

- $$\frac{\text{Strength of base } (BOH)_1}{\text{Strength of base } (BOH)_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

- $K_a = K_{a_1} \times K_{a_2} \times K_{a_3}$ (For tribasic acid)
  $K_{a_1} > K_{a_2} > K_{a_3}$

- Strong acids have very weak conjugate bases.

IONISATION CONSTANT OF WATER AND ITS IONIC PRODUCT

$$\underset{\text{Acid}}{H_2O_{(l)}} + \underset{\text{Base}}{H_2O_{(l)}} \rightleftharpoons \underset{\substack{\text{Conjugate}\\\text{acid}}}{H_3O^+_{(aq)}} + \underset{\substack{\text{Conjugate}\\\text{base}}}{OH^-_{(aq)}}$$
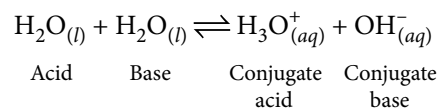
The dissociation constant is given as :

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]}$$

Ionic product of water (K_w)

$K_w = [H^+][OH^-]$

At 298 K, $[OH^-] = [H^+] = 1.0 \times 10^{-7}$ M

$\therefore K_w = (1 \times 10^{-7} \text{ M})^2 = 1 \times 10^{-14} \text{ M}^2$

$K_a \times K_b = K_w$

THE pH SCALE

- pH may be defined as negative logarithm of hydronium ion concentration.

$$\text{pH} = -\log [H_3O^+]$$

- $pK_w = \text{pH} + \text{pOH} = 14$

$pK_w = pK_a + pK_b = 14$

- pH of a solution can be determined with pH paper or more accurately by pH meter.

SALT HYDROLYSIS

The reaction of the cation or anion of the salt with water to produce acidic or basic solution, is called salt hydrolysis.

Degree of hydrolysis : The degree of hydrolysis of a salt is defined as the fraction of the total salt which is hydrolysed.

- Salts of weak acid and strong base

$$K_h = \frac{K_w}{K_a} \; ; h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a \cdot C}}$$

$$\text{pH} = -\frac{1}{2}(\log K_w + \log K_a - \log C)$$

- Salts of strong acid and weak base

$$K_h = \frac{K_w}{K_b} \; ; \; h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_b \cdot C}}$$

$$\text{pH} = -\frac{1}{2}(\log K_w - \log K_b + \log C)$$

- Salts of weak acid and weak base

$$K_h = \frac{K_w}{K_a K_b} \; ; h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a K_b}}$$

$$\text{pH} = \frac{1}{2}(pK_w + pK_a - pK_b)$$

BUFFER SOLUTIONS

- A buffer solution is defined as a solution which any change in its pH value even when small amounts of acid or base are added to it.

- Acidic buffer : It is the solution of a mixture of a weak acid and its salt with a strong base, *e.g.*, $CH_3COOH + CH_3COONa$.

- Basic buffer : It is the solution of a mixture of a weak base and its salt with a strong acid, *e.g.*, $NH_4OH + NH_4Cl$.

pH of acidic buffer (Henderson Hasselbalch equation)

$$\text{pH} = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= pK_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

pH of Buffer Mixture

pH of basic buffer (Henderson Hasselbalch equation)

$$\text{pOH} = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{pH} = pK_a + \log \frac{[\text{Base}]}{[\text{Conjugate acid}]}$$

SOLUBILITY EQUILIBRIA AND SOLUBILITY PRODUCT OF SPARINGLY SOLUBLE SALTS

Solubility product of an electrolyte at a specified temperature may be defined as the product of the molar concentration of its ions in a saturated solution, each concentration raised to the power equal to the number of ions produced on dissociation of one molecule of the electrolyte.

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

$$K_{sp} = [A^{y+}]^x[B^{x-}]^y$$
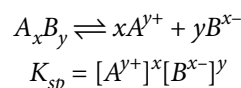
COMMON ION EFFECT

If to an ionic equilibrium, $AB \rightleftharpoons A^+ + B^-$, a salt containing a common ion (*AC* or *BD*) is added, the equilibrium shifts in the backward direction. This is called common ion effect.

Applications of Solubility Product and Common Ion Effect

- In the precipitation of salts, a salt precipitates if K_{sp} < ionic product.

- In the removal of hardness of water.

- In qualitative analysis.

- In fractional precipitation.

iNFO SHOTS

'Chemical equilibrium based model' for describing the strength of sludge !

A new model, based on chemical equilibrium theory, was established to evaluate the strength of sludges in biological wastewater treatment systems. The effectiveness of this model was demonstrated by the experimental results with an anaerobic hydrogen producing sludge. The Gibbs free energy of adhesion ($\Delta G°$) under shear could also be calculated using this model. The equilibrium constant $K°$ and $\Delta G°/RT$ at a shear intensity of 800 per second were estimated to be 6.54 ± 0.12 and 1.88 ± 0.02, respectively. The two parameters could be used to evaluate the strength of the hydrogen producing sludge.

REDOX REACTIONS

Chemical reactions involve transfer of electrons from one chemical substance to another. These electron-transfer reactions are termed as oxidation-reduction or redox reactions.

OXIDATION AND REDUCTION

Oxidation

Oxidation is a process which involves addition of oxygen, removal of hydrogen, addition of non-metal, removal of metal, increase in +ve charge, loss of electrons and increase in oxidation number, *e.g.*,

(i) Addition of oxygen : $2Mg + O_2 \rightarrow 2MgO$

(ii) Removal of hydrogen : $H_2S + Cl_2 \rightarrow 2HCl + S$

(iii) Addition of non-metal : $Fe + S \rightarrow FeS$

(iv) Removal of metal : $2KI + H_2O_2 \rightarrow 2KOH + I_2$

(v) Increase in +ve charge : $Fe^{2+} \rightarrow Fe^{3+} + e^-$

(vi) Loss of electrons (also known as de-electronation)
$H_2^0 \rightarrow 2H^+ + 2e^-$

Reduction

Reduction is just reverse of oxidation. Reduction is a process which involves removal of oxygen, addition of hydrogen, removal of non-metal, addition of metal, decrease in +ve charge, gain of electrons and decrease in oxidation number, *e.g.*,

(i) Removal of oxygen : $CuO + C \rightarrow Cu + CO$

(ii) Addition of hydrogen : $Cl_2 + H_2 \rightarrow 2HCl$

(iii) Removal of non-metal :
$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$

(iv) Addition of metal : $HgCl_2 + Hg \rightarrow Hg_2Cl_2$

(v) Decrease in +ve charge : $Fe^{3+} \rightarrow Fe^{2+}$

(vi) Gain of electrons (also known as electronation)
$Zn_{(aq)}^{2+} + 2e^- \rightarrow Zn_{(s)}$

Oxidising and Reducing Agents

An oxidising agent is a substance in which the oxidation number of its element decreases while a reducing agent is a substance in which the oxidation number of its element increases.

- **Oxidation number :** Charge on an atom produced by donating or accepting electrons is called oxidation number or oxidation state, *e.g.*,
  - For homonuclear species like N_2, Cl_2, H_2, P_4, S_8, etc., oxidation state is zero.
  - Oxidation state of H is +1 but –1 when combined with non-metals.
  - Oxidation state of oxygen is –2, but in peroxide it is –1. In OF_2, it is +2 as oxidation state of fluorine is always –1.

Types of Redox Reactions

- **Combination reaction :** The reaction in which two atoms or molecules combine together to form a third molecule, *e.g.*,

$$\overset{0}{C} + \overset{0}{O_2} \longrightarrow \overset{+4\,-2}{C O_2};$$
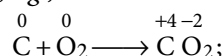
- **Decomposition reaction or intramolecular redox reaction :** The reaction in which a molecule breaks down to form two or more components out of which one must be in the elemental state, *e.g.*,

$$\overset{+1\ -2}{2H_2 O} \overset{\Delta}{\longrightarrow} \overset{0}{2H_2} + \overset{0}{O_2}$$
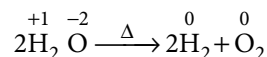
- **Displacement reaction or intermolecular redox reaction :** The reaction in which an atom or ion in a compound is replaced by an atom or ion of some other element, *e.g.*,

$$X + YZ \longrightarrow XZ + Y$$

(a) **Metal displacement reaction :** The reaction in which a metal in the compound is displaced by some other metal in the elemental state, *e.g.*,

$$\overset{+2}{C}uSO_4 + \overset{0}{Z}n \longrightarrow \overset{0}{C}u + \overset{+2}{Z}nSO_4$$
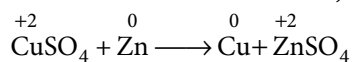
(b) **Non-metal displacement reaction :** The reaction in which a metal or a non-metal displaces another non-metal from its compound, *e.g.*,

$$2\overset{0}{N}a + 2\overset{+1}{H}_2O \longrightarrow 2Na\overset{+1}{O}H + \overset{0}{H}_2$$
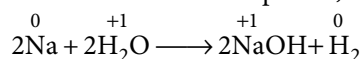
- **Disproportionation reaction or auto-redox reaction :** The reaction in which the same species is simultaneously oxidised as well as reduced, *e.g.*,

$$2H_2\overset{-1}{O}_2 \longrightarrow 2H_2\overset{-2}{O} + \overset{0}{O}_2$$
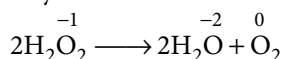
Applications of Redox Reactions

- In extraction of metals, *e.g.*,
$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$
- In electrochemical cells.
- In photosynthesis.
- In quantitative analysis.

BALANCING OF REDOX REACTIONS

By Oxidation Number Method

- Identify the element whose oxidation number have changed.
- Calculate the increase or decrease in oxidation number per atom and thereby identify oxidising and reducing agents. If more than one atom of the same element is involved, find total increase or decrease in oxidation number by multiplying with the number of atoms involved.
- Multiply the formula of oxidising and reducing agents by suitable integers so that
  total increase = total decrease.
- Balance all atoms other than H and O.
- Finally balance H and O atoms by adding H_2O molecules.
  - For acidic medium, first balance O– atoms by adding H_2O molecules to the side deficient in O and H^+ ions to the side deficient in hydrogen.
  - For basic medium, first balance O– atoms by adding H_2O molecules to the side deficient in O. Then, to balance H add H_2O molecules to the side deficient in H add equal number of OH^- ions to the other side.

By Ion-electron/Half-reaction Method

- Find the atoms whose oxidation numbers undergo a change.
- Split the reaction in two half equations, oxidation half-reaction and reduction half- reaction.
- Balance each half-reaction by balancing all other elements except H and O.
- Balance the oxidation numbers of the half- reactions by adding electrons to the side necessary.
- Balance the charge on the two sides of the half-reaction by adding H^+ ions (if medium is acidic) or adding OH^- ions (if medium is basic).
- Balance H and O by adding H_2O molecules to the side deficient.
- Multiply the two half-reaction by suitable integers so that, on adding, electrons gained in one are cancelled by the electrons lost in the other.

Equivalent Weights of Oxidising and Reducing Agents

Eq. wt. of oxidising agent
$$= \frac{\text{Molecular weight}}{\substack{\text{No. of electrons gained by one molecule} \\ \text{or} \\ \text{Change in O.No. per mole}}}$$

Eq. wt. of reducing agent
$$= \frac{\text{Molecular weight}}{\substack{\text{No. of electrons lost by one molecule} \\ \text{or} \\ \text{Change in O.No. per mole}}}$$

REDOX REACTIONS AS THE BASIS FOR TITRATIONS

Redox titrations can be used to determine the exact amount of an oxidising agent (or a reducing agent) in a given solution by titrating it against the standard solution (whose normality or molarity is known) of a suitable reducing agent (or the oxidising agent) in presence of an indicator.

Types of Redox Titrations

- **Potassium permanganate titration :** In this titration, reducing agents like $FeSO_4$, Mohr's salt $[(NH_4)_2SO_4.FeSO_4.6H_2O]$, H_2O_2, oxalic acid $(COOH)_2$, sodium oxalate $(COONa)_2$, etc. are directly titrated against $KMnO_4$ as the oxidising agent in acidic medium, *e.g.*,

$$\underset{\text{Ferrous ion}}{5Fe^{2+}_{(aq)}} + \underset{\text{Permanganate ion}}{MnO^-_{4(aq)}} + 8H^+_{(aq)} \longrightarrow$$
$$\underset{\text{Ferric ion}}{5Fe^{3+}_{(aq)}} + Mn^{2+}_{(aq)} + 4H_2O_{(l)}$$
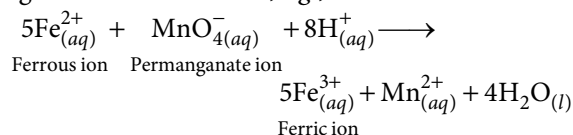
- **Potassium dichromate titration :** In this titration, reducing agents given in potassium permanganate titration are directly titrated against $K_2Cr_2O_7$ as the oxidising agent in acidic medium. *e.g.*,

$$6Fe^{2+}_{(aq)} + Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 6Fe^{3+}_{(aq)} + 7H_2O_{(l)}$$
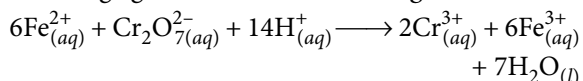
- **Ceric sulphate titration :** In this titration, the reducing agents such as Fe^{2+} salts, Cu^+ salts, nitrites, arsenites, oxalates, etc. are directly titrated against ceric sulphate, $Ce(SO_4)_2$ as the oxidising agent.

$$\underset{\text{Ferrous ion}}{Fe^{2+}_{(aq)}} + \underset{\text{Ceric ion}}{Ce^{4+}_{(aq)}} \longrightarrow \underset{\text{Ferric ion}}{Fe^{3+}_{(aq)}} + \underset{\text{Cerous ion}}{Ce^{3+}_{(l)}}$$
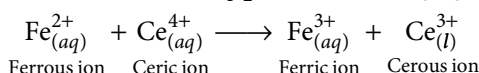
- **Iodimetric titration :** This titrations involve the direct use of iodine as the oxidising agent (in neutral or slightly acidic medium) using starch as an indicator. The various reducing agents used in these titrations are thiosulphates, sulphites, arsenites and antimonites.

$$\underset{\text{Thiosulphate ion}}{I_{2(aq)} + 2S_2O^{2-}_{3(aq)}} \longrightarrow \underset{\text{Tetrathionate ion}}{2I^-_{(aq)} + S_4O^{2-}_{6(aq)}}$$
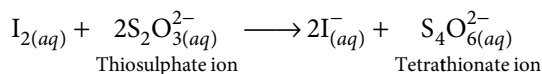
- **Iodometric titration :** This titration is carried out in two steps. In the first step, oxidising agents such as $KMnO_4$, $K_2Cr_2O_7$, $CuSO_4$, peroxides, etc. are treated with an excess of KI when I_2 is liberated quickly and quantitatively.

$$2MnO^-_{4(aq)} + 16H^+_{(aq)} + 10I^-_{(aq)} \longrightarrow 2Mn^{2+}_{(aq)} + 5I_{2(s)} + 8H_2O_{(l)}$$
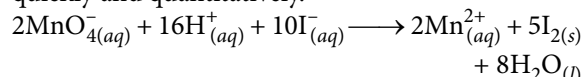
In the second step, the liberated iodine is titrated against a standard solution of sodium thiosulphate using starch as an indicator.

Electrochemical Cell

- It is a device which converts chemical energy produced in an indirect redox reaction into electrical energy.
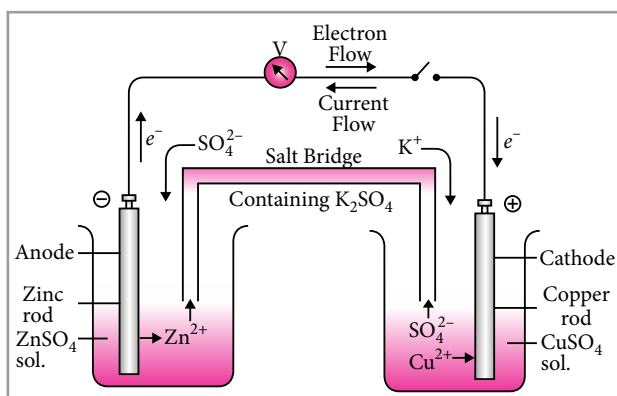
- Representation of an electrochemical cell
  $Zn \mid Zn^{2+} (C_1) \parallel Cu^{2+} (C_2) \mid Cu$

- Redox couple is defined as a combination of the oxidised and reduced forms of the same substance taking part in an oxidation or reduction half reaction.

- At anode : $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$
- At cathode : $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$

Important generalisation :

- Oxidation occurs at the anode while reduction occurs at the cathode.
- Anode acts as the negative pole while cathode acts as the positive pole.
- Electrons flow from anode to cathode in the external circuit while current flows from cathode to anode.
- Chemical energy of the redox reaction occurring in the galvanic cell is converted into electrical energy.

> By convention, the standard electrode potential ($E°$) of hydrogen electrode is 0.00 volt.
> A negative $E°$ means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
> A positive $E°$ means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

- The electrode potential is termed as oxidation potential if the electrode loses electrons and is called the reduction potential if the electrode gains electrons.

Electrode Potential

- **Electrode potential :** The tendency of an electrode to lose or gain electrons.

- If the concentration of electrolytes is taken as unity (1 mol L^{-1}) or if any gas appears in the electrode reaction, it is taken at 1 atm pressure and temperature is taken as 298 K, then the electrode potentials is called standard electrode potential ($E°$).

Electromotive series

A list of oxidising agents, arranged in decreasing order of their strength is called the activity or electromotive or electrochemical series.

Applications :

- To compare the relative strength of oxidising and reducing agents.
- Comparison of reactivity of metals.
- To predict whether a metal will liberate hydrogen from the aqueous solution of acids or not.

iNFO SHOTS

Chemical oxidation with Fenton's Reagents !

Fenton's reagent generates hydroxyl radicals through the reaction of ferrous ion and hydrogen peroxide :

$$Fe^{2+} + H_2O_2 \longrightarrow {}^\bullet OH + Fe^{3+} + OH^\bullet$$
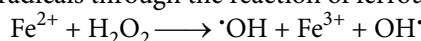
The hydroxyl radical is a powerful oxidising agent, second only to fluorine. Now, the process is self replicating since the reaction of ferric ion with hydrogen peroxide to generate the perhydroxyl radical also occurs :

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + {}^\bullet OOH + H^+$$
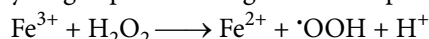
The perhydroxyl radical is a weaker oxidizer (between hydrogen peroxide and permanganate). But more importantly the process generates further ferrous ions that in turn stimulate further reaction with hydrogen peroxide to produce more hydroxyl radicals. The hydroxyl radical can react with almost any hydrocarbon to produce carbon dioxide as a final product (as chlorides if a chlorinated hydrocarbon is treated).

SPEED PRACTICE

1. Calculate the pH of a solution formed by mixing of 0.2 M NH_4Cl and 0.1 M NH_3. The pK_b of ammonia is 4.75.
   (a) 8   (b) 7.67   (c) 8.95   (d) 10.55

2. For a gaseous phase reaction, $A + 2B \rightleftharpoons AB_2$, $K_c = 0.3475$ at 200 °C. When 2 moles of B are mixed with one mole of A, the total pressure required to convert 60% of A to AB_2 is
   (a) 190.5 atm   (b) 181.5 atm
   (c) 101.0 atm   (d) 281.5 atm.

3. The change in the oxidation number of S in H_2S and SO_2 in the following industrial reaction :
   $2H_2S_{(g)} + SO_{2(g)} \longrightarrow 3S_{(s)} + H_2O_{(g)}$, will be
   (a) –2 to 0, +4 to 0   (b) –2 to 0, +4 to –1
   (c) –2 to –1, +4 to 0   (d) –2 to –1, +4 to –2

4. For a sparingly soluble salt A_pB_q, the relationship of its solubility product (K_{sp}) with its solubility (S) is
   (a) $K_{sp} = S^{p+q} \cdot p^p \cdot q^q$ (b) $K_{sp} = S^{p+q} \cdot p^q \cdot q^q$
   (c) $K_{sp} = S^{pq} \cdot p^q \cdot q^q$ (d) $K_{sp} = S^{pq} \cdot (pq)^{p+q}$

5. A 20 litre container at 400 K contains $CO_{2(g)}$ at pressure 0.4 atm and an excess of SrO (neglect the volume of solid SrO). The volume of the container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO_2 attains its maximum value, will be
   (Given that : $SrCO_{3(s)} \rightleftharpoons SrO_{(s)} + CO_{2(g)}$, $K_p = 1.6$ atm)
   (a) 10 litre   (b) 4 litre
   (c) 2 litre   (d) 5 litre.   **(NEET 2017)**

6. Which of the following is a set of reducing agents?
   (a) HNO_3, Fe^{2+}, F_2 (b) F^-, Cl^-, MnO_4^-
   (c) I^-, Na, Fe^{2+} (d) $Cr_2O_7^{2-}$, CrO_4^{2-}, Na

7. The ionisation constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3.19 as compared to its solubility in pure water?
   (a) 2   (b) 3.32   (c) 4   (d) 4.32

8. Which set represents an odd nature with respect to oxidation number per atom of underlined atoms ?
   (a) $H_2\underline{S}O_5$, $H_2\underline{S}_2O_8$, $K_2\underline{Cr}_2O_7$
   (b) $\underline{Cr}O_5$, $\underline{Cr}O_4^{2-}$, $\underline{S}O_4^{2-}$
   (c) $H\underline{N}O_2$, $\underline{N}_2O_3$, $\underline{N}F_3$
   (d) $\underline{N}H_4^+$, $\underline{N}_3H$, $\underline{N}H_3$

9. MY and NY_3, two nearly insoluble salts, have the same K_{sp} values of 6.2×10^{-13} at room temperature. Which statement would be true in regard MY and NY_3?

(a) The salts MY and NY_3 are more soluble in 0.5 M KY than in pure water.

(b) The addition of the salt of KY to solution of MY and NY_3 will have no effect on their solubilities.

(c) The molar solubilities of MY and NY_3 in water are identical.

(d) The molar solubility of MY in water is less than that of NY_3. **(NEET Phase-I 2016)**

10. The degree of dissociation of PCl_5 (α) obeying the equilibrium : $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is related to the pressure at equilibrium by

(a) $\alpha \propto P$

(b) $\alpha \propto \dfrac{1}{\sqrt{P}}$

(c) $\alpha \propto \dfrac{1}{P^2}$

(d) $\alpha \propto \dfrac{1}{P^4}$

11. What will occur if a block of copper metal is dropped into a beaker containing a solution of 1 M $ZnSO_4$?

(a) The copper metal will dissolve with evolution of oxygen gas.

(b) The copper metal will dissolve with evolution of hydrogen gas.

(c) No reaction will occur.

(d) The copper metal will dissolve and zinc metal will be deposited. **(JEE Main Online 2016)**

12. The rate of formation of the complex $[Fe(dipy)_3]^{2+}$ at 25 °C in following the reaction

$Fe^{2+} + 3dipy \rightleftharpoons [Fe(dipy)_3]^{2+}$

is given as, 1.45×10^{13} $[Fe^{2+}]$ $[dipy]^3$

The rate of disappearance of complex is 1.22×10^{-4} $[Fe(dipy)_3]^{2+}$. The stability constant of complex will be

(a) 1.19×10^{17}

(b) 2.45×10^{17}

(c) 1.00×10^{17}

(d) 2.30×10^{17}

13. The degree of dissociation of PCl_5 at a certain temperature and under atmospheric pressure is 0.2. Calculate the pressure at which it will be half dissociated at the same temperature.

(a) 2 atm

(b) 0.225 atm

(c) 0.123 atm

(d) 2.50 atm

14. In which of the following reactions, hydrogen peroxide acts as an oxidizing agent?

(a) $I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$

(b) $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$

(c) $2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$

(d) $HOCl + H_2O_2 \rightarrow H_3O^+ + Cl^- + O_2$

(JEE Main Online 2017)

15. Maximum oxidation state is present in

(a) CrO_2Cl_2

(b) MnO_2

(c) $[Fe(CN)_6]^{3-}$

(d) MnO

16. A sparingly soluble salt gets precipitated only when the ionic product becomes greater than its solubility product. If the solubility of $BaSO_4$ in water is 8×10^{-4} mol dm^{-3}. Calculate its solubility in 0.01 mol dm^{-3} of H_2SO_4.

(a) 6×10^{-5} mol dm^{-3}

(b) 8×10^{-4} mol dm^{-3}

(c) 6×10^{-7} mol dm^{-3}

(d) 8×10^{-6} mol dm^{-3}

17. In acidic medium, H_2O_2 changes $Cr_2O_7{}^{2-}$ to CrO_5 which has two ($-O-O-$) bonds. Oxidation state of Cr in CrO_5 is

(a) +5

(b) +3

(c) +6

(d) −10

18. Consider the following reactions in which all the reactants and the products are in gaseous state.

$2PQ \rightleftharpoons P_2 + Q_2$; $K_1 = 2.5 \times 10^5$

$PQ + \dfrac{1}{2}R_2 \rightleftharpoons PQR$; $K_2 = 5 \times 10^{-3}$

The value of K_3 for the equilibrium,

$\dfrac{1}{2}P_2 + \dfrac{1}{2}Q_2 + \dfrac{1}{2}R_2 \rightleftharpoons PQR$, is

(a) 2.5×10^{-3}

(b) 2.5×10^3

(c) 1.0×10^{-5}

(d) 5×10^3

19. 5 g mixture of $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$ is completely oxidised by 5.5 mL of 0.1 M $KMnO_4$ in acidic medium. The percentage of $FeSO_4 \cdot 7H_2O$ in mixture is

(a) 15.29

(b) 30.58

(c) 20.24

(d) 25.29

20. In the disproportionation reaction,

$3HClO_3 \longrightarrow HClO_4 + Cl_2 + 2O_2 + H_2O$, the equivalent mass of the oxidizing agent is (molar mass of $HClO_3 = 84.45$)

(a) 16.89 (b) 32.22 (c) 84.45 (d) 28.15

21. The % yield of ammonia as a function of time in the reaction, $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$, $\Delta H < 0$ at (P, T_1) is given in the graph. If this reaction is conducted at (P, T_2), with $T_2 > T_1$, the % yield of ammonia as a function of time is represented by
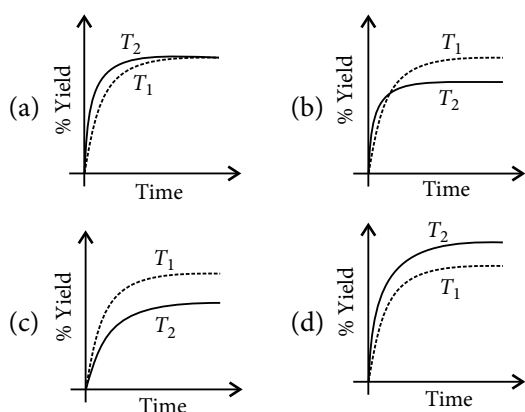
(JEE Advanced 2015)

22. In a reversible reaction $A \rightleftharpoons B$, the initial concentration of A and B are a and b in moles per litre and the equilibrium concentration are $(a - x)$ and $(b + x)$ respectively, express x in terms of k_f, k_b, a and b.

(a) $\dfrac{k_f a - k_b b}{k_f + k_b}$ (b) $\dfrac{k_f a - k_b b}{k_f - k_b}$

(c) $\dfrac{k_f a - k_b b}{k_f k_b}$ (d) $\dfrac{k_f a + k_b b}{k_f + k_b}$

23. If $E^\circ_{M^+/M} = -1.2$ V, $E^\circ_{X_2/X^-} = 1.1$ V and $E^\circ_{O_2/H_2O} = 1.23$ V then on electrolysis of aqueous solution of salt MX, the products obtained are
(a) M, X_2 (b) H_2, X_2 (c) H_2, O_2 (d) M, O_2

24. NH_4CN is a salt of weak acid HCN ($K_a = 6.2 \times 10^{-10}$) and a weak base NH_4OH ($K_b = 1.8 \times 10^{-5}$) then molar solution of NH_4CN will be
(a) neutral   (b) strongly acidic
(c) strongly basic   (d) weakly basic.

25. Equivalent weight of potassium permanganate in alkaline solution is equal to
(a) $\dfrac{1}{5} \times$ Mol.wt.   (b) $\dfrac{1}{6} \times$ Mol.wt.
(c) $\dfrac{1}{3} \times$ Mol.wt.   (d) $\dfrac{1}{10} \times$ Mol.wt.

26. A weak acid HX has p$K_a = 5$. The per cent degree of hydrolysis of 0.1 M solution of its salt NaX is
(a) 0.001%   (b) 0.01%
(c) 0.1%   (d) 0.15%

27. Hot concentrated sulphuric acid is a moderately strong oxidising agent. Which of the following reactions does not show oxidising behaviour?
(a) $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$
(b) $S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$
(c) $C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$
(d) $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$
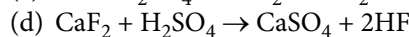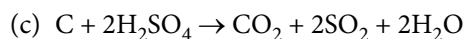
(NEET Phase-II 2016)

28. What is the molecular state of sulphur as reactant in the given reaction :
Sulphur + $12OH^- \longrightarrow 4S^{2-} + 2S_2O_3^{2-} + 3H_2O$
(a) S_8^{2-} (b) S_4^{2-} (c) S_8 (d) S_8^-
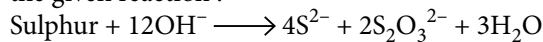
29. If the salt M_2X, QY_2 and PZ_3 have the same solubilities, their K_{sp} values are related as
(a) $K_{sp}(M_2X) = K_{sp}(QY_2) < K_{sp}(PZ_3)$
(b) $K_{sp}(M_2X) > K_{sp}(QY_2) = K_{sp}(PZ_3)$
(c) $K_{sp}(M_2X) < K_{sp}(QY_2) = K_{sp}(PZ_3)$
(d) $K_{sp}(M_2X) > K_{sp}(QY_2) > K_{sp}(PZ_3)$
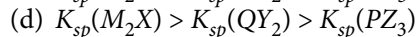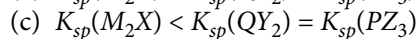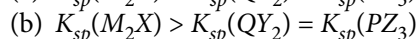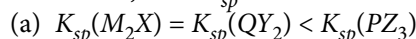
30. In which case oxidation number of Cr has been affected?
(a) $2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$
(b) $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$
(c) $(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + 4H_2O + N_2$
(d) $CrO_2Cl_2 + 2OH^- \longrightarrow CrO_4^{2-} + 2HCl$
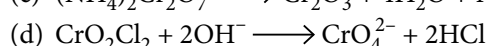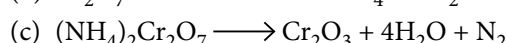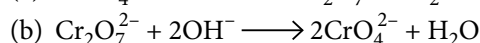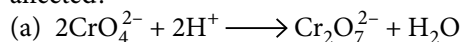
SOLUTIONS

1. **(c)** : $pOH = pK_b + \log \dfrac{[\text{Salt}]}{[\text{Base}]}$

$$= 4.75 + \log \dfrac{0.2}{0.1} = 4.75 + \log 2$$

$$= 4.75 + 0.3010 = 5.0510 \approx 5.05$$

Now, $pH = 14 - pOH = 14 - 5.05 = 8.95$

2. **(b)** :

	A	$+$	$2B$	$\rightleftharpoons$	AB_2
Initial mole	1		2		0
Moles at equilibrium	$(1-x)$		$(2-2x)$		x

Total moles at equilibrium = $1 - x + 2 - 2x + x$
$$= 3 - 2x$$

Let pressure at equilibrium be P,

Now, $p'_{AB_2} = \left[\dfrac{x}{3-2x}\right]P$; $p'_A = \left[\dfrac{1-x}{3-2x}\right]P$;

$p'_B = \left[\dfrac{2-2x}{3-2x}\right]P$

$K_p = \dfrac{x \cdot P}{(3-2x) \cdot P \dfrac{(1-x)}{(3-2x)} \cdot P^2 \dfrac{(2-2x)^2}{(3-2x)^2}}$

$K_p = \dfrac{x \cdot (3-2x)^2}{P^2(1-x)(2-2x)^2}$ ...(i)

Given that, $x = 0.6$ and $\Delta n = -2$
$\therefore \quad K_p = K_c(RT)^{\Delta n}$
$$= 0.3475 \times (0.0821 \times 473)^{-2} \quad ...(ii)$$

From eqn. (i) and (ii),
$0.3475 \times (0.0821 \times 473)^{-2}$

$$= \frac{0.6(3-1.2)^2}{P^2(1-0.6)(2-1.2)^2} = \frac{0.6 \times (1.8)^2}{P^2(0.4)(0.8)^2}$$

$\therefore \quad P = 181.5$ atm

3. **(a) :**
$$\overset{\text{Oxidation}}{\underset{\text{Reduction}}{2\overset{-2}{H_2}S_{(g)} + \overset{+4}{S}O_{2(g)} \longrightarrow 3\overset{0}{S}_{(s)} + 2H_2O_{(g)}}}$$

4. **(a) :** $A_pB_q \rightleftharpoons pA + qB$
   $\ S \qquad pS \quad qS$

   Then, $K_{sp} = [A]^p [B]^q = (pS)^p (qS)^q = p^p S^p \cdot q^q S^q$
   $\phantom{Then, K_{sp} = [A]^p [B]^q = (pS)^p (qS)^q} = S^{p+q} \cdot p^p \cdot q^q$

5. **(d) :** $SrCO_{3(s)} \rightleftharpoons SrO_{(s)} + CO_{2(g)}$; $K_p = 1.6$ atm
   $K_p = p_{(CO_2)}$ $(\because \ p_{(SrO)} = p_{(SrCO_3)} = 1)$; $p_{CO_2} = 1.6$

   $\therefore$ Maximum pressure of $CO_2 = 1.6$ atm
   Let the maximum volume of the container when pressure of CO_2 is 1.6 atm be V L.
   During the process, $PV = $ constant
   $\therefore \quad P_1V_1 = P_2V_2 \Rightarrow 0.4 \times 20 = 1.6 \times V$

   $\Rightarrow \quad V = \dfrac{0.4 \times 20}{1.6} = 5$ L

6. **(c)**

7. **(b) :** For silver benzoate (C_6H_5COOAg),
   $K_{sp} = [C_6H_5COO^-][Ag^+] = 2.5 \times 10^{-13}$ ...(i)
   If S' is the solubility of silver benzoate in pure water, then

   $$S' = \sqrt{K_{sp}} = \sqrt{2.5 \times 10^{-13}} = 5 \times 10^{-7} \text{ mol L}^{-1}$$

   pH $= 3.19 \Rightarrow -\log[H^+] = 3.19$
   $\log[H^+] = -3.19$
   $[H^+] = 6.457 \times 10^{-4}$ M
   For benzoic acid in aqueous solution,
   $C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+$
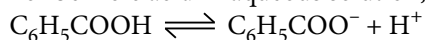
   $$K_a = \frac{[C_6H_5COO^-][H^+]}{[C_6H_5COOH]} \qquad \text{...(ii)}$$

   $$\frac{[C_6H_5COO^-]}{[C_6H_5COOH]} = \frac{K_a}{[H^+]} = \frac{6.46 \times 10^{-5}}{6.457 \times 10^{-4}} = \frac{1}{10}$$

   Suppose solubility of silver benzoate in buffer solution is y mol L^{-1} then most of the benzoate ions are converted into benzoic acid molecules (which remain almost ionised), we have
   $y = [Ag^+] = [C_6H_5COO^-] + [C_6H_5COOH]$
   $ = [C_6H_5COO^-] + 10[C_6H_5COO^-]$
   $ = 11[C_6H_5COO^-]$

$\therefore \ [C_6H_5COO^-] = \dfrac{y}{11}$

$K_{sp} = [C_6H_5COO^-][Ag^+]$

i.e., $2.5 \times 10^{-13} = \dfrac{y}{11} \times y \Rightarrow y^2 = 2.75 \times 10^{-12}$

$y = 1.66 \times 10^{-6}$

$\therefore \quad \dfrac{y\,(\text{solubility in buffer})}{x\,(\text{solubility in water})} = \dfrac{1.66 \times 10^{-6}}{5 \times 10^{-7}} = 3.32$

8. **(d)**

9. **(d) :** For $MY : K_{sp} = S_1^2$

   $\Rightarrow \quad S_1 = \sqrt{K_{sp}} = \sqrt{6.2 \times 10^{-13}}$
   $ = 7.87 \times 10^{-7}$ mol L^{-1}

   For $NY_3 : K_{sp} = 27S_2^4$
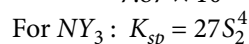
   $\Rightarrow \quad S_2 = \sqrt[4]{\dfrac{6.2 \times 10^{-13}}{27}} = 3.89 \times 10^{-4}$ mol L^{-1}

   Hence, molar solubility of MY in water is less than that of NY_3.

10. **(b)**

11. **(c) :** No reaction will occur. As reduction potential of Zn^{2+} ions to Zn atom is lower than that for Cu^{2+} ions. Hence, Cu metal cannot displace Zn^{2+} ions in $ZnSO_4$ solution.
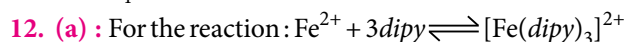
12. **(a) :** For the reaction : $Fe^{2+} + 3dipy \rightleftharpoons [Fe(dipy)_3]^{2+}$
    $r_{forward} = k_f \times [Fe^{2+}][dipy]^3 = 1.45 \times 10^{13} [Fe^{2+}][dipy]^3$
    $r_{backward} = k_b \times [Fe(dipy)_3]^{2+} = 1.22 \times 10^{-4} [Fe(dipy)_3]^{2+}$

    At equilibrium, $r_f = r_b$ and $K_c = \dfrac{k_f}{k_b} = \dfrac{[Fe(dipy)_3]^{2+}}{[Fe^{2+}][dipy]^3}$

    Also, stability constant of complex = Equilibrium
    constant of reaction $= \dfrac{k_f}{k_b}$

    $= \dfrac{1.45 \times 10^{13}}{1.22 \times 10^{-4}} = 1.19 \times 10^{17}$

13. **(c) :** If α is the degree of dissociation at certain temperature under the atmospheric pressure, then

    $$ PCl_5 \rightleftharpoons PCl_3 + Cl_2$$
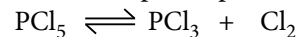
    Initial conc. $ 1 0 0$
    At equilibrium $ 1-\alpha \alpha \alpha$

    Now, $K_p = \dfrac{\alpha^2}{1-\alpha^2} P$

    Putting $P = 1$ atm and $\alpha = 0.2$

    $K_p = \dfrac{(0.2)^2}{1-(0.2)^2} \times 1 = 0.041$

When $\alpha = \dfrac{1}{2} = 0.5$, then let pressure is P'

$$K_p = \dfrac{\alpha^2}{1-\alpha^2} \cdot P' \Rightarrow 0.041 = \dfrac{(0.5)^2 P'}{1-(0.5)^2}$$

$$P' = \dfrac{(0.041)[1-(0.5)^2]}{(0.5)^2} = 0.123 \text{ atm}$$

14. (b)   **15. (a)**

16. (a) : $BaSO_{4(s)} \rightleftharpoons Ba^{2+} + SO_4^{2-}$
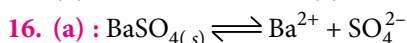
Solubility of $BaSO_4 = 8 \times 10^{-4} \text{ mol dm}^{-3}$

$\therefore \quad [Ba^{2+}] = [SO_4^{2-}] = 8 \times 10^{-4} \text{ mol dm}^{-3}$

$\quad K_{sp} = [Ba^{2+}][SO_4{}^{2-}] = (8 \times 10^{-4})^2$

$\quad = 64 \times 10^{-8}$

Now, $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$

$\therefore \quad [SO_4^{2-}]$ produced from 0.01 mol dm^{-3} of $H_2SO_4 = 0.01$ M

If x is the solubility of $BaSO_4$ in H_2SO_4, then

$[Ba^{2+}] = x$, $[SO_4^{2-}] = x + 0.01$

Since K_{sp} is constant for a given salt,

$K_{sp} = [Ba^{2+}][SO_4^{2-}]$

$= x(x + 0.01) = 64 \times 10^{-8}$

or $\quad x^2 + 0.01\,x - 64 \times 10^{-8} = 0$

$\Rightarrow \quad x = 6 \times 10^{-5} \text{ mol dm}^{-3}$

17. (c) : $CrO_5 : x + 4(-1) + 1(-2) = 0 \Rightarrow x = +6$

18. (c) : $2PQ \rightleftharpoons P_2 + Q_2$; $K_1 = \dfrac{[P_2][Q_2]}{[PQ]^2} = 2.5 \times 10^5$

$$PQ + \dfrac{1}{2}R_2 \rightleftharpoons PQR;\ K_2 = \dfrac{[PQR]}{[PQ][R_2]^{1/2}} = 5 \times 10^{-3}$$

$$\dfrac{1}{2}P_2 + \dfrac{1}{2}Q_2 + \dfrac{1}{2}R_2 \rightleftharpoons PQR$$
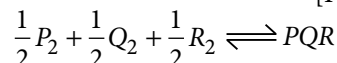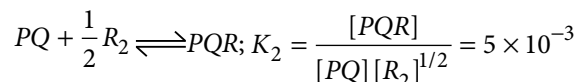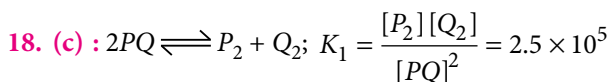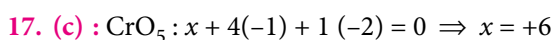
$$K_3 = \dfrac{[PQR]}{[P_2]^{1/2}[Q_2]^{1/2}[R_2]^{1/2}}$$

$$= \dfrac{K_2}{\sqrt{K_1}} = \dfrac{5 \times 10^{-3}}{\sqrt{2.5 \times 10^5}} = 1 \times 10^{-5}$$

19. (a) : $Mn^{7+} + 5e^- \longrightarrow Mn^{2+}$

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$
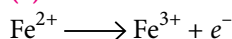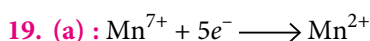
Meq. of $KMnO_4$ = Meq. of $FeSO_4 \cdot 7H_2O$

$$5.5 \times 0.1 \times 5 = \dfrac{w}{278} \times 1000$$

$\therefore \quad w = 0.7645$

$\therefore \quad$ % of $FeSO_4 \cdot 7H_2O = \dfrac{0.7645}{5} \times 100 = 15.29\%$

20. (a) :
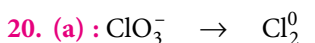
ClO_3^-	$\rightarrow$	Cl_2^0
$x - 6 = -1$		$x = 0$
$x = +5$		$x = 0$ (x = Oxidation number)

$$\text{Equivalent mass} = \dfrac{\text{Molecular mass}}{\text{Oxidation number}} = \dfrac{84.45}{5} = 16.89$$

21. (b) : $N_{2(g)} + 3H_{2(g)} \underset{Endo}{\overset{Exo}{\rightleftharpoons}} 2NH_{3(g)}$; $\Delta H < 0$
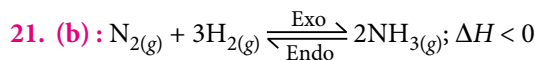
Initially, with increase in temperature ($T_2 > T_1$) % yield increases.

Afterwards, equilibrium is reached and if the temperature is increased, *i.e.*, heat is supplied to the system, then according to Le Chatelier's principle, the equilibrium will shift in the backward direction, where the heat is absorbed. Hence, the % yield decreases.

22. (a) : $\underset{(a-x)}{A} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \underset{(b+x)}{B}$, $\ K_c = \dfrac{k_f}{k_b} = \dfrac{b+x}{a-x}$
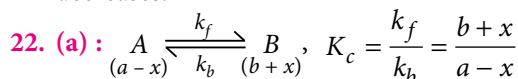
$$x = \dfrac{k_f a - k_b b}{k_f + k_b}$$

23. (b)

24. (d) : Since $K_b > K_a$, the solution will be slightly basic.

25. (c)

26. (b) : Hydrolysis reaction is

$X^- + H_2O \rightleftharpoons HX + OH^-$
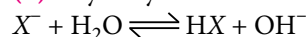
For a salt of weak acid with strong base,

$$K_h = \dfrac{K_w}{K_a} = Ch^2 \Rightarrow \dfrac{10^{-14}}{10^{-5}} = 0.1 \times h^2 \Rightarrow h^2 = 10^{-8}$$

$\therefore \quad h = 10^{-4}$

% hydrolysis = $10^{-4} \times 100 = 10^{-2} = 0.01\%$

27. (d)

28. (c) : Let sulphur be as $(S_n)^x$,

where, x = charge

n = number of sulphur atoms

$(S_n)^x + 12OH^- \longrightarrow 4S^{2-} + 2S_2O_3^{2-} + 3H_2O$
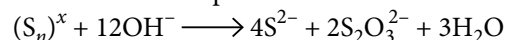
Charge balanced : $x + (-12) = -8 - 4$ $\therefore$ $x = 0$

Sulphur balanced : $n = 4 + 4 = 8$

Thus, molecular state of sulphur is S_8.

29. (a) : For the solubility of a salt like A_xB_y

$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$
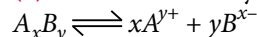
If s is the solubility

$[A^{y+}] = xs$, $[B^{x-}] = ys$

$K_{sp} = (xs)^x \cdot (ys)^y = x^x y^y s^{x+y}$

For $M_2X (x = 2, y = 1)$; $K_{sp} = 4s^3$

$QY_2 (x = 1, y = 2)$; $K_{sp} = 4s^3$

$PZ_3 (x = 1, y = 3)$; $K_{sp} = 27s^4$

30. (c)

$\diamond \diamond$

EXAMİNER'S MİND CLASS XI

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI.
This year JEE (Main & Advanced)/NEET/AIIMS have drawn their papers heavily from NCERT books.

Section - I	Q. 1 to 10 Only One Option Correct Type MCQs.
Section - II	Q. 11 to 13 More than One Options Correct Type MCQs.
Section - III	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.
Section - IV	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.
Section - V	Q. 20 to 22 Assertion Reason Type MCQs having Only One Option Correct. Mark the correct choice as : (a) If both assertion and reason are true and reason is the correct explanation of assertion. (b) If both assertion and reason are true but reason is not the correct explanation of assertion. (c) If assertion is true but reason is false. (d) If both assertion and reason are false.
Section - VI	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).

STATES OF MATTER

SECTION - I

Only One Option Correct Type

1. If the density of a certain gas at 30 °C and 768 torr is 1.35 kg m^{-3} then its density at STP will be
   (a) 1.48 kg m^{-3} (b) 0.125 kg m^{-3}
   (c) 2.48 kg m^{-3} (d) 1.80 kg m^{-3}

2. A refrigeration tank holding 5 L freon gas ($C_2Cl_2F_4$) at 25 °C and 3 atm pressure developed a leak. When the leak was discovered and repaired, the tank had lost 76.0 g of the gas. The pressure of the gas remaining in the tank at 25 °C is
   (a) 0.50 atm   (b) 0.83 atm
   (c) 0.58 atm   (d) 1.90 atm

3. At what temperature, the rate of diffusion of N_2 would be 1.625 times the rate of effusion of SO_2 at 50 °C?
   (a) 110 K   (b) 173 K   (c) 373 K   (d) 273 K

4. Longest mean free path stands for
   (a) H_2 (b) N_2 (c) O_2 (d) Cl_2

5. At which temperature, average velocity of oxygen molecule is equal to the *rms* velocity at 27 °C?
   (a) 90.98 °C   (b) 60.6 °C
   (c) 80.57 °C   (d) 75.82 °C

6. At which location in the inside surface of the closed container shown in figure will the number of gaseous molecular collisions per unit area be the greatest? (Ignore the effects of gravity.)

   (a) Square *A* (top centre)
   (b) Square *B* (center side)
   (c) Square *C* (bottom centre)
   (d) The number of collisions is the same at *A*, *B* and *C*.

7. The pressure of a 1 : 4 mixture of dihydrogen and dioxygen enclosed in a vessel is one atmosphere. What would be the partial pressure of dioxygen?
   (a) 0.8×10^5 atm   (b) 0.008 Nm^{-2}
   (c) 8×10^4 Nm^{-2} (d) 0.25 atm

8. The compressibility of gas is less than unity at STP. Therefore,
   (a) $V_m > 22.4$ L   (b) $V_m < 22.4$ L
   (c) $V_m = 22.4$ L   (d) $V_m > 44.8$ L

9. The distribution of molecular speeds for CO_2 at different temperatures is given below, which of the following statements is incorrect?
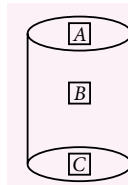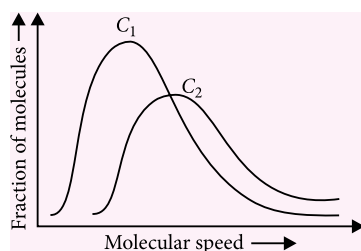
(a) It represents Maxwell's distribution curve.
(b) Temperature of C_2 graph is more than that of C_1.
(c) The average velocity of molecules in C_2 graph is more than C_1.
(d) Velocity $\propto \dfrac{1}{\sqrt{M}}$, therefore, molecular mass of molecules in $C_1 > C_2$.

10. Pick out the wrong statement(s).
  (i) Vapour pressure of a liquid is the measure of the strength of intermolecular attractive forces.
  (ii) Surface tension of a liquid acts perpendicular to the surface of the liquid.
  (iii) Vapour pressures of all liquids are same at their freezing points.
  (iv) Liquids with stronger intermolecular attractive forces are more viscous than those with weaker intermolecular forces.
  (a) (ii), (iii) and (iv) only
  (b) (ii) and (iii) only
  (c) (i), (ii) and (iii) only
  (d) (iii) only

SECTION - II
More than One Options Correct Type

11. The van der Waals' parameters of two gases are given as :

	$a(\text{dm}^6\ \text{bar mol}^{-2})$	$b(\text{dm}^3\ \text{mol}^{-1})$
Gas A	6.5	0.056
Gas B	18.0	0.011

Considering these values, which of the following statements are correct?
  (a) Critical volume of A < Critical volume of B
  (b) Critical pressure of A > Critical pressure of B
  (c) Critical temperature of A < Critical temperature of B
  (d) Ease of liquefaction of A > Ease of liquefaction of B

12. Which of the followings are correct about Charles' law?
  (a) $(\partial V/\partial T)_P = \text{Constant}$
  (b) $V \propto T$ at constant P and n
  (c) $V \propto P$ at constant T, n
  (d) $V \propto T$ at constant P, n

13. If a graph is plotted between $\log V$ and $\log T$ for 2 moles of a gas at constant pressure of 0.0821 atm, then which of the following statements are correct?
  (a) The curve is straight line with slope –1.
  (b) The curve is straight line with slope + 1.
  (c) The intercept on y-axis is equal to 2.
  (d) The intercept on y-axis is equal to 0.3010.

SECTION - III
Paragraph Type
Paragraph for Questions 14 and 15

Rate of effusion is a process in which gas comes out of the container into vacuum through a fine hole.

$$\text{Rate of effusion} = k\,\frac{P}{\sqrt{M}}$$

The two containers A and B have the same volume, container A contains 6 moles of He and 2 moles of O_2 but container B contains only 5 moles of N_2. Both the containers are separately kept in vacuum at the same temperature. Both the containers have very small orifices of the same area through which the gases leak out.

14. The mole fraction of O_2 in the mixture which is effusing out of the container A is
  (a) 0.895 (b) 0.105 (c) 0.623 (d) 0.325

15. The ratio of rate of effusion of N_2 with that of mixture of He and O_2 is
  (a) 0.0497 (b) 0.367 (c) 0.497 (d) 0.83

Paragraph for Questions 16 and 17

The behaviour of real gas may be represented by Berthelot's equation :

$$P = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}$$

16. The unit of constant a is
  (a) $\text{Pa m}^6\ \text{mol}^{-2}$ (b) $\text{Pa m}^3\ \text{mol}^{-1}$
  (c) $\text{Pa m}^6\ \text{K mol}^{-2}$ (d) $\text{atm L}^2\ \text{mol}^{-2}$

17. The Boyle temperature for the Bethelot's equation is given by the expression
  (a) $T_B = \dfrac{1}{Rb}$ (b) $T_B = \dfrac{a}{\sqrt{Rb}}$
  (c) $T_B = \sqrt{\dfrac{a}{Rb}}$ (d) $T_B = \dfrac{b}{Ra}$

SECTION - IV
Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists :

	List I		List II
P.	Mean free path	1.	$\propto T$
Q.	Root mean square velocity	2.	$\propto 1/d$
R.	Effusion rate	3.	$\propto \sqrt{T}$
S.	Average kinetic energy	4.	$\propto 1/V$

	P	Q	R	S
(a)	4	3	2	1
(b)	1	2	3	4
(c)	4	3	1	2
(d)	4	1	2	3

19. Match the List I with List II and select the correct answer using the codes given below the lists :

	List I		List II
(P)	Pressure *vs.* temperature graph at constant molar volume	1.	Isotherms
(Q)	Pressure *vs.* volume graph at constant temperature	2.	Isochores
(R)	Volume *vs.* temperature graph at constant pressure	3.	Isobars

	P	Q	R
(a)	2	1	3
(b)	1	2	3
(c)	3	2	1
(d)	1	3	2

SECTION - V
Assertion Reason Type

20. **Assertion :** Considering the Van der Waals' quation of state $(P + a/V^2) + (V - b) = R$ for ammonia (NH_3) and nitrogen (N_2), the value of a for NH_3 is larger than that of N_2.
Reason : Ammonia has a lower molecular weight than nitrogen.

21. **Assertion :** At higher peaks of mountains, people suffer from high altitude sickness (sluggish feeling, breathlessness, etc.) due to lesser oxygen intake during respiration.
Reason : Air at sea level is dense because it is compressed by the mass of the air above it. The atmospheric pressure at higher peaks of mountains is lower, causing the air at those heights to be much less denser than at sea level.

22. **Assertion :** In Maxwell—Boltzmann distribution of speeds, the curve broadens at higher temperature.
Reason : At a particular temperature, the individual speed of molecules as well as the distribution of speeds remains the same.

SECTION - VI
Integer Value Correct Type

23. A V dm^3 flask contains gas A and another flask of 2 V dm^3 contains gas B at the same temperature. If density of gas A is 3.0 g dm^{-3} and of gas B is 1.5 g dm^{-3} and molecular mass of $A = \dfrac{1}{2}$ molecular mass of B, then the ratio of pressure exerted by gases (P_A/P_B) is

24. A column of Hg of 10 cm in length is contained in the middle of a narrow 1 m long tube which is closed at both ends. Both the halves of the tube contained air at a pressure 76 cm of Hg. By what distance will the column of Hg be displaced (in cm) if the tube is held vertical?

25. At 400 K, the root mean square (*rms*) speed of a gas X (molecular weight = 40) is equal to the most probable speed of gas Y at 60 K. The molecular weight of the gas Y is

THE s-BLOCK ELEMENTS

SECTION - I
Only One Option Correct Type

1. Calculate heat of solution of sodium chloride from following data.
Hydration energy of Na^+ = – 389.4 kJ/mol
Hydration energy of Cl^- = – 382.3 kJ/mol
Lattice energy of NaCl = – 776 kJ/mol
(a) – 4.3 kJ/mol   (b) – 4.5 kJ/mol
(c) 4.3 kJ/mol   (d) – 4.6 kJ/mol

2. Which of the following compounds are formed when magnesium metal burns in air followed by hydrolysis?
(a) $MgSO_4$, MgO, $MgCO_3$
(b) MgO, Mg_3N_2, $Mg(OH)_2$
(c) MgO, Mg_3N_2, $MgCO_3$
(d) $Mg(OH)_2$, MgO, $MgCO_3$

3. From the following sets, choose the incorrect set :
I. Oxidising nature : $I_2 > Br_2 > Cl_2 > F_2$
II. IE_1 : Na < Li < B < Be

III. $EA_1 : N < P < O < S$
IV. Aqueous ion radius : $Na^+ < Mg^{2+} < Al^{3+}$
(a) Only I (b) I and II
(c) I, II and III (d) All of these

4. Beryllium chloride has a linear structure in the solid state but in the vapour phase it tends to form a chlorine-bridge dimer. This is due to
(a) its small size
(b) its electron deficient nature
(c) its high ionisation enthalpy
(d) its high lattice energy.

5. Based on lattice energy and other considerations, which one of the following alkali metal chlorides is expected to have highest melting point?
(a) LiCl (b) NaCl (c) KCl (d) RbCl

6. Select the correct order of solubility in water.
(a) $CaCO_3 > KHCO_3 > NaHCO_3$
(b) $KHCO_3 > NaHCO_3 > CaCO_3$
(c) $NaHCO_3 > KHCO_3 > CaCO_3$
(d) $CaCO_3 > NaHCO_3 > KHCO_3$

7. Be and Al exhibit many properties which are similar. But the two elements differ in
(a) forming covalent bonds
(b) forming polymeric hydrides
(c) exhibiting maximum covalency in compounds
(d) exhibiting amphoteric nature in their oxides.

8. Solubility and thermal stability both increase down the group for
(a) hydroxides of alkaline earth metals $[M(OH)_2]$
(b) fluorides of alkali metals (MF)
(c) perchlorates of alkali metals ($MClO_4$)
(d) hydrides of alkali metals (MH).

9. Which of the following alkaline earth metal sulphates has highest solubility in water?
(a) $BaSO_4$ (b) $SrSO_4$ (c) $CaSO_4$ (d) $BeSO_4$

10. The set representing the correct order of ionic radii is
(a) $Na^+ > Li^+ > Mg^{2+} > Be^{2+}$
(b) $Li^+ > Na^+ > Mg^{2+} > Be^{2+}$
(c) $Mg^{2+} > Be^{2+} > Li^+ > Na^+$
(d) $Li^+ > Be^{2+} > Na^+ > Mg^{2+}$

SECTION - II
More than One Options Correct Type

11. When chlorine is passed through NaOH solution under different dilutions, the main products formed are
(a) NaCl, NaClO (b) NaCl, $NaClO_2$
(c) NaCl, $NaClO_3$ (d) NaCl, $NaClO_4$

12. The compounds formed upon combustion of sodium metal in excess air are
(a) Na_2O_2 (b) Na_2O (c) NaO_2 (d) NaOH

13. Which of the following statements are correct for Be and Al?
(a) Both are rendered passive by conc. HNO_3.
(b) Both have sp-hybridisation in their compounds.
(c) Both form amphoteric oxides.
(d) Both form ionic hydrides.

SECTION - III
Paragraph Type
Paragraph for Questions 14 and 15

Alkali metals are oxidised on exposure to air. When heated in excess of air they burn strenuously forming different types of oxides. The stability of these oxides can be explained on the basis of size of the cation and anion.

14. Which of the following oxides is formed when potassium is heated in excess of oxygen?
(a) KO_2 (b) K_2O_2 (c) KO (d) K_2O

15. Lithium on heating in the presence of excess of oxygen forms
(a) Li_2O_2 (b) LiO (c) LiO_2 (d) Li_2O

Paragraph for Questions 16 and 17

A suspension of inorganic salt X when saturated with ammonia and carbon dioxide forms ammonium sulphate, a nitrogenous fertiliser. A gas Z and a solid is produced when it is heated at very high temperature. Gas Z produces white turbidity in aqueous solution and produces green colour with $Cr_2O_7^{2-}$ solution in acidic medium.

16. Inorganic salt X is
(a) $MgSO_4 . 7H_2O$ (b) $CaSO_4 . 2H_2O$
(c) $Na_2SO_4 . 10H_2O$ (d) $CaCO_3$

17. Green coloured compound produced by the reaction of $Cr_2O_7^{2-}$ and Z is
(a) K_2CrO_4 (b) K_2CrO_2
(c) $[Cr(H_2O)_6]_2(SO_4)_3$ (d) Cr_2O_3

SECTION - IV
Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists :

List I	List II
(P) Ra	1. Do not impart any colour to Bunsen flame
(Q) Fr	2. Form covalent hydride
(R) Mg	3. Form amphoteric oxide
(S) Be	4. Radioactive

	P	Q	R	S
(a)	4	2,4	3,1	4
(b)	2,1,3	4	1	1
(c)	4	4	1	2, 3
(d)	2, 3, 4	1	4,1	4

19. Match the List I with List II and select the correct answer using the codes given below the lists :

List I		List II	
(P)	Major constituent of Portland cement	1.	$CaSiO_3$
(Q)	Plaster of Paris	2.	Ca_3SiO_5
(R)	Solvay's process	3.	$(CaSO_4)_2 \cdot H_2O$
(S)	Fly ash	4.	Na_2CO_3

	P	Q	R	S
(a)	2	3	4	1
(b)	4	3	1	2
(c)	2	1	4	3
(d)	1	4	2	3

SECTION - V

Assertion Reason Type

20. **Assertion :** Lithium chloride is predominantly covalent compound.

Reason : Electronegativity difference between Li and Cl is small.

21. **Assertion :** Sulphur is estimated as $BaSO_4$ and not as $MgSO_4$.

Reason : The ionic radius of Mg^{2+} is smaller than that of Ba^{2+} ion.

22. **Assertion :** BaO reacts with HCl solution to produce $BaCl_2$ solution.

Reason : BaO is amphoteric oxide.

SECTION - VI

Integer Value Correct Type

23. Ammonia and hydrogen are evolved on heating calcium ammoniate. How many moles of ammonia are evolved when 1.5 moles of calcium hexaammoniate are heated?

24. Out of given hydroxides, find the number of hydroxide(s) which can form salt with CO_2.
NaOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$

25. Total number of moles of water in 1 mole of epsom salt is

SOLUTIONS

STATES OF MATTER

1. **(a) :** $\because d = \dfrac{PM}{RT}$

$\therefore$ For the same gas at two different pressures and temperatures, $\dfrac{d_1}{d_2} = \dfrac{P_1}{P_2} \times \dfrac{T_2}{T_1}$

$d_1 = 1.35$ Kg m^{-3}, $P_1 = 768$ torr, $T_1 = 303$ K

$d_2 = ?$, $P_2 = 760$ torr, $T_2 = 273$ K (P_2 and T_2 at STP)

$\therefore \dfrac{1.35}{d_2} = \dfrac{768}{760} \times \dfrac{273}{303} \Rightarrow d_2 = 1.48$ kg m^{-3}

2. **(b) :** Moles of gas initially present, $n = \dfrac{PV}{RT}$

$= \dfrac{(3 \text{ atm})(5 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm} / \text{mol} \cdot \text{K})(298 \text{ K})} = 0.613$ mol

Mass of gas initially present

$= (0.613 \text{ mol}) \times \left(\dfrac{171 \text{ g}}{\text{mol}}\right) = 105$ g

The remaining quantity of the gas = 105 – 76 = 29 g

Number of moles of remaining gas (n)

$= (29 \text{ g}) \times \left(\dfrac{1 \text{ mol}}{171 \text{ g}}\right) = 0.17$ mol

Pressure of remaining gas, $(P) = \dfrac{nRT}{V}$

$= \dfrac{(0.17 \text{mol}) \times (0.0821 \text{ L} \cdot \text{atm} / \text{mol} \cdot \text{K}) \times (298 \text{ K})}{(5 \text{ L})}$

$= 0.83$ atm

3. **(c) :** $\dfrac{r_{N_2}}{r_{SO_2}} = \sqrt{\dfrac{T_{N_2} M_{SO_2}}{T_{SO_2} M_{N_2}}}$

$\dfrac{r_{N_2}}{r_{SO_2}} = \dfrac{1.625}{1} = \sqrt{\dfrac{T_{N_2} \times 64}{323 \times 28}}$

$\therefore T_{N_2} = \dfrac{(1.625)^2 \times 323 \times 28}{64} = 373$ K

4. **(a) :** The mean free path $\lambda = \dfrac{1}{\sqrt{2\pi\sigma^2 N}}$

or $\lambda \propto \dfrac{1}{\sigma^2}$ [σ is molecular diameter]

Thus, the path is largest for smallest σ. Here σ is smallest for H_2.

5. (c) : Root mean square velocity $= \left(\dfrac{3RT}{M}\right)^{1/2}$

Average velocity $= \left(\dfrac{8RT}{\pi M}\right)^{1/2}$

Now, average velocity = root mean square velocity

$$\left(\dfrac{8RT}{\pi M}\right)^{1/2} = \left(\dfrac{3R \times 300}{M}\right)^{1/2}$$

$\therefore \quad T = \dfrac{900 \times 22}{7 \times 8} = 353.57\,\text{K}$

$= 353.57 - 273 = 80.57\,°C$

6. (d)

7. (c) : Let the number of moles of dihydrogen and dioxygen be 1 and 4.

Mole fraction of $O_2 = \dfrac{4}{5}$

Partial pressure of dioxygen
$$= \text{Mole fraction} \times \text{Total pressure}$$
$$= \dfrac{4}{5} \times 1 = 0.8\,\text{atm}$$
$$= 0.8 \times 10^5\,\text{N m}^{-2} = 8 \times 10^4\,\text{N m}^{-2}$$

8. (b) : $\because\ Z < 1 \ \Rightarrow\ \dfrac{PV}{nRT} < 1$

Thus, $V_m < 22.4$ L

9. (d) : Velocity $\propto \dfrac{1}{\sqrt{M}}$, but from this relation we cannot predict molecular mass of molecules in $C_1 > C_2$ or curves C_1 and C_2 are for same gas *i.e.*, CO_2 at two different temperatures.

10. (d)   **11. (a,c)**

12. (a,b) : Charles' law, $V \propto T$

13. (b,d) : $PV = nRT$

$\log V = \log T + \log \dfrac{nR}{P}$

Slope $= \tan\theta = \tan 45° = 1$

Intercept $= \log \dfrac{nR}{P} = \log\left[\dfrac{2 \times 0.0821}{0.0821}\right] = 0.3010$

14. (b) : $\dfrac{r_{O_2}}{r_{He}} = \dfrac{2}{6}\sqrt{\dfrac{4}{32}} = 0.118$

Let rate of effusion of O_2 be x moles and rate of effusion of He = y moles.

Then, $\dfrac{x}{y} = 0.118$

$x = 0.118\,y \quad$ or $\quad y = 8.474\,x$

Total moles in container $A = x + y$
$$= x + 8.474x = 9.474x$$

Now, mole fraction of O_2 effusing out

$$= \dfrac{x}{9.474x} = 0.105$$

15. (c) : Average molecular mass of mixture in container $A = M_{\text{mix}} = x_{O_2}M_{O_2} + x_{He}M_{He}$
$$= 0.105 \times 32 + 0.895 \times 4 = 6.94$$

$\dfrac{r_{N_2}}{r_{\text{mix}}} = \sqrt{\dfrac{M_{\text{mix}}}{M_{N_2}}} = \sqrt{\dfrac{6.94}{28}} = 0.497$

16. (c) : The unit of a is the same as that of the expression pTV_m^2, *i.e.*, Pa m^6 K mol^{-2}.

17. (c)   **18. (a)**

19. (a)   **20. (b)**

21. (a)

22. (c) : Speed distribution curve broadens at higher temperature because number of molecules moving at higher speed increases. At a particular temperature, the individual speed of molecules keeps changing but the distribution of speeds remains the same.

23. (4) : Using equation, $PV = \dfrac{w}{M}RT$ or $P = \dfrac{d}{M}RT$

For gas A, $P_A = \dfrac{3}{M_A} \times R \times T$

For gas B, $P_B = \dfrac{1.5}{M_B} \times R \times T$

$\therefore\ \dfrac{P_A}{P_B} = \dfrac{2 \times M_B}{M_A} = \dfrac{2 \times 2 \times M_A}{M_A} = 4$

24. (3) : Let initially the length of air column on each side be L cm, then

$2L + 10 = 100$ cm

$\therefore\ L = 45$ cm
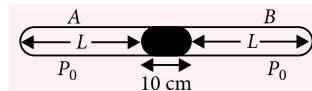
If the tube is held vertically, let the Hg column be displaced downwards by y cm to attain the same pressure above and below the column of Hg. Then,

$P_B + 10 = P_A \qquad\qquad …(1)$

Pressures are taken in terms of length of Hg.

For end A : Since mole remains same on two sides.

$\dfrac{P_0 \times L \times a}{RT} = \dfrac{P_A \times (L - y) \times a}{RT} \quad …(2)$

$\therefore\ P_A = \dfrac{LP_0}{(L - y)} \qquad\qquad …(3)$

For end B :

$\therefore\ \dfrac{P_0 \times L \times a}{RT} = \dfrac{P_B \times (L + y) \times a}{RT} \quad …(4)$

$$\therefore \quad P_B = \frac{LP_0}{(L+y)} \qquad \ldots(5)$$

By Eqs. (1), (3) and (5),

$$\left[\frac{LP_0}{L+y}\right] + 10 = \frac{LP_0}{(L-y)}$$

Putting $L = 45$ cm and $P_0 = 76$ cm and on solving, we get

$$y = 2.9478 \approx 3 \text{ cm}$$

25. (4): Given, $T_1 = 400$ K, $T_2 = 60$ K
Molecular weight of X, $M_1 = 40$

Let molecular weight of Y be M_2

$$v_{rms\,(X)} = \sqrt{\frac{3RT_1}{M_1}}, v_{mp\,(Y)} = \sqrt{\frac{2RT_2}{M_2}}$$

Given, $v_{rms(X)} = v_{mp(Y)}$

$$\therefore \quad \sqrt{\frac{3R \times 400}{40}} = \sqrt{\frac{2R \times 60}{M_2}}$$

$$30 = \frac{120}{M_2} \implies M_2 = 4$$

THE *s*-BLOCK ELEMENTS

1. (c): Hydration energy of NaCl = $-389.4 - 382.3$
$$= -771.7 \text{ kJ}$$
$\Delta H_{solution}$ = Hydration energy – Lattice energy
$$= -771.7 - (-776) = +4.3 \text{ kJ/mol}$$

2. (b): $2Mg + O_2 \longrightarrow 2MgO$
(from air)
$3Mg + N_2 \longrightarrow Mg_3N_2$
(from air)
Hydrolysis of MgO and Mg_3N_2 with water :
$MgO + H_2O \longrightarrow Mg(OH)_2$
$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$
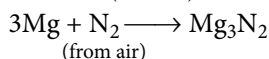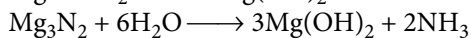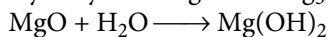
3. (a): Order of oxidising strength of halogens :
$$F_2 > Cl_2 > Br_2 > I_2$$
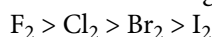
4. (b)

5. (b): The melting point decreases down the group as lattice energy decreases with increase in atomic number. However, LiCl has covalent character due to very small size of Li^+ ion. Hence, melting point of NaCl is highest amongst the alkali metal chlorides.

6. (b): $CaCO_3$ is insoluble in water.
Solubility of bicarbonates of group 1 increases down the group.

7. (c)

8. (a): Order of thermal stability and solubility in water of alkaline earth metal hydrides :
$Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$
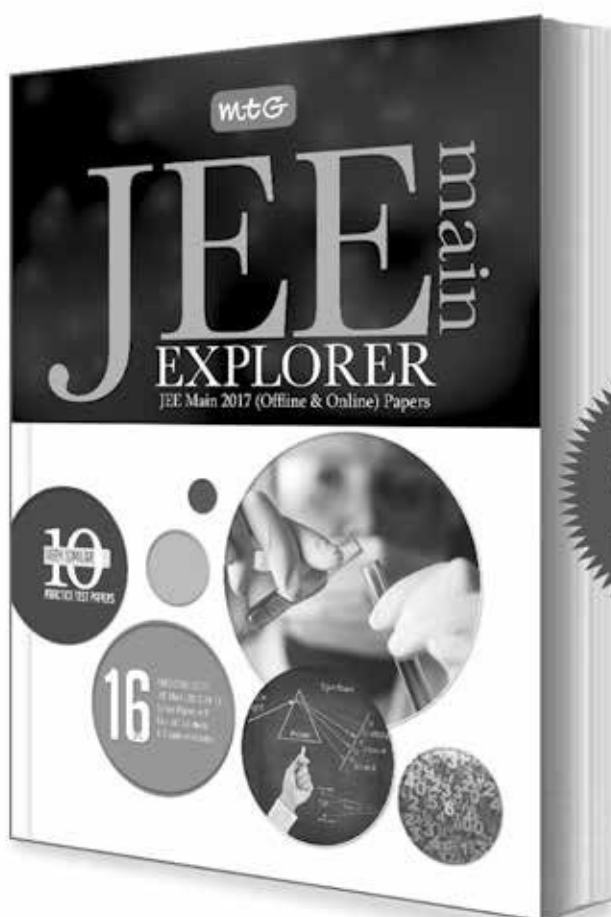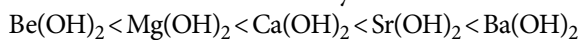
9. (d): Among alkaline earth metal sulphates, lattice enthalpy remains almost constant but hydration enthalpy decreases down the group. Thus, $BeSO_4$ has highest solubility in water.

10. (a): The ionic radii of alkali metal ions are larger than those of the corresponding alkaline earth metal ions. Also, ionic radii increase down the group. Therefore, the ionic radii decrease in the order : $Na^+ > Li^+ > Mg^{2+} > Be^{2+}$

11. (a,c): $Cl_2 + 2NaOH \longrightarrow NaCl + NaClO + H_2O$
(Cold and dilute) Sodium hypochlorite
$3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$
(hot and conc.) Sodium chlorate
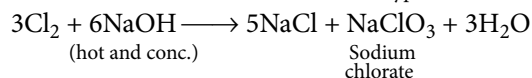
12. (a, b): $4Na + O_2 \rightarrow 2Na_2O$
$4Na + 2O_2 \rightarrow 2Na_2O_2$
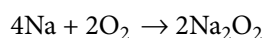
13. (a,c)   14. (a)   15. (d)   16. (b)

17. (c): $Cr_2O_7^{2-} + SO_{2(g)} \longrightarrow Cr^{3+}_{(aq)} + SO_{4(aq)}^{2-}$
(in acidic solution)

18. (c)   19. (a)   20. (c)   21. (b)

22. (c): $BaO + H_2O \longrightarrow Ba(OH)_2$
(Basic)
$BaO + 2HCl_{(aq)} \longrightarrow BaCl_2 + H_2O$
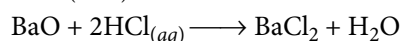
23. (8): $3[Ca(NH_3)_6]^{2+} \longrightarrow Ca_3N_2 + 16NH_3 + 3H_2$
3 moles   16 moles
1.5 moles   8 moles

24. (7): All hydroxides are alkaline, hence they can form salt with acidic gas, CO_2.

25. (7): Epsom salt : $MgSO_4 \cdot 7H_2O$

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MPP-6 CLASS XII		ANSWER		KEY
1. (a)	**2.** (d)	**3.** (d)	**4.** (d)	**5.** (c)
6. (b)	**7.** (b)	**8.** (d)	**9.** (c)	**10.** (c)
11. (a)	**12.** (b)	**13.** (d)	**14.** (d)	**15.** (a)
16. (b)	**17.** (d)	**18.** (b)	**19.** (c)	**20.** (a,b,c)
21. (b,d)	**22.** (b,c,d)	**23.** (a,b,c)	**24.** (4)	**25.** (5)
26. (6)	**27.** (c)	**28.** (c)	**29.** (a)	**30.** (a)

ACE
YOUR WAY CBSE XI
Series 4

CHAPTERWISE PRACTICE PAPER : EQUILIBRIUM | REDOX REACTIONS

Time Allowed : 3 hours   Maximum Marks : 70

GENERAL INSTRUCTIONS

(i)   All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v)   Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. Classify the following species into acids and bases according to Lewis concept :
   S^{2-}, H^+, OH^-, BF_3, Ni^{2+}, F^-
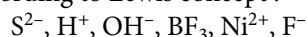
2. Write down the conjugate base of $[Al(H_2O)_6]^{3+}$.

3. At what concentration of $M^+_{(aq)}$ will its electrode potential become equal to its standard electrode potential?

4. Calculate the oxidation number of nitrogen in nitrous acid and nitric acid.

5. Define solubility product.

6. Consider the following equilibrium :
   $$SO_{2(g)} + \frac{1}{2}O_{2(g)} \xrightleftharpoons{K_1} SO_{3(g)}$$
   $$2SO_{3(g)} \xrightleftharpoons{K_2} 2SO_{2(g)} + O_{2(g)}$$
   What is the relation between K_1 and K_2?

7. Calculate the oxidation number of sulphur in $S_2O_8^{2-}$ ion and $S_4O_6^{2-}$ ion.

8. Write equilibrium expression (K_p and K_c) for each of the following reactions :
   (i) $Fe_2O_{3(s)} + 3H_{2(g)} \rightleftharpoons 2Fe_{(s)} + 3H_2O_{(g)}$
   (ii) $CO_{2(g)} + C_{(s)} \rightleftharpoons 2CO_{(g)}$
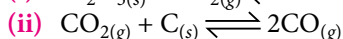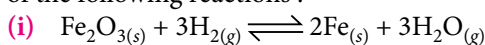
9. 16.4 mL volume of 0.14 M $KMnO_4$ solution is required to oxidise 20.0 mL of $FeSO_4$ solution in acidic medium. What is the concentration of $FeSO_4$ solution?

10. Why does the following reaction occur?
    $$XeO_{6(aq)}^{4-} + 2F_{(aq)}^- + 6H_{(aq)}^+ \longrightarrow XeO_{3(g)} + F_{2(g)} + 3H_2O_{(l)}$$
    What conclusion about the compound Na_4XeO_6 i.e., XeO_6^{4-} can be drawn from the reaction?

    OR
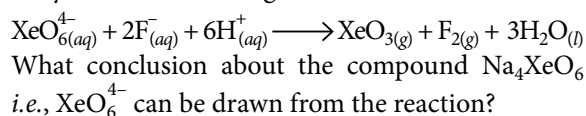
    Nitric acid is an oxidising agent and reacts with PbO but it does not react with PbO_2. Explain, why?

11. Determine the solubilities of silver chromate, ferric hydroxide and lead chloride at 298 K from their solubility product constants given below. Determine also the molarities of individual ions.

Salt	K_{sp} value
Silver chromate	1.1×10^{-12}
Ferric hydroxide	1.0×10^{-38}
Lead chloride	1.6×10^{-5}

12. The ionisation constant of phenol is 1.0×10^{-10}. What is the concentration of phenolate ion in 0.05 M

solution of phenol? What will be its degree of ionisation if the solution is 0.01 M in sodium phenolate?

13. Depict the galvanic cell in which the reaction, $Zn_{(s)} + 2Ag^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$, takes place and answer the following :
   (i) which of the electrode is negatively charged?
   (ii) the direction of the current in the cell, and
   (iii) individual reaction at each electrode.

14. At 473 K, equilibrium constant, K_c for the decomposition of phosphorus pentachloride, PCl_5 is 8.3×10^{-3}. If the decomposition is depicted as,
$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \; ; \; \Delta_r H° = 124.0 \text{ kJ mol}^{-1},$$
then
   (i) write an expression for K_c for the reaction.
   (ii) what is the value of K_c for the reverse reaction at the same temperature?
   (iii) what would be the effect on K_c if more PCl_5 is added?

15. At 46 °C, K_p for the reaction; $3\,N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ is 0.66 atm. Compute the per cent dissociation of N_2O_4 at 46 °C and at total pressure 380 torr. What are the partial pressures of N_2O_4 and NO_2 at equilibrium?

16. For the formation of ammonia, the equilibrium constant data at 673 K and 773 K are 1.64×10^{-4} and 1.44×10^{-5} respectively. Calculate the heat of reaction ($R = 8.314$ J K^{-1} mol^{-1}).

<div align="center">**OR**</div>

Calculate the hydronium ion concentration of solution containing 0.200 mol of $HC_2H_3O_2$ in 1.00 L of solution. What is the per cent ionisation of the acid? ($K_a = 1.80 \times 10^{-5}$)

17. Classify the following redox reactions with reason :
   (i) $2Pb(NO_3)_{2(s)} \longrightarrow 2PbO_{(s)} + 4NO_{2(g)} + O_{2(g)}$
   (ii) $NaH_{(s)} + H_2O_{(l)} \longrightarrow NaOH_{(aq)} + H_{2(g)}$
   (iii) $2NO_{2(g)} + 2OH^-_{(aq)} \longrightarrow NO^-_{2(aq)} + NO^-_{3(aq)} + H_2O_{(l)}$

18. Answer the following :
   (i) Will the pH of water be same at 4°C and 25°C? Explain.
   (ii) The concentration of hydrogen ions in a sample of soft drink is 3.8×10^{-3} M. What is its pH?

19. The ionisation constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13}. How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water?

20. With the help of standard electrode potentials, select the reducing agent that can reduce the following ions to their metallic state :
   (i) $Ag^+_{(aq)}$ **(ii)** $Al^{3+}_{(aq)}$ **(iii)** $Ni^{2+}_{(aq)}$

21. Answer the following :
   (i) What is the oxidation state of copper in $YBa_2Cu_2O_7$, which shows superconductivity? (Assume that the rare earth element yttrium is in its usual +3 oxidation state).
   (ii) Liquid ammonia ionises to a slight extent. At $-50°C$, its ionic product is $K_{NH_3} = [NH_4^+][NH_2^-] = 10^{-30}$. How many amide ions, NH_2^-, are present per mm^3 of pure liquid ammonia?

22. Write the half-reactions for the following redox reactions :
   (i) $2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(aq)}$
   (ii) $Zn_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + H_{2(g)}$
   (iii) $Al_{(s)} + 3Ag^+_{(aq)} \longrightarrow Al^{3+}_{(aq)} + 3Ag_{(s)}$

23. Acids find wide applications in different industries like fertilizer, textile, leather industry, etc. At home, their use for cleaning toilets is very common. However, in recent times, bad elements are misusing these acids. For example, incidents of acid throwing on face, thereby causing burns on the face, are being often reported. Balloons filled with acids are thrown on the passers-by on holi. A mixture of acids is used by the miscreants to cheat women in the name of cleaning their gold jewellery.
   (i) Which two acids are mixed to dissolve gold and in what ratio ? What is the mixture called?
   (ii) Name the reaction when acid is treated with base along with example.
   (iii) Calculate the pH of vinegar with hydrogen ion concentration 1.738×10^{-4} M.
   (iv) What values are expressed in the above paragraph?

24. **(i)** What will be the effect on equilibrium for the given reaction;
   $$2N_2O_{(g)} + O_{2(g)} \rightleftharpoons 4NO_{(g)}; \Delta H > 0$$
      (a) when volume of vessel increases?
      (b) temperature decreases?
   (ii) Calculate the pH of the following solutions :
      (a) 2 g of TlOH dissolved in water to give 2 L of solution.
      (b) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution.
      (c) 0.3 g of NaOH dissolved in water to give 200 mL of solution.
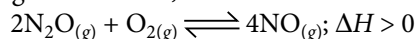
OR

(i) The progress of the reaction, $A \rightleftharpoons nB$, with time is represented in the given figure.

On the basis of above graph, determine :
- **(a)** the value of n
- **(b)** the equilibrium constant, K.

(ii) (a) Ammonium chloride is acidic in liquid ammonia solvent. Explain, why?

(b) Why does solubility of CO_2 decrease with rise in temperature?

25. Identify the substance oxidised, reduced, oxidising agent and reducing agent for each of the following reactions :

(i) $2AgBr_{(s)} + C_6H_6O_{2(aq)} \longrightarrow 2Ag_{(s)} + 2HBr_{(aq)} + C_6H_4O_{2(aq)}$

(ii) $HCHO_{(l)} + 2[Ag(NH_3)_2]^+_{(aq)} + 3OH^-_{(aq)} \longrightarrow 2Ag_{(s)} + HCOO^-_{(aq)} + 4NH_{3(aq)} + 2H_2O_{(l)}$

(iii) $HCHO_{(l)} + 2Cu^{2+}_{(aq)} + 5OH^-_{(aq)} \longrightarrow Cu_2O_{(s)} + HCOO^-_{(aq)} + 3H_2O_{(l)}$

(iv) $N_2H_{4(l)} + 2H_2O_{2(l)} \longrightarrow N_{2(g)} + 4H_2O_{(l)}$

(v) $Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \longrightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$

OR

Starting with the correctly balanced half-reactions, write the overall ionic reaction for the following changes :

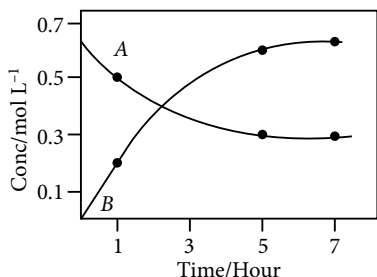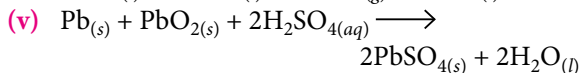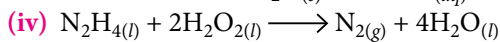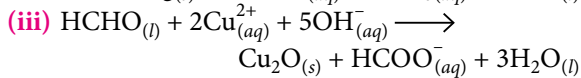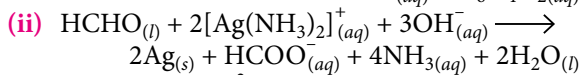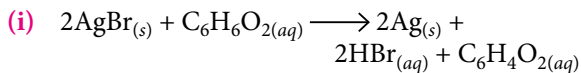**(i)** Chloride ion is oxidised to Cl_2 by $\mathbf{MnO_4^-}$ in acidic solution.

(ii) Nitrous acid (HNO_2) reduces MnO_4^- in acidic solution.

(iii) Nitrous acid (HNO_2) oxidises $\mathbf{I^-}$ to I_2 in acidic solution.

(iv) Chlorate ion ($\mathbf{ClO_3^-}$) oxidises Mn^{2+} to $MnO_{2(s)}$ in acidic solution

(v) Chromite ion ($\mathbf{CrO_3^-}$) is oxidised by H_2O_2 in strongly basic solution.

Also find out the change in the oxidation numbers of the atoms printed in bold letters.

26. (i) Write van't Hoff reaction isotherm. Using this equation deduce that if $K > 1$, the reaction proceeds more in the forward direction.

(ii) A graph plotted between $\log_{10} K_c$ and $1/T$ is straight line with intercept 10 and slope equal to 0.5. Calculate
- **(a)** pre-exponential factor A.
- **(b)** heat of reaction at 298 K.
- **(c)** equilibrium constant at 298 K.
- **(d)** equilibrium constant at 800 K assuming ΔH remains constant in between 298 K and 800 K.

OR

(i) Consider the following reaction, which occurs at 300 K and at constant pressure,
$$P_{(g)} + Q_{(g)} \rightleftharpoons R_{(g)} + 2S_{(g)}$$
Under standard conditions, entropy change and internal energy change are 100 cal K^{-1} and -90.0 kcal, respectively. Calculate equilibrium constant for the reaction.
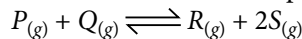
(ii) (a) What are the expression for equilibrium constant for heterogeneous and homogeneous equilibria? Explain with examples.

(b) What is the effect of adding inert gas on equilibrium?

SOLUTIONS

1. Lewis acids are H^+, BF_3, Ni^{2+} whereas Lewis bases are S^{2-}, OH^-, F^-.

2. $\underset{\text{Acid}}{[Al(H_2O)_6]^{3+}} \xrightleftharpoons{H_2O} \underset{\text{Conjugate base}}{[Al(OH)(H_2O)_5]^{2+}} + H_3O^+$
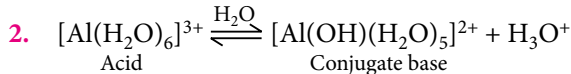
3. When the concentration of metal ion is 1 molar *i.e.*, 1 mol/L, its electrode potential is measured as standard electrode potential.

4. Nitrous acid *i.e.*, HNO_2
$+1 + x - 2 \times 2 = 0$
$x = +3$
Nitric acid *i.e.*, HNO_3
$+1 + x - 2 \times 3 = 0$
$x = +5$
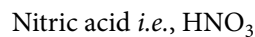
5. It is the product of the molar concentrations of ions of an electrolyte where each concentration terms raised to the power of their coefficients in the balanced chemical equation in a saturated solution.

6. $SO_{2(g)} + \frac{1}{2}O_{2(g)} \xrightleftharpoons{K_1} SO_{3(g)}$; $K_1 = \dfrac{[SO_3]}{[SO_2][O_2]^{1/2}}$

$2SO_{3(g)} \xrightleftharpoons{K_2} 2SO_{2(g)} + O_{2(g)}$; $K_2 = \dfrac{[SO_2]^2[O_2]}{[SO_3]^2}$
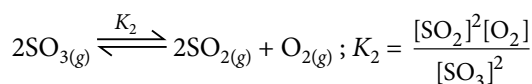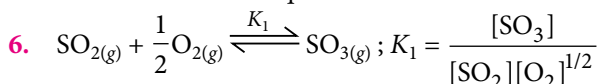
$K_1 \times K_2 = \dfrac{[SO_3]}{[SO_2][O_2]^{1/2}} \times \dfrac{[SO_2]^2[O_2]}{[SO_3]^2}$

$$K_1 \times K_2 = \frac{[SO_2][O_2]^{1/2}}{[SO_3]}$$

$$K_1 \times K_2 = \frac{1}{K_1} \Rightarrow K_1 = \frac{1}{\sqrt{K_2}}$$

7. In $S_2O_8^{2-}$, there is one peroxide bond (—O—O—) therefore, two oxygen atoms having oxidation number -1 (*i.e.*, O_2^{2-}) and for the other six oxygen atoms, the oxidation number is -2.

$S_2O_8^{2-} = 2x + (-2 \times 6) + (-1 \times 2) = -2$

$2x = +12 \Rightarrow x = +6$

In $S_4O_6^{2-}$, two S-atoms have oxidation state $+5$ while another two S-atoms have 0 oxidation state.

$$\underset{S_4O_6^{2-}}{{}^{-}O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}{}^{+5}-S\overset{0}{}-S\overset{0}{}-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}{}^{+5}O^{-}}$$

8. (i) Concentration of pure solids is taken as unity.

$[Fe_2O_{3(s)}] = [Fe_{(s)}] = 1$

The equilibrium constants, K_p and K_c are :

$$K_p = \frac{p_{H_2O}^3}{p_{H_2}^3} \text{ and } K_c = \frac{[H_2O]^3}{[H_2]^3}$$

(ii) Carbon is present in solid phase, $[C_{(s)}] = 1$

The equilibrium constants, K_p and K_c are :

$$K_p = \frac{p_{CO}^2}{p_{CO_2}} \text{ and } K_c = \frac{[CO]^2}{[CO_2]}$$

9. $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

$n_1M_1V_1 = n_2M_2V_2 \Rightarrow 5 \times 0.14 \times 16.4 = 1 \times 20.0 \times M_2$

$\therefore M_2 = \dfrac{0.14 \times 16.4 \times 5}{20.0} = 0.574$ M

10. $XeO_6^{4-}{}_{(aq)} + 2F^-{}_{(aq)} + 6H^+{}_{(aq)} \rightarrow XeO_{3\,(g)} + F_{2(g)} + 3H_2O_{(l)}$

In this reaction, oxidation number of Xe decreases from $+8$ (in XeO_6^{4-}) to $+6$ (in XeO_3) while that of F increases from -1 (in F^-) to 0 (in F_2). Therefore, XeO_6^{4-} is reduced while F^- is oxidised. From this reaction, it is concluded that Na_4XeO_6 is a stronger oxidising agent than F_2.

OR

Nitric acid is an oxidising agent and reacts with PbO to give a simple acid-base reaction without any change in oxidation state. In PbO_2, Pb is in $+4$ oxidation state and cannot be oxidised further, hence no reaction takes place between PbO_2 and HNO_3.

$\underset{\text{Salt}}{2PbO + 4HNO_3 \rightarrow 2Pb(NO_3)_2} + 2H_2O$ (Acid-base reaction)
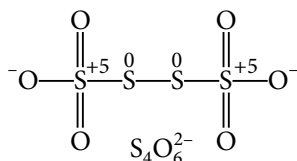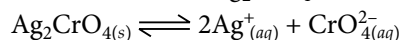
$PbO_2 + HNO_3 \longrightarrow$ No reaction

11. Silver chromate, (Ag_2CrO_4)

$Ag_2CrO_{4(s)} \rightleftharpoons 2Ag^+{}_{(aq)} + CrO_4^{2-}{}_{(aq)}$

$K_{sp} = 4S^3 = 1.1 \times 10^{-12} \Rightarrow S = 6.50 \times 10^{-5}$ M

$\therefore [Ag^+] = 2 \times 6.50 \times 10^{-5} = 1.30 \times 10^{-4}$ M and

$[CrO_4^{2-}] = 6.50 \times 10^{-5}$ M

Ferric hydroxide, $[Fe(OH)_3]$;

$Fe(OH)_{3(s)} \rightleftharpoons Fe^{3+}{}_{(aq)} + 3OH^-{}_{(aq)}$
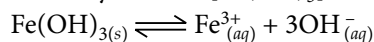
$K_{sp} = 27S^4 = 1.0 \times 10^{-38} \Rightarrow S = 1.38 \times 10^{-10}$ M

$[Fe^{3+}] = 1.38 \times 10^{-10}$ M and $[OH^-] = 3 \times 1.38 \times 10^{-10}$

$\qquad\qquad\qquad\qquad\qquad = 4.14 \times 10^{-10}$ M

Lead chloride, $(PbCl_2)$;

$PbCl_{2(s)} \rightleftharpoons Pb^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)}$
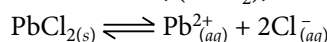
$K_{sp} = 4S^3 = 1.6 \times 10^{-5} \Rightarrow S = 1.59 \times 10^{-2}$ M

$[Pb^{2+}] = 1.59 \times 10^{-2}$ M and $[Cl^-] = 2 \times 1.59 \times 10^{-2}$

$\qquad\qquad\qquad\qquad\qquad = 3.18 \times 10^{-2}$ M

12.
$$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$$

Initial concentration:	0.05 M	0	0
After dissociation:	0.05 − x	x	x

$\therefore K_a = \dfrac{x \times x}{0.05 - x} = 1.0 \times 10^{-10}$ (Given)

$\dfrac{x^2}{0.05} = 1.0 \times 10^{-10}$ $[\because 0.05 - x \approx 0.05]$

$x^2 = 5 \times 10^{-12} \Rightarrow x = 2.23 \times 10^{-6}$ M

In presence of 0.01 M C_6H_5ONa, suppose y is the amount of phenol dissociated, then at equilibrium

$[C_6H_5OH] = 0.05 - y \approx 0.05$ M

$[C_6H_5O^-] = 0.01 + y \approx 0.01$ M, $[H^+] = y$ M

$\therefore K_a = \dfrac{(0.01)(y)}{0.05} = 1.0 \times 10^{-10}$ (Given)

$y = 5 \times 10^{-10}$ M

$\therefore \alpha = \dfrac{y}{C} = \dfrac{5 \times 10^{-10}}{0.05} = 1 \times 10^{-8}$

13.

$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel Ag^{+}_{(aq)} \mid Ag_{(s)}$
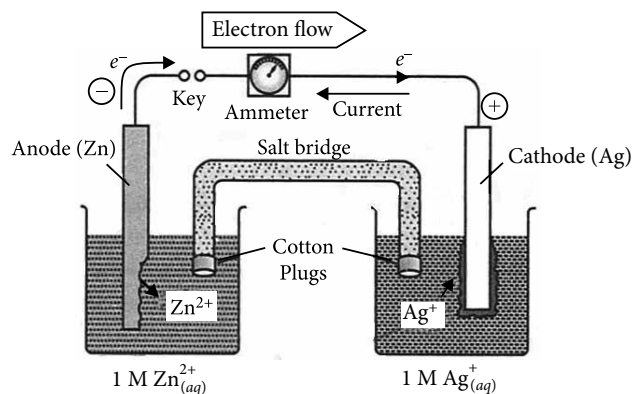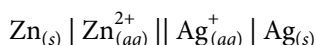
(i) Zinc electrode (anode).

(ii) Current will flow from silver to zinc in the external circuit.

(iii) At anode ; $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^{-}$

At cathode ; $Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)}$

14. (i) $K_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]}$

(ii) $K_{c \text{ (reverse reaction)}} = \dfrac{1}{K_{c(\text{forward reaction})}}$

$= \dfrac{1}{8.3 \times 10^{-3}} \approx 120.5$

(iii) When more PCl_5 is added to the reaction mixture, the concentrations of PCl_3 and Cl_2 will increase in such a way that the value of K_c remains unchanged.

15. $K_p = \dfrac{p^2_{(NO_2)}}{p_{(N_2O_4)}} = 0.66$

$p_{(NO_2)} + p_{(N_2O_4)} = 380 \text{ torr} = 0.500 \text{ atm}$

$\dfrac{p^2_{(NO_2)}}{0.500 - p_{(NO_2)}} = 0.66$

$p^2_{(NO_2)} + 0.66\, p_{(NO_2)} - 0.33 = 0$

$p_{(NO_2)} = 0.332 \text{ atm and } p_{(N_2O_4)} = 0.168 \text{ atm}$

Since each mol of N_2O_4 which dissociates produces 2 mol of NO_2, the per cent dissociation is given by

$\dfrac{0.5\, p_{(NO_2)}}{P_{\text{Total}}} = \dfrac{0.5\,(0.332 \text{ atm})}{[0.5\,(0.332) + 0.168]\,\text{atm}} \times 100 = 50\%$

16. $K_{p_1} = 1.64 \times 10^{-4} ; T_1 = 673 \text{ K}$

$K_{p_2} = 1.44 \times 10^{-5} ; T_2 = 773 \text{ K}$

Using van't Hoff equation,

$\log\left(\dfrac{K_{p_2}}{K_{p_1}}\right) = \dfrac{\Delta H}{2.303R}\left(\dfrac{T_2 - T_1}{T_2 T_1}\right)$

$\therefore \ \log \dfrac{1.44 \times 10^{-5}}{1.64 \times 10^{-4}} = \dfrac{\Delta H}{8.314 \times 2.303}\left(\dfrac{773 - 673}{773 \times 673}\right)$

$-1.0565 = \dfrac{\Delta H}{19.147}\left(\dfrac{100}{520229}\right)$

$\therefore \ \Delta H = \dfrac{-1.0565 \times 19.147 \times 520229}{100}$

$= -105236 \text{ J} = -105.236 \text{ kJ}$

OR

$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$
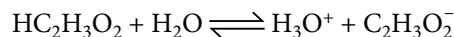
$K_a = \dfrac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.80 \times 10^{-5}$

At equilibrium, let $[H_3O^+] = x$, then $[C_2H_3O_2^-] = x$ and $[HC_2H_3O_2] = 0.200 - x$

$\dfrac{x^2}{0.200 - x} = 1.80 \times 10^{-5}$

$x^2 + (1.80 \times 10^{-5})x - (3.60 \times 10^{-6}) = 0$

Application of the quadratic formula yields

$x = \dfrac{-1.80 \times 10^{-5} \pm \sqrt{(3.24 \times 10^{-10}) + (1.44 \times 10^{-5})}}{2}$

$= 1.89 \times 10^{-3} \text{ M} = [H_3O^+]$

$\% \text{ ionised} = \dfrac{[C_2H_3O_2^-]}{[HC_2H_3O_2]_{\text{original}}} \times 100$

$= \dfrac{1.89 \times 10^{-3}}{0.200} \times 100 = 0.945 \%$

The acid is less than 1% ionized.

17. (i) $\overset{+2}{2Pb}\overset{+5}{(N}\overset{-2}{O_3)}_{2(s)} \xrightarrow{\text{Heat}} \overset{+2}{2Pb}\overset{-2}{O}_{(s)} + \overset{+4-2}{4NO_2(g)} + \overset{0}{O_2(g)}$

Lead nitrate decomposes to form three products and therefore, it is a decomposition reaction.

(ii) $\overset{+1\ -1}{NaH}_{(s)} + \overset{+1\ -2}{H_2O}_{(l)} \longrightarrow \overset{+1\ -2+1}{NaOH}_{(aq)} + \overset{0}{H_2(g)}$

Hydrogen of water has been displaced by hydride ion to form dihydrogen gas. Therefore, it is a displacement reaction.

(iii) $\overset{+4}{2NO_2(g)} + 2OH^-_{(aq)} \longrightarrow \overset{+3}{NO_2^-}_{(aq)} + \overset{+5}{NO_3^-}_{(aq)} + H_2O_{(l)}$
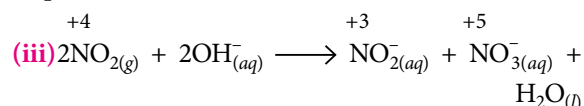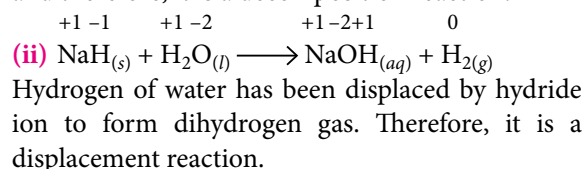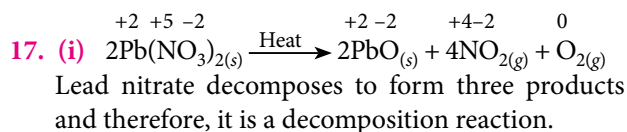
In this reaction, the +4 oxidation state of nitrogen (in NO_2) decreases to +3 (in NO_2^-) and increases to +5 (in NO_3^-). Therefore, it is a disproportionation reaction.

18. (i) No, in aqueous solution, $[H^+][OH^-] = K_w$
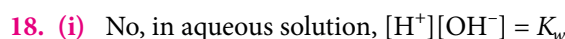
For pure water, $[H^+] = [OH^-]$

So, $[H^+]^2 = K_w$ or $[H^+] = \sqrt{K_w}$

The value of K_w increases with increase in temperature.

So, $K_{w(25°C)} > K_{w(4°C)}$

$\Rightarrow [H^+]_{25°C} > [H^+]_{4°C}$

Now, we know that, $\text{pH} = -\log[H^+] = \log\dfrac{1}{[H^+]}$

Therefore, $\text{pH}_{(25°C)} < \text{pH}_{(4°C)}$

(ii) $[H^+] = 3.8 \times 10^{-3}$ M

$pH = -\log[H^+] = -\log(3.8 \times 10^{-3})$

$= 3 \log 10 - \log 3.8 = 3 - 0.5797 = 2.4203 \approx 2.42$

19. Suppose S is the molar solubility of silver benzoate in water, then

$C_6H_5COOAg_{(s)} \rightleftharpoons C_6H_5COO^-_{(aq)} + Ag^+_{(aq)}$
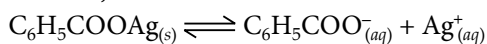
$K_{sp} = S^2$ ∴ $S = \sqrt{2.5 \times 10^{-13}} = 5.0 \times 10^{-7}$ M

If the solubility of salt of weak acid of ionisation constant K_a is S', then K_{sp}, K_a and S' are related to each other at pH = 3.19.

∴ $[H^+] = 6.46 \times 10^{-4}$ M

$$K_{sp} = S'^2 \left[\frac{K_a}{K_a + [H^+]} \right],$$

$$S' = \left\{ \frac{2.5 \times 10^{-13}}{\left[\dfrac{6.46 \times 10^{-5}}{6.46 \times 10^{-5} + 6.46 \times 10^{-4}} \right]} \right\}^{1/2}$$

$$S' = \left\{ \frac{2.5 \times 10^{-13} \times 7.106 \times 10^{-4}}{6.46 \times 10^{-5}} \right\}^{1/2}$$

$$= (2.75 \times 10^{-12})^{1/2} = 1.658 \times 10^{-6} \text{ M}$$

∴ The ratio $\dfrac{S'}{S} = \dfrac{1.658 \times 10^{-6}}{5.0 \times 10^{-7}} = 3.32$

Silver benzoate is 3.32 times more soluble in buffer of pH 3.19 than in pure water.

20. (i) $E^\circ_{Ag^+/Ag} = +0.80$ V

Any reductant having E° value lower than + 0.80 V, will be able to reduce Ag^+ to Ag. Some typical reductants which can reduce Ag^+ to Ag are Zn, Cu, Mg, Na, etc.

(ii) $E^\circ_{Al^{3+}/Al} = -1.66$ V

Any reductant having E° value lower than –1.66 V, will be able to reduce Al^{3+} to Al. Some typical reductants are Mg, Na, Ca, etc.

(iii) $E^\circ_{Ni^{2+}/Ni} = -0.25$ V

Any reductant having E° value lower than –0.25 V, will be able to reduce Ni^{2+} to Ni. Some typical reductants are Zn, Al, Mg, Na, etc.

21. (i) Let the oxidation state of copper is x, then

$1 \times (+3) + 2 \times (+2) + 3x + 7 \times (-2) = 0$

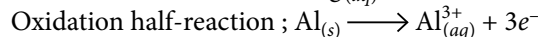$3 + 4 + 3x - 14 = 0$

$3x = 7$; $x = 7/3$

(ii) $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

$K = x^2 = 10^{-30}$ thus, $x = 10^{-15}$ M $= [NH_2^-]$

$$\left(\frac{10^{-15} \text{ mol}}{L} \right) \left(\frac{1 \text{ L}}{10^6 \text{ mm}^3} \right) \left(\frac{6 \times 10^{23} \text{ ions}}{\text{mol}} \right)$$

$= 600$ ions/mm³

22. (i)

$$2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \xrightarrow[\text{Reduction}]{\text{Oxidation}} 2Fe^{2+}_{(aq)} + I_{2(aq)}$$

Reduction half-reaction ; $2Fe^{3+}_{(aq)} + 2e^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)}$

Oxidation half-reaction ; $2I^-_{(aq)} \longrightarrow I_{2(aq)} + 2e^-$

(ii)

$$Zn_{(s)} + 2H^+_{(aq)} \xrightarrow[\text{Oxidation}]{\text{Reduction}} Zn^{2+}_{(aq)} + H_{2(g)}$$

Reduction half-reaction ; $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

Oxidation half-reaction ; $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$

(iii)

$$Al_{(s)} + 3Ag^+_{(aq)} \xrightarrow[\text{Reduction}]{\text{Oxidation}} Al^{3+}_{(aq)} + 3Ag_{(s)}$$

Reduction half-reaction ; $3Ag^+_{(aq)} + 3e^- \longrightarrow 3Ag_{(s)}$

Oxidation half-reaction ; $Al_{(s)} \longrightarrow Al^{3+}_{(aq)} + 3e^-$

23. (i) Concentrated hydrochloric acid and concentrated nitric acid are mixed in the ratio of 1 : 3 by volume. The mixture is called 'aqua regia'.

(ii) Neutralization reaction :

$HCl + NaOH \longrightarrow NaCl + H_2O$
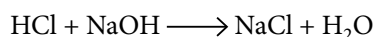
(iii) $pH = -\log[H^+]$

$= -\log[1.738 \times 10^{-4}] = 3.76$

(iv) (a) The acid should not be easily or readily available in the market. In fact, a law has been enforced that sale of acid can be done only after showing one's identification proof.

(b) You should not give your gold jewellery for cleaning to the unknown people visiting your home.

(c) As good citizens, we should not use acid balloons on holi.

24. (i) (a) When volume of vessel increases, pressure will decrease. As the forward reaction is accompanied by increase in number of moles, the decrease in the pressure will favour forward reaction (according to Le Chatelier principle).

(b) As ΔH is +ve, the reaction is endothermic, decrease of temperature will favour the direction in which heat is released *i.e.*, backward direction.

(ii) (a) Concentration of TlOH in solution

$$= \frac{2 \text{ g} / 221.4 \text{ g mol}^{-1}}{2 \text{ L}} = 0.0045 \text{ mol L}^{-1}$$

Assuming complete ionisation of TlOH,

$[OH^-] = 0.0045$ mol L⁻¹

So, $[H^+] = K_w/[OH^-] = (1 \times 10^{-14} / 0.0045)$ mol L⁻¹

$= 2.22 \times 10^{-12}$

$pH = -\log[H^+] = -\log(2.22 \times 10^{-12}) = 11.65$

(b) Concentration of $Ca(OH)_2$ in the solution,

$$[Ca(OH)_{2(aq)}] = \dfrac{\dfrac{0.3\ g}{74\ g/mol}}{0.5\ L} = 8.1 \times 10^{-3}\ mol/L$$

Assuming complete ionisation of $Ca(OH)_2$, we can write

$$[OH^-] = 2 \times [Ca(OH)_{2(aq)}] = 2 \times 8.1 \times 10^{-3}$$
$$= 0.0162\ mol\ L^{-1}$$

So, $[H^+] = K_w/[OH^-] = (1 \times 10^{-14}/0.0162)\ mol\ L^{-1}$
$$= 6.173 \times 10^{-13}\ mol\ L^{-1}$$

$pH = -\log[H^+] = -\log(6.173 \times 10^{-13}) = 12.21$

(c) Concentration of NaOH in the solution.

$$= \dfrac{(0.3\ g\ /\ 40\ g\ mol^{-1}) \times 1000\ mL/L}{200\ mL}$$
$$= 0.0375\ mol\ L^{-1}$$

So, $[OH^-] = 0.0375\ mol\ L^{-1}$
$$[H^+] = K_w/[OH^-] = (1 \times 10^{-14}/0.0375)\ mol\ L^{-1}$$
$$= 2.67 \times 10^{-13}\ mol\ L^{-1}$$

So, $pH = -\log[H^+] = -\log(2.67 \times 10^{-13}) = 12.57$

OR

(i) (a) From the graph, it is clear that in 1 to 5 h,
$$\Delta[A] = (0.3 - 0.5)\ mol\ L^{-1} = -0.2\ mol\ L^{-1}$$

$\Delta[B] = (0.6 - 0.2)\ mol\ L^{-1} = 0.4\ mol\ L^{-1}$

The amount of B formed is double the amount of A consumed. So, in the equation, $A \rightleftharpoons nB$,
At equilibrium, n is 2.

(b) $[A]_{eq} = 0.3\ mol\ L^{-1}$; $[B]_{eq} = 0.6\ mol\ L^{-1}$

$$K_{eq} = \dfrac{[B]^2}{[A]} = \dfrac{(0.6\ mol\ L^{-1})^2}{0.3\ mol\ L^{-1}} = 1.2\ mol\ L^{-1}$$

(ii) (a) Liquid NH_3 undergoes self ionisation according to the reaction,

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

According to the solvent system concept of acid and base, the strongest acid and base that can exist in a self-ionising solvent are the characteristic cation and anion respectively. Thus, in liquid ammonia the strongest acid is NH_4^+ and the strongest base is NH_2^-. Thus, all ammonium salts act as acids and amides act as bases in liquid NH_3.

(b) $CO_{2(g)} + nH_2O_{(l)} \rightleftharpoons CO_{2(aq)}$

The process occurs with decrease in randomness. Since this reaction is feasible, it must be exothermic in the forward direction. Therefore, the increase of temperature pushes the reaction in the backward direction, thereby decreasing the solubility.

25. (i)

$$\overset{+1}{2AgBr_{(s)}} + C_6H_6O_{2(aq)} \longrightarrow \overset{0}{2Ag_{(s)}} + 2HBr_{(aq)} + C_6H_4O_{2(aq)}$$

(Reduction / Oxidation indicated)

AgBr : Reduced ; $C_6H_6O_{2(aq)}$: Oxidised
AgBr : Oxidising agent ; $C_6H_6O_{2(aq)}$: Reducing agent

(ii)

$$HCHO_{(l)} + 2[\overset{+1}{Ag}(NH_3)_2]^+_{(aq)} + 3OH^- \longrightarrow \overset{0}{2Ag_{(s)}} + HCOO^-_{(aq)} + 4NH_{3(aq)} + 2H_2O_{(l)}$$

(Reduction / Oxidation indicated)

$[Ag(NH_3)_2]^+_{(aq)}$: Reduced ; $HCHO_{(l)}$: Oxidised
$[Ag(NH_3)_2]^+_{(aq)}$: Oxidising agent ;
$HCHO_{(l)}$: Reducing agent

(iii)

$$HCHO_{(l)} + 2\overset{+2}{Cu}^{2+}_{(aq)} + 5OH^-_{(aq)} \longrightarrow \overset{+1}{Cu_2}O_{(s)} + HCOO^-_{(aq)} + 3H_2O_{(l)}$$

(Reduction / Oxidation indicated)

$Cu^{2+}_{(aq)}$: Reduced ; $HCHO_{(l)}$: Oxidised
$Cu^{2+}_{(aq)}$: Oxidising agent; $HCHO_{(l)}$: Reducing agent

(iv)

$$\overset{-2}{N_2}H_{4(l)} + 2\overset{-1}{H_2O_2}_{(l)} \longrightarrow \overset{0}{N_{2(g)}} + 4\overset{-2}{H_2O}_{(l)}$$

(Reduction / Oxidation indicated)

H_2O_2 : Reduced ; $N_2H_{4(l)}$: Oxidised
H_2O_2 : Oxidising agent ; $N_2H_{4(l)}$: Reducing agent

(v)

$$\overset{0}{Pb_{(s)}} + \overset{+4}{Pb}O_{2(s)} + 2H_2SO_{4(aq)} \longrightarrow \overset{+2}{2Pb}SO_{4(s)} + 2H_2O_{(l)}$$

(Reduction / Oxidation indicated)

PbO_2 : Reduced ; $Pb_{(s)}$: Oxidised
$PbO_{2(s)}$: Oxidising agent ; $Pb_{(s)}$: Reducing agent

OR

(i) Chloride ion is oxidised to Cl_2 by MnO_4^- in acidic solution. The two half-reactions are,
Oxidation half-reaction :
$$[2Cl^- \longrightarrow Cl_2 + 2e^-] \times 5$$
Reduction half-reaction :
$$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
Net ionic reaction :
$$2MnO_4^- + 10Cl^- + 16H^+ \longrightarrow 5Cl_2 + 2Mn^{2+} + 8H_2O$$

Here, the oxidation number of Mn changes from +7 (in MnO_4^-) to +2 (in Mn^{2+}).

(ii) Nitrous acid (HNO_2) reduces MnO_4^- in acidic solution. The two half-reactions are,
Oxidation half-reactions :
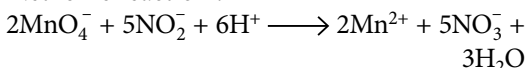$[HNO_2 + H_2O \longrightarrow HNO_3 + 2H^+ + 2e^-] \times 5$
Reduction half-reaction :
$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$
Net reaction :
$2MnO_4^- + 5HNO_2 + 6H^+ \longrightarrow 2Mn^{2+} + 5HNO_3 + 3H_2O$
Net ionic reaction :
$2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$
Here, the oxidation number of N changes from +3 (in HNO_2) to +5 (in HNO_3).

(iii) Nitrous acid (HNO_2) oxidises I^- to I_2 in the acidic solution. The two half-reactions are,
Oxidation half-reaction :
$2I^- \longrightarrow I_2 + 2e^-$
Reduction half-reaction :
$[HNO_2 + H^+ + e^- \longrightarrow NO + H_2O] \times 2$
Net reaction :
$2HNO_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2NO + 2H_2O$
Here, the oxidation number of N changes from +3 (in HNO_2) to +2 (in NO).
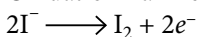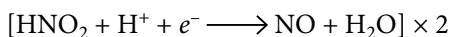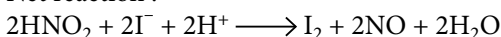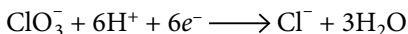
(iv) Chlorate ion (ClO_3^-) oxidises Mn^{2+} to $MnO_{2(s)}$ in acidic solution. The two half-reactions are,
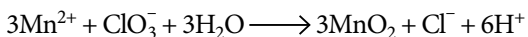Oxidation half-reaction :
$[Mn^{2+} + 2H_2O \longrightarrow MnO_2 + 4H^+ + 2e^-] \times 3$
Reduction half-reaction :
$ClO_3^- + 6H^+ + 6e^- \longrightarrow Cl^- + 3H_2O$
Net ionic reaction :
$3Mn^{2+} + ClO_3^- + 3H_2O \longrightarrow 3MnO_2 + Cl^- + 6H^+$
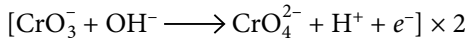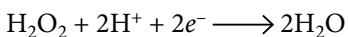Here, the oxidation number of Cl changes from +5 (in ClO_3^-) to –1 (in Cl^-).

(v) Chromite ion (CrO_3^-) is oxidised by H_2O_2 in strongly basic solution. The two half-reactions are,
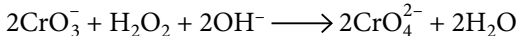Oxidation half-reaction :
$[CrO_3^- + OH^- \longrightarrow CrO_4^{2-} + H^+ + e^-] \times 2$
Reduction half-reaction :
$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$
Net ionic reaction :
$2CrO_3^- + H_2O_2 + 2OH^- \longrightarrow 2CrO_4^{2-} + 2H_2O$
Here, the oxidation number of Cr changes from +5 (in CrO_3^-) to +6 (in CrO_4^{2-}).

26. (i) $\Delta G° = -RT \ln K$
or $K = e^{-\Delta G°/RT}$ (called van't Hoff reaction isotherm)
If $\Delta G°$ is –ve, $e^{-\Delta G°/RT}$ is +ve, *i.e.*, > 1. This means that $K > 1$. But $K > 1$ implies that the reaction proceeds in the forward direction, *i.e.,* products are present in larger amount.

(ii) van't Hoff isochore is :
$$\log_{10} K = \log_{10} A - \frac{\Delta H}{2.303RT}$$
(a) Thus, intercept = $\log_{10} A = 10$
$\therefore \quad A = 10^{10}$
(b) Also, slope = $\tan \theta = 0.5 = -\dfrac{\Delta H}{2.303R}$
$\therefore \quad \Delta H = -2.303$ cal mol^{-1}
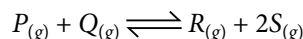**(c)** $\log_{10} K = 10 + \dfrac{2.303}{2.303 \times 2 \times 298}$
$\therefore \quad K = 1.004 \times 10^{10}$
(d) $\log_{10} K = 10 + \dfrac{2.303}{2.303 \times 2 \times 800}$
$\therefore \quad K = 1.001 \times 10^{10}$

OR

(i) The reaction is
$P_{(g)} + Q_{(g)} \rightleftharpoons R_{(g)} + 2S_{(g)}$
Given that, $\Delta U° = -90.0$ kcal, $\Delta S° = 100$ cal K^{-1},
$T = 300$ K
Using $\quad \Delta H° = \Delta U° + \Delta n_g RT$
$= (-90.0 \times 10^3) + (1 \times 2.0 \times 300)$
$(\because \Delta n_g = 1, R = 2.0$ cal K^{-1} $mol^{-1})$
$= -89,400$ cal
but, $\Delta G° = \Delta H° - T\Delta S° = -89,400 - (300 \times 100)$
$(\because \Delta S° = 100$ cal $K^{-1})$
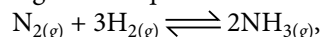$= -1,19,400$ cal
Now using $\Delta G° = -2.303$ $RT \log K_p$
$\log K_p = -\dfrac{(-1,19,400)}{2.303 \times 2 \times 300} = 86.4$
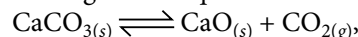$\therefore \quad K_p = 2.5 \times 10^{86}$

(ii) (a) Considering a chemical equation for homogeneous equilibria :
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)},$
$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}, K_p = \frac{p_{NH_3}^2}{p_{N_2} \times p_{H_2}^3}$$
For heterogeneous equilibria :
$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)},$
Taking $\quad [CaCO_{3(s)}] = 1$ and $[CaO_{(s)}] = 1$
$\therefore \quad K_c = [CO_2] \quad \Rightarrow \quad K_p = p_{CO_2}$
(b) There is no effect when $(n_p = n_r)_{gaseous}$. Effect is observed when $(n_p \neq n_r)_{gaseous}$ and reaction takes place at constant pressure. At constant volume, there is no effect because adding inert gas at constant volume does not change molar concentrations. When $(n_p > n_r)_{gaseous}$,
e.g., $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$, on adding inert gas equilibrium shifts forward.

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MPP-6 | MONTHLY Practice Problems

Class XI

This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Hydrogen | Redox Reactions

Total Marks : 120

Time Taken : 60 Min.

NEET / AIIMS
Only One Option Correct Type

1. Hydrogen can be placed in group 17 because
   (a) it is light
   (b) it contains one electron only
   (c) it forms hydrides like halides
   (d) it has isotopes D and T.

2. The gases that bleach the colour of flowers by reduction and oxidation respectively are
   (a) CO and Cl_2
   (b) SO_2 and Cl_2
   (c) H_2S and Br_2
   (d) NH_3 and SO_2

3. Hydrogen can be prepared by mixing steam and water gas at 500 °C in the presence of O_3 and Cr_2O_3. This process is called
   (a) Nelson process
   (b) Serpeck's process
   (c) Bosch process
   (d) Parkes process.

4. The reaction, $3ClO^-_{(aq)} \longrightarrow ClO^-_{3(aq)} + 2Cl^-_{(aq)}$ is an example of
   (a) oxidation reaction
   (b) reduction reaction
   (c) disproportionation reaction
   (d) decomposition reaction.

5. Choose the incorrect statement.
   (a) Hardness of water depends upon its soap consuming power.
   (b) Temporary hardness is due to bicarbonates of calcium and magnesium.
   (c) Permanent hardness is due to soluble sulphates, chlorides and nitrates of calcium and magnesium.
   (d) Permanent hardness can be removed by boiling hard water.

6. Oxidation numbers of iodine in IO_3^-, IO_4^-, KI and I_2 respectively are
   (a) –1, –1, 0, +1
   (b) +3, +5, +7, 0
   (c) +5, +7, –1, 0
   (d) –1, –5, –1, 0

7. Hydrogen gas will not reduce
   (a) heated cupric oxide
   (b) heated ferric oxide
   (c) heated stannic oxide
   (d) heated aluminium oxide.

8. For the redox reaction,
   $MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$
   the correct stoichiometric coefficients of MnO_4^-, $C_2O_4^{2-}$ and H^+ respectively are
   (a) 2, 16, 5
   (b) 2, 5, 16
   (c) 16, 5, 2
   (d) 5, 16, 2

9. Dilute solution of H_2O_2 can be concentrated by
   (a) evaporation on a water bath
   (b) dehydration in a vacuum desiccator
   (c) distillation under reduced pressure
   (d) all of these.

10. Which of the following have been arranged in the decreasing order of oxidation number of sulphur?
    (a) $S_2O_6^{2-} > S_2O_7^{2-} > S_2O_3^{2-} > S_8$
    (b) $H_2SO_4 > SO_2 > H_2S > H_2S_2O_8$
    (c) $SO_2^{2+} > SO_4^{2-} > SO_3^{2-} > HSO_4^-$
    (d) $H_2SO_5 > H_2SO_3 > SCl_2 > H_2S$

11. Which of the following statements is not true?
    (a) Ordinary water is electrolysed more rapidly than heavy water.
    (b) Reaction between H_2 and Cl_2 is much faster than between D_2 and Cl_2.

(c) D_2O freezes at lower temperature than H_2O.

(d) Bond dissociation energy of D_2 is greater than H_2.

12. HBr and HI can reduce H_2SO_4, HCl can reduce $KMnO_4$ and HF can reduce _____.

(a) H_2SO_4 (b) $K_2Cr_2O_7$

(c) $KMnO_4$ (d) none of these

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

(a) If both assertion and reason are true and reason is the correct explanation of assertion.

(b) If both assertion and reason are true but reason is not the correct explanation of assertion.

(c) If assertion is true but reason is false.

(d) If both assertion and reason are false.

13. **Assertion :** At room temperature, the ratio of *ortho* and *para* hydrogen is 3 : 1.

Reason : Hydrogen molecules of in which the spins of both the nuclei are in same direction is known as *para* hydrogen.

14. **Assertion :** Fe reacts with HCl to produce H_2 gas.

Reason : Fe is a better reducing agent than H_2.

15. **Assertion :** H_2O_2 has higher boiling point than H_2O.

Reason : The dipole moment of H_2O_2 is little more than that of H_2O.

### JEE MAIN / JEE ADVANCED

Only One Option Correct Type

16. The non-existence of PbI_4 and $PbBr_4$ is due to

(a) highly oxidising nature of Pb^{4+} ions

(b) highly reducing nature of I^- and Br^- ions

(c) larger ionic sizes of Pb^{4+}, Br^- and I^- ions

(d) both (a) and (b).

17. H^+ ion always gets associated with other atoms or molecules because

(a) ionisation enthalpy of hydrogen resembles that of alkali metals

(b) its reactivity is similar to halogens

(c) it resembles both alkali metals and halogens

(d) loss of an electron from hydrogen atom results in a nucleus of very small size as compared to other atoms or ions due to which it cannot exist in free state.

18. The volume strength of 3.57 M solution of hydrogen peroxide is

(a) 30 volume   (b) 25 volume

(c) 20 volume   (d) 40 volume.

19. Consider the following reactions :

I. $AlH_3 + H^- \longrightarrow AlH_4^-$

II. $H_2O + H^- \longrightarrow H_2 + OH^-$
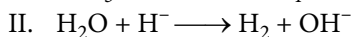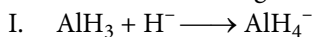
Select the correct statement from the following :

(a) H^- is a Lewis acid in I and a Lewis base in II.

(b) H^- is a Lewis base in I and a Bronsted base in II.

(c) H^- is a Lewis acid in I and a Bronsted base in II.

(d) H^- is a Lewis base in both I and II.

More than One Options Correct Type

20. Which of the following reactions are not feasible?

(a) $I^- + Fe^{2+} \longrightarrow$ (b) $F_2 + 2NaCl \longrightarrow$

(c) $Cl_2 + 2NaF \longrightarrow$ (d) $I_2 + 2NaBr \longrightarrow$

21. Among the hydrides given below, which are reasonably good acids?
(a) NH_3 (b) HF   (c) HN_3 (d) NaH

22. Oxidation states of nitrogen are correctly given for

Compound	Oxidation state
(a) $[Co(NH_3)_5Cl]Cl_2$	−3
(b) NH_2OH	−1
(c) $(N_2H_5)_2SO_4$	+2
(d) Mg_3N_2	+3

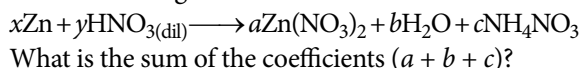**23.** Which of the following have lower value for D_2O than for H_2O?
(a) Molecular mass   (b) Dielectric constant
(c) Ionization constant (d) Viscosity

Integer Answer Type

24. In alkaline medium, ClO_2 oxidises H_2O_2 to O_2 and itself gets reduced to Cl^-, then how many moles of H_2O_2 will be oxidised by two moles of ClO_2?

25. The percentage strength of 10 volume of H_2O_2 (approximately) is

26. In the following reaction :
$$xZn + yHNO_{3(dil)} \longrightarrow aZn(NO_3)_2 + bH_2O + cNH_4NO_3$$
What is the sum of the coefficients $(a + b + c)$?

Comprehension Type

Temporary hardness is due to the presence of soluble $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ whereas permanent hardness is due to the presence of $CaCl_2$, $MgCl_2$, $CaSO_4$ and $MgSO_4$. The process of removal of Ca^{2+} and Mg^{2+} ion is called softening of water.

27. Which of the following is not present in clear hard water?
(a) $Mg(HCO_3)_2$ (b) $CaCl_2$
(c) $MgSO_4$ (d) $MgCO_3$

28. Chemical A is used to remove temporary hardness. A reacts with sodium carbonate to generate caustic soda. When CO_2 is bubbled through a solution of A, it turns cloudy. What is the chemical formula of A?

(a) $CaCO_3$ (b) CaO
(c) $Ca(OH)_2$ (d) $Ca(HCO_3)_2$

Matrix Match Type

29. Match the half-reactions given in Column I with change in oxidation number given in Column II and choose the correct option using the codes given below.

Column I	Column II
(A) $Cl^- \longrightarrow ClO_4^-$	(p) 4
(B) $Cr^{3+} \longrightarrow CrO_5$	(q) 8
(C) $C_{(s)} \longrightarrow CO_{2(g)}$	(r) 0
(D) $CrO_2^{2+} \longrightarrow CrO_4^{2-}$	(s) 3

	A	B	C	D
(a)	p	r	s	q
(b)	q	s	p	r
(c)	q	p	r	s
(d)	p	s	q	r

30. Match the Column I with Column II and choose the correct option using the codes given below.

Column I		Column II
(A)	Syngas	(p) Causes sequestration of Ca^{2+} and Mg^{2+} ions
(B)	Hydride gap	(q) Repeated electrolysis of water
(C)	Calgon	(r) Elements of groups 7, 8 and 9
(D)	Heavy water	(s) $CO + H_2$

	A	B	C	D
(a)	s	r	p	q
(b)	r	s	q	p
(c)	p	r	s	q
(d)	q	p	r	s

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Keys are published in this issue. Search now! ☺

SELF CHECK ✏

Check your score! If your score is

No. of questions attempted ......
No. of questions correct ......
Marks scored in percentage ......

> 90%	EXCELLENT WORK !	You are well prepared to take the challenge of final exam.
90-75%	GOOD WORK !	You can score good in the final exam.
74-60%	SATISFACTORY !	You need to score more next time.
< 60%	NOT SATISFACTORY!	Revise thoroughly and strengthen your concepts.

NEET | JEE
ESSENTIALS

Class XII

Maximise your chance of success, and high rank in NEET, JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

Unit 4 | *d*- and *f*-Block Elements | Coordination Compounds

d- AND *f*-BLOCK ELEMENTS

- The *d*-block of the periodic table contains the elements of the group-3 to 12 in which the *d*-orbitals are progressively filled in each of the four long periods.

- In *f*-block, 4*f*- and 5*f*-orbitals are progressively filled. These elements are formal members of group-3 but they have taken out to form a separate *f*-block of the periodic table.

CHEMISTRY OF *d*-BLOCK ELEMENTS

Elements which have incompletely filled *d*-subshell in their ground state or in any one of their oxidation states, are called *d*-block elements. All the *d*-block elements except Zn, Cd and Hg, are transition elements. These elements have completely filled *d*-subshell in their ions, that is why they are not considered as transition elements.

ELECTRONIC CONFIGURATION

General configuration : $(n - 1)d^{1\text{-}10}\,ns^{0\text{--}2}$
Here, $(n - 1)$ stands for inner shell and n for outermost shell or *s*-orbital.
As half-filled (d^5) and fully filled (d^{10}) configurations are more stable. So, Cr and Cu show exceptional electronic configuration in 3*d*-series.

First Transition Series	Second Transition Series	Third Transition Series	Fourth Transition Series
Sc (21) $\Rightarrow$ [Ar]$3d^1 4s^2$	Y(39) $\Rightarrow$ [Kr] $4d^1 5s^2$	La(57) $\Rightarrow$ [Xe] $4f^0\,5d^1 6s^2$	Ac(89) $\Rightarrow$ [Rn]$5f^0\,6d^1 7s^2$
Ti (22) $\Rightarrow$ [Ar]$3d^2 4s^2$	Zr(40) $\Rightarrow$ [Kr] $4d^2 5s^2$	Hf(72) $\Rightarrow$ [Xe]$4f^{14} 5d^2 6s^2$	Rf(104) $\Rightarrow$ [Rn] $5f^{14}\,6d^2 7s^2$
V(23) $\Rightarrow$ [Ar]$3d^3 4s^2$	Nb(41) $\Rightarrow$ [Kr]$4d^4 5s^1$	Ta(73) $\Rightarrow$ [Xe]$4f^{14} 5d^3 6s^2$	Db(105) $\Rightarrow$ [Rn] $5f^{14}\,6d^3 7s^2$
Cr(24) $\Rightarrow$ [Ar]$3d^5 4s^1$	Mo(42) $\Rightarrow$ [Kr]$4d^5 5s^1$	W (74) $\Rightarrow$ [Xe] $4f^{14} 5d^4 6s^2$	Sg(106) $\Rightarrow$ [Rn]$5f^{14}\,6d^4 7s^1$
Mn(25) $\Rightarrow$ [Ar]$3d^5 4s^2$	Tc(43) $\Rightarrow$ [Kr]$4d^5 5s^2$	Re(75) $\Rightarrow$ [Xe]$4f^{14} 5d^5 6s^2$	Bh(107) $\Rightarrow$ [Rn]$5f^{14}\,6d^5 7s^2$
Fe(26) $\Rightarrow$ [Ar]$3d^6 4s^2$	Ru(44) $\Rightarrow$ [Kr]$4d^7 5s^1$	Os(76) $\Rightarrow$ [Xe]$4f^{14} 5d^6 6s^2$	Hs(108) $\Rightarrow$ [Rn] $5f^{14}\,6d^6 7s^2$
Co(27) $\Rightarrow$ [Ar]$3d^7 4s^2$	Rh(45) $\Rightarrow$ [Kr]$4d^8 5s^1$	Ir(77) $\Rightarrow$ [Xe] $4f^{14} 5d^7 6s^2$	Mt(109) $\Rightarrow$ [Rn] $5f^{14}\,6d^7 7s^2$
Ni(28) $\Rightarrow$ [Ar]$3d^8 4s^2$	Pd(46) $\Rightarrow$ [Kr]$4d^{10} 5s^0$	Pt(78) $\Rightarrow$ [Xe] $4f^{14}\,5d^9 6s^1$	Ds(110) $\Rightarrow$ [Rn]$5f^{14} 6d^9 7s^1$
Cu(29) $\Rightarrow$ [Ar]$3d^{10} 4s^1$	Ag(47) $\Rightarrow$ [Kr]$4d^{10}\,5s^1$	Au(79) $\Rightarrow$ [Xe] $4f^{14}\,5d^{10} 6s^1$	Rg(111) $\Rightarrow$ [Rn]$5f^{14} 6d^{10} 7s^1$
Zn(30) $\Rightarrow$ [Ar]$3d^{10} 4s^2$	Cd(48) $\Rightarrow$ [Kr]$4d^{10} 5s^2$	Hg(80) $\Rightarrow$ [Xe]$4f^{14} 5d^{10} 6s^2$	Cn(112) $\Rightarrow$ [Rn]$5f^{14} 6d^{10} 7s^2$

GENERAL PROPERTIES OF *d*-BLOCK ELEMENTS

Metallic Character

Due to presence of strong metallic bonds, the transition metals are hard, possess high densities and high enthalpies of atomisation. Scandium has least density whereas Iridium has the highest density among the transition metals.

Atomic and Ionic Sizes

Trends in atomic radii of transition elements

The atomic radii first decreases, at the middle becomes almost constant and then increases towards the end of the period.
In first transition series, atomic radii decrease from Sc to Cr, remain almost constant till Cu and then increase.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
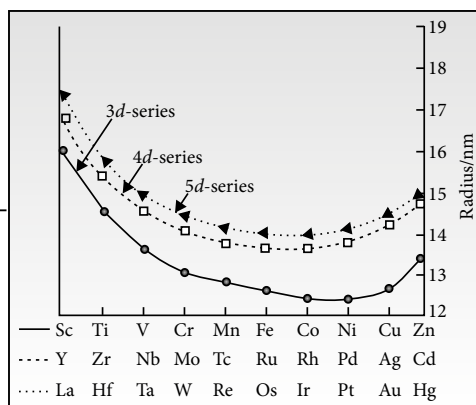
The elements of second and third transition series belonging to a particular group have almost equal atomic radii. This is due to the intervention of the 4*f*-orbitals which must be filled before the 5*d* series of elements begins. The filling of 4*f*-orbitals before 5*d*-orbitals results in a regular decrease in atomic radii known as **lanthanoid contraction**.

Ionisation Enthalpy

- The ionisation enthalpy of *d*-block elements are higher than those of *s*-block elements and are lower than those of *p*-block elements.
- In a particular transition series, ionisation enthalpy increases gradually but quite slowly among *d*-block elements.
- Extra stability of half filled and fully filled orbital give rise to high ionisation enthalpy.

Oxidation state
- Variable oxidation states arise due to participation of $(n-1)d$ and ns-electrons.
- The element which shows the greatest number of oxidation state occur in or near the middle of the series, *e.g.*, Mn
- In + 2 and +3 oxidation states, the bonds formed are mostly ionic.
- In a group of *d*-block elements, the higher oxidation states are more stable for heavier elements.
- Low oxidation states such as +1, 0 or negative are also possible.

Sc   + 3
Ti   (+ 2), + 3, + 4
V   + 2, + 3, + 4, + 5
Cr   (+1), + 2, + 3, (+ 4), (+ 5), + 6
Mn   + 2, + 3, + 4, (+ 5), + 6, + 7
Fe   + 2, + 3, (+ 4), (+ 5), (+ 6)
Co   + 2, + 3, (+4)
Ni   + 2, + 3, + 4
Cu   + 1, + 2
Zn   + 2

Y   + 3
Zr   (+ 3), + 4
Nb   (+ 2), + 3, (+ 4), + 5
Mo   + 2, + 3, + 4, + 5, + 6
Tc   + 2, + 4, (+ 5), + 7
Ru   + 2, + 3, + 4, (+ 5), (+ 6), (+ 7), (+ 8), 0, –2
Rh   + 2, + 3, + 4, (+ 6)
Pd   + 2, (+ 3), +4
Ag   + 1, (+ 2), (+ 3)
Cd   + 2

La   + 3
Hf   (+ 3), + 4
Ta   (+ 2), (+ 3), (+ 4), + 5
W   + 2, (+ 3), + 4, + 5, + 6
Re   (– 1), (+ 1), (+ 2), (+ 3), + 4, + 5, (+ 6), + 7
Os   + 2, + 3, + 4, + 6, + 8
Ir   + 2, + 3, + 4, (+ 6)
Pt   + 2, (+ 3), + 4, (+ 5), (+ 6)
Au   + 1, + 3
Hg   +1, + 2

*Oxidation states, which are in brackets, are unstable while underlined oxidation states are stable.

Standard Reduction Potential

- Lower the electrode potential *i.e.*, more negative the standard reduction potential of the electrode, more stable is the oxidation state of the transition metal in the aqueous medium.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$E^{\circ}_{(M^{2+}/M)}$ in volts (V)	—	−1.63	−1.18	−0.91	−1.18	−0.44	−0.28	−0.25	+0.34	−0.76
$E^{\circ}_{(M^{3+}/M^{2+})}$ in volts (V)	−2.08	−0.37	−0.26	−0.41	+1.57	+0.77	+1.97	—	—	—

Trends in $E^{\circ}_{M^{2+}/M}$:

- No regular trend due to irregular variation of ionisation energies and sublimation energies.
- Except copper, all other elements have negative reduction potential values.
- The values of E° for Mn, Zn and Ni are more negative than expected from general trend.

Trends in $E^{\circ}_{M^{3+}/M^{2+}}$:

- E° value for Sc^{3+}/Sc^{2+} is very low reflect the stability of Sc^{3+} which is due to noble gas configuration.
- E° value for Mn^{3+}/Mn^{2+} is high shows that Mn^{2+} is very stable which is due to d^5 configuration.
- E° values for the redox couple M^{3+}/M^{2+} indicate Mn^{3+} and Co^{3+} are strongest oxidising agents.

SOME MORE PROPERTIES

Formation of Interstitial Compounds
- Small non-metallic atoms such as, H, B, C, N etc. are able to occupy interstitial spaces of the lattices of the *d*-block elements to form interstitial compounds.

Colour
- Most of the compounds of transition metals are coloured in the solid as well as in aqueous solution.
- Colour arises due to *d-d* transition.
- Transition elements with completely filled or completely empty *d*-orbitals are colourless, *e.g.*, Cu^+, Ag^+, Au^+, Zn^{2+}, Cd^{2+}, etc.

Catalytic properties
- Catalytic properties are due to unpaired electrons in their *d*-orbitals, *e.g.*, V_2O_5, cobalt, Ni, etc.

Tendency to form complexes
Due to small size, high nuclear charge and vacant *d*-orbitals they can accept lone pairs of electrons donated by the ligands, *e.g.*, $[Fe(CN)_6]^{3-}$, etc.

Magnetic properties
- Most of the compounds are paramagnetic due to presence of unpaired electrons.
- $\mu_{eff} = \sqrt{n(n+2)}$ B.M. where, n = number of unpaired electrons.
- Magnetic moment first increases from d^1 to d^5 and then decreases.

Alloy formation
Due to similar atomic radii and other characteristics, they form alloy very readily.

SOME IMPORTANT COMPOUNDS OF *d*-BLOCK ELEMENTS

Potassium Dichromate ($K_2Cr_2O_7$)	Potassium Permanganate ($KMnO_4$)
Preparation : $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$	**Preparation :** $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$ $3K_2MnO_4 + 4HCl \longrightarrow 2KMnO_4 + MnO_2 +$ $\quad\quad\quad\quad\quad\quad\quad\quad\quad 2H_2O + 4KCl$
Properties : • Orange coloured crystalline compound which is soluble in water. • On strong heating, it decomposes with the evolution of oxygen. $4K_2Cr_2O_7 \longrightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$ • On heating with alkalies, a yellow solution results due to formation of chromate. $K_2Cr_2O_7 + 2KOH \longrightarrow 2K_2CrO_4 + H_2O$ (Orange) (Yellow) • In the solution, dichromate ions exist in equilibrium with chromate ions. $Cr_2O_7^{2-} + H_2O \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} 2CrO_4^{2-} + 2H^+; pH = 4$ (Orange) (Yellow) • In acidic medium, it acts as a strong oxidising agent. $\overset{(+6)}{Cr_2O_7^{2-}} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ • **Chromyl chloride test :** Test for chloride ion. When a mixture of a metal chloride and potassium dichromate is heated with conc. H_2SO_4, orange-red vapours of chromyl chloride are evolved. $K_2Cr_2O_7 + 6H_2SO_4 + 4NaCl \longrightarrow$ $\quad 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$ chromyl chloride $CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O$ Yellow soln. $Na_2CrO_4 + (CH_3COO)_2 Pb \longrightarrow 2CH_3COONa + PbCrO_4$ Yellow ppt.	**Properties :** • Deep purple coloured crystalline solid, moderately soluble in water. • On heating, it decomposes to give O_2. $2KMnO_4 \xrightarrow[513\,K]{\Delta} K_2MnO_4 + MnO_2 + O_2$ • With conc. H_2SO_4, it gives Mn_2O_7 which on heating decomposes to MnO_2. $2KMnO_4 + 2H_2SO_4 \longrightarrow 2KHSO_4 + Mn_2O_7$ $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad + H_2O$ $2Mn_2O_7 \xrightarrow{\Delta} 4MnO_2 + 3O_2$ • In alkaline solution, it acts as an oxidising agent. $2KMnO_4 + H_2O \xrightarrow{Weakly\ alkaline} 2MnO_2 +$ $\quad\quad\quad\quad\quad\quad\quad\quad 2KOH + 3[O]$ • In neutral solution, it acts as a moderate oxidising agent. $2KMnO_4 + H_2O \longrightarrow 2MnO_2 + 2KOH +$ $\quad\quad\quad\quad\quad\quad\quad\quad 3[O]$ • In acidic solution, it acts as a strong oxidising agent. $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4$ $\quad\quad\quad\quad\quad\quad\quad\quad + 3H_2O + 5[O]$
Uses : • As a volumetric reagent. • Preparation of several chromium compounds. • In dyeing, chrome tanning, photography, etc.	**Uses :** • As a strong oxidising agent in laboratory. • Alkaline potassium permanganate is known as Baeyer's reagent used for the testing unsaturation. • As a disinfectant and germicide.

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Surface Chemistry

Surface chemistry is the study of chemical reactions at interfaces. It is closely related to surface engineering which aims at modifying the chemical composition of a surface for desired improvement. Surface science has importance in catalysis, electrochemistry and geochemistry.

Applications of Adsorption

Adsorption finds extensive applications in research laboratories and in industries. It can be used to remove certain classes of pollutants from air and industrial waste water.

In Gas Masks

Gas masks are used to adsorb poisonous gases (e.g., Cl_2, CO, oxides of sulphur etc.) and thus purify the air for breathing. Activated charcoal is used for this purpose.

Removal of Colouring Matter from Solution

Many substances such as sugar, juice and vegetable oils (having coloured impurities) can be decolourised by using adsorbents like activated charcoal or fuller's earth, e.g., animal charcoal is used as a decolouriser in the manufacture of cane sugar.

Heterogeneous Catalysis

Mostly heterogeneous catalytic reactions proceed through the adsorption of gaseous reactants on solid catalyst, e.g.,
- Finely powdered nickel is used for the hydrogenation of oils.
- Finely divided vanadium pentaoxide (V_2O_5) is used in the Contact process for the manufacture of sulphuric acid.

In Curing Disease

Some drugs can adsorb the germs and kill them hence, save us from diseases.

Separation of Inert Gases

Due to the difference in degree of adsorption of gases by charcoal, a mixture of inert gases can be separated by adsorption on coconut charcoal at different temperatures.

In Industries

Smoke Precipitation

Smoke is a big problem for environment as it is the major cause of air pollution. Coagulation of the dispersed colloidal particles (smoke) occurs on metal plates before allowing them to pass through the chimney.

To chimney (gases free from dust)
Point electrode
High voltage source
Plate electrode
Gases carrying dust and smoke
Precipitated dust and smoke
Cottrell Precipitator

Purification of Drinking Water

Addition of the electrolyte (like alum) for water purification is based on the fact that impure water is a colloidal system.

Coagulant added
impurities
Coagulant forms precipitate, trapping impurities
Precipitate and trapped impurities settle to bottom

Artificial Rain

Due to mixing of oppositely charged sand or common salt with the clouds to bring about coagulation of water particles.

Silver iodide aids the formation of ice crystals
The ice crystals become large enough to fall and create snow
Silver iodide particles reach the targeted cloud
Silver iodide is released by a plane or ground-based generator

Applications of Colloids

Colloids have very vast applications from food products to industries like rubber etc.

In Nature and Everyday Life

Food Articles

Number of food articles that we eat, are colloidal in nature, e.g.,
- Milk : Fat dispersed in water.
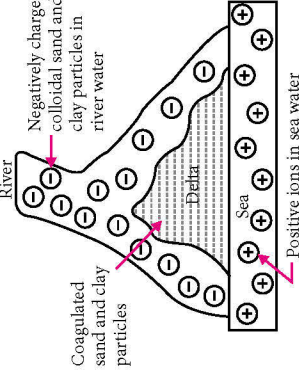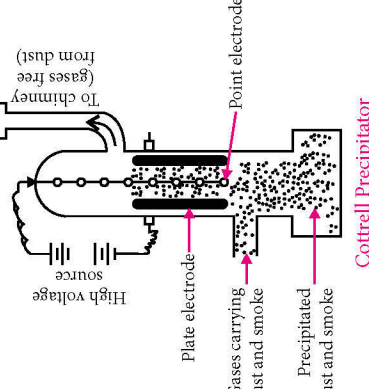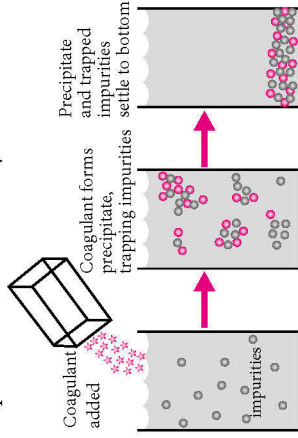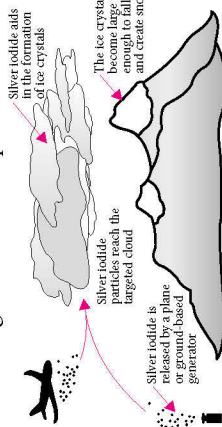- Bread : Air dispersed in baked dough.

Medicines

- Colloidal medicines are more effective as they are easily absorbed in the body, e.g.,
  - Silver colloid : Germicidal
  - Copper colloid : Anticancer
  - Mercury colloid : Antisyphilis
- Colloidal dispersion of gelatin is used in coating over tablets and granules.

Blood Coagulation

Blood consists of negatively charged colloidal particles (albuminoid substances). On applying ferric chloride solution, it causes coagulation of blood to form a clot which stops further bleeding.

Formation of Delta

Formation of delta shaped heap of sand, clay, etc. where river falls into sea due to coagulation of sand/clay particles by electrolytes present in sea water.

River
Negatively charged colloidal sand and clay particles in river water
Coagulated sand and clay particles
Delta
Sea
Positive ions in sea water

Trends and Anomalies in s- and p-Block Elements

Generally in a group, elements show a regular trend in their physical and chemical properties with increase in their atomic numbers. But some of the elements show exceptional behaviour and anomalies.

Anomalous Behaviour of First Element of Group

Due to
- Small size
- High ionization enthalpy
- Absence of d-orbitals in valence shell
- High electronegativity

Anomalous Behaviour of Lithium

- Melting and boiling points are comparatively high.
- Lithium forms nitride while other alkali metals do not.
$$6Li + N_2 \rightarrow 2Li_3N$$
- Lithium hydroxide and carbonate decompose on heating, while other alkali metal hydroxides and carbonates do not.
$$2LiOH \xrightarrow{\Delta} Li_2O + H_2O \qquad Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2\uparrow$$

Anomalous Behaviour of Beryllium

- Beryllium is harder than other group members.
- Beryllium does not react with water even at high temperature.
- Beryllium forms covalent compounds. Because of covalent character salts of beryllium are easily hydrolysed.
$$BeCO_3 + 4H_2O \rightarrow [Be(H_2O)_4]^{2+} + CO_3^{2-}$$

Anomalous Behaviour of Boron

- Boron is hard and has high melting and boiling points.
- Boron forms only covalent compounds while others form both ionic and covalent compounds.
- The oxide and hydroxide of boron are weakly acidic.
$$B_2O_3 + 2NaOH \rightarrow 2NaBO_2 + H_2O$$
$$B(OH)_3 + NaOH \rightarrow NaBO_2 + 2H_2O$$

Anomalous Behaviour of Carbon

- Due to small size and high electronegativity, carbon has a strong tendency to form $p\pi$-$p\pi$ multiple bonds.
- Carbon has high tendency of catenation. Tendency for catenation : C >> Si > Ge ≈ Sn >> Pb

Stability of Hydrides

- LiH > NaH > KH > RbH > CsH
- $CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$

Lewis Acid Character

- $BI_3 > BBr_3 > BCl_3 > BF_3$

Stability of Nitrates

- $Be(NO_3)_2 < Mg(NO_3)_2 < Ca(NO_3)_2 < Sr(NO_3)_2 < Ba(NO_3)_2$

General Trends in Properties of s- and p-Block Compounds

Carbonates and Bicarbonates Stability

- $Li_2CO_3 < Na_2CO_3 < K_2CO_3 < Rb_2CO_3 < Cs_2CO_3$
- $LiHCO_3 < NaHCO_3 < KHCO_3 < RbHCO_3 < CsHCO_3$
- $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$

Basic Strength, Solubility and Stability of Hydroxides

- $LiOH < NaOH < KOH < RbOH < CsOH$
- $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$
- $B(OH)_3 < Al(OH)_3 < Ga(OH)_3 < In(OH)_3 < Tl(OH)_3$

Acidic — Amphoteric — Basic

Solubility and Basic Strength of Oxides

- $Li_2O < Na_2O < K_2O < Rb_2O < Cs_2O$
- $BeO < MgO < CaO < SrO < BaO$

Amphoteric — Strongly basic

- $B_2O_3 < Al_2O_3 < Ga_2O_3 < In_2O_3 < Tl_2O_3$

Weakly acidic — Amphoteric — Basic

Stability of Peroxides and Superoxides

- $Na_2O_2 < K_2O_2 < Rb_2O_2 < Cs_2O_2$
- $NaO_2 < KO_2 < RbO_2 < CsO_2$
- $MgO_2 < CaO_2 < SrO_2 < BaO_2$

Solubility in Water

- $LiF < NaF < KF < RbF < CsF$
- $LiCl < NaCl < KCl < RbCl < CsCl$
- $NaF < NaCl < NaBr < NaI$
- $BeCl_2 > MgCl_2 > CaCl_2 > SrCl_2 > BaCl_2$
- $BF_3 < BCl_3 < BBr_3$

Stability of Halides

- $CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$
- $CF_4 > CCl_4 > CBr_4 > Cl_4$
- $PbX_2 > SnX_2 > GeX_2 > SiX_2$

Solubility of Sulphates

- $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$

Stability of Sulphate

- $BeSO_4 < MgSO_4 < CaSO_4 < SrSO_4$

CHEMISTRY OF *f*-BLOCK ELEMENTS

The elements in which the last electron enters the antipenultimate energy level, *i.e.*, $(n - 2)$ *f*-orbitals, are called *f*-block or inner transition elements.

General electronic configuration : $(n - 2) f^{1-14} (n - 1) d^{0-1} ns^2$

LANTHANOIDS

The elements in which the last electron enters one of the 4*f*-orbitals, are called lanthanides or lanthanons.

Name of the elements	Symbol (Ln)	At. No. (Z)	Electronic configuration	Oxidation states
Lanthanum	La	57	$[Xe] 5d^1 6s^2$	+ $\underline{3}$
Cerium	Ce	58	$[Xe]4f^1 5d^1 6s^2$	+ $\underline{3}$, + 4
Praseodymium	Pr	59	$[Xe]4f^3 5d^0 6s^2$	+ $\underline{3}$, + 4
Neodymium	Nd	60	$[Xe]4f^4 5d^0 6s^2$	+ 2, + $\underline{3}$, + 4
Promethium	Pm	61	$[Xe]4f^5 5d^0 6s^2$	+ $\underline{3}$
Samarium	Sm	62	$[Xe]4f^6 5d^0 6s^2$	+ 2, + $\underline{3}$
Europium	Eu	63	$[Xe]4f^7 5d^0 6s^2$	+ 2, + $\underline{3}$
Gadolinium	Gd	64	$[Xe]4f^7 5d^1 6s^2$	+ $\underline{3}$
Terbium	Tb	65	$[Xe]4f^9 5d^0 6s^2$	+ $\underline{3}$, + 4
Dysprosium	Dy	66	$[Xe]4f^{10} 5d^0 6s^2$	+ $\underline{3}$, + 4
Holmium	Ho	67	$[Xe]4f^{11} 5d^0 6s^2$	+ $\underline{3}$
Erbium	Er	68	$[Xe]4f^{12} 5d^0 6s^2$	+ $\underline{3}$
Thulium	Tm	69	$[Xe]4f^{13} 5d^0 6s^2$	+ 2, + $\underline{3}$
Ytterbium	Yb	70	$[Xe]4f^{14} 5d^0 6s^2$	+ 2, + $\underline{3}$
Lutetium	Lu	71	$[Xe] 4f^{14} 5d^1 6s^2$	+ $\underline{3}$

*Underlined oxidation states are stable.

Lanthanoid Contraction

> **Lanthanoid contraction**
> The regular decrease in atomic and ionic radii of lanthanoids with increasing atomic number, is known as lanthanoid contraction.

> **Cause of lanthanoid contraction**
> Lanthanoid contraction is caused due to increase in nuclear charge which outweighs the imperfect shielding of *f*-electrons.
>
> Due to almost same ionic radii, their chemical properties are similar. Hence, these are difficult to separate.

> **Consequences of lanthanoid contraction**
> Due to decrease in size from La^{3+} to Lu^{3+}, the basic strength of their hydroxides decreases.
>
> Due to similarity in size, 2nd and 3rd rows of transition elements resemble each other more closely than do the first and second rows.

Chemical Properties of Lanthanoids
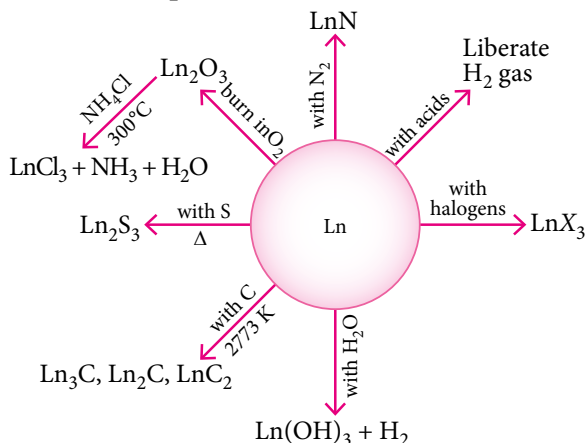
- Ln + N$_2$ → LnN (with N$_2$)
- Ln + O$_2$ → Ln$_2$O$_3$ (burn in O$_2$)
- Ln + NH$_4$Cl → LnCl$_3$ + NH$_3$ + H$_2$O (300°C)
- Ln + S → Ln$_2$S$_3$ (with S, Δ)
- Ln + C → Ln$_3$C, Ln$_2$C, LnC$_2$ (with C, 2773 K)
- Ln + H$_2$O → Ln(OH)$_3$ + H$_2$ (with H$_2$O)
- Ln + acids → Liberate H$_2$ gas (with acids)
- Ln + halogens → LnX$_3$ (with halogens)

ACTINOIDS

Name of the elements	Symbol	At. No. (Z)	Electronic configuration	Oxidation states
Actinium	Ac	89	$[Rn]6d^1, 7s^2$	+ $\underline{3}$
Thorium	Th	90	$[Rn]6d^2, 7s^2$	+ 3, + $\underline{4}$
Protactinium	Pa	91	$[Rn]5f^2, 6d^1, 7s^2$	+ 3, + 4, + $\underline{5}$
Uranium	U	92	$[Rn]5f^3, 6d^1, 7s^2$	+ 3, + 4, + 5, + $\underline{6}$
Neptunium	Np	93	$[Rn]5f^4, 6d^1, 7s^2$	+ 3, + 4, + $\underline{5}$, + 6, + 7
Plutonium	Pu	94	$[Rn]5f^6, 6d^0, 7s^2$	+ 3, + $\underline{4}$, + 5, + 6, + 7
Americium	Am	95	$[Rn]5f^7, 6d^0, 7s^2$	+ $\underline{3}$, + 4, + 5, + 6
Curium	Cm	96	$[Rn]5f^7, 6d^1, 7s^2$	+ $\underline{3}$, + 4
Berkelium	Bk	97	$[Rn]5f^9, 6d^0, 7s^2$	+ $\underline{3}$, + 4
Californium	Cf	98	$[Rn]5f^{10}, 6d^0, 7s^2$	+ 2, + $\underline{3}$
Einsteinium	Es	99	$[Rn]5f^{11}, 6d^0, 7s^2$	+ 2, + $\underline{3}$
Fermium	Fm	100	$[Rn]5f^{12}, 6d^0, 7s^2$	+ 2, + $\underline{3}$
Mendelevium	Md	101	$[Rn]5f^{13}, 6d^0, 7s^2$	+ 2, + $\underline{3}$
Nobelium	No	102	$[Rn]5f^{14}, 6d^0, 7s^2$	+ 2, + 3
Lawrencium	Lr	103	$[Rn]5f^{14}, 6d^1, 7s^2$	+ $\underline{3}$

*Underlined oxidation states are stable.

COMPARISON OF LANTHANOIDS AND ACTINOIDS

Similarities

- The elements of both the series show mainly +3 oxidation state.
- The elements of both the series are electropositive in nature. They are reactive metals and act as strong reducing agents.
- Actinoids exhibit actinoid contraction like lanthanoid contraction. These contractions are due to the poor shielding effect of electrons residing in $(n-2)$ f-orbitals.
- Cations with unpaired electrons in both the series are paramagnetic.

Dissimilarities

S.N.	Lanthanoids	Actinoids
1.	Except promethium, all the remaining lanthanides are non-radioactive.	All the actinides are radioactive.
2.	Besides +3 oxidation state, lanthanides in some cases show +2 and +4 oxidation states.	Besides +3 oxidation state, actinides show a variety of oxidation states like +2, +4, +5, +6 and +7.
3.	Oxides and hydroxides of lanthanides are less basic.	Oxides and hydroxides of actinides are more basic.
4.	Most of the tripositive ions are colourless.	Most of the tripositive and tetrapositive ions are coloured.

INFO SHOTS

Transition Metal Silicides !

Transition metal silicides, a distinct class of semiconducting materials that contain silicon, demonstrate superior oxidation resistance, high temperature stability and low corrosion rates, which make them promising for a variety of future developments in electronic devices.

COORDINATION COMPOUNDS

- A coordination compound contains a central metal atom or ion surrounded by a number of oppositely charged ions or neutral molecules, called ligands.
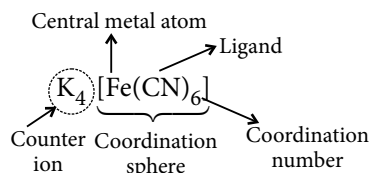
Types of Ligands

Monodentate
Only one donor atom is present, *e.g.,*
NH_3, H_2O, CN^-, NO_2^-, CO

Bidentate
Two donor atoms are present, *e.g.,* ethylenediamine (*en*)

$$CH_2 \!-\! \overset{..}{N}H_2$$
$$|$$
$$CH_2 \!-\! \overset{..}{N}H_2$$

oxalato (*ox*)
$$COO^-$$
$$|$$
$$COO^-$$
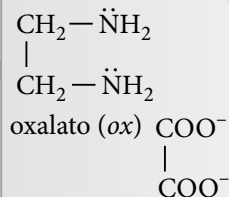
Tridentate
Three donor atoms are present, *e.g.,*

$$H\overset{..}{N}\!\!\overset{\displaystyle /(CH_2)_2\overset{..}{N}H_2}{\underset{\displaystyle \backslash (CH_2)_2\overset{..}{N}H_2}{}}$$
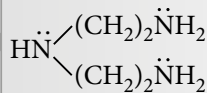
Diethylenetriamine (*dien*)

Polydentate
Tetradentate : Triethylenetetraamine (*trien*)
Pentadentate : Ethylenediaminetriacetate ion
Hexadentate : Ethylenediaminetetraacetate ion
(EDTA)

Chelating ligands
A bidentate or a polydentate ligand is known as chelating ligand if on coordination it results in the formation of a closed or cyclic ring structure. The complex thus formed are called chelates.

$$\left[\begin{array}{c} CH_2\!-\!H_2N \\ | \\ CH_2\!-\!H_2N \end{array} \!\!\! \searrow \!\! Cu \!\! \nearrow \!\!\! \begin{array}{c} NH_2\!-\!CH_2 \\ | \\ NH_2\!-\!CH_2 \end{array} \right]^{2+}$$
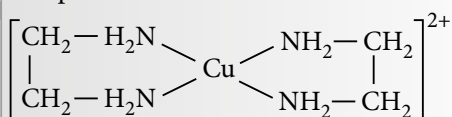
EAN Rule

EAN = Z – O.N + 2(C.N)
Z = Atomic number of central metal atom
O.N. = Oxidation number of central metal atom
C.N. = Coordination number of central metal atom

WERNER'S THEORY

- Metal possesses two types of valencies, *i.e.,* primary valency (ionisable) and secondary valency (non-ionisable).
- Primary valency corresponds to the oxidation state of the central metal and secondary valency represents the coordination number of the metal.
- Primary valencies are satisfied by negative ions, while secondary valencies may be satisfied by neutral or negative ions.

—— Secondary valency
----- Primary valency
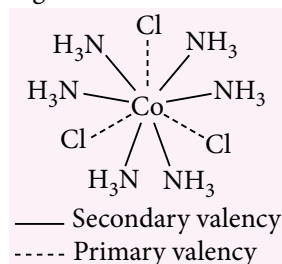
- Negative ion can satisfy both primary and secondary valencies at the same time.

NOMENCLATURE OF COORDINATION COMPOUNDS

Rules for nomenclature :
- Positive ion is named first followed by negative ion.
- Negative ligands are named by adding suffix – o.
- Positive ligands are named by adding suffix – ium.
- Neutral ligands are named as such without adding any suffix or prefix.
- Ligands are named in alphabetical order.
- Name of the ligands is written first followed by name of metal with its oxidation number mentioned in roman numerals in simple parenthesis.
- Number of the polysyllabic ligands *i.e.,* ligands which have numbers in their name, is indicated by prefixes bis, tris, tetrakis, etc.
- When both cation and anion are complex ions, the metal in negative complex is named by adding suffix -ate.

Ligand	Name in complexes	Ligand	Name in complexes
Azide (N_3^-)	Azido	Oxalate ($C_2O_4^{2-}$)	Oxalato
Bromide (Br^-)	Bromido	Oxide (O^{2-})	Oxo
Chloride (Cl^-)	Chlorido	Ammonia (NH_3)	Ammine
Cyanide (CN^-)	Cyano	Carbon monoxide (CO)	Carbonyl
Fluoride (F^-)	Fluorido	Ethylene-diamine (*en*)	Ethylene-diamine

Hydroxide (OH^-)	Hydroxo	Pyridine (C_5H_5N)	Pyridine
Carbonate (CO_3^{2-})	Carbonato	Water (H_2O)	Aqua

Few examples illustrate the nomenclature :

- $[Pt(NH_3)_6]Cl_4$ – Hexaammineplatinum(IV) chloride
- $[Cu(en)_2]SO_4$ – *bis*(ethane-1,2-diamine)copper(II) sulphate
- $K_4[Fe(CN)_6]$ – Potassium hexacyanoferrate(II)
- $[Pt(NH_3)_4Cl_2][PtCl_4]$ – Tetraamminedichlorido--platinum(IV) tetrachloridoplatinate(II)

Isomerism in Coordination Compounds

Stereoisomerism

Ionisation isomerism
- Isomerism arises in the compounds which have same molecular formula but give different ions in solution, *e.g.*, $[Co(NH_3)_5Br]SO_4$, $[Co(NH_3)_5SO_4]Br$.

Linkage isomerism
- Occurs in the complex compounds which contain ambidentate ligand. *e.g.*, $[Co(NH_3)_5NO_2]Cl_2$ or $[Co(NH_3)_5ONO]Cl_2$

Coordination (position) isomerism
- Exhibited by polynuclear complexes by interchanging the position of ligands. *e.g.*,

$$\left[(NH_3)_4Co \overset{NH}{\underset{OH}{<}} Co(NH_3)_2Cl_2 \right]^{2+} \quad \text{OR} \quad \left[(NH_3)_3ClCo \overset{NH}{\underset{OH}{<}} Co(NH_3)_3Cl \right]^{2+}$$

Structural Isomerism

Hydrate or solvate isomerism
- Isomerism arises when different number of water molecules are present inside and outside the coordination sphere, *e.g.*, $CrCl_3 \cdot 6H_2O$ exists in three isomeric forms. $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]H_2O.Cl_2$, $[Cr(H_2O)_4Cl_2]Cl.2H_2O$

Polymerisation isomerism
- Isomerism arises in the compounds which have same stoichiometric composition but different molecular composition. $[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_4][PtCl_4]$

Coordination isomerism
- Isomerism arises when both complex cation and complex anion are present. $[Pt(NH_3)_4][CuCl_4]$ and $[PtCl_4][Cu(NH_3)_4]$

Stereoisomerism

Geometrical

Optical

Tetrahedral complexes : Optical isomerism is possible but no isomer has been isolated.

Square planar complexes : Optical isomerism is not possible.

Tetrahedral Complex
Geometrical isomerism is not possible

Square planar complex

Structure	No. of isomers
$Mabcd$	3
$Mabc_2$	2 (cis-trans)
Ma_2b_2	2 (cis-trans)
$M(ab)_2$	2 (cis-trans)

Isomers of $Mabcd$:

Octahedral complex

Ma_2b_4	2 (cis-trans)
$M(aa)_2b_2$	2 (cis-trans)
$M(aa)_2bc$	2 (cis-trans)
Ma_3b_3	2 (fac/mer)

Isomers of Ma_3b_3:

Facial or 'fac'   Meridional or 'mer'

Octahedral complexes :
Octahedral complexes like $Ma_2b_2c_2$, $Mabcdef$, $[M(AA)_3]^{n\pm}$, $[M(AA)_2a_2]^{n\pm}$ $[M(AA)_2ab]$ and $[M(AB)_3]$ show optical isomerism.

Isomers of $[Ma_2b_2c_2]^{n\pm}$:

cis-d-isomer   cis-l-isomer

*AA and AB are bidentate ligands.

BONDING IN COORDINATION COMPOUNDS

- For explaining the nature of bonding and different properties of coordination compounds such as colour, geometry and magnetic properties, some theories has been developed.

Valence Bond Theory (VBT)

- The central atom uses its number of empty s-, p- and d-atomic orbitals which is equal to its coordination number.
- These empty orbitals hybridise together to form hybrid orbitals.
- The non-bonding electrons of the metal occupy the inner orbitals.
- The d-orbitals participating in the process of hybridization in octahedral complexes may either be $(n-1)d^2sp^3$, inner or low spin complexes or nsp^3d^2 outer or high spin complexes.

Coordination number	Type of hybridization	Geometry	Examples
2	sp	Linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$[Ni(CO)_4]$, $[NiX_4]^{2-}$, $[ZnCl_4]^{2-}$, $[CuX_4]^{2-}$ (where $X = Cl^-, Br^-, I^-$)
	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$ $[Ni(NH_3)_4]^{2+}$
5	sp^3d	Trigonal bipyramidal	$[Fe(CO)_5]$, $[SbF_5]^{2-}$
6	d^2sp^3 or sp^3d^2	Octahedral	$[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$ $[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$

Differences between inner orbital and outer orbital complexes :

S.N.	Inner orbital octahedral complexes or low spin complexes	Outer orbital octahedral complexes or high spin complexes
1.	The complexes are formed by strong ligands and showing d^2sp^3-hybridisation.	The complexes are formed by weak ligands and showing sp^3d^2-hybridisation.
2.	These complexes generally possess less number of unpaired electrons *i.e.*, they show either low or no magnetic moment.	These complexes generally possess greater number of unpaired electrons *i.e.*, they show high magnetic moment.
3.	These are less reactive *i.e.*, more stable. Substitution reactions are difficult to occur.	These are reactive *i.e.*, less stable. Substitution reactions are easy to occur.

Crystal Field Theory (CFT)

- According to crystal field theory, the bonding in complexes is purely electrostatic.

- The complex is regarded as a combination of a central metal ion surrounded by ligands which act as point charges or point dipoles.

- Interaction between positively charged central metal ion or atom and the negatively charged ligands are of two types.
    - The attractive forces arise due to the positive metal ion and the negatively charged ligands or the negative end of a polar neutral molecules.
    - The repulsive forces arise between the lone pairs on the ligands and electrons in the *d*-orbitals of the metal or atom.

- In a free transition metal or ion, there are five *d*-orbitals which are designated as d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$ and d_{z^2}. The five *d*-orbitals are split into two sets, depending on the nature of their orientation in space. This splitting known as crystal field splitting.

- The splitting is different in different structures with different coordination numbers. The crystal field splitting (Δ_o) depends upon the nature of the ligands. The ligands which cause only a small degree of crystal field splitting are called weak field ligands while those which cause a large degree of splitting are called strong field ligands.

$$\text{Strong} \quad\quad\quad\quad \text{Weak}$$
$$CO > CN^- > NO_2^- > en > NH_3 \approx Py > EDTA > H_2O > ox > OH^- > F^- > NO_3^- > Cl^- > SCN^- > Br^- > I^-$$
$$\text{Relative ligand field strengths}$$

- In octahedral complexes, e_g orbitals are of higher energy than that of t_{2g} orbitals.
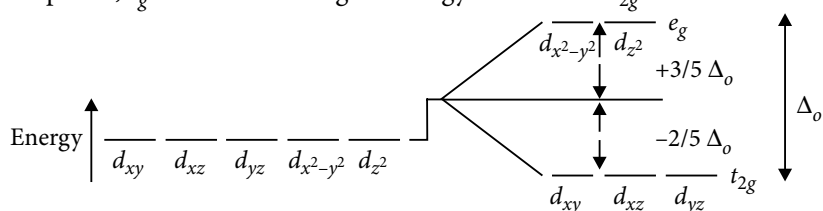
Splitting of *d*-orbitals in an octahedral complex

- In tetrahedral complexes, *e* orbitals are of lower energy than t_2 orbitals.
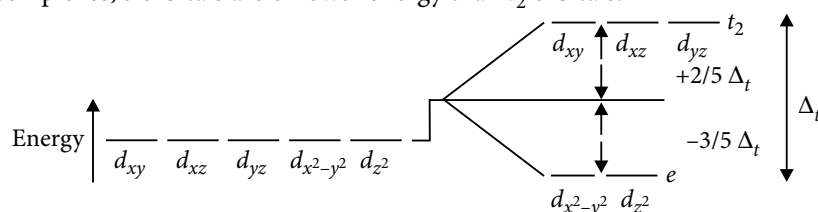
Splitting of *d*-orbitals in a tetrahedral complex

Splitting in tetrahedral complexes (Δ_t) is considerably less than in octahedral complexes (Δ_o) *i.e.*, $\Delta_t \approx 4/9\ \Delta_o$

Calculation of CFSE

- In an octahedral complex, each electron occupying t_{2g} orbital results in lowering of energy by $-0.40\ \Delta_o$ (or -4 Dq). Similarly, each electron occupying e_g orbital results in increase of energy by $+0.60\ \Delta_o$ (or $+6$ Dq). Thus, CFSE $= (-0.4x + 0.6y)\ \Delta_o$

  where, x = number of electrons occupying t_{2g} orbitals and y = number of electrons occupying e_g orbitals. Negative value of CFSE indicates net lowering in energy, *i.e.*, gain in stability.

Calculation of CFSE Values for d^1 to d^{10} Configurations

Metal ion configuration	Low spin state (strong field ligand)	CFSE (Δ_o/Dq)	High spin state (weak field ligand)	CFSE (Δ_o/Dq)
d^1	$t_{2g}^1\ e_g^0$	$-0.4 \times 1 = -0.4\ \Delta_o$ or -4 Dq	$t_{2g}^1\ e_g^0$	$-0.4 \times 1 = -0.4\ \Delta_o$ or -4 Dq
d^2	$t_{2g}^2\ e_g^0$	$-0.4 \times 2 = -0.8\ \Delta_o$ or -8 Dq	$t_{2g}^2\ e_g^0$	$-0.4 \times 2 = -0.8\ \Delta_o$ or -8 Dq
d^3	$t_{2g}^3\ e_g^0$	$-0.4 \times 3 = -1.2\ \Delta_o$ or -12 Dq	$t_{2g}^3\ e_g^0$	$-0.4 \times 3 = -1.2\ \Delta_o$ or -12 Dq
d^4	$t_{2g}^4\ e_g^0$	$-0.4 \times 4 = -1.6\ \Delta_o$ or -16 Dq	$t_{2g}^3\ e_g^1$	$-0.4 \times 3 + 0.6 = -0.6\ \Delta_o$ or -6 Dq
d^5	$t_{2g}^5\ e_g^0$	$-0.4 \times 5 = -2.0\ \Delta_o$ or -20 Dq	$t_{2g}^3\ e_g^2$	$-0.4 \times 3 + 2 \times 0.6 = 0.0\ \Delta_o$ or 0 Dq
d^6	$t_{2g}^6\ e_g^0$	$-0.4 \times 6 = -2.4\ \Delta_o$ or -24 Dq	$t_{2g}^4\ e_g^2$	$-0.4 \times 4 + 2 \times 0.6 = -0.4\ \Delta_o$ or -4 Dq
d^7	$t_{2g}^6\ e_g^1$	$-0.4 \times 6 + 0.6 = -1.8\ \Delta_o$ or -18 Dq	$t_{2g}^5\ e_g^2$	$-0.4 \times 5 + 2 \times 0.6 = -0.8\ \Delta_o$ or -8 Dq
d^8	$t_{2g}^6\ e_g^2$	$-0.4 \times 6 + 2 \times 0.6 = -1.2\ \Delta_o$ or -12 Dq	$t_{2g}^6\ e_g^2$	$-0.4 \times 6 + 2 \times 0.6 = -1.2\ \Delta_o$ or -12 Dq
d^9	$t_{2g}^6\ e_g^3$	$-0.4 \times 6 + 3 \times 0.6 = -0.6\ \Delta_o$ or -6 Dq	$t_{2g}^6\ e_g^3$	$-0.4 \times 6 + 3 \times 0.6 = -0.6\ \Delta_o$ or -6 Dq
d^{10}	$t_{2g}^6\ e_g^4$	$-0.4 \times 6 + 4 \times 0.6 = 0.0\ \Delta_o$ or 0 Dq	$t_{2g}^6\ e_g^4$	$-0.4 \times 6 + 4 \times 0.6 = 0.0\ \Delta_o$ or 0 Dq

Similarly, for tetrahedral complex CFSE $= (-0.6\ x + 0.4\ y)\ \Delta_t$

- The actual configuration adopted by the complex is decided by the relative values of Δ_o and P, where P represents the energy required for electron pairing in a single orbital.

- If Δ_o is less than $P(\Delta_o < P)$, we have weak field, the fourth electron will enter one of the e_g orbitals giving the configuration, $t_{2g}^3 e_g^1$. It will be high spin complex.

- If Δ_o is more than $P(\Delta_o > P)$, we have strong field and the pairing will occur in the t_{2g} orbitals with e_g orbitals remaining unoccupied giving the configuration, t_{2g}^4. It will be low spin complex.

STABILITY OF COORDINATION COMPOUNDS

- Consider the following reaction
  $$M + 4L \rightleftharpoons ML_4 \qquad \text{...(i)}$$
  The equilibrium constant for the reaction is called the stability constant and is represented by β_4.

  $$\beta_4 = \frac{[ML_4]}{[M][L]^4}$$

Larger the stability constant, higher is the proportion of ML_4 that exists in solution.

$$M + L \rightleftharpoons ML\ ; \qquad K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \rightleftharpoons ML_2\ ; \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \rightleftharpoons ML_3\ ; \qquad K_3 = \frac{[ML_3]}{[ML_2][L]}$$

$$ML_3 + L \rightleftharpoons ML_4\ ; \qquad K_4 = \frac{[ML_4]}{[ML_3][L]}$$
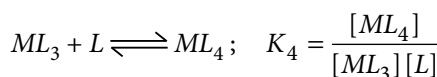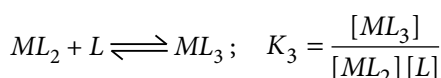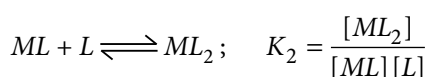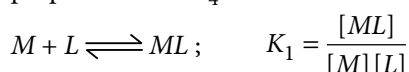
K_1, K_2 etc. referred to as stepwise stability constants. Overall stability constant, $\beta_4 = K_1 \times K_2 \times K_3 \times K_4$,

or, $\beta_4 = \dfrac{[ML_4]}{[M][L]^4}$

The instability constant or the dissociation constant of coordination compounds is defined as the reciprocal of the formation constant (stability constant).

ORGANOMETALLIC COMPOUNDS

Organometallic compounds :
Compounds in which metal is directly attached to carbon, are called organometallic compounds.

Sigma bonded compounds	π-bonded compounds	σ and π bonded compounds
Metal carbon bond is sigma bond. *e.g.*, R – Mg – X, R_2Zn, $(CH_3)_4Sn$, $(C_2H_5)_4Pb$ etc.	Metal and ligands form a bond that involve π-electrons of ligands. *e.g.,* ferrocene, zeise's salt, etc.	These compound possess both σ -and π- bonding between M and ligands. *e.g.,* $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$ etc.

BONDING OF METAL CARBONYLS

- In a metal carbonyl, the metal-carbon bond possesses both the σ- and π-character. A σ-bond between metal and carbon atoms is formed when a vacant hybrid orbital of the metal atom overlaps with an orbital on C atom of carbon monoxide containing a lone pair of electrons.

Vacant orbital on metal | Lone pair | σ-overlap $M \leftarrow C$ bond
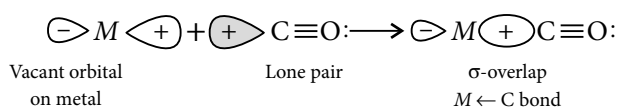
Formation of π-bond is caused when a filled orbital of the metal atom overlaps with a vacant antibonding π* orbital of C atom of carbon monoxide. This overlap is also called back donation of electrons by metal atom to carbon *i.e.*, synergic bonding.

Filled metal *d*-orbital | Empty π*2*p* orbital of CO | $M \rightarrow C$ bond π-overlap
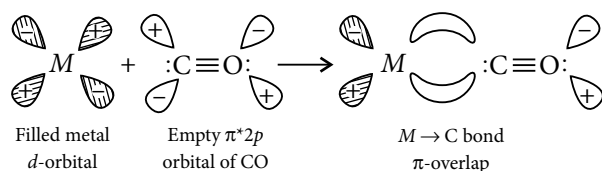
The π-overlap is perpendicular to the nodal plane of σ-bond.

IMPORTANCE OF COORDINATION COMPOUNDS
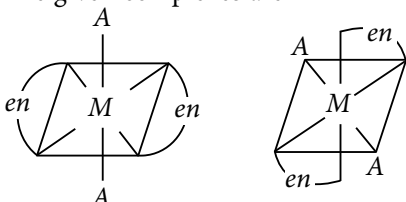
- In both qualitative and quantitative methods of analysis.
- In metallurgical operations.
- In photography.
- **In electroplating :** Metal complexes release metal slowly and thus give a uniform coating *i.e.*, electroplating of the metal on the desired object.
- **In biological processes :** Coordination compounds are essential in storage and transport of oxygen as electron transfer agents, acts as catalysts and are used in photosynthesis.
- **In medicinal field :** The complex of Ca with EDTA is used for treatment of lead poisoning. *Cis*-platin is used as an antitumor agent.

iNFO SHOTS

Some Recent Developments in Coordination Chemistry

Catalysts of the type $(R_3Q)_2MX_2$ (*R* is an alkyl, aryl, or phenoxy group ; *Q* is P, As, or Sb ; *M* is Ni, Pd, or Pt, *X* is a halogen or halogenoid are recently developed. In the presence of such a substance, polyunsaturated compounds, especially esters of long chain fatty acids are hydrogenated until one double bond remains. The hydrogenation is preceded by *cis-trans* rearrangement of the double bond and migration of the double bonds along the carbon chain ocours for a conjugated system. Another research project has shown that certain bacteria can utilize the nitrogen from *d*-[Co(*en*)$_3$]Cl$_3$ but that *l*-[Co(*en*)$_3$]Cl$_3$ inhibits their growth.

SPEED PRACTICE

1. Which of the following ions does not liberate hydrogen gas on reaction with dilute acids?
   (a) Mn^{2+} (b) Ti^{2+} (c) V^{2+} (d) Cr^{2+}
   (JEE Main Online 2017)

2. The IUPAC name of $[Ni(NH_3)_4]\,[NiCl_4]$ is
   (a) tetrachloronickel(II) tetraamminenickel(II)
   (b) tetraamminenickel(II) tetrachloronickel(II)
   (c) tetraamminenickel(II) tetrachloronickelate(II)
   (d) tetrachloronickel(II) tetraamminenickelate(0).

3. Which of the following statement(s) is/are correct?
   (I) The size of the lanthanide M^{3+} ions decreases as the atomic number of M increases.
   (II) Lanthanoids show limited number of oxidation states.
   (III) Like transition metals, coordination number six is very common in lanthanide complexes.
   (a) I only   (b) I and II only
   (c) I and III only   (d) III only

4. Which one of the following cyano complex would exhibit the lowest value of paramagnetic behaviour?
   (a) $[Cr(CN)_6]^{3-}$ (b) $[Co(CN)_6]^{3-}$
   (c) $[Fe(CN)_6]^{3-}$ (d) $[Mn(CN)_6]^{3-}$

5. Which of the following statements about the transition elements is not true?
   (a) All the transition elements are predominantly metallic.
   (b) In aqueous solution, many of their simple ions are coloured.
   (c) Most of the transition elements show pronounced catalytic activity.
   (d) Most of the transition elements show only one valency.

6. The given complexes are

   (a) geometrical isomers (b) position isomers
   (c) optical isomers   (d) identical.

7. Which of the following combination will produce H_2 gas?
   (a) Cu metal and conc. HNO_3
   (b) Zn metal and $NaOH_{(aq)}$
   (c) Au metal and $NaCN_{(aq)}$ in the presence of air
   (d) Fe metal and conc. HNO_3
   (JEE Advanced 2017)

8. Wilkinson's catalyst used as a homogeneous catalyst in the hydrogenation of alkenes contains
   (a) iron   (b) aluminium
   (c) rhodium   (d) cobalt.

9. Acidified potassium dichromate on reaction with sulphite is reduced to
   (a) CrO_2Cl_2 (b) CrO_4^{2-}
   (c) Cr^{3+} (d) Cr^{2+}.

10. The number of geometrical isomers of $[Co(NH_3)_3\,(NO_2)_3]$ is
    (a) 2   (b) 3   (c) 4   (d) 0

11. Pyrolusite (MnO_2) is used to prepare $KMnO_4$ as given:
    $$MnO_2 \xrightarrow{\text{I}} MnO_4^{2-} \xrightarrow{\text{II}} MnO_4^{-}$$
    here, I and II are
    (a) fused with KOH/air, electrolytic oxidation
    (b) fused with conc. HNO_3/air, electrolytic oxidation
    (c) fused with KOH/air, electrolytic reduction
    (d) all of the above.

12. Among $[Ni(CO)_4]$, $[NiCl_4]^{2-}$, $[Co(NH_3)_4Cl_2]Cl$, $Na_3[CoF_6]$, Na_2O_2 and CsO_2, the total number of paramagnetic compounds is
    (a) 2   (b) 3   (c) 4   (d) 5
    (JEE Advanced 2016)

13. The lanthanide contraction is responsible for the fact that
    (a) Zr and Y have about the same radius
    (b) Zr and Nb have similar oxidation states
    (c) Zr and Hf have about the same radius
    (d) Zr and Zn have the same oxidation state.

14. Which of the following are square planar complexes?
    (1) $[AuCl_4]^-$ (2) $[PtCl_4]^{2-}$
    (3) $[MnBr_4]^{2-}$ (4) $[Cu(NH_3)_4]^{2+}$
    (a) 1 and 2 only   (b) 2 and 3 only
    (c) 2 and 4 only   (d) 1, 2 and 4 only

15. How many moles of iodine are liberated when 1 mole of potassium dichromate reacts with potassium iodide?
(a) 1   (b) 2   (c) 3   (d) 4

16. Which of the following is a π-acid ligand?
(a) NH_3 (b) CO
(c) F^- (d) $H_2N–CH_2–CH_2–NH_2$

17. The reason for greater range of oxidation states in actinoids is attributed to
(a) actinoid contraction
(b) $5f$, $6d$ and $7s$ levels having comparable energies
(c) $4f$ and $5d$ levels being close in energies
(d) the radioactive nature of actinoids.

[NEET 2017]

18. Ammonia forms the complex ion, $[Cu(NH_3)_4]^{2+}$ with copper ions in alkaline solutions but not in acidic solution. This is because
(a) in acidic solutions, protons coordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are thus, not available
(b) in alkaline solutions, insoluble $Cu(OH)_2$ is precipitated which is soluble in excess of any alkali
(c) copper hydroxide is an amphoteric substance
(d) in acidic solutions, hydration protects copper ions.

19.
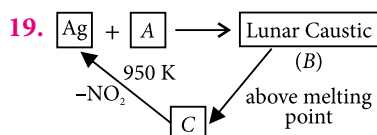
A, *B* and *C* are respectively
(a) HNO_3, $AgNO_3$, $AgNO_2$
(b) $NaNO_2$, $AgNO_2$, Ag_2NO
(c) $NaNO_2$, $AgNO_3$, $AgNO_2$
(d) HNO_3, $AgNO_2$, $Ag_2O_2 + N_2$

20. The metal ion in complex *A* has EAN identical to the atomic number of krypton. *A* is
(At. no. of Cr = 24, Fe = 26, Pd = 46)
(a) $[Pd(NH_3)_6]Cl_4$ (b) $[Cr(NH_3)_5Cl]SO_4$
(c) $Na_4[Fe(CN)_6]$ (d) $K_3[Fe(CN)_6]$

21. The 'spin only' magnetic moment of Ni^{2+} in aqueous solution would be
(a) 0 B.M.   (b) 1.73 B.M.
(c) 2.83 B.M.   (d) 4.90 B.M.

22. Jahn-Teller effect is not observed in high spin complexes of
(a) d^7 (b) d^8 (c) d^4 (d) d^9

[NEET Phase-II 2016]

23. The electronic configuration of gadolinium $(Z = 64)$ is
(a) $[Xe]4f^8 5d^0 6s^2$ (b) $[Xe]4f^3 5d^5 6s^2$
(c) $[Xe]4f^6 5d^2 6s^2$ (d) $[Xe]4f^7 5d^1 6s^2$.
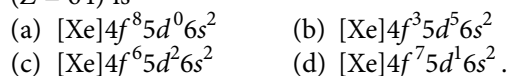
24. In a complex ML_2, stepwise formation constants for
$$M + L \rightleftharpoons ML$$
$$ML + L \rightleftharpoons ML_2$$
are 4 and 3. Hence, overall stability constant for the reaction, $M + 2L \rightleftharpoons ML_2$ is
(a) 12   (b) 7   (c) 1.33   (d) 0.75
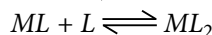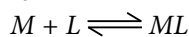
25. In the standardisation of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent weight of $K_2Cr_2O_7$ is
(a) mol wt/2   (b) mol wt/6
(c) mol wt/3   (d) same as mol wt.

26. Which of the following has longest C—O bond length? (Free C—O bond length in CO is 1.128 Å).
(a) $[Fe(CO)_4]^{2-}$ (b) $[Mn(CO)_6]^+$
(c) $Ni(CO)_4$ (d) $[Co(CO)_4]^-$

[NEET Phase-I 2016]

27. The correct order of ionic radii of Ce, La, Pm and Yb in +3 oxidation state is
(a) $La^{3+} < Pm^{3+} < Ce^{3+} < Yb^{3+}$
(b) $La^{3+} < Ce^{3+} < Pm^{3+} < Yb^{3+}$
(c) $Yb^{3+} < Ce^{3+} < Pm^{3+} < La^{3+}$
(d) $Yb^{3+} < Pm^{3+} < Ce^{3+} < La^{3+}$

28. Crystal field stabilisation energy for high spin d^4 octahedral complex is
(a) $-0.6\,\Delta_o$ (b) $-0.8\,\Delta_o$
(c) $-1.6\,\Delta_o + P$ (d) $-1.2\,\Delta_o$

29. Cerium $(Z = 58)$ is an important member of the lanthanoids. Which of the following statements about cerium is incorrect?
(a) The +4 oxidation state of cerium is not known in solutions.
(b) The +3 oxidation state of cerium is more stable than +4 oxidation state.
(c) The common oxidation states of cerium are +3 and +4.
(d) Cerium (IV) acts as an oxidising agent.

30. Which one of the following complexes shows optical isomerism?
(a) $[Co(NH_3)_3Cl_3]$
(b) $cis[Co(en)_2Cl_2]Cl$
(c) $trans[Co(en)_2Cl_2]Cl$
(d) $[Co(NH_3)_4Cl_2]Cl$ (*en* = ethylenediamine)

[JEE Main 2016]

SOLUTIONS

1. (a) : The third ionisation energy of Mn is too high due to stable half-filled $3d$-orbital. Hence, it cannot further get oxidised to liberate hydrogen.

2. (c)   **3. (b)**

4. (b) : CN^- is a strong field ligand, thus, causes pairing of electrons in $3d$-orbitals.

$[Cr(CN)_6]^{3-}$:
Cr^{3+} : $[Ar]3d^3$

; 3 unpaired electrons
d^2sp^3

$[Co(CN)_6]^{3-}$:
Co^{3+} : $[Ar]3d^6$

; No unpaired electron
d^2sp^3

$[Fe(CN)_6]^{3-}$:
Fe^{3+} : $[Ar]3d^5$

; 1 unpaired electron
d^2sp^3

$[Mn(CN)_6]^{3-}$:
Mn^{3+} : $[Ar]3d^4$

; 2 unpaired electrons
d^2sp^3
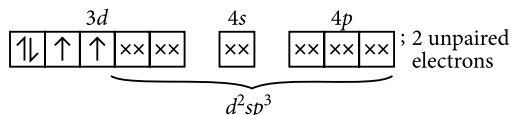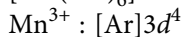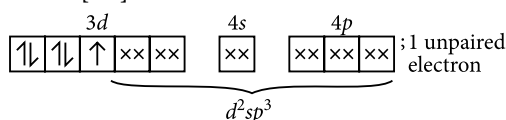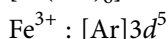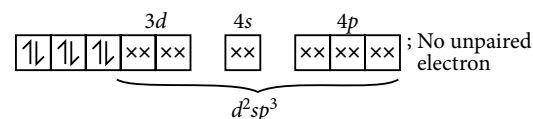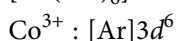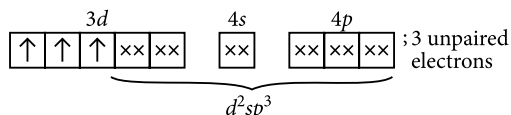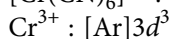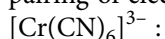
Greater the number of unpaired electrons, higher is the paramagnetism.

5. (d)   **6. (d)**

7. (b) :

(a) $\underset{\text{Copper}}{Cu} + \underset{\text{Nitric acid}}{4HNO_3(conc.)} \rightarrow \underset{\text{Copper nitrate}}{Cu(NO_3)_2}$
$+ \underset{\text{Nitrogen dioxide}}{2NO_2} + \underset{\text{Water}}{2H_2O}$

(b) $\underset{\text{Zinc}}{Zn} + \underset{\substack{\text{Sodium} \\ \text{hydroxide}}}{2NaOH_{(aq)}} \rightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + \underset{\text{Hydrogen}}{H_2}$

(c) $\underset{\text{Gold}}{4Au} + \underset{\substack{\text{Sodium} \\ \text{cyanide}}}{8NaCN} + \underset{\text{Oxygen}}{O_2} + \underset{\text{Water}}{2H_2O} \rightarrow$
$\underset{\text{Sodium dicyanoaurate (I)}}{4Na[Au(CN)_2]} + \underset{\text{Sodium hydroxide}}{4NaOH}$
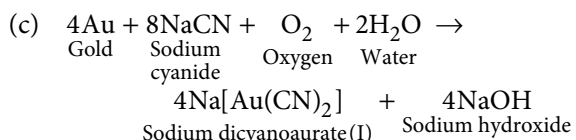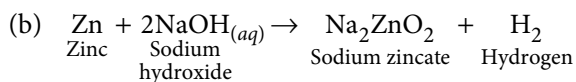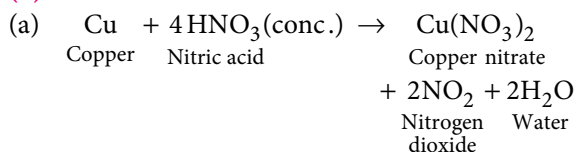
(d) Conc. HNO_3 makes iron passive. Relatively cold concentrated HNO_3 will react with Fe.

$\underset{\text{Iron}}{Fe} + \underset{\text{Nitric acid}}{6HNO_3} \rightarrow \underset{\text{Iron nitrate}}{Fe(NO_3)_3} + \underset{\substack{\text{Nitrogen} \\ \text{dioxide}}}{3NO_2} + \underset{\text{Water}}{3H_2O}$
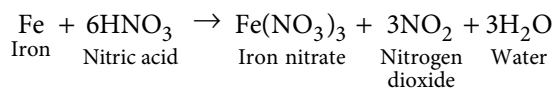
8. (c) : Wilkinson's catalyst is $(Ph_3P)_3RhCl$.

9. (c) : $Cr_2O_7^{2-} + 8H^+ + 3SO_3^{2-} \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$
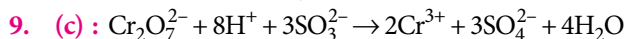
10. (a) : The given complex exhibits two geometrical isomers (i) *facial* and (ii) *meridional*.

'Facial'   'Meridional'

11. (a) : $MnO_2 \xrightarrow[\text{air}]{\text{Fused with KOH}} MnO_4^{2-}$

$MnO_4^{2-} \xrightarrow{\text{Electrolytic oxidation}} MnO_4^-$

12. (b) : $[Ni(CO)_4]$:

sp^3 hybridisation, diamagnetic
(CO is a strong field ligand)

$[NiCl_4]^{2-}$:

sp^3 hybridisation, paramagnetic
(Cl^- is a weak field ligand)

$[Co(NH_3)_4Cl_2]^+$:

d^2sp^3 hybridisation, diamagnetic
(NH_3 is a strong field ligand)

$[CoF_6]^{3-}$:

sp^3d^2 hybridisation, diamagnetic
(F^- is a weak field ligand)
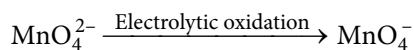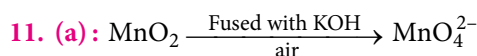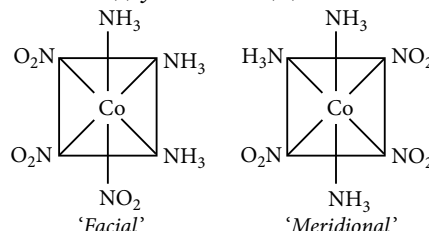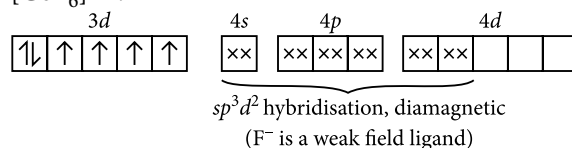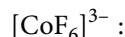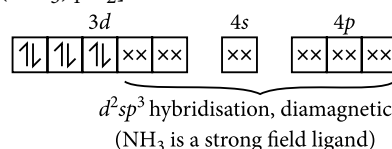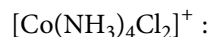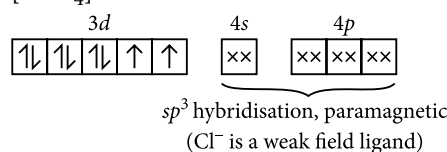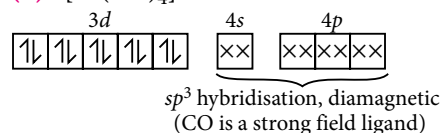
Na_2O_2 contains O_2^{2-} (peroxide ion) which is diamagnetic. CsO_2 contains O_2^- (superoxide ion) which is paramagnetic.

13. (c)

14. (d) : (1) $[AuCl_4]^-$: highly charged species with $5d^8$ configuration, has greater CFSE and thus, $\Delta_t > P$ and so, dsp^2 hybridisation.
(2) $[PtCl_4]^{2-}$: $5d^8$ configuration, has greater CFSE and thus, $\Delta_t > P$ and so, dsp^2 hybridisation.

(3) $[MnBr_4]^{2-}$: sp^3 hybridisation as Br^- is a weak field ligand.

(4) $[Cu(NH_3)_4]^{2+}$: dsp^2 hybridisation, one d-electron jumps to $4p$-orbital, leaving behind one empty d-orbital for dsp^2 hybridisation.

15. (c) : Iodine is liberated from potassium iodide.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3$$
$$+ 4H_2O + 3[O]$$
$$[2KI + H_2SO_4 + [O] \longrightarrow K_2SO_4 + I_2 + H_2O] \times 3$$

$$\overline{K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3}$$
$$+ 7H_2O + 3I_2$$
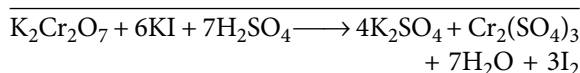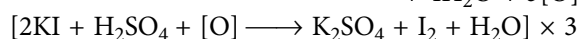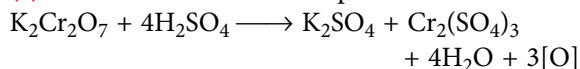
16. (b)

17. (b) : Actinoids have a greater range of oxidation states due to comparable energies of $5f$, $6d$ and $7s$ orbitals. Hence, all their electrons can take part in bond formation.

18. (a) : In acidic solution, NH_3 forms a coordinate bond with H^+ to form NH_4^+ ion which does not have a lone pair of electrons on N to act as a ligand.

19. (a) :
$$\underset{\substack{\text{(cold and dil.)} \\ (A)}}{3\,Ag + 4\,HNO_3} \longrightarrow \underset{\substack{\text{(Lunar caustic)} \\ (B)}}{3AgNO_3}$$
$$+ 2H_2O + NO$$

$$\underset{(B)}{2AgNO_3} \xrightarrow{\text{Above melting point}} \underset{(C)}{2AgNO_2} + O_2$$

$$AgNO_2 \xrightarrow{950\,K} Ag + NO_2$$
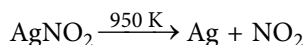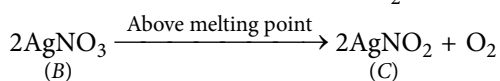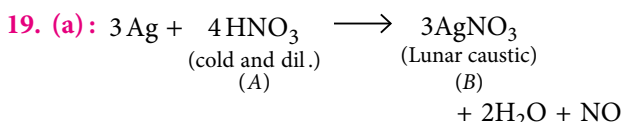
20. (c) : Atomic number of krypton = 36

Effective atomic number (EAN) = atomic number of the metal – number of electrons lost in ion formation + number of electrons gained from the donor atoms of the ligands.

EAN of $[Pd(NH_3)_6]Cl_4 = 46 – 4 + 12 = 54$

EAN of $[Cr(NH_3)_5Cl]SO_4 = 24 – 3 + 12 = 33$

EAN of $Na_4[Fe(CN)_6] = 26 – 2 + 12 = 36$

EAN of $K_3[Fe(CN)_6] = 26 – 3 + 12 = 35$

21. (c) : Ni^{2+} = [Ar] $3d^8$

$$\overset{3d}{\boxed{\uparrow\downarrow\,|\,\uparrow\downarrow\,|\,\uparrow\downarrow\,|\,\uparrow\,|\,\uparrow}}$$

Magnetic moment $= \sqrt{n(n+2)}$ B.M.

$= \sqrt{2(2+2)} = \sqrt{8}$ B.M. = 2.83 B.M.

22. (b) : In octahedral complexes, Jahn-Teller effect is most pronounced when an odd number of electrons occupy the e_g orbitals. This situation arise in complexes with the configuration d^9, low spin d^7 or high spin d^4 complexes, all of which have doubly degenerated ground states.

Number of d-electrons	1	2	3	4		5		6		7		8	9	10
High/low spin				HS	LS	HS	LS	HS	LS	HS	LS			
Strength of J-T effect	W	W		S	W			W	W		W	S		S

W = Weak Jahn-Teller effect
S = Strong Jahn-Teller effect
Blank = No Jahn-Teller effect

23. (d)

24. (a) : $\beta_{overall} = K_1 \times K_2 = 4 \times 3 = 12$

25. (b) : $Cr_2O_7^{2-} + 8H^+ + 3S_2O_3^{2-} \rightarrow 2Cr^{3+} + 3SO_4^{2-}$
$$+ 3S + 4H_2O$$
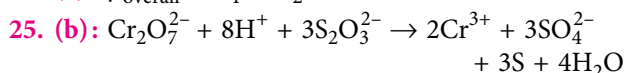
Eq. wt. $= \dfrac{\text{Mol.wt.}}{6}$

26. (a) : As the negative charge on metal carbonyl complex increases, back π–bonding increases and hence, the bond length of $M-C$ bond decreases while the bond length of $C-O$ bond increases.

Thus, $[Fe(CO)_4]^{2-}$ have longest $C-O$ bond length.

27. (d)

28. (a) : Electronic configuration of octahedral high spin complex (d^4)

$$\uparrow \quad \_ \qquad e_g$$
$$\uparrow \quad \uparrow \quad \uparrow \qquad t_{2g}$$
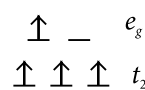
CFSE $= (–0.4 \times 3 + 0.6 \times 1)\Delta_o = (–1.2 + 0.6)\Delta_o = –0.6$

29. (a) : Ce(58) can attain stable f^0 configuration in +4 oxidation state and therefore, Ce can exhibit +4 oxidation state.

Ce^{4+} : [Xe] $4f^0$
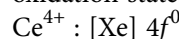
30. (b) : $[Co(NH_3)_3Cl_3]$ has two geometrical isomers but both are optically inactive due to plane of symmetry.

$cis[Co(en)_2Cl_2]Cl$ is optically active.
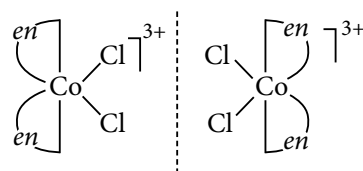
Non-superimposable

$trans[Co(en)_2Cl_2]Cl$ is optically inactive due to plane of symmetry.

$[Co(NH_3)_4Cl_2]Cl$ has two geometrical isomers but both are optically inactive due to plane of symmetry.

◈◈

EXAMINER'S MIND CLASS XII
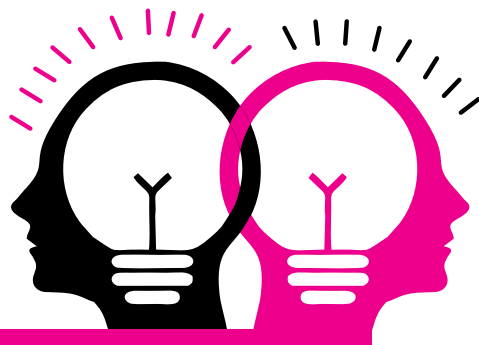
The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII.
This year JEE (Main & Advanced)/NEET/AIIMS have drawn their papers heavily from NCERT books.

Section - I	Q. 1 to 10 Only One Option Correct Type MCQs.
Section - II	Q. 11 to 13 More than One Options Correct Type MCQs.
Section - III	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.
Section - IV	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.
Section - V	Q. 20 to 22 Assertion Reason Type MCQs having Only One Option Correct. Mark the correct choice as : (a) If both assertion and reason are true and reason is the correct explanation of assertion. (b) If both assertion and reason are true but reason is not the correct explanation of assertion. (c) If assertion is true but reason is false. (d) If both assertion and reason are false.
Section - VI	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).

d- AND f-BLOCK ELEMENTS

SECTION - I

Only One Option Correct Type

1. In anhydride of chromic acid (CrO_3), Cr has d^0 configuration but it is bright orange coloured solid. the colour is due to
   (a) d–d transition
   (b) charge transfer from $L \rightarrow M$
   (c) charge transfer from $M \rightarrow L$
   (d) p–d transition.

2. The colourless species is
   (a) VCl_3
   (b) $VOSO_4$
   (c) Na_3VO_4
   (d) $[V(H_2O)_6SO_4] \cdot H_2O$

3. In the following reaction,

   $$Z \xleftarrow[\text{acids}]{\text{with}} \text{Ln} \xrightarrow{\text{with } H_2O} X$$
   $$\downarrow \text{burns in } O_2$$
   $$Y$$
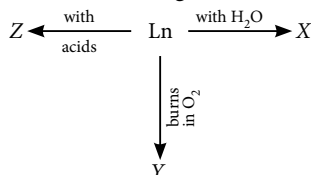
   The X, Y and Z respectively are
   (a) Ln_2O_3, H_2, $Ln(OH)_3 + H_2$
   (b) $Ln(OH)_3 + H_2$, Ln_2O_3, H_2
   (c) H_2, Ln_2O_3, $Ln(OH)_3 + H_2$
   (d) $Ln(OH)_3 + H_2$, $LnNO_2$, H_2

4. The given graph represents the trend in melting point of transition metals.
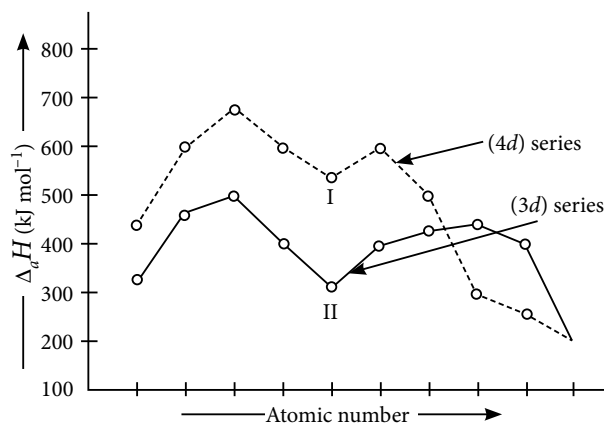
   (a) I – Mo, II – Cr
   (b) I – Ru, II – Fe
   (c) I – Tc, II – Mn
   (d) None of these

5. Oxides of which metal are used as phosphors in television screens and fluorescent surface?
   (a) W
   (b) Tb
   (c) Ac
   (d) All of these

6. Which of the following exhibits only + 3 oxidation state?
(a) U (b) Th (c) Ac (d) Pa

7. Acidified potassium permanganate is decolourised by
(a) laughing gas
(b) bleaching powder
(c) white vitriol
(d) hydrogen peroxide.

8. Complete the given reaction.
$2Mn^{2+} + 5\ \underline{(i)}\ + 8H_2O \rightarrow 2\ \underline{(ii)}\ + 10\ \underline{(iii)}\ + 16H^+$

	(i)	(ii)	(iii)
(a)	SO_4^{2-}	MnO_4^-	$S_2O_8^{2-}$
(b)	$S_2O_8^{2-}$	MnO_4^-	SO_4^{2-}
(c)	MnO_4^-	$S_2O_8^{2-}$	SO_4^{2-}
(d)	$S_2O_8^{2-}$	SO_4^{2-}	MnO_4^-

9. When an oxide of manganese (*P*) is fused with KOH in the presence of an oxidising agent and dissolved in water, it gives a dark green solution of compound (*Q*). Compound (*Q*) disproportionates in neutral or acidic solution to give purple compound (*R*). An alkaline solution of compound (*R*) oxidises potassium iodide solution to a compound (*S*) and compound (*P*) is also formed. Compounds *P* to *S* are

	P	Q	R	S
(a)	MnO_4^-	KIO_3	MnO_2	K_2MnO_4
(b)	MnO_2	K_2MnO_4	MnO_4^-	KIO_3
(c)	MnO_2	MnO_4^-	K_2MnO_4	KIO_3
(d)	K_2MnO_4	MnO_2	MnO_4^-	KIO_3

10. There are 14 elements in actinoid series. Which of the following elements does not belong to this series?
(a) U (b) Np (c) Tm (d) Fm

SECTION - II
More than One Options Correct Type

11. Select the correct options with respect to indicated properties :
(a) $Ce(OH)_3 > Gd(OH)_3 > Lu(OH)_3$ (Basic strength)
(b) $UO_2^{2+} > UO_2^+ > UF_4$ (Oxidation number of uranium in fluoride and oxocations of uranium)
(c) $Ce^{3+} > Pr^{3+} > Pb^{3+} > Lu^{3+}$ (size of lanthanide ions)
(d) $Lu^{3+} < Eu^{3+} < La^{3+} < Y^{3+}$ (Size)

12. Which of the following statement(s) is (are) correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4?

(a) Orange red vapours are evolved.
(b) The vapours when passed through NaOH solution, a yellow coloured solution is obtained.
(c) Chlorine gas is also evolved.
(d) Chromyl chloride is formed.

13. Mercurous ion can be represented as
(a) Hg^+ (b) $-Hg^+-Hg^+-$
(c) Hg_2^{2+} (d) Hg^{2+}

SECTION - III
Paragraph Type

Paragraph for Questions 14 and 15

Transition metal compounds are coloured due to *d-d* transitions and charge transfer. Colour due to *d-d* transition is shown by transition metal compounds having d^1 to d^9 electrons whereas few compounds containing d^0 and d^{10} configurations are coloured due to charge transfer transitions.

14. The purple colour of $[Ti(H_2O)_6]^{3+}$ ion is due to
(a) unpaired *d*-electron
(b) transfer of an electron
(c) intermolecular vibrations
(d) presence of water molecules.

15. For the same transition metal ion, the colour of its compounds will depend upon
(a) temperature of the reaction
(b) pressure of the reaction
(c) nature of ligands or Lewis bases attached to the metal ion
(d) concentration of the ligands.

Paragraph for Questions 16 and 17

The element Cu, Ag and Au show oxidation states of +1, +2 and +3. However, the only simple hydrated ions found in solution are Cu^{2+} and Ag^+. The univalent ions Cu^+ and Au^+ disproportionate in water and as a result they only exist as insoluble compounds or complexes. Cu(+3), Ag(+3) and Ag(+2) are so strong oxidising agents that they oxidise water. Thus, they only occur when stabilised in complexes, or as insoluble compounds.

16. Cu is very slowly oxidised in moisture to '*x*', often seen in electrical circuits. The '*x*' is
(a) $CuSO_4 . 5H_2O$ (b) $CuCO_3$
(c) $Cu(OH)_2$ (d) $Cu(OH)_2 . CuCO_3$

17. $Au + aqua\ regia \longrightarrow$ '*y*'
About '*y*' which of the following is/are correct?
(a) '*y*' is $H[AuCl_4]$ and a square planar complex.
(b) '*y*' is $H[AuCl_4]$ and a tetrahedral complex.
(c) '*y*' is $AuCl_3$ and a triangular planar compound.
(d) '*y*' is $H_3[AuCl_6]$ and an octahedral complex.

SECTION - IV

Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists :

List I (Metal ion)	List II (μ_{eff} (B.M.))
A. Cr^{3+}	(p) $\sqrt{35}$
B. Fe^{2+}	(q) $\sqrt{30}$
C. Ni^{2+}	(r) $\sqrt{24}$
D. Mn^{2+}	(s) $\sqrt{15}$
	(t) $\sqrt{8}$

	A	B	C	D
(a)	p	r	t	s
(b)	q	r	t	p
(c)	s	r	t	p
(d)	s	t	r	p

19. Match the List I with List II and select the correct answer using the codes given below the lists :

List I Property of a metal (M)	List II Metal (M)
A. "M" produces H_2 with KOH solution	(p) Au
B. "M" produces M^{2+} ion when reacts with dil. HCl	(q) Zn
C. "M" does not dissolve in dil. HCl but dissolves in dil. HNO_3	(r) Hg
D. "M" does not dissolve in conc. HCl, HNO_3 or H_2SO_4	(s) Fe

	A	B	C	D
(a)	p,s	r	q	s
(b)	s	p,q	r,p	p
(c)	p,q	s	p,q	r
(d)	q	q,s	r	p

SECTION - V

Assertion Reason Type

20. **Assertion :** The compound $UO_2(NO_3)_2$ is called uranyl nitrate.
    Reason : $UO_2(NO_3)_2$ contains uranyl (UO_2^{2+}) cation.

21. **Assertion :** Lanthanoids show a limited number of oxidation state whereas actinoids show a large number of oxidation states.
    Reason : Energy gap between $4f$, $5d$ and $6s$ subshells is small whereas that between $5f$, $6d$ and $7s$ subshells is large.

22. **Assertion :** Permanganate titrations in presence of hydrochloric acid are unsatisfactory.
    Reason : Hydrochloric acid is oxidised to chlorine by MnO_4^-.

SECTION - VI

Integer Value Correct Type

23. How many Cr—O bonds are equivalent in dichromate anion?

24. Acidified potassium dichromate reacts with potassium iodide and oxidises it to I_2. The oxidation state of chromium in the products of the reaction is $+x \cdot x$ refers to

25. Total number of reagents from the following that would react with $KI_{(aq)}$ to produce I_2.
    $CuSO_4$, $FeSO_4$, $Hg(NO_3)_2$, $KMnO_4/H^+$, $K_2Cr_2O_7/H^+$

ELECTROCHEMISTRY

SECTION - I

Only One Option Correct Type

1. In the electrolysis of aqueous NaCl, how long would you pass a current of 1.0 A through the cell to convert 1.0 L solution of 1 M concentration into 1 M NaOH?
   (a) 12.6 hr
   (b) 20.4 hr
   (c) 26.8 hr
   (d) 30.2 hr

2. What is the energy which may be obtained from a lead storage battery in which 0.100 mol lead is consumed? Assume a constant concentration of 10.0 M H_2SO_4. (Given that $E^\circ_{(PbO_2/PbSO_4)}$ = 1.70 V and $E^\circ_{(Pb/PbSO_4)}$ = 0.31 V.)
   (a) 43 kJ   (b) 99 kJ   (c) 32 kJ   (d) 90 kJ

3. An unknown metal M displaces nickel from nickel (II) sulphate solution but does not displace manganese from manganese sulphate solution. Which order represents the correct order of reducing power?

(a) $Mn > Ni > M$ (b) $Ni > Mn > M$
(c) $Mn > M > Ni$ (d) $M > Ni > Mn$

4. 3.80 g of metal M is deposited at the cathode by passing 0.2 F of electricity through the solution of metal chloride. The formula of the metal chloride is (Atomic mass of M = 57)
(a) MCl (b) MCl_2 (c) MCl_3 (d) MCl_4

5. When a direct current is passed through an aqueous concentrated solution of NaCl
1.   pH of the solution decreases
2.   metallic sodium will be deposited at the cathode
3.   chlorine gas will be liberated at the anode
4.   pH of the solution increases.
Which of the statements given above are correct?
(a) 1 and 2   (b) 2 and 3
(c) 3 and 4   (d) 1 and 3

6. Equivalent conductance of $BaCl_2$, H_2SO_4 and HCl are x_1, x_2 and x_3 S cm^2 $equiv^{-1}$ at infinite dilution. If specific conductance of saturated $BaSO_4$ solution is y S cm^{-1} then K_{sp} of $BaSO_4$ is

(a) $\dfrac{10^3 y}{2(x_1 + x_2 - 2x_3)}$ (b) $\dfrac{10^6 y^2}{(x_1 + x_2 - 2x_3)^2}$

(c) $\dfrac{10^6 y^2}{4(x_1 + x_2 - 2x_3)^2}$ (d) $\dfrac{x_1 + x_2 - 2x_3}{10^6 y^2}$

7. On the basis of the electrochemical theory of corrosion, the reaction occurring at the cathode is
(a) $O_{2(g)} + 4H^+_{(aq)} + 4e^- \longrightarrow 2H_2O_{(l)}$

(b) $Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^-$

(c) $Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^-$

(d) $H_{2(g)} + 2OH^-_{(aq)} \longrightarrow 2H_2O_{(l)} + 2e^-$

8. Consider the galvanic cell,
$Pb_{(s)} | Pb^{2+}_{(aq)}(x_1M) || Cu^{2+}_{(aq)}(x_2M) | Cu_{(s)}$, $E^\circ_{cell} = 0.47$ V
Which of the following graphs represents the variation of E_{cell} (y-axis) with $log[Cu^{2+}]/[Pb^{2+}]$ (x-axis).

(a)
(b)
(c)
(d)
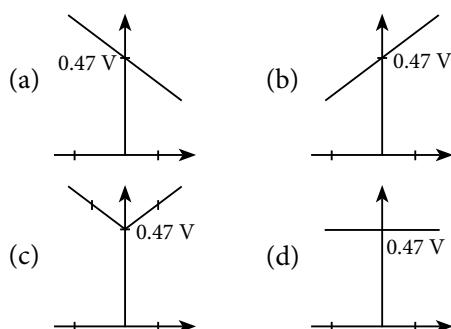
9. The EMF of the cell,
Pt | Ce^{4+}(90%), Ce^{3+}(10%) | normal calomel electrode,
is 1.464 V at 25°C. Find the value of equilibrium constant of the reaction :
$2Ce^{3+} + 2H^+ \longrightarrow 2Ce^{4+} + H_2$
The electrode potential of the normal calomel electrode is + 0.28 V.
(a) 2.38×10^{38} (b) 1.08×10^{42}
(c) 1.67×10^{39} (d) 3.24×10^{44}

10. The Gibbs energy for the decomposition of Al_2O_3 at 500 °C is as follows :
$$\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2, \Delta_r G = +966 \text{ kJ mol}^{-1}$$
The potential difference needed for electrolytic reduction of Al_2O_3 at 500 °C is atleast
(a) 2.5 V   (b) 5.0 V
(c) 4.5 V   (d) 3.0 V

SECTION - II
More than One Options Correct Type

11. Which of the following statements are true for a standard hydrogen electrode?
(a) The hydrogen ion concentration is 1 M.
(b) Temperature is 25 °C.
(c) Pressure of hydrogen is 1 atmosphere.
(d) It contains a metallic conductor which does not absorb hydrogen.

12. The correct relationships among the following are :
(a) $E_{cell} = \dfrac{RT}{nF} \ln K$
(b) Cell constant (G^*) = Conductivity (κ) × Resistance (R)
(c) 1 S m^{-1} = 100 S cm^{-1}
(d) Equilibrium constant (K) = $e^{-\Delta G^\circ/RT}$

13. E°_{cell} = 1.1 V for Daniell cell. Which of the following expressions are correct description of state of equilibrium in this cell?
(a) $1.1 = K_c$ (b) $\dfrac{2.303RT}{2F} \log K_c = 1.1$
(c) $\log K_c = \dfrac{2.2}{0.059}$ (d) $\log K_c = 1.1$

SECTION - III
Paragraph Type

Paragraph for Questions 14 and 15
Electrochemical series is series of elements arranged in increasing order of their reduction potential. For hydrogen, $E^\circ_{H^+/H_2} = 0$. The metals above H_2 have –ve reduction potential, they are more reactive than

hydrogen whereas metals below hydrogen are less reactive than H_2. Reduction potential of metal depends upon (i) sublimation energy, (ii) ionization energy and (iii) hydration energy of ions.

14. Which of the following is the best reducing agent?
(a) Li (b) Na (c) K (d) Cs

15. Which of the following cannot displace H_2 from dil. acid?
(a) Ag (b) Zn (c) Mg (d) Pb

Paragraph for Questions 16 and 17

Weak electrolytes do not dissociate completely even at infinite dilution. Hence, it is not possible to determine their molar conductivity at infinite dilution ($\Lambda°$) experimentally. The problem was solved by Kohlrausch by putting forward Kohlrausch law. This law not only helped to find $\Lambda°$ for weak electrolytes but also helped to find degree of dissociation of weak electrolytes at any concentration and also the dissociation constant of the weak electrolyte. Knowing the ionic conductances of the cations and anions at infinite dilution their ionic mobilities (speed of the ion under a potential gradient of 1 volt/cm) can also be calculated.

16. Given that $\Lambda_m°$ values of $BaCl_2$, $Ba(OH)_2$ and NH_4Cl in Ω^{-1} cm^2 mol^{-1} are 240.6, 461 and 129.8 respectively. The $\Lambda_m°$ for NH_4OH in Ω^{-1} cm^2 mol^{-1} will be
(a) 350.2 (b) 240.0 (c) 175.1 (d) 119.7

17. If a centinormal solution of NH_4OH has molar conductivity equal to 9.6 Ω^{-1} cm^2 mol^{-1}, the per cent dissociation of NH_4OH at this dilution will be
(a) 8% (b) 12% (c) 6% (d) 4%

SECTION - IV
Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists :

List I (Quantity)	List II (Units)
(A) Conductance	(p) Ω^{-1} m^{-1}
(B) Conductivity	(q) Siemen
(C) Molar conductivity	(r) m^2 s^{-1} V^{-1}
(D) Ionic mobility	(s) S m^2 mol^{-1}

	A	B	C	D
(a)	p	q	s	r
(b)	q	p	s	r
(c)	q	p	r	s
(d)	s	p	q	r

19. An aqueous solution of X is added slowly to an aqueous solution of Y as shown in List I. The variation in conductivity of these reactions is given in List II. Match the List I with List II and select the correct answer using the codes given below the lists :

List I	List II
(A) $(C_2H_5)_3N + CH_3COOH$ (X) (Y)	(p) Conductivity decreases and then increases

(B) $KI(0.1M)$
    (X)
    $+ AgNO_3(0.01M)$
        (Y)
	(q) Conductivity decreases and then does not change much

(C) $CH_3COOH + KOH$ (X) (Y)	(r) Conductivity increases and then does not change much
(D) $NaOH + HI$ (X) (Y)	(s) Conductivity does not change much and then increases

	A	B	C	D
(a)	r	s	q	p
(b)	s	r	q	p
(c)	q	r	s	p
(d)	p	s	r	q

SECTION - V
Assertion Reason Type

20. **Assertion :** In an electrolytic cell, anode is positive electrode.
Reason : In a galvanic cell, anode is a negative electrode.

21. **Assertion :** Equivalent conductance increases with dilution for an electrolytic solution.
Reason : The number of ions in one litre of electrolytic solution increases with dilution.

22. **Assertion :** H_2—O_2 fuel cell gives a constant voltage throughout its life.
Reason : In this fuel cell, H_2 reacts with OH^- ions yet the overall concentration of OH^- ions does not change.

SECTION - VI
Integer Value Correct Type

23. An alloy of Pb-Ag weighing 1.08 g was dissolved in dilute HNO_3 and the volume made upto 100 mL. A silver electrode was dipped in the solution and EMF of the cell set up

$Pt_{(s)}, H_{2(g)} | H^+ (1 M) || Ag^+_{(aq)} | Ag_{(s)}$

was 0.62 V. The percentage of Ag in the alloy is
[E^o_{cell} = 0.80 V, 2.303 RT/F = 0.06 at 25°C]

24. In the electrolysis of acidulated water, it is desired to obtain hydrogen at the rate of 42 cc per minute

at STP conditions. The current passed in amperes should be nearly equal to

25. A certain current liberates 0.500 g of H_2 in 2.00 hr. The mass of oxygen (in gram) that can be liberated by the same current in the same time is

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SOLUTIONS

d- AND *f*-BLOCK ELEMENTS

1. **(b):** The colour of CrO_3 (d^0 configuration) is due to charge transfer from ligand (oxygen) to metal (chromium).

2. **(c):** Na_3VO_4 contains vanadium in + 5 oxidation state which has empty *d*-orbitals and is thus colourless.

3. **(b):** Lanthanoids react with dilute acids to liberate H_2 gas and they form oxides and hydroxides of the type M_2O_3 and $M(OH)_3$.

4. **(c)**

5. **(b):** Oxides of terbium (Tb) are used as green phosphors in coloured TV tubes and fluorescent lamps.

6. **(c):** U exhibits + 3, + 4, + 5, + 6 oxidation states. Th exhibits + 3, + 4 ; Ac exhibits + 3 only and Pa exhibits + 3, + 4, + 5 oxidation states.

7. **(d)**   8. **(b)**

9. **(b):** $P = MnO_2, Q = K_2MnO_4, R = KMnO_4, S = KIO_3$

$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$
$\quad$ (P) $\qquad\qquad\qquad$ Green (Q)

$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$
$\qquad\qquad$ Purple (R)

$2MnO_4^- + H_2O + KI \longrightarrow 2MnO_2 + 2OH^- + KIO_3$
$\qquad\qquad\qquad$ (P) $\qquad\qquad\qquad$ (S)

10. **(c):** Actinoid series has elements from atomic no. 90 to 103. Thulium (Tm) has atomic no. 69 and hence, it is a lanthanide element.

11. **(a, b, c):** Eu and Lu are the members of lanthanide series. Due to the lanthanide contraction, the size of Eu, Lu and La will follow the order, Lu < Eu < La. The element Y belongs to the fifth period while Lu belongs to the sixth period. Thus, the order of size is
$Y^{3+} < Lu^{3+} < Eu^{3+} < La^{3+}$
U^{4+} in UF_4; U^{5+} in UO_2^+; U^{6+} in UO_2^{2+}
as the size of M^{3+} decreases covalent character increases in M—O bond hence the basic strength decreases.

12. **(a, b, d):** This is chromyl chloride test.
$K_2Cr_2O_7 + 6H_2SO_4 + 4NaCl \longrightarrow 2KHSO_4$
$\qquad\qquad + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$
$\qquad\qquad\qquad$ chromyl chloride (orange red vapour)
$4NaOH + CrO_2Cl_2 \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O$
$\qquad\qquad\qquad$ (yellow)

13. **(b, c)**   14. **(a)**
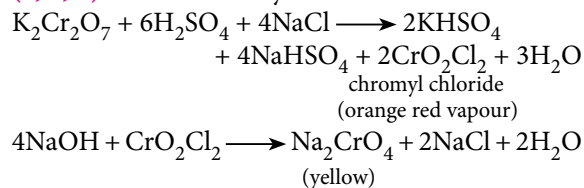
15. **(c):** Colour of the compounds of the same transition metal ion depends upon the nature of ligands attached to it. For example, $[CuCl_4]^{2-}$ is greenish yellow, $[Cu(H_2O)_4]^{2+}$ is blue but $[Cu(NH_3)_4]^{2+}$ is violet or deep blue.

16. **(d):** Copper is not affected by dry air at ordinary temperature but when exposed to air and moisture, it is covered by a thin film.
$2Cu + H_2O + CO_2 + O_2 \longrightarrow Cu(OH)_2 \cdot CuCO_3$
$\qquad\qquad\qquad$ (Basic carbonate)

17. **(a):** Aqua regia contain nascent chlorine. With nascent chlorine Au is first oxidised to $AuCl_3$ then in excess HCl, $AuCl_3$ form soluble complex, $H[AuCl_4] \cdot H[AuCl_4]$ is dsp^2 hybridised and hence square planar.

18. **(c):** Cr^{3+}, = [Ar] $3d^3$, n = 3, $\mu = \sqrt{15}$ B.M.
Fe^{2+}, = [Ar] $3d^6$, n = 4, $\mu = \sqrt{24}$ B.M.
Ni^{2+}, = [Ar] $3d^8$, n = 2, $\mu = \sqrt{8}$ B.M.
Mn^{2+}, = [Ar] $3d^5$, n = 5, $\mu = \sqrt{35}$ B.M.

19. **(d):** $Zn + 2KOH \longrightarrow K_2ZnO_2 + H_2\uparrow$
$Zn + 2HCl \longrightarrow ZnCl_2 + H_2\uparrow$
$Fe + 2HCl \longrightarrow FeCl_2 + H_2\uparrow$
$Hg \begin{cases} \xrightarrow{dil.\ HCl} \text{No reaction} \\ \xrightarrow{dil.\ HNO_3} Hg_2(NO_3)_2 + NO\uparrow \end{cases}$
Au does not react with HNO_3 or H_2SO_4 or HCl, etc.

20. **(a)**

21. **(c):** Energy gap between 4*f*, 5*d* and 6*s* is large thus lanthanoids show limited number of oxidation states, whereas that between 5*f*, 6*d* and 7*s* is small. Thus, actinoids show large number of oxidation states.

22. (a): MnO_4^- ion reacts with Cl^- to produce Cl_2 and Mn^{2+}.

23. (6)

24. (3): During the reaction $K_2Cr_2O_7$ is converted to $Cr_2(SO_4)_3$.

$$K_2\overset{+6}{Cr_2}O_7 + 7H_2SO_4 + 6KI \longrightarrow 4K_2SO_4 + \overset{+3}{Cr_2}(SO_4)_3 + 7H_2O + 3I_2$$

25. (3): $2Cu^{2+} + 4I^- \longrightarrow \underset{\text{Cuprous iodide}}{Cu_2I_2} + I_2$

$$2I^- \xrightarrow{MnO_4^-/H^+} I_2$$

$$2I^- \xrightarrow{Cr_2O_7^{2-}/H^+} I_2$$
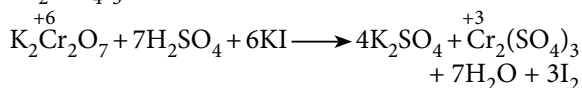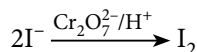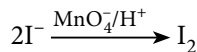
(I^- converts into I_2 when it reacts with oxidising agents)

ELECTROCHEMISTRY

1. (c): Q for 1 mol H^+ = 1 mol OH^- = 1F

$Q = I \times t$, and $I = 1$ A

$t = 96500$ s $= \dfrac{96500}{60 \times 60} = 26.8$ hours

2. (a): Overall cell reaction in lead storage battery is

$$PbO_{2(s)} + Pb_{(s)} + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_{4(s)} + 2H_2O$$

$E^\circ_{cell} = E^\circ_{OP} + E^\circ_{RP} = 0.31 + 1.70 = 2.01$ V

According to Nernst equation,

$$E_{cell} = E^\circ_{cell} - \left(\frac{0.0591}{2}\right)\log\frac{1}{[H^+]^4[SO_4^{2-}]^2}$$

$$= 2.01 - \frac{0.0591}{2}\log\frac{1}{(20)^4 \times (10)^2} = 2.22 \text{ V}$$

By use of 1 mole Pb, 2 mole electrons (2 F charge) are transferred and by 0.1 mole Pb, charge transfer

= 0.2 F = 0.2 × 96500 C = 19300 C

Electrical energy obtained = $Q \times V$

= 19300 × 2.22 = 42.846 kJ

3. (c)

4. (c): Equivalent mass of metal $= \dfrac{3.80}{0.2} = 19$

$19 = \dfrac{57}{n} \Rightarrow n = 3$ (n = valency)

Thus, the formula of the metal chloride will be MCl_3.

5. (c)

6. (c): $\Lambda_{BaSO_4} = \Lambda_{BaCl_2} + \Lambda_{H_2SO_4} - 2 \times \Lambda_{HCl}$

$= x_1 + x_2 - 2x_3$

$\Lambda_{BaSO_4} = \dfrac{1000 \times \kappa}{N}$ $\therefore$ Normality $= \dfrac{10^3 \times y}{x_1 + x_2 - 2x_3}$

Molarity $= \dfrac{10^3 \times y}{2(x_1 + x_2 - 2x_3)}$

For $BaSO_4$, $K_{sp} = (s)^2 = \left[\dfrac{10^3 \times y}{2(x_1 + x_2 - 2x_3)}\right]^2$

$= \dfrac{10^6 y^2}{4(x_1 + x_2 - 2x_3)^2}$

7. (a)

8. (b): Cell reaction:

$$Pb_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Pb^{2+}_{(aq)} + Cu_{(s)}$$
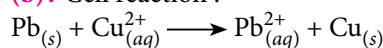
$$E_{cell} = E^\circ_{cell} + \frac{0.0592}{2}\log\frac{[Cu^{2+}]}{[Pb^{2+}]}$$

9. (b): $E_{cell} = E_c - E_a = 1.464$ V

$$E_{Ce^{4+}|Ce^{3+}} = E^\circ_{Ce^{4+}|Ce^{3+}} - \frac{0.059}{1}\log\frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$= E^\circ_{Ce^{4+}|Ce^{3+}} - \frac{0.059}{1}\log\frac{10}{90}$$

$$E_{cell} = E_{cal} - E_{Ce^{4+}|Ce^{3+}}$$

$$1.464 = E_{cal} - \left[\left(E^\circ_{Ce^{4+}|Ce^{3+}} - 0.059\log\frac{1}{9}\right)\right]$$

$$1.464 = 0.28 - \left(E^\circ_{Ce^{4+}|Ce^{3+}} - 0.059\log\frac{1}{9}\right)$$

$$E^\circ_{Ce^{4+}|Ce^{3+}} = -1.24 \text{ V}$$

Now, $2Ce^{3+} + 2H^+ \rightleftharpoons 2Ce^{4+} + H_2$
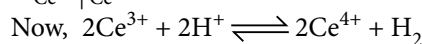
At Equilibrium $E_{cell} = 0$

$\therefore$ $E^\circ = \dfrac{0.059}{2}\log K$

At anode, $2Ce^{3+} \longrightarrow 2Ce^{4+} + 2e^-$ (Oxidation)

At cathode, $2H^+ + 2e^- \longrightarrow H_2$ (Reduction)

Cell reaction, $2Ce^{3+} + 2H^+ \longrightarrow 2Ce^{4+} + H_2$
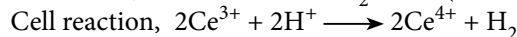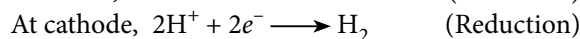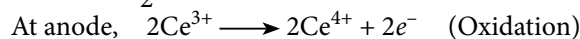
$E^\circ_{cell} = E^\circ_{red(cathode)} - E^\circ_{red(anode)}$

$= E^\circ_{red(H_2)} - E^\circ_{red(Ce^{4+}|Ce^{3+})} = 0 - (-1.24) = 1.24$ V

$\therefore$ $E^\circ = \dfrac{0.059}{2}\log K$

$1.24 = \dfrac{0.059}{2}\log K$

$\log K = 42.03 \Rightarrow K = 1.08 \times 10^{42}$

10. (a): $\dfrac{2}{3}Al_2O_3 \longrightarrow \dfrac{4}{3}Al + O_2$,

$\Delta_r G = +966$ kJ mol^{-1}

Thus, $2O^{2-} \longrightarrow O_2 + 4e^-$, $n = 4$
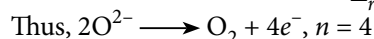
$\Delta G = -nFE$ $\therefore$ $966 \times 10^3 = -4 \times 96500 \times E$

or $E = -2.50$ V

Thus, minimum potential difference required = 2.50 V

11. (a, b, c)　　　**12. (b, d)**

13. (b, c) : Nernst equation is

$$E = E° - \frac{2.303RT}{nF} \log Q_c$$

At equilibrium, $E = 0$ and $Q_c = K_c$

$$\therefore \quad E° = \frac{2.303RT}{nF} \log K_c$$

$$1.1 = \frac{2.303RT}{2F} \log K_c$$

$$\text{or} \quad 1.1 = \frac{0.059}{2} \log K_c$$

$$\frac{2.2}{0.059} = \log K_c$$

K_c or $\log K_c \neq 1.1$

14. (a) : Li is the best reducing agent because it has lowest standard reduction potential and Li^+ is the most stable due to greater hydration energy.

15. (a)

16. (b) : $\Lambda°_m(NH_4OH) = \lambda°_{NH_4^+} + \lambda°_{OH^-}$

$$= \Lambda°_m(NH_4Cl) + \frac{1}{2}\Lambda°_m(Ba(OH)_2) - \frac{1}{2}\Lambda°_m(BaCl_2)$$

$$= 129.8 + \frac{1}{2}(461) - \frac{1}{2}(240.6)$$

$$= 129.8 + 230.5 - 120.3 = 240 \ \Omega^{-1} \ cm^2 \ mol^{-1}$$

17. (d) : Degree of dissociation (α)

$$= \frac{\Lambda^c_m}{\Lambda°_m} = \frac{9.6}{240} = 0.04 = 4\%$$

18. (b)

19. (a) : A : $\underset{(X)}{(C_2H_5)_3N} + \underset{(Y)}{CH_3COOH} \rightarrow CH_3COO^-_{(aq)}$

$$+ (C_2H_5)_3NH^+$$
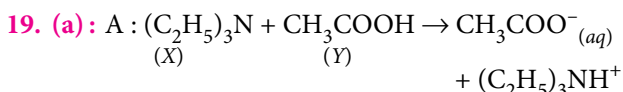
Initially conductivity increases due to ion formation after that it becomes practically constant because X alone cannot form ions.

B : $\underset{(X)}{KI(0.1\ M)} + \underset{(Y)}{AgNO_3(0.01\ M)} \rightarrow AgI\downarrow + KNO_3$
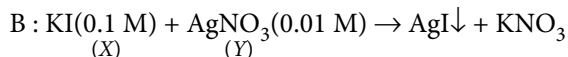
Number of ions in the solution remains constant until all the $AgNO_3$ precipitated as AgI. Thereafter conductance increases due to increase in number of ions.

C : $\underset{(X)}{CH_3COOH} + \underset{(Y)}{KOH} \rightarrow CH_3COOK + H_2O$
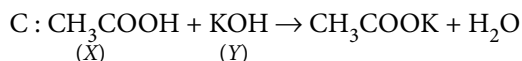
Initially conductance decreases due to the decrease in the number of OH^- ions thereafter it slowly increases due to increase in number of H^+ ions.

D : $\underset{(X)}{NaOH} + \underset{(Y)}{HI} \rightarrow NaI + H_2O$
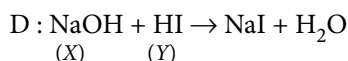
Initially it decreases due to decrease in H^+ ions and then increases due to increase in OH^- ions.

20. (b)　　　　**21. (a)**

22. (b) : Electrode reaction occuring in the H_2—O_2 fuel cell is

Anode : $2[H_{2(g)} + 2OH^-_{(aq.)} \longrightarrow 2H_2O_{(l)} + 2e^-]$

Cathode : $O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)}$

Overall reaction : $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$
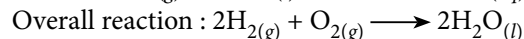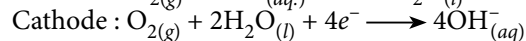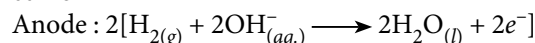
23. (1) : $H_2 + 2Ag^+ \longrightarrow 2H^+ + 2Ag$

$$E_{cell} = E°_{cell} - \frac{2.303RT}{nF} \log \frac{1}{[Ag^+]^2} \qquad [\because \ n = 2]$$

$$0.62 = 0.80 + 0.06 \log [Ag^+]$$

$$\log[Ag^+] = \frac{-0.18}{0.06} = -3$$

$$[Ag^+] = 1.0 \times 10^{-3} \ M$$

$$= 1.0 \times 10^{-3} \times 108 = 0.108 \ g \ L^{-1}$$

$\therefore$ Amount of Ag in 100 mL solution = 0.0108 g

$$\therefore \quad \%Ag = \frac{0.0108}{1.08} \times 100 = 1$$

24. (6) : $2H^+ + 2e^- \longrightarrow H_2$

Thus, 1 mole of H_2, *i.e.,* 22400 cc at STP requires $2F = 2 \times 96500$ coulombs

$$\therefore \quad 42 \ cc \ at \ STP \ require = \frac{2 \times 96500}{22400} \times 42$$

$$= 361.9 \ coulombs$$

As $Q = I \times t$

$$\therefore \quad I = \frac{Q}{t} = \frac{361.9 \ C}{60 \ s} \simeq 6 \ ampere$$

25. (4) : According to Faraday's first law,

$w = ZIt$

Given, it is same for H_2 and O_2.

$$\frac{w_{H_2}}{w_{O_2}} = \frac{Z_{H_2}}{Z_{O_2}} \quad \Rightarrow \quad \frac{w_{H_2}}{w_{O_2}} = \frac{E_{H_2}}{E_{O_2}}$$

$$\frac{0.500}{w_{O_2}} = \frac{1}{8} \quad \Rightarrow \quad w_{O_2} = 4.00 \ g$$

....◇◇

MPP-6 CLASS XI			**ANSWER**	**KEY**

1.	(c)	**2.**	(b)	**3.**	(c)	**4.**	(c)	**5.**	(d)
6.	(c)	**7.**	(d)	**8.**	(b)	**9 .**	(d)	**10.**	(d)
11.	(c)	**12.**	(d)	**13.**	(c)	**14.**	(d)	**15.**	(b)
16.	(a)	**17.**	(d)	**18.**	(d)	**19.**	(b)		
20.	(a, c, d)			**21.**	(b,c)	**22.**	(a,b)	**23.**	(b,c)
24.	(5)	**25.**	(3)	**26.**	(8)	**27.**	(d)	**28.**	(c)
29 .	(b)	**30.**	(a)						

ACE
YOUR WAY CBSE XII

Series 5

CHAPTERWISE PRACTICE PAPER : HALOALKANES AND HALOARENES/ALCOHOLS, PHENOLS AND ETHERS

Time Allowed : 3 hours   Maximum Marks : 70

GENERAL INSTRUCTIONS

(i)   All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v)   Q. no. 23 is a value based question and carry 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. Why is ethyl chloride a gas whereas ethyl iodide a liquid at room temperature?

2. Arrange the following compounds in increasing order of their acidic strengths : Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol.

3. Which will have a higher boiling point : 1-chlorobutane or 2-methyl-2-chlorobutane? Give reason.

4. Which is the most suitable reagent for the conversion of $RCH_2OH \longrightarrow RCHO$?

5. Why iodoform has appreciable antiseptic property?

6. How do you account for the fact that unlike phenol, 2,4-dinitrophenol and 2, 4, 6-trinitrophenol are soluble in aqueous sodium carbonate solution?

7. Write the common and IUPAC names for the isomers of molecular formula C_4H_9Br and classify them as to whether they are 1°, 2° or 3°.

8. What is Jones reagent? Give the product of reaction of the following compounds with Jones reagent.

(i) (cyclohexyl group with H and CH₂OH)

(ii) $CH_3CH{=}CHCH(OH)CH_3$
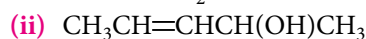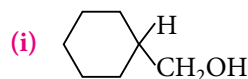
9. How will you distinguish between the following?
   (a) Chloroform and carbon tetrachloride
   (b) Ethyl chloride and vinyl chloride

OR

RCl is treated with Li in ether to form R—Li. R—Li reacts with water to form *iso*-pentane. R—Cl also reacts with sodium to form 2, 7-dimethyloctane. What is the structure of R—Cl?

10. When *tert*-butanol and *n*-butanol are separately treated with a few drops of dil. $KMnO_4$ in one case only, the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate formed?

11. Explain the following :
    (a) Chloroform is kept with a little amount of ethyl alcohol in a dark brown coloured bottle.
    (b) Hydrogen atom of chloroform is acidic in nature.

(c) Free radical halogenation of alkanes is seldom used for laboratory preparation of alkyl halides.

12. A mixture of phenol and propanoic acid reacts with bromine water to give 66.2 g of precipitate. The 40 g mixture of phenol and propanoic acid is titrated with 1 M of sodium hydroxide solution and requires 300 mL of NaOH at equivalence point. Calculate the weight percentage of phenol and propanoic acid.

13. Predict the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene.
(i) 1-Bromo-1-methylcyclohexane
(ii) 2-Chloro-2-methylpropane
(iii) 3-Bromo-2,2,3-trimethylpentane

14. Write the structures of the major products expected from the following reactions :
(i) Mononitration of 3-methylphenol
(ii) Dinitration of 3-methylphenol
(iii) Mononitration of phenyl ethanoate.

15. Explain why primary allylic and benzylic halides show greater reactivity towards S_N1 mechanism than primary alkyl halides.

16. Explain :
(a) Alcohols have higher boiling points than alkanes, ethers and alkyl halides of comparable molecular masses.
(b) Ethanol cannot be used as a solvent with Grignard reagent or $LiAlH_4$.
(c) The relative acidity of alcohols is in the order of $3° < 2° < 1° < CH_3OH$.

17. Write the mechanism for the reaction of HI with methoxymethane.

18. Predict the order of reactivity of the following compounds in S_N1 and S_N2 reactions :
(a) The four isomeric bromobutanes
(b) $C_6H_5CH_2Br$, CH_3CH_2Br, CH_3—$CH(Br)CH_3$, $(CH_3)_3CBr$

19. Answer the following questions :
(i) What is meant by chirality of a compound? Give an example.
(ii) Which one of the following compounds is more easily hydrolysed by KOH and why? $CH_3CHClCH_2CH_3$ or $CH_3CH_2CH_2CH_2Cl$
(iii) Which one undergoes S_N2 reaction faster and why?

 I or Cl
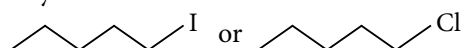
20. How will you obtain
(a) Ethanol from methanol (three steps)?
(b) *tert*-Butyl alcohol from *iso*-butyl alcohol?
(c) Acetamide from ethyl alcohol?

OR

(a) Write the IUPAC name of the following :
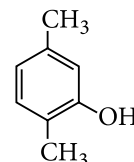
(b) Give reasons for the following :
(i) Phenol is a stronger acid than alcohol.
(ii) Alcohols are comparatively more soluble in water than the corresponding hydrocarbons.

21. A sweet smelling organic compound *A* is slowly oxidised by air in presence of light to a highly poisonous gas. On warming with silver powder, it forms a gaseous substance *B*, which is also produced by the action of calcium carbide on water. Identify *A* and *B* and write the chemical equations for the reactions involved.

22. How will you convert the following?
(i) Phenol to anisole
(ii) Propan-2-ol to 2-methylpropan-2-ol
(iii) Aniline to phenol

23. Ravi Prasad, a farmer has 25 acres of land. He noticed some infection on the leaves of his field crops. He called his friend Raghav, who advised him to use DDT. However, Mr. Prasad preferred to use dry powder of neem leaves as an insecticide.
(i) Why does Ravi Prasad prefer using neem powder?
(ii) Write the structure and IUPAC name of DDT?
(iii) Write two side effects of DDT?
(iv) Write the values associated with Ravi Prasad's decision.

24. Answer the following questions :
(a) How is 1-propoxypropane synthesised from propan-1-ol?
(b) Write the chemical equations for the reactions of the hydrogen iodide with
(i) 1-propoxypropane
(ii) Methoxybenzene
(iii) Benzyl ethyl ether.

OR

(a) Write the final product(s) in each of the following reactions :

(i) $CH_3CH_2-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{Cu/573\ K}$

(ii) $C_6H_5-OH \xrightarrow[\text{(ii) H}^+]{\text{(i) CHCl}_3 + \text{aq. NaOH}}$
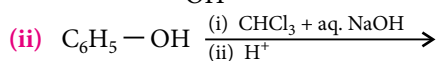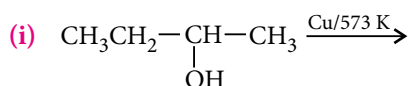
(b) Name the reagents which are used in the following conversions :

(i) A primary alcohol to an aldehyde

(ii) Butan-2-one to butan-2-ol

(iii) Phenol to 2, 4, 6-tribromophenol

25. Complete the following reactions :

(a) $CH_3CH_2COOAg \xrightarrow{Br_2} ? \xrightarrow{\text{alc. KOH}}$

(b) $CH_3CH_2CH_2Cl \xrightarrow{CH_3C\equiv CNa}$

(c) $\langle\!\bigcirc\!\rangle-CH_2-CH=CH_2 + HBr \xrightarrow{Peroxide}$

(d) $CH_3\underset{\underset{CH_3}{|}}{CHI} \xrightarrow[\text{Dry ether}]{Na}$

(e) $CH_3CH=CH_2 \xrightarrow{HBr} ? \xrightarrow{\text{aq. KOH}} ?$
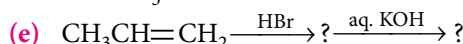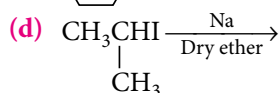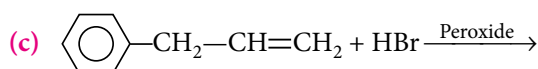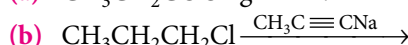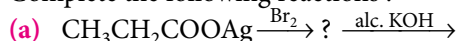
OR

Primary alkyl halide (A) C_4H_9Br reacts with alcoholic KOH to give compound (B). Compound (B) reacts with HBr to give (C) which is an isomer of (A). When (A) reacts with Na metal, it forms a compound (D) C_8H_{18} that is different from the compound formed when n-butyl bromide reacts with sodium. Give the structural formula of (A), (B), (C), (D) and write the equations for all the reactions involved.

26. An aromatic compound 'A' on treatment with $CHCl_3$/KOH gives two compounds 'B' and 'C'. Both B and C give the same product 'D' when distilled with zinc dust. Oxidation of D gives E having molecular formula $C_7H_6O_2$. The sodium salt of E on heating with soda-lime gives F which may also be obtained by distilling A with zinc dust. Identify A to F and write the reactions involved.

OR

Name the reagents used in the following reactions :

(i) Oxidation of a primary alcohol to carboxylic acid.

(ii) Oxidation of a primary alcohol to an aldehyde.

(iii) Dehydration of propan-2-ol to propene.

(iv) Butan-2-one to butan-2-ol.

(v) Formaldehyde to ethanol.

SOLUTIONS

1. Ethyl iodide has greater molecular mass than ethyl chloride and therefore, has greater van der Waals' forces. Thus, it is a liquid at room temperature.

2. Increasing order of acidic strength of the given compounds is :
Propan-1-ol < 4-methylphenol < phenol < 3-nitrophenol < 3, 5-dinitrophenol < 2, 4, 6-trinitrophenol
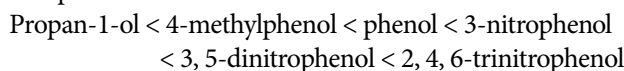
3. 2-Methyl-2-chlorobutane has higher boiling point than 1-chlorobutane because with increase in carbon number of alkyl group, boiling point increases.

4. Pyridinium chlorochromate (PCC) is used to oxidise alcohols to aldehydes and prevents further oxidation of aldehydes to carboxylic acids.
$$RCH_2OH \xrightarrow[\text{CH}_2\text{Cl}_2 \text{ solvent}]{PCC} RCHO + H_2O$$
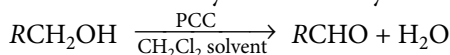
5. Iodoform has antiseptic properties because on coming in contact with organic matter of skin, it decomposes to give free iodine which acts as an antiseptic.

6. Nitro group is an electron withdrawing group and it stabilises the phenoxide ion by dispersing the negative charge on the oxygen. As a result, the acidic strength of nitrophenol is more than that of phenol. With increase in number of $-NO_2$ groups, the acidic strength increases. Thus, 2,4-dinitrophenol and 2,4,6-trinitrophenol are more acidic than phenol. Therefore, both easily release H^+ ions. These stabilised phenoxide ions react with aq. solution of Na_2CO_3 and give corresponding sodium salt of nitrophenols and dissolve in solution with evolution of CO_2 gas.

7. Following are the isomers of molecular formula C_4H_9Br with their common and IUPAC names :

$CH_3CH_2CH_2CH_2Br$; $CH_3CH_2CHBrCH_3$
(1-Bromobutane) (2-Bromobutane)
n-Butyl bromide sec-Butyl bromide
(1° Bromide) (2° Bromide)

$CH_3-\underset{\underset{}{|}}{\overset{\overset{CH_3}{|}}{CH}}-CH_2Br$; $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br$
(1-Bromo-2-methylpropane) (2-Bromo-2-methylpropane)
iso-butyl bromide tert-butyl bromide
(1° Bromide) (3° Bromide)
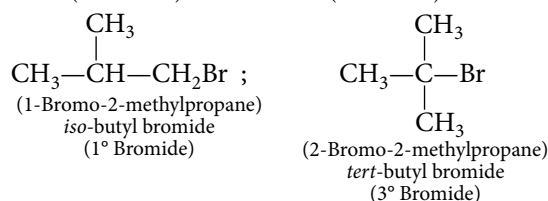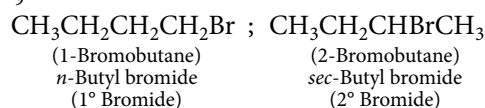
8. Jones reagent is CrO_3 in aqueous acetone and dilute sulphuric acid solution. It is a mild oxidising reagent thus, it oxidises alcohols without oxidising or rearranging double bonds.

(i) $\langle\!\!\!\bigcirc\!\!\!\rangle\!\!<^H_{CH_2OH} \xrightarrow[\text{acetone}]{CrO_3\text{ in}} \langle\!\!\!\bigcirc\!\!\!\rangle\!\!<^H_{COOH}$

(ii) $CH_3CH=CHCH(OH)CH_3 \xrightarrow[\text{acetone}]{CrO_3\text{ in}}$
$CH_3CH=CHCOCH_3$
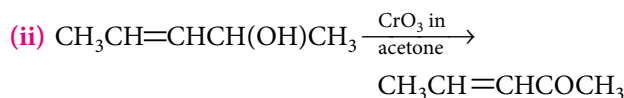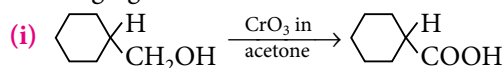
9. (a) Chloroform gives carbylamine test, *i.e.*, when heated with aliphatic or aromatic primary amines and alcoholic KOH, offensive smell of isocyanide is produced. CCl_4 does not give this test.

(b) Ethyl chloride reacts with alcoholic silver nitrate to give a white precipitate of silver chloride. Vinyl chloride does not give this test.

OR

$$R—Li + H_2O \longrightarrow CH_3—\underset{\underset{CH_3}{|}}{CH}—CH_2—CH_3 + LiOH$$

iso-pentane

$$R—Cl + 2Na + Cl—R \rightarrow CH_3\underset{\underset{CH_3}{|}}{CH}CH_2CH_2CH_2CH_2\underset{\underset{CH_3}{|}}{CH}CH_3$$

2, 7-dimethyloctane
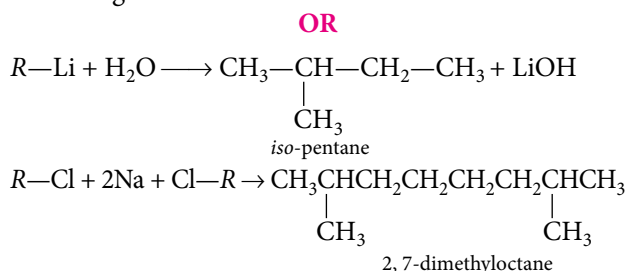
The structure of RCl is, $CH_3—\underset{\underset{CH_3}{|}}{CH}—CH_2—CH_2Cl$

10. $\underset{n\text{-butanol}}{\diagup\!\!\diagdown\!\!\diagup\text{OH}} \xrightarrow{\text{dil. KMnO}_4} \diagup\!\!\diagdown\!\!\diagup^{\text{CHO}} + \underset{\text{Brown}}{MnO_2\downarrow}$

$$CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—OH \xrightarrow{\text{dil. KMnO}_4} \text{No reaction}$$

tert-butanol
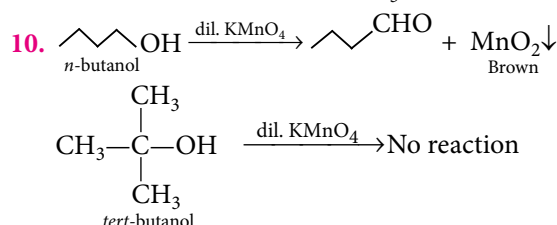
11. (a) When exposed to sunlight and air, chloroform slowly oxidises into phosgene. Phosgene is extremely poisonous gas. To prevent the oxidation, it is stored in dark brown coloured bottle and 1% ethyl alcohol is added. This retards the oxidation and converts phosgene into harmless ethyl carbonate.

$CHCl_3 + [O] \longrightarrow COCl_2 + HCl$;
$COCl_2 + 2C_2H_5OH \longrightarrow (C_2H_5)_2CO_3 + 2HCl$
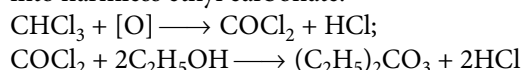
(b) Chlorine is more electronegative than carbon. Due to three chlorine atoms, the carbon acquires partial positive charge due to $-I$ effect. The carbon atom, thus, attracts the electron pair of C–H bond towards itself and making the release of H^+ easier.

(c) Several isomeric monosubstituted alkyl halides are formed because alkanes have different types of hydrogen atoms. Their separation is difficult. Thus, free radical halogenation method is not used unless the parent hydrocarbon possesses equivalent hydrogen atoms.

12. Bromine water reacts with phenol only.

Mol. wt. = 94 g   Mol. wt. = 331 g
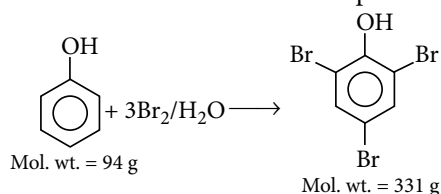
331 g of precipitate is formed from 94 g of phenol.

$\therefore$ 66.2 g of precipitate is formed from $= \dfrac{94}{331} \times 66.2$.

$= 18.8$ g phenol

Moles of phenol $= \dfrac{18.8\,g}{94\,g\,/\,mol} = 0.2$ mol

Now, number of moles of NaOH $= 0.3$ L $\times 1$ M $= 0.3$ mol
At equivalence point,
Propanoic acid + phenol = 0.3 mol
Propanoic acid + 0.2 mol = 0.3 mol
Propanoic acid = 0.1 mol
Weight of propanoic acid = 0.1 mol $\times$ 74 g/mol = 7.4 g

Weight % of propanoic acid $= \dfrac{7.4}{40} \times 100 = 18.5\%$

Weight % of phenol $= \dfrac{18.8}{40} \times 100 = 47\%$

13. (i) In 1-bromo-1-methylcyclohexane, the β-hydrogens on either side of the Br-atom are equivalent, therefore, only one alkene is formed.

1-Methylcyclohexene
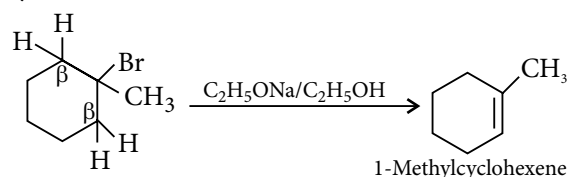
(ii) All the nine β-hydrogens in 2-chloro-2-methylpropane are equivalent, hence on treatment with $C_2H_5ONa/$ C_2H_5OH, it gives a single alkene.

2-Methylpropene
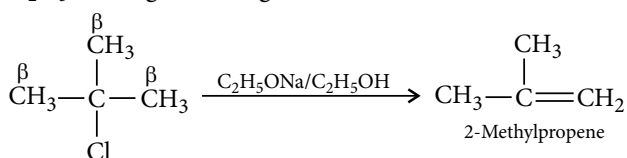
(iii) 3-Bromo-2, 2, 3-trimethylpentane has two different sets of β-hydrogens and therefore, can give two alkenes (I and II). But according to Saytzeff rule, more substituted alkene (II), being more stable is the major product

$(CH_3)_3CC(Br)(CH_3)CH_2CH_3$
3-Bromo-2, 2, 3-trimethylpentane

2-Ethyl-3,3-dimethylbut-1-ene

3,4,4-Trimethylpent-2-ene
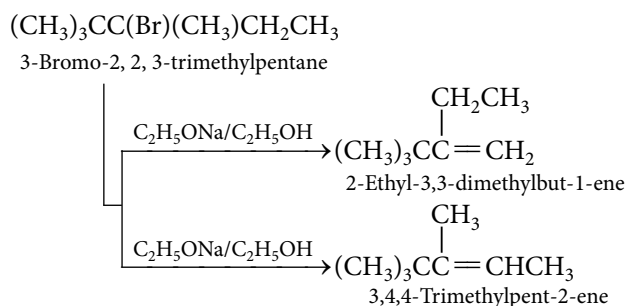
14. Both —OH and —CH$_3$ groups are *o*- and *p*-directing. Therefore, position 2,4 and 6 are activated. But due to steric hindrance, substitution does not occur at position 2, *i.e.*, in between two groups.

(i)

3-Methylphenol

$\xrightarrow[\text{Nitration}]{\text{HNO}_3 + \text{H}_2\text{SO}_4}$

4-Nitro-3-methylphenol   2-Nitro-5-methylphenol

(ii)

3-Methylphenol

$\xrightarrow[\text{Dinitration}]{\text{HNO}_3 + \text{H}_2\text{SO}_4}$

2,4-Dinitro-5-methylphenol
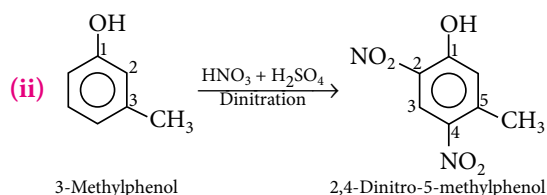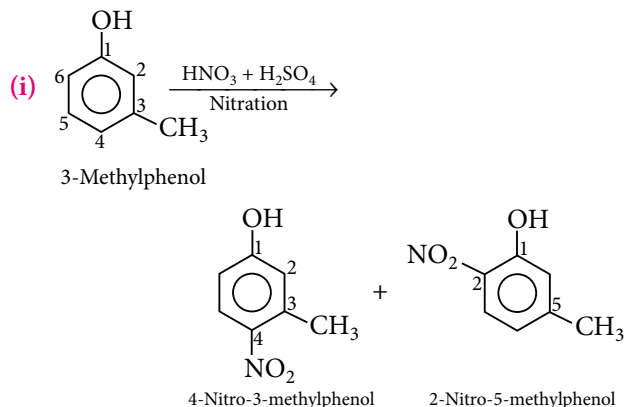
(iii) —OCOCH$_3$ is *o,p*-director but due to steric hindrance, *p*-product predominates.

Phenyl ethanoate

$\xrightarrow[+ \text{H}_2\text{SO}_4]{\text{Conc.HNO}_3}$

4-Nitrophenyl ethanoate (major)   2-Nitrophenyl ethanoate
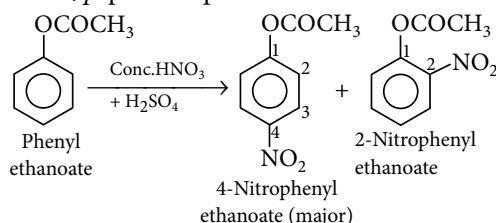
15. Primary allylic and benzylic halides show greater reactivity towards S_N1 mechanism than primary alkyl halides. This can be explained in terms of stability of intermediate *i.e.*, carbocations formed in the reaction. Allylic and benzylic carbocations are more stable than primary alkyl carbocations due to resonance.

$$CH_2 = CH - \overset{+}{C}H_2 \leftrightarrow \overset{+}{C}H_2 - CH = CH_2$$
Allyl carbocation

Benzyl carbocation
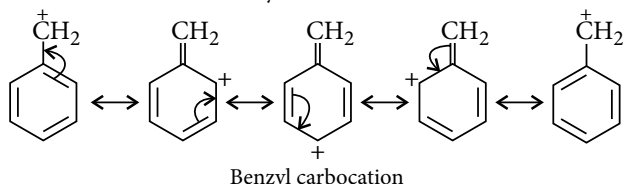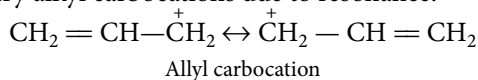
16. (a) O—H bond of alcohols is highly polarised. This gives rise to intermolecular hydrogen bonding, *i.e.*, molecules are brought nearer to each other and held together by attractive forces. No such hydrogen bonding exists in alkanes, ethers and alkyl halides. This is the reason why the boiling points of alcohols are higher than alkanes, ethers and alkyl halides of comparable molecular masses.

(b) Ethanol being acidic readily reacts with strongly basic *R* of Grignard reagent to form alkane.
$$CH_3CH_2OH + RMgX \longrightarrow \underset{\text{Alkane}}{R - H} + CH_3CH_2OMgX$$
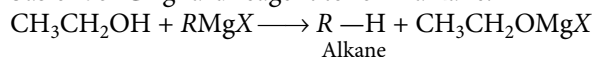
LiAlH$_4$ reacts with alcohol to form hydrogen.
$$4CH_3CH_2OH + LiAlH_4 \longrightarrow LiAl(OCH_2CH_3)_4 + 4H_2\uparrow$$
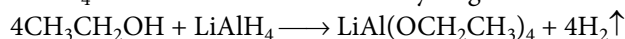
(c) The decreasing order of acidity from CH$_3$OH to 3° alcohol is attributed due to +*I* effect of alkyl group which intensify the charge on the base RO^- and the removal of proton becomes difficult.

17. With equimolar amounts of HI and methoxymethane, a mixture of methyl alcohol and methyl iodide are formed by the following mechanism:

Step I. $CH_3 - \ddot{O} - CH_3 + H - I \xrightarrow[\text{Fast}]{\text{Protonation}}$
Methoxymethane

Dimethyl oxonium ion

Step II. $I^- + CH_3 - \overset{H}{\underset{..}{\overset{+}{O}}} - CH_3 \xrightarrow[\text{Slow}]{S_N2}$

$$\underset{\text{Methyl iodide}}{CH_3 - I} + \underset{\text{Methyl alcohol}}{CH_3OH}$$
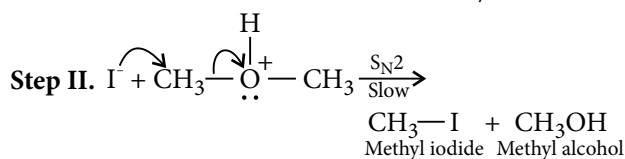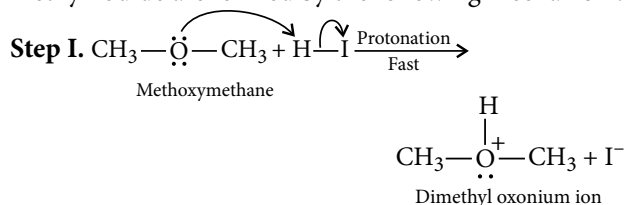
If excess of HI is used, methyl alcohol formed in Step II is also gets converted into methyl iodide.

18. (a) In S_N1 reaction, the order of reactivity depends upon the stability of the intermediate carbocations. Hence, the order of reactivity is : CH$_3$CH$_2$CH$_2$CH$_2$Br < (CH$_3$)$_2$CHCH$_2$Br < CH$_3$CH$_2$CH(Br)CH$_3$ < (CH$_3$)$_3$CBr. The reactivity in S_N2 reactions follows the reverse order of S_N1 as the steric hindrance around the electrophilic carbon increases. Thus, the order of reactivity in S_N2 reaction shown by these bromo butanes is : CH$_3$CH$_2$CH$_2$CH$_2$Br > (CH$_3$)$_2$CHCH$_2$Br > CH$_3$CH$_2$CH(Br)CH$_3$ > (CH$_3$)$_3$CBr.

(b) For S_N1 reaction the order of reactivity :
C$_6$H$_5$CH$_2$Br > (CH$_3$)$_3$CBr > CH$_3$CH(Br)CH$_3$ > CH$_3$CH$_2$Br
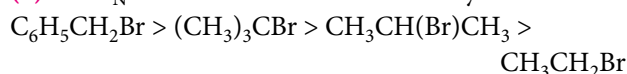
Similarly for S_N2 reaction :
CH$_3$CH$_2$Br > CH$_3$CH(Br)CH$_3$ > (CH$_3$)$_3$CBr > C$_6$H$_5$CH$_2$Br

19. (i) Chirality is a necessary and sufficient condition for the existence of enantiomers.

e.g.,
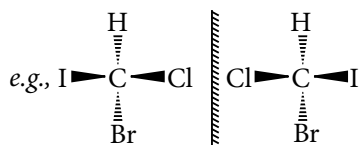
(ii) $CH_3CH_2CHCH_3$ (with Cl substituent) hydrolyses easily with KOH because it is a secondary halide.

(iii) As iodide is a better leaving group because of its larger size than chloride therefore, (pentyl iodide) undergoes S_N2 reaction faster than (pentyl chloride).

20. (a) $CH_3OH \xrightarrow{HI} CH_3I \xrightarrow[Et_2O]{Mg}$

$CH_3MgI \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) HCHO}} CH_3CH_2OH$

(b) $CH_3-\underset{\underset{CH_3}{|}}{C}HCH_2OH \xrightarrow[443 K]{\text{conc. } H_2SO_4} CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2$

$\xrightarrow{HBr} CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow{KOH_{(aq.)}} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

(c) $C_2H_5OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH$

$\xrightarrow{NH_3} CH_3COONH_4 \xrightarrow{Heat} CH_3CONH_2$
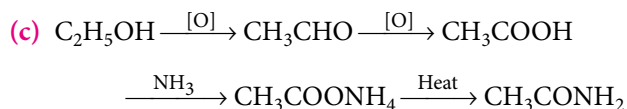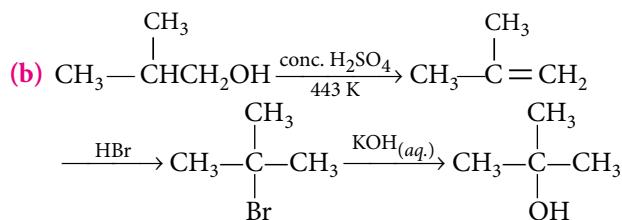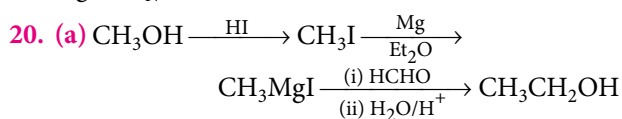
OR

(a) 2, 5-Dimethylphenol

(b) (i) Due to formation of resonance stabilised conjugate base i.e. phenoxide ion from phenol, phenol is more acidic than alcohol as it forms less stable alkoxide ion as a conjugate base.

(ii) Due to intermolecular H-bonding in alcohols, they are more soluble in water than hydrocarbons of comparable molar masses.

21. Since the compound B is produced by the action of calcium carbide on water the compound B must be ethyne.

$$CaC_2 + 2H_2O \longrightarrow HC \equiv CH + Ca(OH)_2$$
Cal. carbide Ethyne (B)
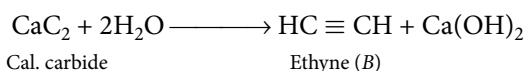
Since the compound (B), i.e., ethyne is produced by warming compound (A) with silver powder, therefore, compound (A) must be chloroform.

$$2CHCl_3 + 6Ag \xrightarrow{\Delta} HC \equiv CH + 6AgCl$$
Chloroform (A) Ethyne (B)
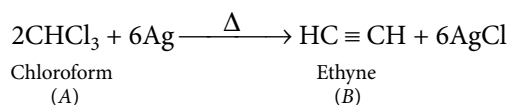
Chloroform is slowly oxidised by air in presence of light to a highly poisonous gas, i.e., phosgene.

$$2CHCl_3 + O_2 \xrightarrow{light} 2COCl_2 + 2HCl$$
Chloroform (A) Phosgene (Poisonous gas)
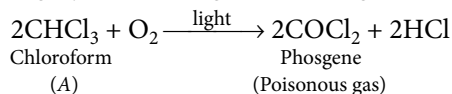
Thus, compound A is chloroform and the compound B is ethyne.

22. (i) Phenol to anisole
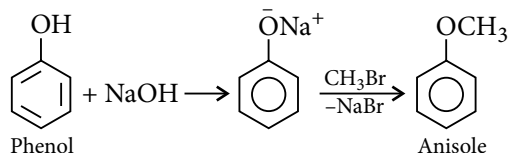
(ii) Propan-2-ol to 2-methylpropan-2-ol
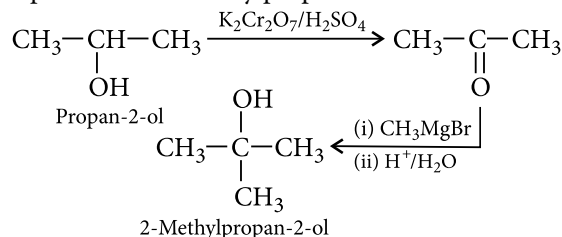
(iii) Aniline to phenol
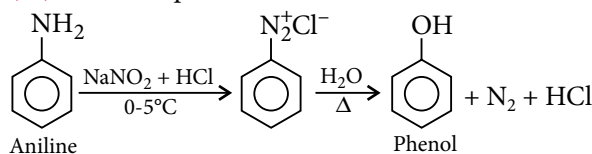
23. (i) Neem powder is biodegradable and does not harm soil.

(ii)

1,1′-(2,2,2,-Trichloroethane -1,1-diyl) bis-(4-chlorobenzene)
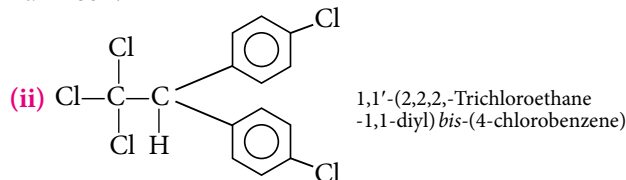
(iii) DDT is not metabolised very rapidly by animals rather it gets deposited and stored in fatty tissues. DDT is highly toxic for aquatic life.

(iv) Application of scientific knowledge and environment concern.

24. (a) $CH_3CH_2CH_2OH + HBr \rightarrow CH_3CH_2CH_2Br + H_2O$

$CH_3CH_2CH_2OH + Na \longrightarrow CH_3CH_2CH_2ONa + \frac{1}{2}H_2$

$CH_3CH_2CH_2Br + CH_3CH_2CH_2ONa$

Williamson synthesis

$CH_3CH_2CH_2 - O - CH_2CH_2CH_3 + NaBr$
1-Propoxypropane

(b) (i) $CH_3CH_2CH_2 — O — CH_2CH_2CH_3 + HI$
1-Propoxypropane   (small amount)

$\downarrow$ 373 K

$CH_3CH_2CH_2I + CH_3CH_2CH_2OH$
1-Iodopropane   1-Propanol

$CH_3CH_2CH_2 — O — CH_2CH_2CH_3 + 2HI$ (excess)

$\downarrow$ 373 K

$2CH_3CH_2CH_2I + H_2O$
1-Iodopropane

(ii) Methoxy benzene $+ HI \xrightarrow{\Delta}$ Phenol $+ CH_3I$ Iodomethane

(iii) Benzyl ethyl ether $+ 2HI \xrightarrow{\Delta, 400\ K}$ Benzyl iodide (major) $+ CH_3CH_2OH$ Ethanol

OR

(a) (i) $CH_3CH_2CH(OH)CH_3 \xrightarrow[573\ K]{Cu} CH_3CH_2C(O)CH_3$ Butan-2-one

(ii) $C_6H_5—OH \xrightarrow[\text{(ii) } H^+]{\text{(i) CHCl}_3 + \text{aq. NaOH}}$ Salicylaldehyde

(b) (i) Copper at 573 K
(ii) Sodium borohydride ($NaBH_4$)/C_2H_5OH
(iii) Bromine water

25. (a) $CH_3CH_2COOAg \xrightarrow{Br_2} CH_3CH_2Br \xrightarrow{\text{alc. KOH}} CH_2{=}CH_2$

(b) $CH_3CH_2CH_2Cl \xrightarrow{CH_3C{\equiv}CNa} CH_3C{\equiv}CCH_2CH_2CH_3 + NaCl$

(c) $\langle\bigcirc\rangle—CH_2—CH{=}CH_2 + HBr \xrightarrow{\text{Peroxide}} \langle\bigcirc\rangle—CH_2—CH_2—CH_2Br$

(d) $2CH_3\underset{CH_3}{CHI} \xrightarrow[\text{Dry ether}]{2Na} CH_3—\underset{CH_3}{CH}—\underset{CH_3}{CH}—CH_3 + 2NaI$

(e) $CH_3CH{=}CH_2 \xrightarrow{HBr} CH_3—\underset{Br}{CH}—CH_3 \xrightarrow{\text{aq. KOH}} CH_3—\underset{OH}{CH}—CH_3$

OR

Reactions involved are

$CH_3—\underset{CH_3}{CH}—CH_2—Br$ (A) $\xrightarrow[\text{Dehydrohalogenation}]{\text{alc. KOH}/\Delta}$ $CH_3—\underset{CH_3}{C}{=}CH_2$ (B)

$CH_3—\underset{CH_3}{C}{=}CH_2$ (B) $+ H—Br \xrightarrow{\text{(Mark. addn)}} CH_3—\underset{Br}{\overset{CH_3}{C}}—CH_3$ (C)

$CH_3—\underset{CH_3}{CH}—CH_2—Br$ (A) $+ 2Na + Br—CH_2—\underset{CH_3}{CH}—CH_3$

$\downarrow$ dry ether (Wurtz reaction)

$CH_3—\underset{CH_3}{CH}—CH_2—CH_2—\underset{CH_3}{CH}—CH_3 + 2NaBr$ (D)

26. The reactions involved are

Phenol (A) $\xrightarrow{\text{CHCl}_3/\text{KOH}}$ o-Hydroxybenzaldehyde (B) $+$ p-Hydroxybenzaldehyde (C)

Phenol (A) $\xrightarrow[\text{distillation}]{\text{Zn (dust)}}$ Benzene (F)

(B/C) $\xrightarrow[\text{distillation}]{\text{Zn (dust)}}$ Benzaldehyde (D)

Benzaldehyde (D) $\xrightarrow{[O]}$ Benzoic acid (E)

Benzoic acid (E) $\xrightarrow[630\ K]{\substack{\text{(i) NaOH} \\ \text{(ii) NaOH / CaO}}}$ Benzene (F)

OR

(i) Acidified solution of $KMnO_4$ (or acidified $K_2Cr_2O_7$).
(ii) Copper/573 K (or pyridinium chlorochromate, PCC, using CH_2Cl_2 as solvent).
(iii) Hot conc. H_2SO_4.
(iv) Lithium aluminium hydride, $LiAlH_4$, using dry ether as solvent.
(v) Methyl magnesium bromide (Grignard reagent) followed by hydrolysis.

◆◆

MPP-6 | MONTHLY Practice Problems

Class XII

This specially designed column enables students to self analyse their extent of understanding of specified chapter. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Haloalkanes and Haloarenes

Total Marks : 120

Time Taken : 60 Min.
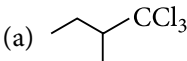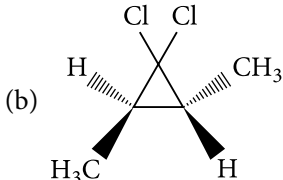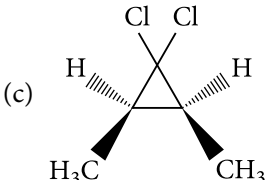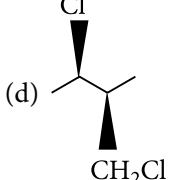
NEET / AIIMS
Only One Option Correct Type

1. In which of the following pairs, the first species is more nucleophilic than the latter?
   (a) H_2NNH_2, NH_3
   (b) HO^-, HOO^-
   (c) F^-, NH_2^-
   (d) HO^-, HS^-

2. Replacement of chlorine of chlorobenzene to give phenol requires drastic conditions but chlorine of 2, 4–dinitrochlorobenzene is readily replaced. This is because
   (a) $-NO_2$ makes the ring electron rich at *ortho-* and *para-* positions
   (b) $-NO_2$ withdraws e^- from *meta*-position
   (c) $-NO_2$ donates e^- at *meta*-position
   (d) $-NO_2$ withdraws e^- from *ortho* and *para*-positions.

3. An alkyl halide with molecular formula $C_6H_{13}Br$ on dehydrohalogenation gave two isomeric alkenes X and Y with molecular formula C_6H_{12}. On reductive ozonolysis, X and Y gave four compounds CH_3COCH_3, CH_3CHO, CH_3CH_2CHO and $(CH_3)_2CHCHO$. The alkyl halide is
   (a) 2, 2-dimethyl-1-bromobutane
   (b) 4-bromo-2-methylpentane
   (c) 2-bromo-2, 3-dimethylbutane
   (d) 3-bromo-2-methylpentane.

4. Identify B and D in the following sequence of reactions.
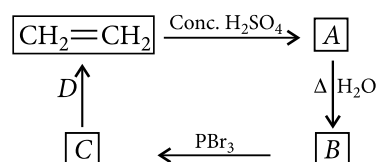
   (a) Methanol and bromoethane
   (b) Ethyl hydrogen sulphate and alcoholic KOH
   (c) Ethyl hydrogen sulphate and aqueous KOH
   (d) Ethanol and alcoholic KOH

5. The fire extinguisher pyrene contains
   (a) CO_2
   (b) CS_2
   (c) CCl_4
   (d) $CHCl_3$

6. The end product in the following reaction is

$$CHCl_3 + (CH_3)_3COK \xrightarrow{(CH_3)_3COH} \underset{\text{Unstable}}{X} \xrightarrow{\text{trans}} \text{Major}$$

7. For the given reaction,
$$R - Cl + NaI \xrightarrow{\text{Acetone}} R - I + NaCl$$
   Which of the following alkyl halides will give the maximum yield?

(a) $CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - Cl$ 　(b) $CH_3 - CH_2 - CH_2 - Cl$

(c) $C_6H_5 - \overset{}{\underset{\underset{\displaystyle CH_3}{|}}{CH}} - Cl$ 　(d) $C_6H_5 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - Cl$

8. $CH_3C \equiv CH \xrightarrow[\text{(HgSO}_4)]{\text{dil. H}_2\text{SO}_4} (B) \xrightarrow[\text{(NaOH)}]{\text{CHCl}_3} (C)$
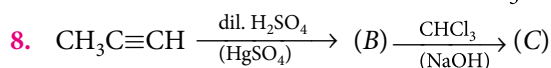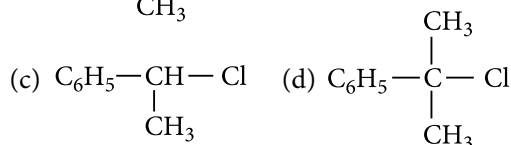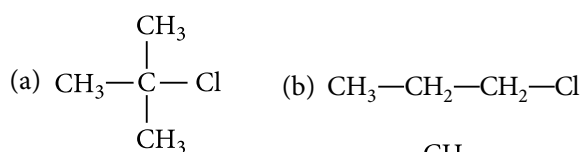
Compound (C) can be used as
(a) an anaesthetic 　(b) an insecticide
(c) a solvent 　(d) a hypnotic.

9. In this given reaction the major intermediate 'X' is

$CH_3 - \overset{}{\underset{\underset{\displaystyle D}{|}}{CH}} - \overset{}{\underset{\underset{\displaystyle CH_3}{|}}{CH}} - CH_3 + Br^\bullet \longrightarrow X + HBr$

(a) 　(b)

(c) 　(d)
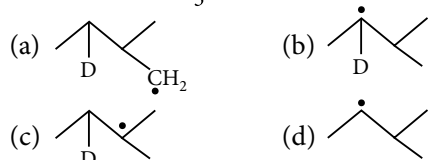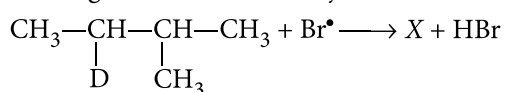
10. Cyanoform is .... than chloroform.
(a) weaker acid 　(b) weaker base
(c) stronger acid 　(d) stronger base

11. The products formed when alcoholic silver nitrite reacts with ethyl bromide are
1. ethyne 　2. ethene
3. nitroethane 　4. ethyl alcohol
5. ethyl nitrite
(a) 3, 5 　(b) 3, 4 　(c) 2, 3, 5 　(d) 1, 5

12. Which of the carbon atoms present in the molecule given below are asymmetric?

$HO \underset{O}{\overset{}{\underset{}{C}}} \overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{\overset{(i)}{C}}} \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{\overset{(ii)}{C}}} \overset{(iii)(iv)}{C} \overset{O}{\underset{H}{}}$
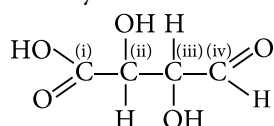
(a) (i), (ii), (iii), (iv) 　(b) (ii), (iii)
(c) (i), (iv) 　(d) (i), (ii), (iii)

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

13. Assertion : 2-Bromobutane on reaction with sodium ethoxide in ethanol gives 1-butene as a major product.
Reason : 1-Butene is more stable than 2-butene.

14. Assertion : Electron withdrawing groups in aryl halides decrease the reactivity towards nucleophilic substitution.
Reason : 2, 4-Dinitrochlorobenzene is less reactive than chlorobenzene towards nucleophilic substitution.

15. Assertion : $CH_3\overset{\overset{\displaystyle Cl}{|}}{CH}CH_2CH_3 \xrightarrow{\text{alc. KOH}}$
$CH_3CH = CHCH_3 + KCl + H_2O$
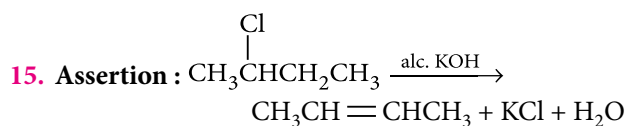
Dehydrohalogenation reaction of 2-chlorobutane gives 2-butene.
Reason : Elimination reaction takes place according to Saytzeff's rule.

JEE MAIN / JEE ADVANCED
Only One Option Correct Type

16.

$H_3C \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}H \xrightarrow{Cl_2/h\nu} \underset{\substack{(N \text{ isomeric} \\ \text{products})}}{C_5H_{11}Cl} \xrightarrow[\text{distillation}]{\text{Fractional}} \underset{\substack{\text{isomeric} \\ \text{products}}}{M}$
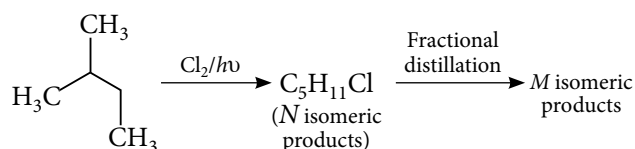
Give the number of N and M.
(a) 6, 6 　(b) 6, 4 　(c) 4, 4 　(d) 3, 3

17. 1-Bromo-3-chlorocyclobutane when treated with two equivalents of Na in the presence of ether, which of the following will be formed?

(a) 　(b)

(c) 　(d)
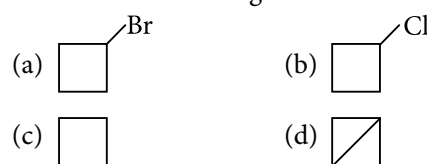
18. From which one of the following, both ethylene and acetylene could be prepared in a single step reaction?
(a) CH_3CH_2OH 　(b) $BrCH_2CH_2Br$
(c) CH_3CH_2Br 　(d) $BrCH_2CH_2OH$

19. 2-Bromobutane reacts with OH^- in H_2O to give 2-butanol. The reaction involves
(a) retention of configuration
(b) inversion of configuration
(c) racemization
(d) mutarotation.

More than One Options Correct Type

20. Consider the following E1/S_N1 reaction:
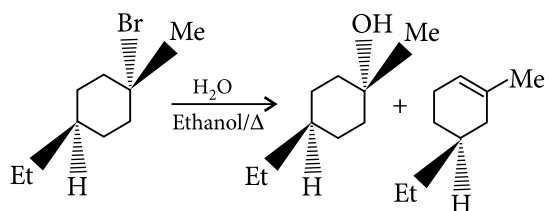
The missing products are

(a)

(b)

(c)

(d)

21. Which of the following reactions are not feasible?

(a)

(b) $CH_3 \overset{CH_3}{\underset{CH_3}{-C-}} Br + RO^- \longrightarrow CH_3 \overset{CH_3}{\underset{CH_3}{-C-}} OR$

(c) $CH_3 \overset{CH_3}{\underset{CH_3}{-C-}} Br + ROH \longrightarrow CH_3 \overset{CH_3}{\underset{CH_3}{-C-}} OR$

(d)
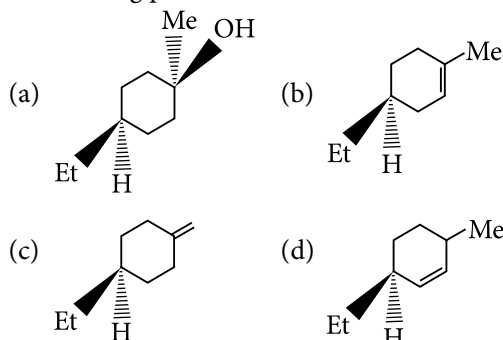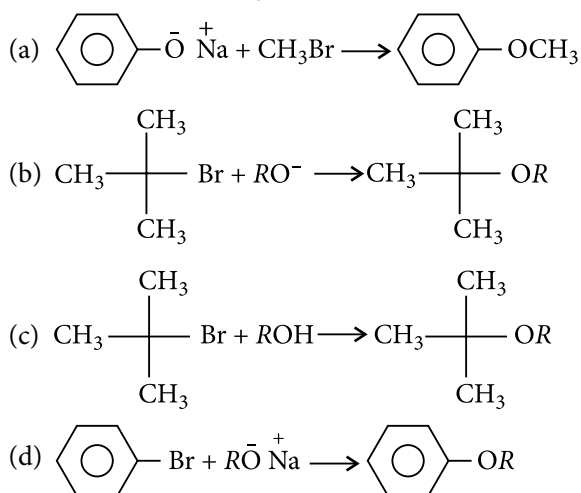
22. In the reaction given below :
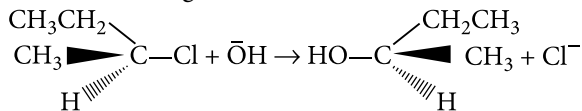
Which of the following statements are not correct?
(a) The reaction proceeds *via* S_N2 mechanism hence inversion of configuration takes place.
(b) The reaction proceeds *via* S_N1 mechanism hence inversion of configuration takes place.
(c) The reaction proceeds *via* S_N2 mechanism hence their is no change in the configuration.
(d) The reaction proceeds *via* S_N1 mechanism hence there is no change in the configuration.

23. Which of the following reactions take place?
(a) $C_2H_5Br + KNO_2 \longrightarrow C_2H_5-O-N=O + KBr$
(b) $C_2H_5Br + AgNO_2 \longrightarrow C_2H_5-N\overset{O}{\underset{O}{\diagup\!\!\!\diagdown}} + AgBr$
(c) $C_2H_5Br + AgCN \longrightarrow C_2H_5NC + AgBr$
(d) $C_2H_5Br + KCN \longrightarrow C_2H_5NC + KBr$

Integer Answer Type

24. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentyl-hexane using alcoholic KOH is

25. In the following monobromination reaction, the number of possible chiral products is
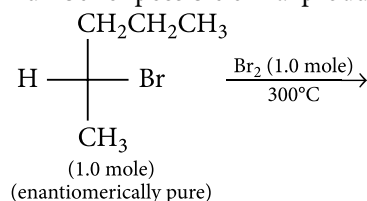
26. Following compound when heated in ethanol, S_N1 reaction occurs involving rearrangement of carbocation.
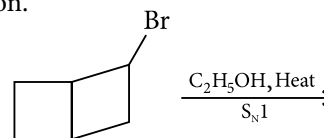
In the major product, how many carbon atoms are present in the single largest ring?

Comprehension Type

Reactivity ratio for primary, secondary and tertiary radical is 1 : 3.8 : 4.5.

The propagation step of monochlorination of alkane involve formation of free radical intermediate.
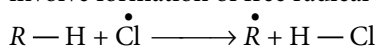
$$R-H + \overset{\bullet}{Cl} \longrightarrow \overset{\bullet}{R} + H-Cl$$

The energy profile for the formation of free radical (P, Q, R) is described in the given graph for the compound (X).

(X)
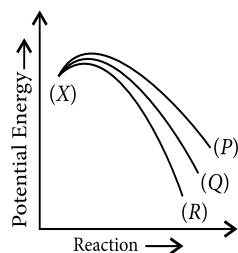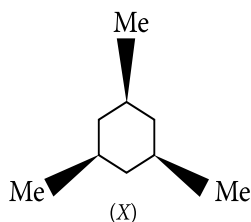
27. For the compound (X), which of the following statements is true for the monochlorination of compound (X) via intermediate (Q).
  (a) Two different products, both optically inactive.
  (b) Two different products, one optically active and other optically inactive.
  (c) Two different products and are diastereomers of each other.
  (d) Only one product is obtained.

28. Which of the following is incorrect for the monochlorination of (X)?
  (a) Via intermediate (P) only one product is obtained.
  (b) Via intermediate (R) two products are obtained which are enantiomers.
  (c) All products obtained are optically inactive.
  (d) The per cent distribution of products formed via intermediate (P) is 19.86%.

Matrix Match Type

29. Match the reaction listed in Column I with their characteristics listed in Column II and choose the correct option using the codes given below.

Column I	Column II
(P) $CHCl_3 + HNO_3 \longrightarrow$ An insecticide and tear gas	(1) Gammaxene
(Q) Benzene $+ Cl_2 \xrightarrow{hv}$ Product	(2) Hunsdiecker reaction

(R) + Chloral $\xrightarrow{\text{Conc.}\ H_2SO_4}$ Product (3) Chloropicrin

(S) Silver acetate $\xrightarrow[CH_3Br]{Br_2 \atop CCl_4}$ (4) Dichlorodiph-enyltrichlo-roethane

(T) $\xrightarrow{Cl_2 \atop hv}$ PhCOCH$_2$Cl Phenacyl chloride

(5) Used as a lachrymator (weeping gas) to disperse the mob by police
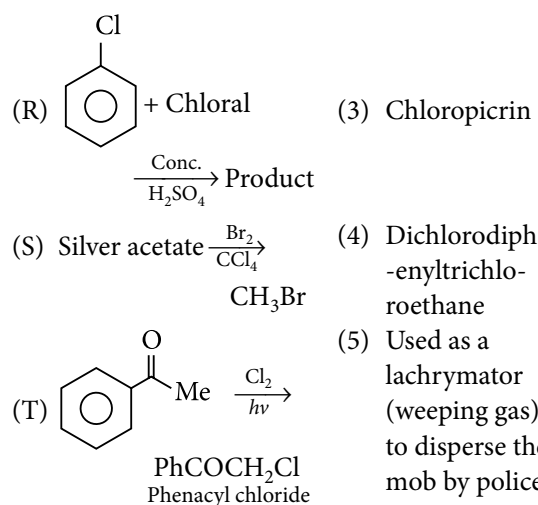
	P	Q	R	S	T
(a)	3	1	4	2	5
(b)	2	1	4	3	5
(c)	5	2	1	3	4
(d)	3	1	2	4	5

30. Match column I with column II and choose the correct option using the codes given below.

Column I	Column II
(P)	(1)
(Q)	(2)
(R)	(3)
(S)	(4)

	P	Q	R	S
(a)	2	1	4	3
(b)	1	1, 3	2	4
(c)	2, 3	1, 2	4	3
(d)	2, 4	1, 4	2	4

Keys are published in this issue. Search now! ☺

CHEMISTRY MUSING

PROBLEM SET 51

*C*hemistry Musing was started from August '13 issue of Chemistry Today. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / JIPMER with additional study material. In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today.
The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue. We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

JEE MAIN/NEET

1. The molal freezing point depression constant of benzene (C_6H_6) is 4.90 K kg mol^{-1}. Selenium exists as a polymer of the type Se_x. When 3.26 g of selenium is dissolved in 226 g of benzene, the observed freezing point is 0.112 °C lower than pure benzene. The correct molecular formula of selenium is
   (a) Se_2 (b) Se_4
   (c) Se_6 (d) Se_8

2. What is the product *E* in the following reaction sequence?

$$\text{(ring)} \xrightarrow[\text{KMnO}_4]{\text{alk.}} A \xrightarrow[\text{AcOH}]{\text{CrO}_3} B \xrightarrow{\text{HCN}} C \xrightarrow{\text{H}_2\text{O/HCl}}$$
$$D \xrightarrow{\text{HI/Red P}} E$$

   (a) (benzene ring)
   (b) cyclohexane with COOH, COOH
   (c) cyclohexane with CH$_3$, CH$_3$
   (d) cyclohexane with O, O
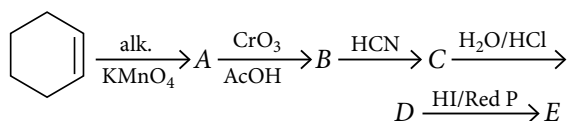
3. At 17 °C, the osmotic pressure of sugar solution is 580 torr. The solution is diluted and the temperature is raised to 57 °C, then the osmotic pressure is found to be 165 torr. The extent of dilution is
   (a) 2 times   (b) 3 times
   (c) 4 times   (d) 5 times.

4. An organic compound *A*, having carbon and hydrogen, adds one mole of hydrogen in the presence of platinum catalyst to form normal hexane. On vigorous oxidation with KMnO$_4$, it gives a single carboxylic acid containing three carbon atoms. What would be the compound *A*?
   (a) Hex-1-ene   (b) Heptanone
   (c) Propanoic acid   (d) Hex-3-ene

5. Which of the following organic compounds does/do not undergo solvolysis?
   (a) (cyclohexadiene with Br)
   (b) (bicyclic with I)
   (c) (cyclohexane with Br)
   (d) Both (b) and (c)
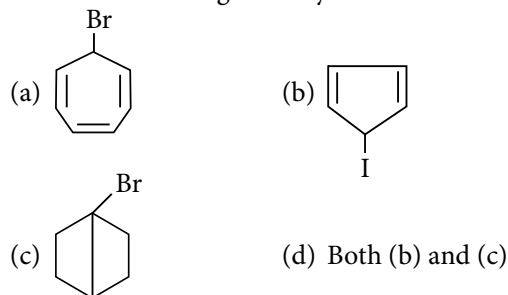
JEE ADVANCED

6. For which of the following reactions, both the gaseous products *X* and *Y* are same? (Do not consider *X* and *Y* as water vapours)
   (a) $Mg_2C_3 + H_2O \longrightarrow X$; $Al_4C_3 + H_2O \longrightarrow Y$
   (b) $NH_4NO_3 \xrightarrow{\Delta} X$; $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} Y$
   (c) $NH_4Cl \xrightarrow{\text{NaOH}_{(aq)}} X$; $NaNO_3 \xrightarrow{\text{Al/NaOH}_{(aq)}} Y$
   (d) $Zn + \text{dil. HNO}_3 \xrightarrow{\text{Cold}} X$; $Ag + \text{dil. HNO}_3 \xrightarrow{\text{Cold}} Y$

COMPREHENSION

Tollen's reagent is used for the detection of aldehyde when a solution of AgNO$_3$ is added to glucose with NH$_4$OH then gluconic acid is formed.

$$Ag^+ + e^- \longrightarrow Ag; E°_{\text{red}} = 0.8 \text{ V}$$

$$C_6H_{12}O_6 + H_2O \longrightarrow \text{Gluconic acid } (C_6H_{12}O_7) + 2H^+ + 2e^-; E°_{\text{ox}} = -0.05 \text{ V}$$

$$Ag(NH_3)_2^+ + e^- \longrightarrow Ag_{(s)} + 2NH_3; E°_{\text{red}} = 0.337 \text{ V}$$
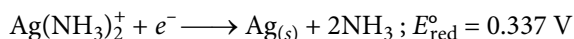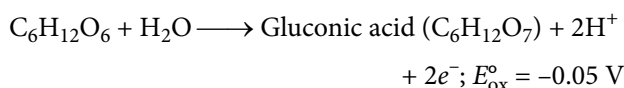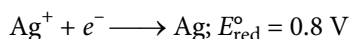
[Use $2.303 \times \dfrac{RT}{F} = -0.0591$ and $\dfrac{F}{RT} = 38.92$ at 298 K]

7. 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) E_{ox} will increase by a factor of 0.65 from E°_{ox}.

(b) E_{ox} will decrease by a factor of 0.65 from E°_{ox}.

(c) E_{red} will increase by a factor of 0.65 from E°_{red}.

(d) E_{red} will decrease by a factor of 0.65 from E°_{red}.

8. Ammonia is always added in this reaction. Which of the following must be correct?

(i) NH_3 combines with Ag^+ to form a complex.

(ii) $[Ag(NH_3)_2]^+$ is a stronger oxidising agent than Ag^+.

(iii) In absence of NH_3 silver salt of gluconic acid is formed.

(iv) NH_3 has affected the standard reduction potential of glucose/gluconic acid electrode.

(a) (i) and (iv) only

(b) (ii) and (iii) only

(c) (i), (ii) and (iii) only

(d) All of these

INTEGER VALUE

9. Following steps are involved in manufacturing of potassium dichromate :

$$\text{Chromite ore} \xrightarrow[\text{in the presence of air}]{\text{Fused with Na}_2\text{CO}_3} \text{Solid mass}$$
$$(X)$$

$$\xrightarrow[\text{and filter}]{\text{Add water}} \begin{cases} \text{Brown residue} \\ \text{Solution} \xrightarrow{\text{conc. H}_2\text{SO}_4} \text{Solution} \\ \quad (Y) \qquad\qquad\qquad\qquad (Z) \end{cases}$$
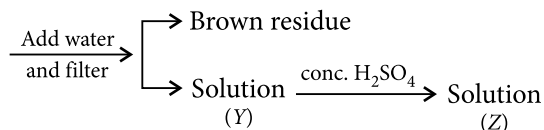
Calculate the difference in the oxidation number of Cr in X and Z.

10. How many of the following compounds have the same osmotic pressure as that of 1 M Na_2SO_4 solution at constant temperature?

1 M KCl, 1.5 M K_2SO_4, 1.5 M NaCl, 2 M $Al_2(SO_4)_3$, 0.5 M $BaSO_4$

◈ ◈

SOLUTION OF SEPTEMBER 2017 CROSSWORD

							¹B		²S	K	A	T	O	L	E			
---	---	---	---	---	---	---	---	---	³Y	---	---	---	---	⁴L	---	---	---	---
				⁵F	L	U	P	I	R	T	I	N	E	⁷C	O	A	G	E	L
⁸T	R	A	U	⁶B	E			T		⁹C	E		¹⁰B		B			
¹¹E	L	E	C	T	R	U	M			¹²H	A	R	T	R	E	E		
				M						L	E		E	L		¹³F		
	¹⁴L	E	W	I	S	I	T	E		X	S		E	L		U		
				O						I	D		I	G				
				N					¹⁵S		E	N	A					
¹⁶Z	Y	M	O	S	C	O	P	¹⁷E		P	R	G	C					
					¹⁸F		O	¹⁹C	A			I						
²⁰D	E	²¹F	L	A	G	R	A	T	I	O	N	N			²²A	T		
		O			I		V	R	D			R	Y					
		N			G		O	N	E			S						
		O			O		S	X			O		²³C					
		F	²⁴K	I	R	C	H	O	F	F	S	²⁵S	U	L	F	L	O	W	E	R
		O			I			²⁶B	A	S	K	E	T	²⁷A	N	E		E
		S			F						L		N			E		
					I			²⁸A			N		I			P		
	²⁹P	A	C	K	I	N	G		A			I					
								A			³⁰C	A	L	I	C	H	E
								T			O						
								E									

JEE Advanced

PRACTICE PROBLEMS

SECTION 1 (Maximum Marks : 24)

This section contains 8 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct. For each question you will be awarded 3 marks if you have darkened only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (–1) mark will be awarded.

1. A 5% solution of glucose (molar mass 180) is isotonic with a 2.5% solution of substance X at the same temperature. The molar mass of X is
   (a) 45   (b) 90   (c) 150   (d) 250

2. Benzene (V.P. = 275 mm) and ethylene chloride (V.P. = 225 mm) form ideal solution. The total pressure made by dissolving 2 moles of benzene and 3 moles of ethylene chloride will be
   (a) 500 mm   (b) 200 mm
   (c) 245 mm   (d) 350 mm.

3. A vessel of volume 6 litres contains 1.4 g of nitrogen at a temperature of 1800 K. Find the pressure of the gas if 40% of its molecules are dissociated into atoms at this temperature.
   (a) 1.72 atm   (b) 2.4 atm
   (c) 24 atm   (d) 3.52 atm

4. A mixture of N_2 and water vapours is admitted into a flask at 760 torr which contains a sufficient solid drying agent, after long time the pressure reached a steady value of 722 torr. If the experiment is done at 27 °C and drying agent increases in weight by 0.9 g, what is the volume of the flask? (Neglect vapour pressure of N_2 gas and volume of drying agent.)
   (a) 38 L   (b) 246.3 L
   (c) 49.26 L   (d) 24.63 L

5. The density of a substance (x) at 1 atm pressure and 500 K temperature is 0.8 kg/m^3. The vapour effuses through a small hole at a rate of 4/5 times slower than oxygen under same conditions. What is the compressibility factor (Z) of the vapour?
   (a) 0.974   (b) 1.35   (c) 1.52   (d) 1.22

6. For one mole of a van der Waals gas when $b = 0$ and $T = 300$ K, the PV vs. $1/V$ plot is shown. The value of the van der Waals constant a (atm. litre^2 mol^{-2}) is

   (a) 1.0   (b) 4.5
   (c) 1.5   (d) 3.0
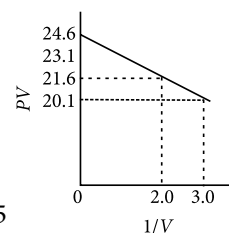
7. Starting out of a trip to the mountains you are requested to inflate the tires of your automobile to a recommended pressure of 3.21×10^5 Pa on a day when the temperature is –5 °C. You drive to the beach where the temperature is 28 °C. Assume that the volume of the tyre has increased by 3%. What is the final pressure in the tyres?
   (a) 350 Pa   (b) 3500 Pa
   (c) 3.5×10^5 Pa   (d) 0.350 Pa

8. A lead storage battery contains a solution of H_2SO_4 38% by weight. At this concentration, van't Hoff factor is 2.50. At what temperature (in Kelvin) will the battery contents freeze? (K_f = 1.86 K kg mol^{-1})
   (a) 243.92   (b) 263.42
   (c) 281.29   (d) 296.16

SECTION 2 (Maximum Marks : 12)

This section contains 3 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which one or more than one answer is correct. For each question you will be awarded 4 marks if you have darkened only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marking in this section.

9. In which of the following pairs of solutions will the values of van't Hoff factor be the same?
   (a) 0.10 M $K_4[Fe(CN)_6]$
        and 0.05 M $K_2SO_4 \cdot (NH_4)_2SO_4 \cdot 24H_2O$
   (b) 0.10 M $K_4[Fe(CN)_6]$ and 0.05 M $Al_2(SO_4)_3$
   (c) 0.10 M NaCl and 0.1 M KCl
   (d) 0.05 M $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ and
        0.2 M $KCl \cdot MgCl_2 \cdot 6H_2O$

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10. 1 mol benzene ($p^{\circ}_{\text{benzene}}$ = 42 mm) and 2 mol toluene ($p^{\circ}_{\text{toluene}}$ = 36 mm) will have
    (a) total vapour pressure 38 mm
    (b) mole fraction of vapours of benzene above liquid mixture is 7/19
    (c) positive deviation from Raoult's law
    (d) negative deviation from Raoult's law.

11. An open ended mercury manometer is used to measure the pressure exerted by a trapped gas as shown in figure. Initially manometer shows no difference in mercury level in both columns as shown in diagram.
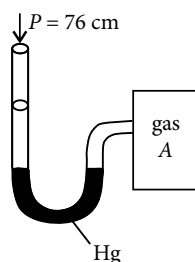
    After sparking 'A' dissociates according to the following reaction

    $A_{(g)} \rightarrow B_{(g)} + 3C_{(g)}$
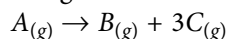
    If pressure of gas 'A' decreases to 0.9 atm then choose the correct statements.
    (Assume temperature is constant and it is 300 K.)
    (a) Total pressure increased to 1.3 atm.
    (b) Total pressure decreased by 0.3 atm.
    (c) Total pressure increased to 988 mm of Hg.
    (d) Difference in mercury level is 228 mm.

SECTION 3 (Maximum Marks : 18)

This section contains 3 paragraphs. Based upon each paragraph, 2 multiple choice questions have to be answered. For each question you will be awarded 3 marks if you have darkened only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (–1) mark will be awarded.

PARAGRAPH 1

1.21 g of benzoic acid (molar mass 121 g mol⁻¹) when dissolved in 100 cm³ solution produces osmotic pressure of 1.73 atm at 300 K. Benzoic acid is known to form dimer in benzene.

12. The calculated average molar mass of benzoic acid in the solution is
    (a) 150 g mol⁻¹   (b) 181 g mol⁻¹
    (c) 172.1 g mol⁻¹   (d) 198 g mol⁻¹

13. The percentage of benzoic acid in the associated state is
    (a) 41%   (b) 48%   (c) 53%   (d) 59%

PARAGRAPH 2

To account for the anomalies in colligative properties due to ionisation or association of molecules, van't Hoff introduced a factor 'i' in the van't Hoff equation ($\pi V = nRT$) of osmotic pressure. The modified equation may thus be written as $\pi V = inRT$

The factor 'i' was defined by the expression,

$$i = \frac{\text{Observed osmotic pressure}}{\text{Calculated osmotic pressure}}$$

Now since osmotic pressure behaves like other colligative properties, the factor 'i' can also be applied to other colligative properties.

Thus, in general,

$$i = \frac{\text{Actual number of particles}}{\text{Number of particles before ionisation (}i.e.\text{, initial)}}$$

or $\quad i = \dfrac{\text{Observed colligative property}}{\text{Calculated colligative property}}$

14. The freezing point of equimolal aqueous solution will be highest for
    (a) $K_3[\text{Fe(CN)}_6]$ (b) Na_2SO_4
    (c) KCl   (d) urea.

15. pH of a 0.01 M monobasic acid is measured to be equal to bond order of CN⁻. Its osmotic pressure at a given temperature T K is
    (a) 0.3 RT (b) 0.11 RT
    (c) 1.1 RT (d) 0.011 RT

PARAGRAPH 3

X and Y are two volatile liquids with molar weights of 10 g mol⁻¹ and 40 g mol⁻¹ respectively. Two cotton plugs, one soaked in X and the other soaked in Y, are simultaneously placed at the ends of a tube of length L = 24 cm, as shown in the figure. The tube is filled with an inert gas at 1 atmosphere pressure and a temperature of 300 K. Vapours of X and Y react to form a product which is first observed at a distance d cm from the plug soaked in X. Take X and Y to have equal molecular diameters and assume ideal behaviour for the inert gas and vapours of both X and Y.
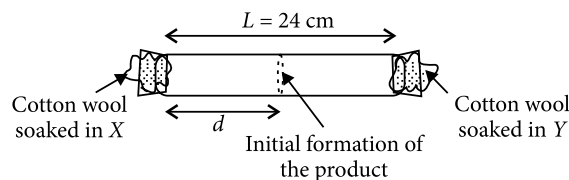
16. The value of d in cm (shown in the figure), as estimated from Graham's law, is
    (a) 8   (b) 12
    (c) 16   (d) 20

17. The experimental value of d is found to be smaller than the estimated using Graham's law. This is due to

(a) larger mean free path for X as compared to that of Y

(b) larger mean free path for Y as compared to that of X

(c) increased collision frequency of Y with the inert gas as compared to that of X with the inert gas

(d) increased collision frequency of X with the inert gas as compared to that of Y with the inert gas.

SECTION 4 (Maximum Marks : 20)

This section contains 5 integer type questions. Answers have to be given in between 0 to 9 in the form of nearest integer. Each question carries 4 marks if you have darkened the correct answer and no negative mark will be awarded for an incorrectly bubbled answer.

18. MX_2 dissociates into M^{2+} and X^- ions in an aqueous solution, with a degree of dissociation (α) of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociation is

19. Oxygen generated by the decomposition of potassium chlorate is collected. The volume of oxygen collected at 47 °C and at atmospheric pressure of 760 mm of Hg is 8.21 L. Calculate the mass of oxygen gas (in g) obtained. (The pressure of water vapour at 47 °C is 76 mm of Hg.)

20. If Pd vs P, where 'P' denotes pressure in atm and 'd' denotes density in g/L, is plotted for He gas at a particular temperature, find the value of $\left[\dfrac{d(Pd)}{dP}\right]_{P=8.21\ atm}$ at 160 K.

21. What volume of 90% sulphuric acid by weight (density = 5 g/L) should be mixed with water to obtain 3 L of 50% solution of sulphuric acid (density = 3 g/L) by weight ?

22. A certain mass of substance when dissolved in 100 g C_6H_6 lowers the freezing point by 1.28 °C. The same mass of solute dissolved in 100 g of water lowers the freezing point by 1.4 °C. If the substance has normal molecular weight in benzene and is completely dissociated in water, into how many ions does it dissociate in water? (K_f for H_2O and C_6H_6 are 1.86 and 5.12 K kg mol^{-1} respectively.)

SECTION 5 (Maximum Marks : 16)

This section contains 2 questions. Each question contains statements given in 2 columns. Statements in the first column have to be matched with statements in the second column. For each question in this section, you will be awarded 8 marks if you have darkened all the bubbles corresponding only to the correct answer and 2 marks for each row. No negative mark will be awarded for an incorrectly bubbled answer.

23. Match the solution in Column I with its nature in Column II.

Column I	Column II
(A) Benzene + Toluene	(p) Non-ideal solution
(B) Ethanol + Water	(q) Ideal solution
(C) Benzene + Chloroform	(r) $\Delta H_{mix} > 0$
(D) Carbon tetrachloride + Chloroform	(s) $\Delta H_{mixing} = 0$

24. Match Column I with Column II.

Column I	Column II
(A) At low pressure	(p) $Z = 1 + \dfrac{pb}{RT}$
(B) At high pressure	(q) $Z = 1 - \dfrac{a}{V_m RT}$
(C) At low density of gas	(r) Gas is more compressible than ideal gas
(D) For H_2 and He at 0 °C	(s) Gas is less compressible than ideal gas

ANSWER KEY

1. (b) 2. (c) 3. (a) 4. (d) 5. (c)
6. (c) 7. (c) 8. (a) 9. (b,c,d) 10. (a, b)
11. (a,c,d) 12. (c) 13. (d) 14. (d) 15. (d)
16. (c) 17. (d) 18. (2) 19. (9) 20. (5)
21. (1) 22. (3)
23. (A) → (q, s); (B) → (p, r); (C) → (p); (D) → (p, r)
24. (A) → (q, r); B → (p, s); C → (q, r); D → (p, s)

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CHEMISTRY MUSING

SOLUTION SET 50

1. **(c):** 1 mol of butane, *i.e.*, C_4H_{10} (=58 g) gives energy = 2658 kJ

or 58 g of C_4H_{10} gives energy = 2658 kJ

11.2 × 1000 g will give energy

$$\Rightarrow \quad \frac{2658 \times 11.2 \times 1000}{58} \Rightarrow 513268.96 \text{ kJ}$$

20000 kJ of energy is required for 1 day.

∴ 513268.96 kJ of energy will be required for

$$= \frac{513268.96}{20000} = 25.66 \text{ days} \approx 26 \text{ days}$$

2. **(a):** Here,

$T_1 = 400 + 273 \text{ K} = 673 \text{ K}$

$(K_p)_1 = 1.64 \times 10^{-4}$

$T_2 = 500 + 273 \text{ K} = 773 \text{ K}$

$\Delta H = -25140$ cal

$$\log \frac{(K_p)_2}{(K_p)_1} = \frac{\Delta H}{2.303 \, R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

Substituting the values in the equation, we get

$$\log \frac{(K_p)_2}{1.64 \times 10^{-4}} = \frac{-25140}{2.303 \times 1.987} \left(\frac{773 - 673}{673 \times 773} \right)$$

$$= -1.0560$$

or $\log (K_p)_2 - \log (1.64 \times 10^{-4}) = -1.0560$

or $\log (K_p)_2 - \log 1.64 + 4 = -1.0560$

or $\log(K_p)_2 = -4.8412$

∴ $(K_p)_2 = 1.44 \times 10^{-5}$

3. **(d):**
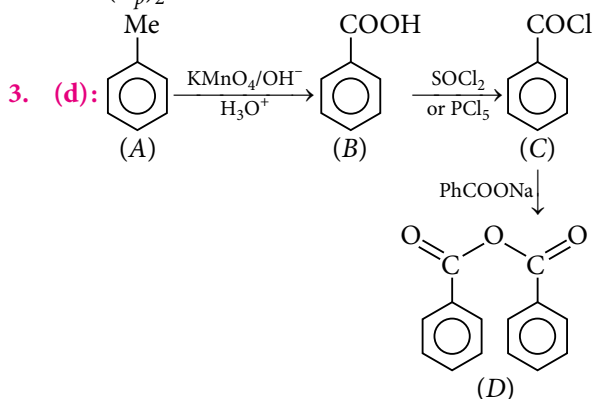
4. **(c):** Coordination number of Cr is six, hence the complex that does not conduct electricity, would not ionise. Hence, NO_2^- and NH_3 ligands are in the coordination sphere and the complex is $[Cr(NH_3)_3(NO_2)_3]$.

The other complex that conducts electricity would ionise. Thus, in this complex H_2O should enter into coordination sphere making atleast one NO_2^- available outside the coordination sphere. This complex is thus, $[Cr(H_2O)(NH_3)_3(NO_2)_2]NO_2$.

5. **(b)**

6. **(d):**
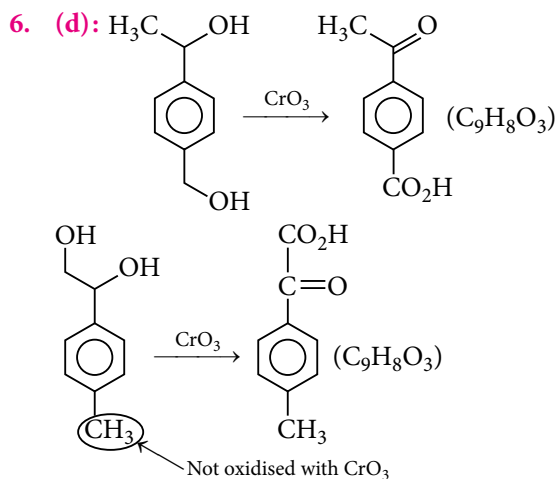
7. **(d):** Yellow powder *X* is S.

8. **(b):** The colourless gas *Y* is SF_6 (octahedral geometry).

$$\underset{X}{S} + 3F_2 \xrightarrow{\Delta} \underset{Y, \text{ colourless gas}}{SF_6}$$
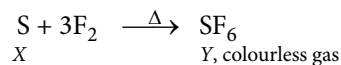
The colourless gas *Z* is SF_4 (trigonal bipyramidal)

$$SCl_2 + 4NaF \longrightarrow \underset{Z}{SF_4} + S_2Cl_2 + 4NaCl$$
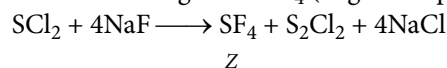
9. **(4)**

10. **(3):** Since the reaction is of the first order,

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

Here, we are given that

$k = 2.2 \times 10^{-5} \text{ sec}^{-1}$

$t = 90 \text{ minutes} = 90 \times 60 = 5400 \text{ sec}$

$$\therefore \quad 2.2 \times 10^{-5} = \frac{2.303}{5400} \log \frac{a}{a - x}$$

or $\log \dfrac{a}{a - x} = 0.0516$

or $\dfrac{a}{a - x} = \text{antilog} \, (0.0516) = 1.126$

or $a = 1.126 \, a - 1.126 \, x$

or $0.126 \, a = 1.126 \, x$

∴ $\dfrac{x}{a} = \dfrac{0.126}{1.126} = 0.112 = 11.2\% = (8.2 + y)\%$

∴ $y = 3$

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