

CBSE 12 CHEMISTRY SET 1 (56/1/1) Question Paper with Solutions

Time Allowed :3 hours	Maximum Marks :70	Total Questions :33
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General Instructions

Read the following instructions very carefully and strictly follow them :

- (i) This question paper contains 33 questions. All questions are compulsory.
- (ii) This question paper is divided into five sections — Section A, B, C, D and E.
- (iii) Section A - questions number 1 to 16 are multiple choice type questions. Each question carries 1 mark.
- (iv) Section B - questions number 17 to 21 are very short answer type questions. Each question carries 2 marks.
- (v) Section C - questions number 22 to 28 are short answer type questions. Each question carries 8 marks.
- (vi) Section D - questions number 29 and 30 are case-based questions. Each question carries 4 marks.
- (vii) Section E - questions number 31 to 33 are long answer type questions. Each question carries 5 marks.
- (viii) There is no overall choice given in the question paper. However, an internal choice has been provided in few questions in all the sections except Section A.
- (ix) Kindly note that there is a separate question paper for Visually Impaired candidates.
- (x) Use of calculators is not allowed.

SECTION A

Questions no. 1 to 16 are Multiple Choice type Questions, carrying 1 mark each

1. Which one of the following first row transition elements is expected to have the highest third ionization enthalpy?

- (A) Iron ($Z = 26$)
- (B) Manganese ($Z = 25$)
- (C) Chromium ($Z = 24$)
- (D) Vanadium ($Z = 23$)

Correct Answer: (B) Manganese ($Z = 25$)

Solution: The third ionization enthalpy of transition elements increases as we move across the period due to increasing nuclear charge. Manganese has a half-filled d-subshell configuration, making it relatively stable and requiring more energy to remove the third electron. Hence, Manganese ($Z = 25$) has the highest third ionization enthalpy.

Quick Tip

For transition elements, the ionization enthalpy increases across the period due to increased nuclear charge and stability of electronic configurations.

2. Which of the following compounds will give a ketone on oxidation with chromic anhydride (CrO_3)?

- (A) $(\text{CH}_3)_2\text{CH} - \text{CH}_2\text{OH}$
- (B) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- (C) $(\text{CH}_3)_3\text{C} - \text{OH}$
- (D)
$$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_3 \\ | \\ \text{OH} \end{array}$$
$$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_3 \\ | \\ \text{OH} \end{array}$$

Correct Answer: (D)

Solution: The compound in option (D) is a secondary alcohol, and upon oxidation with chromic anhydride, it forms a ketone. Chromic anhydride oxidizes alcohols to carbonyl compounds, with secondary alcohols yielding ketones.

Quick Tip

Secondary alcohols are oxidized to ketones, while primary alcohols are oxidized to aldehydes or carboxylic acids with reagents like CrO_3 .

3. Two among the three components of DNA are β -D-2-deoxyribose and a heterocyclic base. The third component is:

- (A) Adenine
- (B) Phosphoric acid
- (C) Sulphuric acid
- (D) Uracil

Correct Answer: (B) Phosphoric acid

Solution: The three components of DNA are β -D-2-deoxyribose (a sugar), a heterocyclic base (either adenine, thymine, cytosine, or guanine), and phosphoric acid, which forms the backbone of the DNA structure by linking the sugars together.

Quick Tip

The components of DNA are sugar, phosphate, and nitrogenous bases. Phosphoric acid plays a crucial role in connecting nucleotides to form the backbone of DNA.

4. For an electrolyte undergoing association in a solvent, the van't Hoff factor:

- (A) is always greater than one
- (B) has negative value
- (C) has zero value
- (D) is always less than one

Correct Answer: (D) is always less than one

Solution: For electrolytes undergoing association, the number of particles in solution decreases because ions form pairs or clusters. This results in a van't Hoff factor less than one, as fewer particles are present than expected based on dissociation alone.

Quick Tip

The van't Hoff factor for association is less than one because the ions combine to form aggregates, reducing the number of particles in solution.

5. For the reaction $X + 2Y \rightarrow P$, the differential form equation of the rate law is:

- (A) $2d[P]/dt = -d[Y]/dt$
- (B) $-d[P]/dt = -d[X]/dt$
- (C) $+d[X]/dt = -d[P]/dt$
- (D) $-2d[Y]/dt = +d[P]/dt$

Correct Answer: (A) $2d[P]/dt = -d[Y]/dt$

Solution: For the reaction $X + 2Y \rightarrow P$, the rate of change of concentration of P is twice that of Y, hence the rate law can be written as:

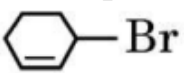
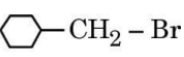
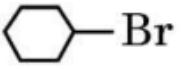
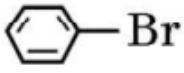
$$\frac{d[P]}{dt} = -\frac{d[Y]}{dt}/2$$

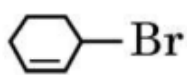
Thus, the correct equation is $2d[P]/dt = -d[Y]/dt$.

Quick Tip

The coefficients in the rate law equation are often determined by the stoichiometry of the reaction. In this case, the change in concentration of Y is double that of P.

6. The compound which undergoes SN_1 reaction most rapidly is:

- (A) 
- (B) 
- (C) 
- (D) 

Correct Answer: (A) 

Solution: In SN_1 reactions, the rate-determining step is the departure of the leaving group. In the case of aromatic compounds, a resonance-stabilized carbocation can form if the leaving group is attached to the ring, which makes the reaction faster. Hence, the phenyl bromide ($\text{C}_6\text{H}_5\text{Br}$) undergoes the reaction most rapidly.

Quick Tip

Aromatic carbocations are stabilized through resonance, which makes the SN_1 reaction faster for compounds where such stabilization can occur.

7. Acetic acid reacts with PCl_5 to give:

- (A) $\text{Cl} - \text{CH}_2 - \text{COCl}$
- (B) $\text{Cl} - \text{CH}_2 - \text{COOH}$
- (C) $\text{CH}_3 - \text{COCl}$
- (D) $\text{CCl}_3 - \text{COOH}$

Correct Answer: (C) $\text{CH}_3 - \text{COCl}$

Solution: When acetic acid reacts with PCl_5 , it forms acyl chloride (CH_3COCl) by replacing the $-\text{OH}$ group with a chlorine atom. This reaction is a typical example of chlorination of carboxylic acids.

Quick Tip

Acyl chlorides can be formed by treating carboxylic acids with reagents like PCl_5 , which replace the hydroxyl group with a chlorine atom.

8. The formation of cyanohydrin from an aldehyde is an example of:

- (A) nucleophilic addition
- (B) electrophilic addition
- (C) nucleophilic substitution
- (D) electrophilic substitution

Correct Answer: (A) nucleophilic addition

Solution: Cyanohydrin formation involves the addition of a nucleophile (cyanide ion) to the carbonyl carbon of an aldehyde, which is characteristic of nucleophilic addition reactions.

Quick Tip

Nucleophilic addition involves the addition of a nucleophile to a polarized electrophilic center, such as the carbonyl group in aldehydes and ketones.

9. In the Arrhenius equation, when $\log k$ is plotted against $1/T$, a straight line is obtained whose:

- (A) slope is $\frac{A}{R}$ and intercept is E_a
- (B) slope is A and intercept is $\frac{-E_a}{R}$
- (C) slope is $\frac{-E_a}{RT}$ and intercept is $\log A$
- (D) slope is $\frac{-E_a}{2.303R}$ and intercept is $\log A$

Correct Answer: (D) slope is $\frac{-E_a}{2.303R}$ and intercept is $\log A$

Solution: The Arrhenius equation is given by:

$$\log k = \frac{-E_a}{2.303R} \cdot \frac{1}{T} + \log A$$

where the slope is $\frac{-E_a}{2.303R}$ and the intercept is $\log A$. This linear relationship is used to determine the activation energy and pre-exponential factor from experimental data.

Quick Tip

In the Arrhenius equation, the slope of the plot of $\log k$ vs. $1/T$ is directly related to the activation energy (E_a) of the reaction.

10. The reaction of an alkyl halide with sodium alkoxide forming ether is known as:

- (A) Wurtz reaction
- (B) Reimer-Tiemann reaction
- (C) Williamson synthesis
- (D) Kolbe reaction

Correct Answer: (C) Williamson synthesis

Solution: The Williamson synthesis is the reaction of an alkyl halide with a sodium alkoxide to form an ether. It is an example of a nucleophilic substitution reaction.

Quick Tip

The Williamson synthesis is a powerful method for preparing ethers and involves an alkoxide nucleophile attacking an alkyl halide.

11. The correct order of the ease of dehydration of the following alcohols by the action of conc. H_2SO_4 is:

- (A) $(CH_3)_3C - OH > (CH_3)_2CH - OH > CH_3CH_2 - OH$
- (B) $(CH_3)_2CH - OH > CH_3CH_2 - OH > (CH_3)_3C - OH$
- (C) $CH_3CH_2 - OH > (CH_3)_2CH - OH > (CH_3)_3C - OH$
- (D) $(CH_3)_2CH - OH > (CH_3)_3C - OH > CH_3CH_2 - OH$

Correct Answer: (A) $(CH_3)_3C - OH > (CH_3)_2CH - OH > CH_3CH_2 - OH$

Solution: The ease of dehydration is based on the stability of the carbocation formed during the reaction. Tertiary alcohols (like $(\text{CH}_3)_3\text{C} - \text{OH}$) undergo dehydration the most easily due to the formation of a stable tertiary carbocation.

Quick Tip

The stability of carbocations increases with the number of alkyl groups attached to the central carbon. Tertiary carbocations are the most stable and lead to the fastest dehydration.

12. Which functional groups of glucose interact to form cyclic hemiacetal leading to pyranose structure?

- (A) Aldehyde group and hydroxyl group at C – 4
- (B) Aldehyde group and hydroxyl group at C – 5
- (C) Ketone group and hydroxyl group at C – 4
- (D) Ketone group and hydroxyl group at C – 5

Correct Answer: (B) Aldehyde group and hydroxyl group at C – 5

Solution: In the pyranose form of glucose, the aldehyde group at C – 1 reacts with the hydroxyl group at C – 5 to form a cyclic hemiacetal. This is a typical reaction in monosaccharides forming a six-membered ring.

Quick Tip

Monosaccharides like glucose can cyclize to form hemiacetals, where the aldehyde group reacts with a hydroxyl group on the same molecule.

For Questions number 13 to 16, two statements are given — one labelled as Assertion (A) and the other labelled as Reason (R). Select the correct answer to these questions from the codes (A), (B), (C) and (D) as given below.

1. Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).
2. Both Assertion (A) and Reason (R) are true, but Reason (R) is *not* the correct explanation of the Assertion (A).
3. Assertion (A) is true, but Reason (R) is false.
4. Assertion (A) is false, but Reason (R) is true.

13. Assertion (A): When NaCl is added to water, a depression in freezing point is observed.
Reason (R): NaCl undergoes dissociation in water.

Correct Answer: (B) Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).

Solution: The depression in freezing point is due to the colligative properties of the solution. Although NaCl dissociates in water, the depression in freezing point is not solely due to dissociation, but to the number of solute particles present.

Quick Tip

Colligative properties, such as freezing point depression, depend on the number of solute particles in solution, not on their nature.

14. Assertion (A): Separation of Zr and Hf is difficult.

Reason (R): Zr and Hf have similar radii due to lanthanoid contraction.

Correct Answer: (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).

Solution: Zr and Hf are very similar in size due to lanthanoid contraction, which makes it difficult to separate them effectively using conventional methods.

Quick Tip

Lanthanoid contraction refers to the steady decrease in ionic radii of the lanthanoids, making elements like Zr and Hf chemically and physically similar.

15. Assertion (A): The pK_a of ethanoic acid is lower than that of $C_1 - CH_2 - COOH$.

Reason (R): Chlorine shows electron withdrawing ($-I$) effect which increases the acidic character of $C_1 - CH_2 - COOH$.

Correct Answer: (D) Assertion (A) is false but Reason (R) is true.

Solution: Chloroacetic acid ($C_1 - CH_2 - COOH$) has a lower pK_a than acetic acid (ethanoic acid), as the electron withdrawing effect of chlorine enhances the acidity. However, the assertion that the pK_a of ethanoic acid is lower is incorrect.

Quick Tip

Electron-withdrawing groups, like chlorine, increase the acidity of carboxylic acids by stabilizing the conjugate base.

16. Assertion (A): Aniline is a stronger base than ammonia.

Reason (R): The unshared electron pair on nitrogen atom in aniline becomes less available for protonation due to resonance.

Correct Answer: (D) Assertion (A) is false but Reason (R) is true.

Solution: Aniline is actually a weaker base than ammonia because the lone pair of electrons on the nitrogen in aniline is delocalized into the benzene ring, making it less available for protonation. The reasoning is true, but the assertion is false.

Quick Tip

In aniline, the lone pair of electrons on nitrogen is involved in resonance with the aromatic ring, reducing its availability for protonation and making it a weaker base than ammonia.

SECTION B

17. Calculate the potential of Iron electrode in which the concentration of Fe^{2+} ion is 0.01 M.

$$E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.45 \text{ V at } 298 \text{ K}$$

[Given: $\log 10 = 1$]

Solution: The Nernst equation is used to calculate the electrode potential at non-standard conditions:

$$E = E^{\circ} - \frac{0.0591}{n} \log \left(\frac{[\text{Fe}^{2+}]}{[\text{Fe}]} \right)$$

Where: - E° is the standard electrode potential, - n is the number of electrons transferred (for Fe^{2+} to Fe , $n = 2$), - $[\text{Fe}^{2+}]$ is the concentration of Fe^{2+} (given as 0.01 M), - $[\text{Fe}]$ is the concentration of solid iron (which is 1 M in standard conditions).

Substituting the given values into the equation:

$$\begin{aligned} E &= -0.45 - \frac{0.0591}{2} \log \left(\frac{1}{0.01} \right) \\ E &= -0.45 - \frac{0.0591}{2} \times (2) = -0.45 + 0.0591 \\ E &= -0.3909 \text{ V} \end{aligned}$$

Thus, the potential of the iron electrode is approximately -0.3909 V .

Quick Tip

The Nernst equation allows you to calculate the potential for an electrode based on the concentration of ions. Remember that the standard potential is measured under standard conditions (1 M concentration, 1 atm pressure).

18. Define molecularity of the reaction. State any one condition in which a bimolecular reaction may be kinetically first order.

Solution: Molecularity of a reaction refers to the number of molecules or ions that must collide simultaneously in an elementary step of the reaction. It is a term used to describe the actual number of reacting particles involved in a single reaction event. For example, a reaction between two molecules is said to be bimolecular.

A bimolecular reaction can be kinetically first order if the concentration of one of the reactants is much larger than the other. In such cases, the rate of reaction depends primarily on the concentration of the limiting reactant, effectively making the reaction behave as if it were first order. This can happen in cases where one reactant is present in excess.

For instance, in the reaction:



If the concentration of B is much higher than A, the rate law will be approximately:

$$\text{Rate} = k[A]$$

Thus, although the reaction is bimolecular, it behaves like a first-order reaction due to the excess of one reactant.

Quick Tip

In cases of bimolecular reactions with excess reactant, the rate depends predominantly on the concentration of the limiting reactant, making the reaction appear to be first order with respect to that reactant.

19. What happens when D-glucose is treated with the following reagents?

(a) HI

(b) Conc. HNO_3

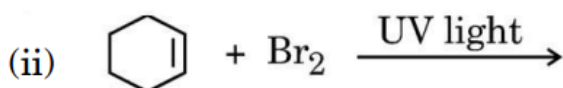
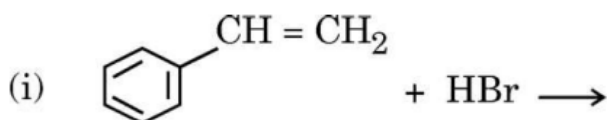
Solution: When D-glucose is treated with HI (hydriodic acid), it undergoes reduction to form hexyl iodide, breaking down into a mixture of smaller molecules such as hexane and iodine. This reaction is a reduction process where the aldehyde group in glucose is reduced.

When D-glucose is treated with concentrated nitric acid (HNO_3), it undergoes oxidation, converting the aldehyde group to a carboxylic acid group, resulting in the formation of glucaric acid. This oxidation occurs at the aldehyde functional group.

Quick Tip

HI is a reducing agent that reduces glucose, while concentrated HNO_3 is an oxidizing agent that converts glucose into glucaric acid, an important process in organic chemistry.

20. (a) Draw the structures of major monohalo products in each of the following reactions:



(b) Give reasons for the following:

- (i) Grignard reagent should be prepared under anhydrous conditions.
- (ii) Alkyl halides give alcohol with aqueous KOH whereas in the presence of alcoholic KOH, alkenes are formed.

Solution: (a) (i) The major product of the reaction between ethene and HBr is 1-bromoethane ($\text{CH}_3\text{CH}_2\text{Br}$).

(ii) The product of the reaction between benzene and Br_2 in UV light is bromobenzene ($\text{C}_6\text{H}_5\text{Br}$).

(b) (i) Grignard reagents are highly reactive and react with water to form hydrocarbons, so they should be prepared under anhydrous conditions to prevent hydrolysis.

(ii) Aqueous KOH leads to nucleophilic substitution, forming alcohols, while alcoholic KOH leads to elimination reactions, producing alkenes.

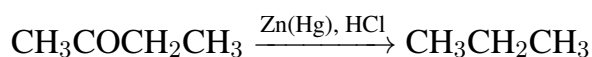
Quick Tip

Grignard reagents require dry conditions to avoid unwanted reactions with moisture. Aqueous KOH favors substitution, and alcoholic KOH promotes elimination to form alkenes.

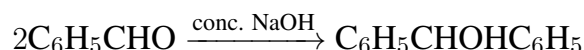
21. Write the chemical equation when:

- (a) Butan-2-one is treated with Zn(Hg) and conc. HCl .
(b) Two molecules of benzaldehyde are treated with conc. NaOH .

Solution: (a) The reaction of butan-2-one with Zn(Hg) and conc. HCl is the Clemmensen reduction, which reduces the ketone to an alkane.



(b) The reaction of benzaldehyde with conc. NaOH is the benzoin condensation, which forms benzoin.



Quick Tip

The Clemmensen reduction removes the carbonyl group, and benzoin condensation couples two benzaldehyde molecules to form benzoin.

22. When a certain conductivity cell was filled with 0.05 M KCl solution, it has a resistance of 100 ohms at 25°C . When the same cell was filled with 0.02 M AgNO_3 solution, the resistance was 90 ohms. Calculate the conductivity and molar conductivity of AgNO_3 solution.

Conductivity of 0.05 M KCl solution = $1.35 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$

Solution:

To calculate the conductivity of AgNO_3 solution, we will use the relationship between the conductivity, resistance, and the cell constant.

The cell constant (G^*) is calculated using the following equation:

$$\text{Cell constant } (G^*) = \text{Conductivity} \times \text{Resistance}$$

For KCl solution:

$$G^* = 1.35 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1} \times 100 \Omega = 1.35 \text{ cm}^{-1}$$

Now, for the AgNO_3 solution, we can use the same cell constant:

$$G^* = 1.35 \text{ cm}^{-1} = \text{Conductivity} \times 90 \Omega$$

$$\text{Conductivity} = \frac{1.35}{90} = 0.015 \text{ S/cm}$$

Next, we calculate the molar conductivity (Λ_m) using the formula:

$$\Lambda_m = \text{Conductivity} \times \frac{1000}{\text{Concentration}}$$

For AgNO_3 solution with concentration 0.02 M:

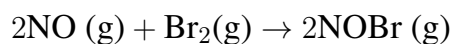
$$\Lambda_m = 0.015 \text{ S/cm} \times \frac{1000}{0.02} = 750 \text{ Scm}^2/\text{mol}$$

Thus, the molar conductivity of the AgNO_3 solution is $750 \text{ Scm}^2/\text{mol}$.

Quick Tip

To calculate molar conductivity, the formula $\Lambda_m = \text{Conductivity} \times \frac{1000}{C}$ is used, where C is the concentration of the solution in mol/L.

23. The following initial rate data were obtained for the reaction:



Expt. No.	[NO]/mol L ⁻¹	[Br ₂]/mol L ⁻¹	Initial Rate (mol L ⁻¹ s ⁻¹)
1	0.05	0.05	1.0×10^{-3}
2	0.05	0.15	3.0×10^{-3}
3	0.15	0.05	9.0×10^{-3}

- (a) What is the order with respect to NO and Br₂ in the reaction?
- (b) Calculate the rate constant (k).
- (c) Determine the rate of reaction when the concentrations of NO and Br₂ are 0.4 M and 0.2 M, respectively.

Solution:

Rate law for the reaction can be expressed as:

$$\text{Rate} = k[\text{NO}]^p[\text{Br}_2]^q$$

Where p is the order with respect to NO and q is the order with respect to Br₂.

- (a) Determining the order with respect to NO (p) Compare experiments 1 and 2 to eliminate the effect of Br₂ concentration and find p . From experiments 1 and 2:

$$\frac{1 \times 10^{-3}}{3 \times 10^{-3}} = \frac{k[0.05]^p[0.05]^q}{k[0.05]^p[0.15]^q}$$

$$\frac{1}{3} = \left(\frac{1}{3}\right)^q \Rightarrow q = 1$$

Determining the order with respect to Br₂ (q) Compare experiments 1 and 3 to eliminate the effect of NO concentration and find p . From experiments 1 and 3:

$$\frac{9 \times 10^{-3}}{1 \times 10^{-3}} = \frac{k[0.15]^p[0.05]^q}{k[0.05]^p[0.05]^q}$$

$$\frac{9}{1} = \left(\frac{3}{1}\right)^p \Rightarrow p = 2$$

Thus, the order with respect to NO is 2 and the order with respect to Br₂s is 1.

- (b) Calculating the rate constant (k) Use the rate law and the data from any experiment to solve for k . Using experiment 1:

$$1 \times 10^{-3} = k[0.05]^2[0.05]$$

$$k = \frac{1 \times 10^{-3}}{(0.05)^3} = 8 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

- (c) Determining the rate when the concentrations of NO and Br₂ are 0.4 M and 0.2 M Now that we have the value of k , we can use it to calculate the rate when [NO] = 0.4 M and [Br₂] = 0.2 M.

$$\text{Rate} = k[\text{NO}]^2[\text{Br}_2]$$

$$\text{Rate} = 8 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1} \times (0.4)^2 \times 0.2$$

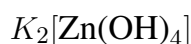
$$\text{Rate} = 8 \times 0.16 \times 0.2 = 2.56 \times 10^{-1} \text{ mol L}^{-1} \text{ s}^{-1}$$

Quick Tip

When determining the order of a reaction with respect to reactants, use the method of comparing experiments with different concentrations of one reactant while keeping others constant. This will help isolate the effect of each reactant on the rate.

24. (a) Write the formula for the following coordination compound: Potassium tetrahydroxidozincate (II)

Solution: The formula for potassium tetrahydroxidozincate (II) is:

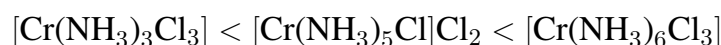


(b) Arrange the following complexes in the increasing order of conductivity of their solution:

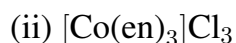
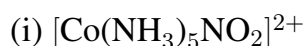


Solution: The conductivity of a compound in solution depends on the number of ions it dissociates into. The more dissociation, the higher the conductivity. For the given complexes: - $[Cr(NH_3)_5Cl]Cl_2$ dissociates into 2 ions. - $[Cr(NH_3)_3Cl_3]$ dissociates into 4 ions. - $[Cr(NH_3)_6Cl_3]$ dissociates into 6 ions.

Thus, the order of conductivity is:



(c) Identify the type of isomerism exhibited by the following complexes:



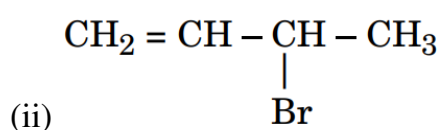
Solution: (i) $[Co(NH_3)_5NO_2]^{2+}$ exhibits linkage isomerism, as the NO ligand can bind through either the nitrogen or the oxygen atom.

(ii) $[Co(en)_3]Cl_3$ exhibits optical isomerism, as the complex is chiral and does not have a plane of symmetry.

Quick Tip

Linkage isomerism occurs when a ligand can coordinate to the metal through two different atoms, while optical isomerism occurs when a molecule lacks any symmetry elements, such as a plane of symmetry, making it non-superimposable on its mirror image.

25. (a) Which of the following is an allylic halide?



Solution: An allylic halide is a compound in which the halogen is attached to a carbon that is adjacent to a double bond. From the given options:

- Option (i): $\text{CH}_3 - \text{CH} = \text{CH} - \text{Br}$ is not an allylic halide because the halogen (Br) is not adjacent to the double bond.

- Option (ii):
$$\begin{array}{c} \text{CH}_2 = \text{CH} - \text{CH} - \text{CH}_3 \\ | \\ \text{Br} \end{array}$$
 is an allylic halide, as the halogen (Br) is attached to the carbon that is adjacent to the double bond.

Thus, the correct allylic halide is option (ii).

Quick Tip

An allylic halide has the halogen attached to a carbon atom that is adjacent to a carbon-carbon double bond. This makes it more reactive in certain reactions, such as allylic substitution.

(b) Out of chlorobenzene and 2,4,6-trinitrochlorobenzene, which is more reactive towards nucleophilic substitution and why?

Solution: 2,4,6-Trinitrochlorobenzene is more reactive towards nucleophilic substitution because the nitro (NO_2) groups present on the benzene ring are electron-withdrawing in nature. These groups pull electron density away from the ring, making the carbon-chlorine bond weaker and easier to break, facilitating nucleophilic attack. In contrast, chlorobenzene does not have such electron-withdrawing groups, making it less reactive towards nucleophilic substitution.

Quick Tip

Electron-withdrawing groups such as nitro (NO_2) increase the reactivity of aromatic compounds in nucleophilic substitution reactions by destabilizing the carbon-halogen bond.

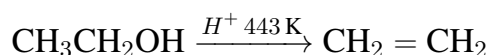
(c) Which isomer of $\text{C}_4\text{H}_9\text{Cl}$ has the lowest boiling point?

Solution: The isomer of $\text{C}_4\text{H}_9\text{Cl}$ with the lowest boiling point is tert-butyl chloride ($(\text{CH}_3)_3\text{C-Cl}$). This is because branching reduces the surface area of the molecule, leading to weaker intermolecular forces (van der Waals forces) and consequently a lower boiling point compared to the straight-chain isomer.

Quick Tip

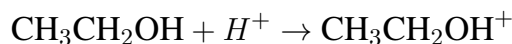
Branched isomers generally have lower boiling points compared to their straight-chain counterparts due to weaker van der Waals forces arising from their reduced surface area.

26. (a) Write the mechanism of the following reaction:

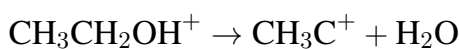


Solution: The mechanism for the dehydration of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) to ethene ($\text{CH}_2=\text{CH}_2$) under acidic conditions involves the following steps:

Step 1: Formation of protonated alcohol (Fast step) Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) reacts with the proton (H^+) to form the protonated alcohol (ethyl oxonium ion).

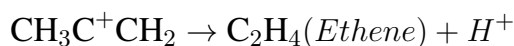


Step 2: Formation of carbocation (Slow step) The protonated alcohol undergoes loss of water to form a carbocation, which is the rate-determining step.

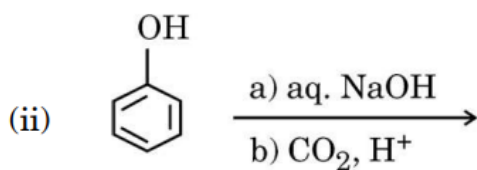
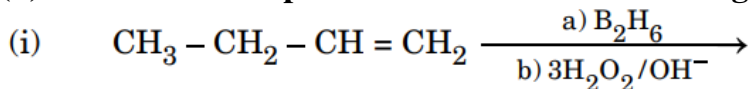


Step 3: Formation of ethene by elimination of a proton (Fast step) The carbocation formed in Step 2 loses a proton to form ethene.

Thus, the overall reaction is:



(b) Write the main product in each of the following reactions:



Solution: For the given reactions:

- (i) The oxidation of the hydroboration product with hydrogen peroxide (H_2O_2) and hydroxide (OH^-) leads to the formation of a diol.

The main product will be ($\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_2\text{OH}$), 1-propanol.

- (ii) Phenol ($\text{C}_6\text{H}_5\text{OH}$) reacts with aqueous NaOH to form phenoxide ion ($\text{C}_6\text{H}_5\text{O}^-$). When phenol reacts with CO_2 in the presence of H^+ , it undergoes carboxylation to form salicylic acid (2-hydroxybenzoic acid).

Main product: Salicylic acid ($\text{C}_6\text{H}_4(\text{OH})\text{COOH}$)

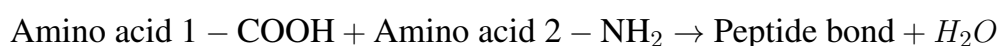
Quick Tip

In reactions of alcohols and phenols, the product formation can be understood by considering the reactivity of the hydroxyl group (-OH) with reagents such as borane, hydrogen peroxide, or carboxylic acids.

27. Answer the following: (any three)

(a) What is peptide linkage?

Solution: A peptide linkage is a covalent bond that joins two amino acids through the carboxyl group ($-COOH$) of one amino acid and the amino group ($-NH_2$) of another, forming a $-CONH-$ bond. This reaction results in the elimination of water (H_2O) and is known as a peptide bond.



(b) What type of bonds hold a DNA double helix together?

Solution: The DNA double helix is held together primarily by hydrogen bonding between the complementary nitrogenous bases. The adenine (A) base forms two hydrogen bonds with thymine (T), and guanine (G) forms three hydrogen bonds with cytosine (C). These hydrogen bonds are essential for the stability of the double helix structure of DNA.

(c) Which one of the following is a polysaccharide? Sucrose, Glucose, Starch, Fructose

Solution: The correct answer is starch. Starch is a polysaccharide composed of long chains of glucose molecules. It serves as a storage carbohydrate in plants. Sucrose and fructose are monosaccharides or disaccharides, and glucose is a monosaccharide.

(d) Give one example each for water-soluble vitamins and fat-soluble vitamins.

Solution: - Water-soluble vitamins: Vitamin B and Vitamin C. - Fat-soluble vitamins: Vitamin A, D, E, K. These vitamins are classified based on their solubility, with water-soluble vitamins dissolving in water and fat-soluble vitamins dissolving in fats and oils.

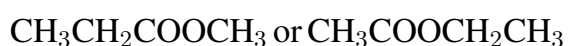
Quick Tip

- Peptide bonds form the backbone of proteins. - Hydrogen bonds are weak but critical for stabilizing the structure of DNA. - Starch is a major energy storage polysaccharide in plants. - Water-soluble vitamins are essential for metabolic processes, while fat-soluble vitamins are stored in fat tissues.

28. Compound (A) ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ gives two compounds (B) and (C). The compound (B) on oxidation with PCC gives compound (D) which upon treatment with dilute NaOH and subsequent heating gives compound (E). Compound (E) on catalytic hydrogenation gives compound (C). The compound (D) is oxidized further to give compound (F) which is found to be a monobasic acid (Molecular weight = 60). Identify the compounds (A), (B), (C), (D), (E) and (F).

Solution:

Identifying Compound (A) The molecular formula of compound (A) is $C_6H_{12}O_2$, which could be either a carboxylic acid or an ester. Upon reduction with $LiAlH_4$, it gives two compounds, indicating the presence of both a carboxyl group and an ester group in compound (A). The most likely structure of compound (A) is ethyl acetate ($CH_3COOCH_2CH_3$).



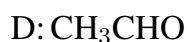
Identifying Compound (B) Upon reduction with $LiAlH_4$, compound (A) gives compound (B), which is likely ethanol (CH_3CH_2OH).



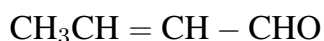
Identifying Compound (C) Upon reduction with $LiAlH_4$, compound (B) (acetaldehyde) gets reduced to propyl alcohol ($CH_3CH_2CH_2OH$). $LiAlH_4$ is a strong reducing agent, typically used to reduce aldehydes to primary alcohols.



Identifying Compound (D) Compound (B) is ethanol ($\text{CH}_3\text{CH}_2\text{OH}$). When ethanol is oxidized using PCC (Pyridinium chlorochromate), it is converted to acetaldehyde (CH_3CHO). This reaction is typical for primary alcohols, where mild oxidants like PCC prevent further oxidation to carboxylic acids.



Identifying Compound (E) Upon catalytic hydrogenation of acetaldehyde (CH_3CHO), acrolein ($\text{CH}_3\text{CH}=\text{CHCHO}$) is formed. This reaction involves the reduction of the carbonyl group in acetaldehyde into an alkene group while keeping the aldehyde functional group intact.



Identifying Compound (F) Upon further oxidation of acrolein ($\text{CH}_3\text{CH}=\text{CHCHO}$), acetic acid (CH_3COOH) is produced. This is a common reaction where aldehydes undergo oxidation to form carboxylic acids.



Quick Tip

- Reduction with LiAlH_4 reduces ester and carboxyl groups to alcohols. - Oxidation with PCC selectively oxidizes alcohols to aldehydes. - Hydrogenation reduces aldehydes to alcohols.

SECTION D

The following questions are case-based questions. Read the case carefully and answer the questions that follow.

29. Batteries and fuel cells are very useful forms of galvanic cells. Any battery or cell that we use as a source of electrical energy is basically a galvanic cell. However, for a battery to be of practical use, it should be reasonably light, compact, and its voltage should not vary appreciably during its use. There are mainly two types of batteries — primary batteries and secondary batteries.

In primary batteries, the reaction occurs only once and after use over a period of time, the battery becomes dead and cannot be reused again, whereas the secondary batteries are rechargeable.

Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. To solve this problem, galvanic cells are designed in such a way that energy of combustion of fuels is directly converted into electrical energy, and these are known as fuel cells. One such fuel cell was used in the Apollo space program.

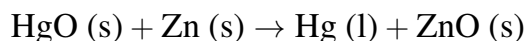
Answer the following questions:

(a) How do primary batteries differ from secondary batteries?

Solution: Primary batteries are not rechargeable, meaning that once the chemical reaction has taken place, the battery cannot be reused. An example is the common alkaline battery, where the zinc undergoes oxidation and the manganese dioxide undergoes reduction, and once the reactants are exhausted, the battery is dead. On the other hand, secondary batteries are rechargeable. For example, a lead-acid battery is a secondary battery where the reaction is reversible, allowing the battery to be recharged by reversing the flow of current.

(b) The cell potential of the Mercury cell is 1.35 V, and remains constant during its life. Give a reason.

Solution: The constant potential of the Mercury cell is due to the fact that the overall reaction does not involve any ion in solution whose concentration can change during the cell's life. The reaction is:

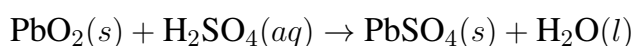


Since the concentration of solid zinc and mercury oxide remains constant throughout the process, the cell's potential remains stable at 1.35 V throughout the life of the battery.

(c) Write the reactions involved in the recharging of the lead storage battery.

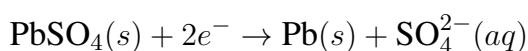
Solution: The lead storage battery undergoes the following reactions during discharging and recharging:

During discharging:

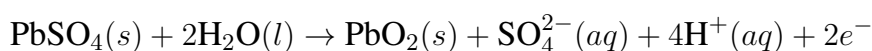


During recharging, the following reactions occur:

Cathode reaction:

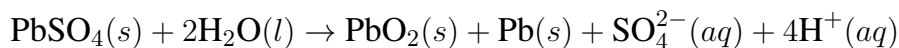


Anode reaction:



OR:

The overall reaction during recharging is:



Additional advantages of fuel cells over other galvanic cells:

- (i) Fuel cells are more efficient because they convert chemical energy directly into electrical energy without the need for mechanical processes, making them more efficient compared to thermal power generation.
- (ii) Fuel cells are pollution-free because they produce only water and heat as byproducts, unlike other batteries or power sources that release harmful gases such as CO₂.

Quick Tip

Primary batteries are single-use, non-rechargeable batteries, while secondary batteries are rechargeable due to reversible reactions. Fuel cells convert energy from combustion into electrical energy and are more efficient and environmentally friendly than conventional methods.

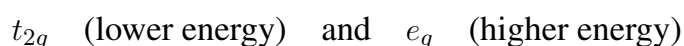
30. The Valence Bond Theory (VBT) explains the formation, magnetic behaviour and geometrical shapes of coordination compounds whereas 'The Crystal Field Theory' for coordination compounds is based on the effect of different crystal fields (provided by ligands taken as point charges), on the degeneracy of d-orbital energies of the central metal atom/ion. The splitting of the d-orbitals provides different electronic arrangements in strong and weak crystal fields. The crystal field theory attributes the colour of the coordination compounds to d-d transition of the electron. Coordination compounds find extensive applications in metallurgical processes, analytical and medicinal chemistry.

Answer the following questions:

(a). What is crystal field splitting energy?

Solution: The energy used in the splitting of degenerate d-orbitals due to the presence of ligands in a definite geometry is called Crystal Field Splitting Energy.

Step 1: Understanding Crystal Field Splitting Energy When ligands approach a transition metal ion, the degeneracy of the d-orbitals is lifted due to electrostatic interactions, causing them to split into two sets of orbitals:



The energy difference between these orbitals is called Crystal Field Splitting Energy (Δ).

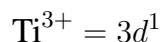
Quick Tip

Crystal Field Splitting Energy (Δ) depends on: - The nature of the ligand (strong field or weak field). - The oxidation state of the metal ion. - The geometry of the complex (octahedral, tetrahedral, square planar).

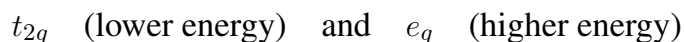
(b). Give reason for the violet colour of the complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ on the basis of crystal field theory.

Solution: The violet colour arises due to the d-d electronic transition within the split d-orbitals.

Step 1: Electronic Configuration of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ For Ti^{3+} , the electronic configuration is:



Step 2: Crystal Field Splitting and d-d Transition In an octahedral field, the d-orbitals split into:



Since Ti^{3+} has one electron, it occupies the t_{2g} orbital as:



Step 3: Cause of Violet Colour When visible light is absorbed, the electron gets excited from the t_{2g} to the e_g orbital, causing a d-d transition. The observed colour (violet) is due to the complementary colour of the absorbed wavelength.

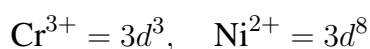
Quick Tip

The colour of transition metal complexes is due to d-d transitions. The nature of ligands and the splitting energy Δ determine the observed colour.

(c). $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is paramagnetic while $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic. Explain why.

Solution: $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is paramagnetic due to unpaired electrons, while $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic due to electron pairing.

Step 1: Electronic Configuration of Cr^{3+} and Ni^{2+}



Step 2: Effect of Ligands on Magnetic Properties - NH_3 is a weak field ligand, so it does not cause electron pairing in $[\text{Cr}(\text{NH}_3)_6]^{3+}$, leaving unpaired electrons in the t_{2g} orbitals. - CN^- is a strong field ligand, so it pairs electrons in $[\text{Ni}(\text{CN})_4]^{2-}$, making it diamagnetic.

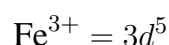
Quick Tip

- Strong field ligands like CN^- cause pairing of electrons, leading to diamagnetic behaviour. - Weak field ligands like NH_3 do not cause pairing, leading to paramagnetism.

OR (c) Explain why $[\text{Fe}(\text{CN})_6]^{3-}$ is an inner orbital complex, whereas $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is an outer orbital complex.

Correct Answer: $[\text{Fe}(\text{CN})_6]^{3-}$ is an inner orbital complex due to strong ligand-induced pairing, whereas $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is an outer orbital complex due to weak ligand-induced hybridization.

Solution: Step 1: Electronic Configuration of Fe^{3+}



Step 2: Effect of Ligands on Hybridization - CN^- is a strong field ligand, causing electron pairing and leading to d^2sp^3 hybridization (inner orbital complex). - H_2O is a weak field ligand, preventing electron pairing and leading to sp^3d^2 hybridization (outer orbital complex).

Quick Tip

- Inner orbital complexes involve d^2sp^3 hybridization with strong ligands. - Outer orbital complexes involve sp^3d^2 hybridization with weak ligands.

SECTION E

31(a)(i). At the same temperature, CO_2 gas is more soluble in water than O_2 gas. Which one of them will have a higher value of K_H and why?

Solution: O_2 gas has a higher K_H value because a higher K_H means lower solubility of the gas in liquid.

Step 1: Understanding Henry's Law Constant (K_H) Henry's law states that:

$$C = K_H P$$

where C is the concentration of the gas in liquid, K_H is Henry's law constant, and P is the partial pressure of the gas.

Step 2: Relationship Between K_H and Solubility

$$K_H \propto \frac{1}{\text{Solubility of Gas}}$$

Since CO_2 is more soluble in water than O_2 , it has a lower K_H value. Thus, O_2 has a higher K_H .

Quick Tip

- A higher K_H means lower solubility of the gas. - A lower K_H means higher solubility of the gas.

(ii). How does the size of blood cells change when placed in an aqueous solution containing more than 0.9% (mass/volume) sodium chloride?

Solution: Blood cells shrink.

Step 1: Understanding Hypertonic Solutions A solution with more than 0.9% NaCl is hypertonic compared to the fluid inside blood cells.

Step 2: Effect on Blood Cells Due to osmosis, water moves out of the blood cells into the hypertonic solution to balance the concentration gradient. This leads to shrinking (crenation) of blood cells.

Quick Tip

- Hypertonic solution: Water leaves the cell, causing shrinkage. - Hypotonic solution: Water enters the cell, causing swelling.

(iii). 1 molal aqueous solution of an electrolyte A_2B_3 is 60% ionized. Calculate the boiling point of the solution.

Solution: $T_b = 374.768$ K (or 374.918 K if considering the boiling point of water as 373.15 K)

Step 1: Boiling Point Elevation Formula The boiling point elevation is given by:

$$\Delta T_b = iK_b m$$

where, $K_b = 0.52 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1}$ (for water), $m = 1 \text{ molal}$, $i = \text{van't Hoff factor}$.

Step 2: Calculation of Van't Hoff Factor The dissociation of A_2B_3 is:



Total particles before dissociation = 1, Total particles after dissociation = 5. Degree of ionization α is given as 60% (0.6).

$$i = 1 + \alpha(n - 1)$$

$$i = 1 + 0.6(5 - 1)$$

$$i = 1 + 2.4 = 3.4$$

Step 3: Calculate Boiling Point Elevation

$$\Delta T_b = 3.4 \times 0.52 \times 1$$

$$\Delta T_b = 1.768 \text{ K}$$

$$T_b = 373 + 1.768 = 374.768 \text{ K}$$

If the boiling point of water is taken as 373.15 K,

$$T_b = 373.15 + 1.768 = 374.918 \text{ K}$$

Quick Tip

- The van't Hoff factor (i) accounts for the number of particles formed in solution. - A higher i results in a greater elevation in boiling point. - Electrolytes with higher ionization lead to larger ΔT_b .

OR

31(b)(i). The vapour pressures of A and B at 25°C are 75 mm Hg and 25 mm Hg, respectively. If A and B are mixed such that the mole fraction of A in the mixture is 0.4, then calculate the mole fraction of B in the vapour phase.

Solution: The mole fraction of B in the vapour phase is 0.33

Step 1: Calculate Total Vapour Pressure Using Raoult's Law,

$$P_T = P_A^0 X_A + P_B^0 X_B$$

Substituting values:

$$P_T = (75 \times 0.4) + (25 \times 0.6)$$

$$P_T = 30 + 15 = 45 \text{ mm Hg}$$

Step 2: Calculate Partial Pressure of B

$$P_B = y_B \times P_T$$

$$y_B = \frac{P_B}{P_T} = \frac{P_B^0 X_B}{P_T}$$

$$y_B = \frac{(25 \times 0.6)}{45} = \frac{15}{45} = \frac{1}{3} = 0.33$$

Quick Tip

- Raoult's Law: The partial vapour pressure of each component in an ideal solution is proportional to its mole fraction. - The component with a lower vapour pressure contributes less to the total vapour pressure.

(ii). Define colligative property. Which colligative property is preferred for the molar mass determination of macromolecules?

Solution: A colligative property depends only on the number of solute particles and not on their nature. Osmotic pressure is the preferred colligative property for molar mass determination of macromolecules.

Step 1: Definition of Colligative Property Colligative properties are solution properties that depend only on the concentration of solute particles and not on their identity.

Examples of Colligative Properties: - Relative lowering of vapour pressure - Boiling point elevation - Freezing point depression - Osmotic pressure

Step 2: Why Osmotic Pressure is Preferred for Macromolecules? - Osmotic pressure ($\pi = CRT$) is highly sensitive to small concentrations, making it ideal for determining the

molar mass of macromolecules like proteins and polymers. - Unlike boiling point elevation or freezing point depression, osmotic pressure is measurable at room temperature, preventing thermal degradation of macromolecules.

Quick Tip

- Colligative properties depend on the number of solute particles, not their identity.
- Osmotic pressure is preferred for macromolecules due to its high sensitivity and suitability at room temperature.

(iii) Why are equimolar solutions of sodium chloride and glucose not isotonic?

Answer: Sodium chloride undergoes dissociation ($i = 2$) in water, while glucose does not ($i = 1$). The osmotic pressure is given by:

$$\pi = iCRT$$

For NaCl, $i = 2$, and for glucose, $i = 1$. Therefore, equimolar solutions of NaCl and glucose do not have the same osmotic pressure and are not isotonic.

Quick Tip

The van 't Hoff factor (i) plays a crucial role in determining osmotic pressure. For ionic compounds like NaCl, i is greater than 1 due to dissociation, whereas for non-electrolytes like glucose, $i = 1$.

32(a). N,N-diethylbenzenesulphonamide is insoluble in alkali. Give reason.

Solution: N,N-diethylbenzenesulphonamide does not contain any hydrogen atom attached to nitrogen, making it non-acidic and thus insoluble in alkali.

Step 1: Understanding the Nature of N,N-Diethylbenzenesulphonamide - In order for a compound to dissolve in alkali, it must have an acidic hydrogen atom that can react with OH^- .

Step 2: Why It Is Insoluble - Sulphonamides that contain a hydrogen attached to nitrogen are acidic and dissolve in alkali. - However, in N,N-diethylbenzenesulphonamide, both hydrogen atoms on nitrogen are replaced by ethyl groups, making it non-acidic and hence, insoluble in alkali.

Quick Tip

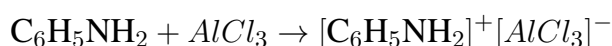
- Only acidic compounds dissolve in alkali. - The absence of an acidic hydrogen makes a compound insoluble in bases.

(b). Aniline does not undergo Friedel-Crafts reaction. Why?

Solution: Due to salt formation with $AlCl_3$, aniline becomes a Lewis base, deactivating the benzene ring.

Step 1: Role of Lewis Acid Catalyst in Friedel-Crafts Reaction - Friedel-Crafts alkylation and acylation require a Lewis acid catalyst like $AlCl_3$ to generate the electrophile.

Step 2: Interaction Between Aniline and $AlCl_3$ - Aniline ($C_6H_5NH_2$) has a lone pair on nitrogen, which interacts with $AlCl_3$, forming a salt.



- This deactivates the benzene ring, making it less reactive toward electrophilic substitution.

Step 3: Conclusion Due to this salt formation, aniline does not undergo Friedel-Crafts reaction.

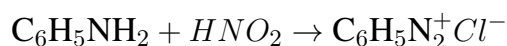
Quick Tip

- $AlCl_3$ forms a salt with aniline, deactivating the benzene ring. - Electrophilic substitution is hindered, preventing Friedel-Crafts reaction.

(c). Write a simple chemical test to distinguish between methylamine and aniline.

Correct Answer: Diazotization Test: Aniline forms a diazonium salt, which gives an orange dye with phenol, whereas methylamine does not.

Solution: Step 1: Diazotization of Aniline - Aniline reacts with nitrous acid (HNO_2) at low temperature ($0-5^\circ C$) to form benzene diazonium chloride.



Step 2: Coupling Reaction with Phenol - The diazonium salt reacts with phenol to form an orange dye. - Methylamine (CH_3NH_2) does not undergo diazotization and does not form the orange dye.

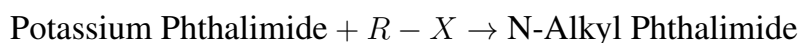
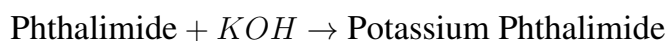
Quick Tip

- Aniline undergoes diazotization and forms a coloured dye. - Methylamine does not form a diazonium salt.

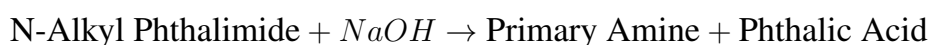
(d). Write the chemical reaction involved in Gabriel phthalimide synthesis.

Solution: Gabriel phthalimide synthesis is used for the preparation of primary amines.

Step 1: Formation of N-Alkyl Phthalimide



Step 2: Hydrolysis to Form Primary Amine



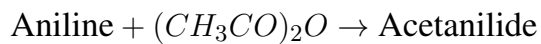
Quick Tip

- Gabriel Phthalimide Synthesis is specific for primary amines. - Secondary and tertiary amines are not formed in this reaction.

(e). How will you convert aniline to p-bromoaniline?

Solution: Aniline is acetylated, then brominated, and finally hydrolyzed to obtain p-bromoaniline.

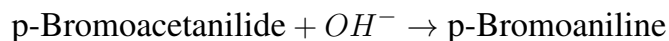
Step 1: Acetylation of Aniline



Step 2: Bromination of Acetanilide



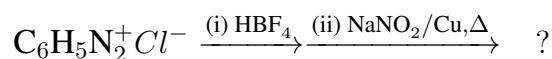
Step 3: Hydrolysis to p-Bromoaniline



Quick Tip

- Direct bromination of aniline gives both ortho and para isomers. - Acetylation controls the reaction to favor p-bromoaniline.

(f). Complete the following reaction:

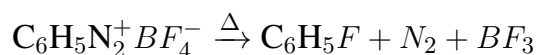


Solution: The given reaction follows the Sandmeyer and Balz-Schiemann reactions, leading to the formation of fluorobenzene and nitrobenzene.

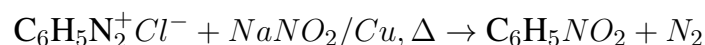
Step 1: Balz-Schiemann Reaction (Fluorination) The first step involves treating benzene diazonium chloride with HBF_4 , forming benzene diazonium tetrafluoroborate.



On heating, it decomposes to form fluorobenzene:



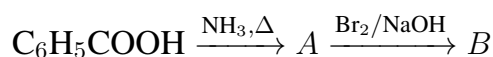
Step 2: Sandmeyer Reaction (Nitration) The second step involves treating benzene diazonium chloride with NaNO_2/Cu , which replaces diazonium with a nitro ($-\text{NO}_2$) group, forming nitrobenzene.



Quick Tip

- The Balz-Schiemann reaction is used to introduce fluorine into the benzene ring. - The Sandmeyer reaction is used to introduce nitro ($-\text{NO}_2$) and other functional groups.

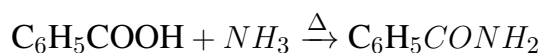
(g). Write the structures of A and B in the following reaction:



Solution: - A = Benzamide ($\text{C}_6\text{H}_5\text{CONH}_2$)

- B = Aniline ($\text{C}_6\text{H}_5\text{NH}_2$)

Step 1: Conversion of Benzoic Acid to Benzamide When benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) is heated with ammonia, it undergoes amide formation, forming benzamide ($\text{C}_6\text{H}_5\text{CONH}_2$).



Step 2: Hoffmann Bromamide Degradation When benzamide ($C_6H_5CONH_2$) reacts with $Br_2/NaOH$, the carbonyl ($-CO$) group is removed, leading to the formation of aniline ($C_6H_5NH_2$).



Quick Tip

- The Hoffmann Bromamide Reaction is used for amide to amine conversion by removing the carbonyl group. - This reaction reduces carbon count by 1, making it useful for amine synthesis.

33 (a) (i) Account for the following :

(1) The melting and boiling points of Zn, Cd, and Hg are low.

Correct Answer: The melting and boiling points of Zn, Cd, and Hg are low due to the absence of unpaired electrons in their d-orbitals, leading to weak metallic bonding between atoms.

Solution: Step 1: Electronic Configuration and Bonding - Zn, Cd, and Hg belong to Group 12 and have a completely filled d^{10} configuration. - The lack of unpaired d-electrons reduces the extent of metallic bonding, making these metals soft with low melting and boiling points.

Step 2: Weak Interatomic Forces - In transition metals, strong metallic bonding arises due to overlapping of d-orbitals. - However, in Zn, Cd, and Hg, fully filled d-orbitals do not contribute to bonding, resulting in weak interatomic forces and low melting/boiling points.

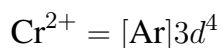
Quick Tip

- Fully filled d-orbitals weaken metallic bonding. - Strong metallic bonding requires unpaired d-electrons.

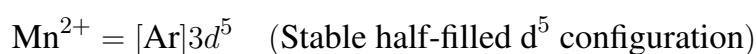
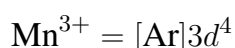
(2). Of the d^4 species, Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidizing.

Correct Answer: Cr^{2+} is strongly reducing because it tends to oxidize to the stable d^3 configuration in Cr^{3+} , while Mn^{3+} is strongly oxidizing as it prefers to reduce to the more stable d^5 configuration in Mn^{2+} .

Solution: Step 1: Electronic Configurations - Chromium (Cr):



- Manganese (Mn):



Step 2: Explanation - Cr^{2+} loses an electron easily to form Cr^{3+} (stable d^3), making it a strong reducing agent. - Mn^{3+} readily gains an electron to form Mn^{2+} (stable d^5), making it a strong oxidizing agent.

Quick Tip

- Stable electronic configurations drive oxidation/reduction tendencies. - Cr^{2+} prefers oxidation to d^3 , Mn^{3+} prefers reduction to d^5 .

(3). E^0 value of Cu^{2+}/Cu is +0.34 V.

Correct Answer: The high atomization enthalpy (ΔH_{atom}^0) and low hydration enthalpy (ΔH_{hydr}^0) of copper make its standard reduction potential (E^0) positive.

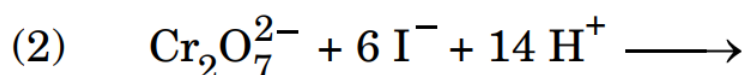
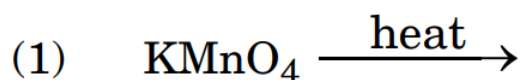
Solution: Step 1: Explanation of E^0 Value - The electrode potential (E^0) depends on: - Atomization enthalpy (ΔH_{atom}^0): The energy required to convert solid Cu to Cu^{2+} is high. - Hydration enthalpy (ΔH_{hydr}^0): Cu^{2+} has low hydration energy, making it less stable in aqueous solution.

Step 2: Effect on E^0 Value - Due to low hydration enthalpy, the reduction of Cu^{2+} to Cu is not highly favored. - Hence, Cu^{2+}/Cu has a positive E^0 value of +0.34 V, indicating that Cu is less reactive than expected.

Quick Tip

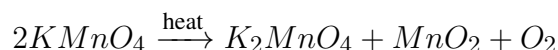
- High atomization enthalpy and low hydration enthalpy make $\text{Cu}^{2+} \rightarrow \text{Cu}$ less favorable, giving a positive E^0 value.

(ii) Complete and balance the following chemical equations:

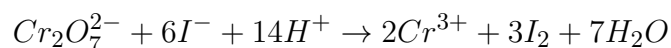


Explanation:

(1): Thermal decomposition of Potassium Permanganate (KMnO_4) - On heating, potassium permanganate (KMnO_4) decomposes to form potassium manganate (K_2MnO_4), manganese dioxide (MnO_2), and oxygen gas (O_2). - This reaction is used in laboratories as a source of oxygen.



(2): Redox Reaction of Dichromate and Iodide in Acidic Medium - Dichromate ($\text{Cr}_2\text{O}_7^{2-}$) acts as an oxidizing agent and oxidizes iodide (I^-) to iodine (I_2) in acidic medium. - The chromium in dichromate is reduced from Cr^{6+} to Cr^{3+} . - The reaction follows the principles of redox balancing, maintaining charge and mass balance.



Quick Tip

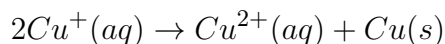
- KMnO_4 decomposition is a key reaction in the production of oxygen in labs. - Dichromate-Iodide reaction is a classic redox reaction where Cr^{6+} is reduced, and I^- is oxidized to I_2 . - Always balance chemical equations by ensuring both mass and charge conservation.

(b)

(i) Out of Cu_2Cl_2 and CuCl_2 , which is more stable in aqueous solution and why?

Solution: CuCl_2 is more stable than Cu_2Cl_2 in aqueous solution because Cu^{2+} is more stable than Cu^+ due to its higher hydration enthalpy ($\Delta_{\text{hyd}}H^\circ$).

In aqueous solution, Cu^+ undergoes disproportionation, as shown in the equation:



(ii) Write the general electronic configuration of f-block elements.

Solution: The general electronic configuration of f-block elements is:

$$(n-2)f^{1-14}(n-1)d^{0-1}ns^2$$

(iii) Predict which of the following will be coloured in aqueous solution and why?

Sc^{3+} , Fe^{3+} , Zn^{2+}

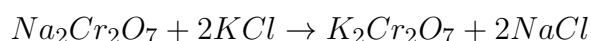
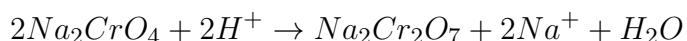
[Atomic numbers: Sc = 21, Fe = 26, Zn = 30]

Solution: Among the given ions, Fe^{3+} is coloured in aqueous solution because it has unpaired electrons in its d-orbital, which allows d-d transitions.

On the other hand: - Sc^{3+} has an empty d-orbital (d^0 configuration), so no d-d transition occurs → Colourless. - Zn^{2+} has a fully filled d-orbital (d^{10} configuration), so no d-d transition occurs → Colourless.

(iv) How can you obtain potassium dichromate from sodium chromate?

Solution: Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) can be obtained from sodium chromate (Na_2CrO_4) through the following reactions:



(v) Why do transition metals and their compounds show catalytic activities?

Solution: Transition metals and their compounds show catalytic activity because: - They can exhibit variable oxidation states, allowing them to form intermediate complexes during reactions. - They can adsorb reactants onto their surface, increasing reaction rates. - Their large surface area provides active sites for catalytic activity.

Quick Tip

- Cu^+ undergoes disproportionation, making CuCl_2 more stable in aqueous solution.
- Fe^{3+} is coloured due to d-d transitions, whereas Sc^{3+} and Zn^{2+} are colourless.
- Potassium dichromate is obtained from sodium chromate via acidification and reaction with KCl.
- Transition metals act as catalysts due to variable oxidation states and large surface area.