Code No. 043

Roll No. ☐☐☐☐☐☐☐

- Please check that this question paper contains **5** printed pages.
- Code number given on the right hand side of the question paper should be written on the title page of the answer-book by the candidate.
- Please check that this question paper contains **33** questions.
- **Please write down the Serial Number of the question before attempting it.**
- 15 minutes time has been allotted to read this question paper. The question paper will be distributed at 10.15 a.m. From 10.15 a.m. to 10.30 a.m., the students will read the question paper only and will not write any answer on the answer-book during this period.

CHEMISTRY–XII

Sample Paper (Solved)

Time allowed: 3 hours *Maximum Marks: 70*

General Instructions:

SECTION A (Objective Type)

1. **Read the passage given below and answer the following questions:** **(1×4=4)**

An iron (III) hydroxide sol can be made to aggregate by the addition of an ionic solution, particularly if the solution contains anions with multiple charges (such as phosphate ions PO_4^{3-}).

Coagulation is the process by which the dispersed phase of a colloid so made to aggregate and thereby separate from the continuous phase.

(*i*) **Colloidal sulphur particles are negatively charged with thiosulfate ions, $S_2O_3^{2-}$, and other ions on the surface of the sulphur. Indicate which of the following could be most effective in coagulating colloidal sulphur.**

(*a*) NaCl (*b*) KCl (*c*) $MgCl_2$ (*d*) $Al_2(SO_4)_3$

(*ii*) **Which of the following ions is most effective in the coagulation of ferric hydroxide sol?**

(*a*) Cl^- (*b*) Br^- (*c*) NO_2^- (*d*) SO_4^{2-}

Or

Which of the following electrolytes will have maximum coagulating value for AgI/Ag$^+$ sol?

(*a*) Na_2S (*b*) Na_3PO_4 (*c*) Na_2SO_4 (*d*) NaCl

(*iii*) **Which of the following anions will have maximum flocculation value for the ferric oxide solution?**

(*a*) Cl^- (*b*) Br^- (*c*) SO_4^{2-} (*d*) $[Fe(CN)_6]^{3-}$

(*iv*) **Which of the following solutions is negatively charged?**

(*a*) Arsenious sulphide (*b*) Aluminium hydroxide

(*c*) Ferric hydroxide (*d*) Silver iodide in $AgNO_3$ solution

2. **Read the passage given below and answer the following questions.**

Since the carbonyl group is polar, since oxygen being more electronegative than carbon, has a greater share of electrons of the double bond. Because of the partial positive charge of the carbonyl carbon, carbonyl compounds are attacked by nucleophiles. Aldehydes are more reactive towards nucleophilic attack than are ketones, because alkyl groups are electron releasing compared to hydrogen. An aldehyde has a greater partial positive charge on its carbonyl carbon, making it more susceptible to attack by a nucleophile. Steric factor also contributes to the greater reactivity of the aldehyde compared with a ketone, because the hydrogen attached to the acyl group of an aldehyde group is smaller than the alkyl group attached to the acyl group of a ketone.

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*a*) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(*b*) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(*c*) Assertion is correct statement but reason is wrong statement.
(*d*) Assertion is wrong statement but reason is correct statement.

(*i*) ***Assertion:*** Aldehydes are more reactive than corresponding ketone for Nucleophilic reactions.
Reason: Due to electron density at functional group carbon which is higher in ketone than in Aldehyde.

(*ii*) ***Assertion:*** In Nucleophilic addition reaction Nucleophile attacks first.
Reason: Nucleophile is highly reactive for carbonyl compounds.

(*iii*) ***Assertion:*** HCHO is more reactive than CH_3COCH_3 towards nucleophilic addition reaction.
Reason: In CH_3COCH_3, $-CH_3$ shows –I effect.

(*iv*) ***Assertion:*** Aliphatic ketones are less reactive than aliphatic aldehyde.
Reason: Rate of electrophilic addition and substitution in aliphatic aldehydes is faster than aliphatic ketones.

Or

Assertion: Carbonyl compounds take part in nucleophillic addition reactions.
Reason: These reactions are initiated by nucleophillic attack at the electron deficient carbon atom.

Following questions (No. 3-11) are Multiple Choice Questions carrying 1 mark each:

3. Standard electrode potentials are

Fe^{2+}/Fe, $E° = -0.44$ V
Fe^{3+}/Fe^{2+} $E° = +0.77$ V

Fe^{2+}, Fe^{3+} and Fe blocks are kept together, then

(*a*) Fe^{3+} increases **(*b*)** Fe^{3+} decreases
(*c*) Fe^{2+}/Fe^{3+} remains unchanged **(*d*)** Fe^{2+} decreases

4. Which of the following set consists only of essential amino acids?

(*a*) Alanine, tyrosine, cysteine **(*b*)** Leucine, lysine, tryptophan
(*c*) Alanine, glutamine, lysine **(*d*)** Leucine, proline, glycine

Or

Glucose molecule reacts with X number of molecules of phenylhydrazine to yield osazone. The value of X is

(*a*) Three **(*b*)** four **(*c*)** one **(*d*)** four

5. In which mode of expression, the concentration of solution remains independent of temperature?

(*a*) Molarity **(*b*)** Normality **(*c*)** Formality **(*d*)** Molality

6. Lanthanide contraction is observed in

(*a*) Gd **(*b*)** At **(*c*)** Xe **(*d*)** Ac

Or

The correct order of ionic radii of γ^{3+}, La^{3+}, Eu^{3+} and Lu^{3+} is

(*a*) $\gamma^{3+} < La^{3+} < Eu^{3+} < Lu^{3+}$ **(*b*)** $Lu^{3+} < \gamma^{3+} < Eu^{3+} < La^{3+}$
(*c*) $Lu^{3+} < Eu^{3+} < La^{3+} < \gamma^{3+}$ **(*d*)** $La^{3+} < Eu^{3+} < Lu^{3+} < \gamma^{3+}$

7. Which of the following factor may be regarded as the main cause of lanthanide contraction?

(*a*) Poor shielding of one of the 4f-electrons by another in the subshell.
(*b*) Effective shielding of one of the 4f-electrons by another in the subshell.
(*c*) Poorer shielding of 5d electrons by 4f electrons.
(*d*) Greater shielding of 5d electrons by 4f electrons.

8. Which among the following complexes has square pyramidal geometry?

(*a*) tetracarbonyl nickel (0) **(*b*)** hexamminecobalt (II) nitrate
(*c*) pentacarbonyl iron (0) **(*d*)** Bis (acetylacetonato) oxovanadium (IV)

Or, **Which of the following statements is correct?**
(CFSE = Crystal Field Splitting Energy)

(*a*) Lower CFSE favours formation of low spin complex.
(*b*) Higher CFSE favours formation of high spin complex.
(*c*) A particular metal ion in a particular oxidation state can form either diamagnetic complexes or paramagnetic complexes only.
(*d*) t_{2g} orbitals are three-fold degenerate while e_g orbitals are two-fold degenerate.

9. **Which gives black precipitate on reaction with CS_2 followed by addition of $HgCl_2$?**

(*a*) $(CH_3)_3\ CNH_2$ (*b*) $(C_2H_5)_2\ NH_2$ (*c*) $(CH_3)_3\ N$ (*d*) all of these

Or, **When aniline is heated with conc. H_2SO_4 at 455-475 K, it forms**

(*a*) Aniline hydrogen sulphate (*b*) m-Aminobenzenesulponic acid
(*c*) Benzenesulphonic acid (*d*) Sulphanilic acid

10. **The end product 'C' in the following sequences of chemical reaction is**

$$CH_3COOH \xrightarrow{CaCO_3} A \xrightarrow{heat} B \xrightarrow{NH_2OH} C$$

(*a*) Acetaldehyde oxime (*b*) Formaldehyde oxime
(*c*) Methyl nitrate (*d*) Acetoxime

11. **How many unit cells are present in a cube-shaped ideal crystal of NaCl of mass 1.00 g?**
[Atomic mass : Na = 23, Cl = 35.5]

(*a*) 5.14×10^{21} (*b*) 1.21×10^{21} (*c*) 5.48×10^{21} (*d*) 2.57×10^{21}

In the following questions (Q. No. 12-16) a statement assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(*a*) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(*b*) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(*c*) Assertion is correct statement but reason is wrong statement.
(*d*) Assertion is wrong statement but reason is correct statement.

12. ***Assertion:*** D (+) – Glucose is dextrorotatory in nature.
Reason: 'D' represents its dextrorotatory nature.
13. ***Assertion:*** Nitrogen is less reactive than molecular oxygen.
Reason: The bond length of Nitrogen is shorter than that of oxygen.
14. ***Assertion:*** Molarity of a solution in liquid state changes with temperature.
Reason: The volume of a solution changes with change in temperature.

Or, ***Assertion:*** 1 M solution of glucose has lower depression in freezing point than 0.1 M solution of urea.
Reason: K_f for both glucose and urea are different.

15. ***Assertion:*** Lower aldehydes and ketones are soluble in water but the solubility decreases as the molecular masses increase.
Reason: Distinction between aldehydes and ketones can be made by Tollen's reagent.
16. ***Assertion:*** The boiling point of alcohol is higher than hydrocarbons of comparable molecular mass.
Reason: Alcohols show intramolecular hydrogen bonding.

SECTION B

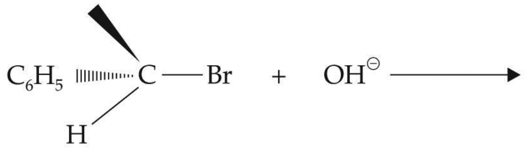
The following questions, Q. No. 17-25 are Short Answer Type I and carry 2 marks each.

17. **Explain why—**

(*i*) the melting point of *p*-dichlorobenzene is higher than *m*-dichlorobenzene?
(*ii*) Grignard reagents should be prepared under anhydrous conditions?

Or

Write the products formed and the steps involved in the following reaction:



Identify the mechanism involved in the above reaction.

18. Will the elevation in boiling point be same if 0.1 mol of Sodium chloride or 0.1 mol of sugar is dissolved in 1 L of water? Explain.

19. (*a*) What is the effect of synergic bonding interactions in a metal carbonyl complex?

(*b*) A metal M combines with the ligand L to form two different complexes namely ML_4 and ML_6. The colours of the two complexes are different. Comment.

Or

The two complexes of nickel, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$, have different structures but possess same magnetic behaviour. Explain.

20. **For the reaction:** $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$.

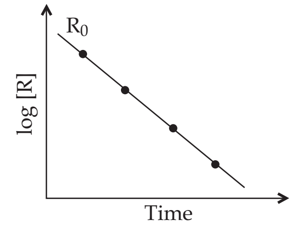
Rate = $k[C_{12}H_{22}O_{11}]$. How is the reaction classified on the basis of order of reaction?

Or

Observe the graph and answer the following questions:

(*a*) If slope is equal to -2.0×10^{-6} sec^{-1}, what will be the value of rate constant?

(*b*) How does the half-life of zero under reaction relate to its rate constant.



21. Rate constant K for first order reaction has been found to be 2.54×10^{-3} sec^{-1}. Calculate its three-fourth life.

22. Haloalkanes undergo nucleophilic substitution whereas haloarenes undergo electrophilic substitution. Explain.

23. **What happens when:**

(*i*) A xenon fluoride is treated with fluoride ion donor?

(*ii*) Sodium azide is thermally decomposed?

24. **How are the following conversions carried out?**

(*i*) Benzyl chloride to benzyl alcohol,

(*ii*) Methyl magnesium bromide to 2-methyl-propan-2-ol.

25. An element occurs in the bcc structure with cell edge of 288 pm. The density of the element is 7.2 g cm^{-3}. How many atoms of the element does 208 g of the element contain?

SECTION C

Q. No. 26-30 are Short Answer Type II carrying 3 marks each.

26. **Name the following:**

(*a*) A transition metal which does not exhibit variation in oxidation state in its compounds.

(*b*) A compound where the transition metal is in the +7 oxidation state.

(*c*) A member of the lanthanoid series which is well known to exhibit +4 oxidation state.

Or, (*i*) For M^{2+}/M and M^{3+}/M^{2+} systems, E° values for some metals are as follows:

$Cr^{2+}/Cr = -0.9$ V　　$Cr^{3+}/Cr^{2+} = -0.4$ V
$Mn^{2+}/Mn = -1.2$ V　　$Mn^{3+}/Mn^{2+} = +1.5$ V
$Fe^{2+}/Fe = -0.4$ V　　$Fe^{3+}/Fe^{2+} = +0.8$ V

Use this data to comment upon—

— the stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} and Mn^{3+}.

— the ease with which iron can be oxidised as compared to the similar process for either Cr or Mn metals.

(*ii*) What can be inferred from the magnetic moment of the complex $K_4[Mn(CN)_6]$, Magnetic moment: 2.2 BM?

27. (*i*) **Illustrate the following reactions:**

(a) Hoffmann bromamide degradation reaction

(b) Coupling reaction

(*ii*) Write a chemical test to distinguish between aniline and ethylamine.

Or, (*a*) **Give reason for the following:**

(*i*) O-Toludine is more basic than aniline.

(*ii*) Tertiary amines do not undergo acetylation reaction.

(*b*) **Write the name reaction—**Hoffman bromamide reaction.

28. The edge length of a unit cell of a metal having molecular mass 75 g/mol is 5A° which crystallises in a cubic lattice. If the density is 2g/cc, then find the radius of the metal atom.

29. (*i*) Name the common types of secondary structure of proteins and give one point of difference.

(*ii*) Give *one* structural difference between amylose and amylopectin.

30. (*i*) **Complete the following chemical equations.**

(a) $NH_4Cl(aq.) + NaNO_2(aq.) \longrightarrow$ *(b)* $P_4 + 3NaOH + 3H_2O \longrightarrow$

(*ii*) Why is $Ka_2 << Ka_1$ for H_2SO_4 in water?

SECTION D

Q. No. 31 to 33 are Long Answer Type carrying 5 marks each.

31. (*a*) **Explain the following:**

(*i*) NF_3 is an exothermic compound whereas NCl_3 is not.

(*ii*) F_2 is most reactive of all the four common halogens.

(*b*) **Complete the following chemical equations:**

(*i*) $C + H_2SO_4 \text{ (conc)} \longrightarrow$ (*ii*) $Cl_2 + \underset{\text{(excess)}}{F_2} \longrightarrow$

Or

(*a*) **Account for the following:**

(*i*) The acidic strength decreases in the order $HCl > H_2S > PH_3$.

(*ii*) Tendency to form pentahalides decreases down the group in group 15 of the periodic table.

(*b*) **Complete the following chemical equations:**

(*i*) $XeF_2 + H_2O \longrightarrow$

(*ii*) $I_2 + \underset{\text{(conc)}}{HNO_3} \longrightarrow$

32. (*a*) Give the equation of reaction for the preparation of phenol from cumene.

(*b*) An alkoxide is a stronger base than hydroxide ion. Justify.

(*c*) **Carry out the following conversions:**

(*i*) Phenol to benzoquinone

(*ii*) Propanone to 2-Methylpropan-2-ol

(*iii*) Propene to propan-1-ol

Or

(*a*) Predict the major product of acid catalysed dehydration of 1-Methylcyclohexanol.

(*b*) You are given benzene, conc. H_2SO_4, NaOH and dil. HCl.
Write the preparation of henol using thesereagents.

(*c*) **Write the equation involved in the following reactions:**

(*i*) Reimer-Tiemannn reaction

(*ii*) Williamson ether synthesis

33. (*a*) State the law which helps to determine the limiting Molar conductivity of weak electrolyte.

(*b*) Calculate limiting molar conductivity of $CaSO_4$ (limiting molar conductivity of calcium and sulphate ions are 119.0 and 160.0 S cm^2 mol^{-1} respectively).

(*c*) Express the relation among the cell constant, the resistance of the solution in the cell and the conductivity of the solution. How is the conductivity of a solution related to its molar conductivity?

Or

(*a*) Define the term degree of dissociation. Write an expression that relates the molar conductivity of a weak electrolyte to its degree of dissociation.

(*b*) **For the cell reaction**

$$Ni_{(s)} \,|\, Ni^{2+}{}_{(aq)} \,||\, Ag^{+}{}_{(aq)} \,|\, Ag_{(s)}$$

Calculate the equilibrium constant at 25 °C. How much maximum work would be obtained by operation of this cell?

($E°_{Ni^2/Ni} = 0.25$ V and $E°_{Ag^+/Ag} = 0.80$ V)

Answer Sheet

SAMPLE PAPER

Code No. **043**

Roll No.

CHEMISTRY

SECTION A

1. **(*i*)** (*d*) $Al_2(SO_4)_3$ **(*ii*)** (*d*) SO_4^{2-} ***Or*** (*b*) Na_3PO_4 **(*iii*)** (*d*) $[Fe(CN)_6]^{3-}$
(*iv*) (*b*) Aluminium hydroxide

2. **(*i*)** **(*a*)** Assertion and reason both are correct statements and reason is correct explanation for assertion.
(*ii*) **(*c*)** Assertion is correct statement but reason is wrong statement.
(*iii*) **(*c*)** Assertion is correct statement but reason is wrong statement.
(*iv*) **(*c*)** Assertion is correct statement but reason is wrong statement.

Or

(*a*) Assertion and reason both are correct statements and reason is the correct explanation for assertion.

3. **(*b*)** Fe^{3+} decreases

4. **(*b*)** Leucine, lysine, tryptophan

Or

(*a*) Three

5. **(*d*)** Molality

6. **(*a*)** Gd

Or

(*b*) $Lu^{3+} < \gamma^{3+} < Eu^{3+} < La^{3+}$

7. **(*a*)** Poor shielding of one of the 4f-electrons by another in the subshell.

8. **(*d*)** Bis (acetylacetonato) oxovanadium (IV)

Or

(*d*) t_{2g} orbitals are three-fold degenerate while e_g orbitals are two-fold degenerate.

9. **(*a*)** $(CH_3)_3CNH_2$

Or

(*d*) Sulphanilic acid

10. **(*b*)** Formaldehyde oxime

11. **(*d*)** 2.57×10^{21}

12. **(*c*)** Assertion is correct statement but reason is wrong statement.

13. **(*a*)** Assertion and reason both are correct statements and reason is correct explanation for assertion.

14. **(*a*)** Assertion and reason both are correct statements and reason is correct explanation for assertion.

Or

(*c*) Assertion is correct statement but reason is wrong statement.

15. **(*b*)** Assertion and reason both are correct statements but reason is not correct explanation for assertion.

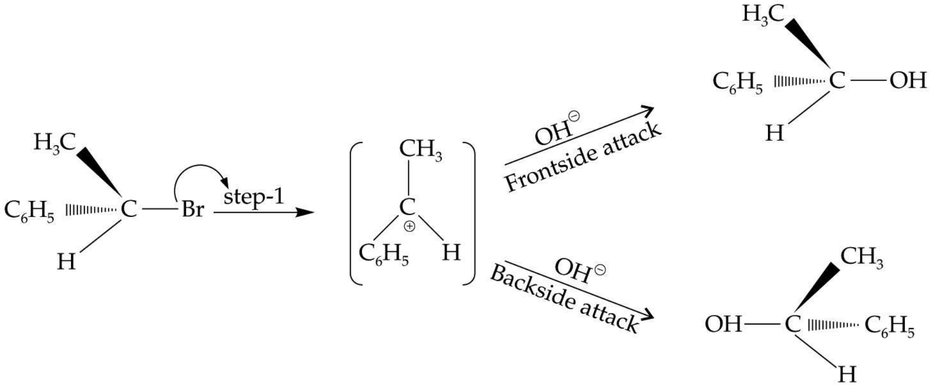
16. **(*c*)** Assertion is correct statement but reason is wrong statement.

SECTION B

17. **(*a*)** (*i*) It is due to symmetry of para-isomer that fits in crystal lattice better as compared to meta-isomer.

(*ii*) Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons.

(*b*) It will follow S_N1 mechanism as a benzyl carbocation is stable because of resonance.



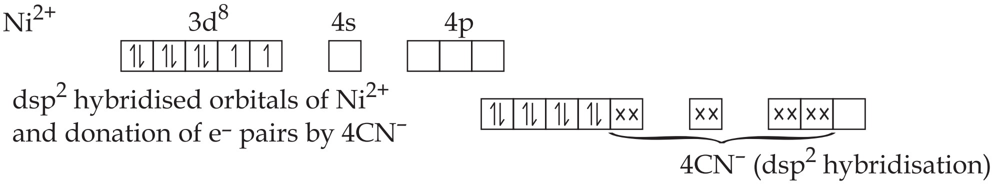
18. No, the elevation in boiling point is not the same. Elevation in boiling point is a colligative property which depends on the number of particles. NaCl is an ionic compound which dissociates in solution to give more number of particles whereas sugar is made up of molecules and thus does not dissociate.

19. **(*a*)** Synergic bonding interaction strengthens the bond between CO and metal.

(*b*) Δt is smaller than Δo. Less energy is absorbed by tetrahedral complexes which results in the colour difference.

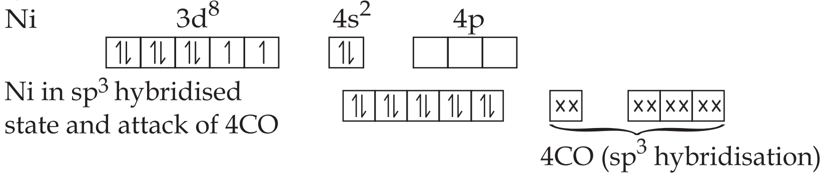
Or

In the complex, $[Ni(CN)_4]^{2-}$ Nickel is in + 2 oxidation state. Due to strong field CN^- ligand all electrons get paired and shows dsp^2 hybridisation with square planar geometry and diamagnetic character.



dsp^2 hybridised orbitals of Ni^{2+}
and donation of e^- pairs by $4CN^-$

In the case of $[Ni(CO)_4]$ Nickel is in zero oxidation state. Due to zero oxidation and strong field CO ligand all electrons get paired showing sp^3 hybridisation with tetrahedral geometry and diamagnetic character.



Ni in sp^3 hybridised
state and attack of 4CO

20. Pseudo first order reaction

Or

(*a*) Slope = $-\dfrac{k}{2.303}$

$k = -2.303 \times -2.0 \times 10^{-6}\ \text{sec}^{-1} = 4.606 \times 10^{-6}\ \text{sec}^{-1}$

(*b*) $t_{1/2} = \dfrac{[A]_0}{2k}$

For zero order reactions, the half-life depends on the initial concentration of reactant and the rate constant.

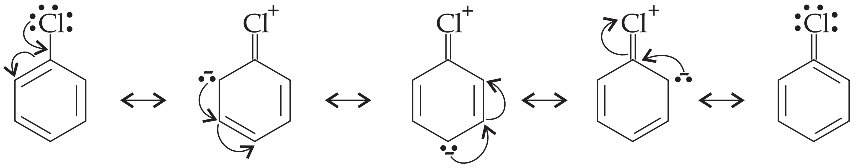
21. **Given:** $a = 1$, $K = 2.54 \times 10^{-3}\ \text{sec}^{-1}$, $x = 3/4$

$$K = \frac{2.303}{t}\log\frac{a}{a-x} \qquad \Rightarrow \quad t = \frac{2.303}{K}\log\frac{a}{a-x}$$

$$\Rightarrow \quad t_{3/4} = \frac{2.303}{2.54 \times 10^{-3}}\log\frac{1}{1-\frac{3}{4}}$$

$$\Rightarrow \quad t_{3/4} = 0.9066 \times 10^{3} \times 0.6021 \qquad \therefore \quad t_{3/4} = \mathbf{5.46 \times 10^{2}\ sec}$$

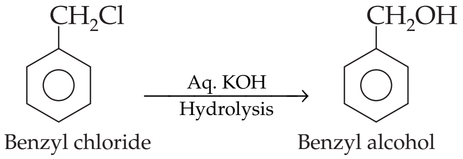
22. Haloarenes (say chlorobenzene) is a resonance hybrid of the following five structures :



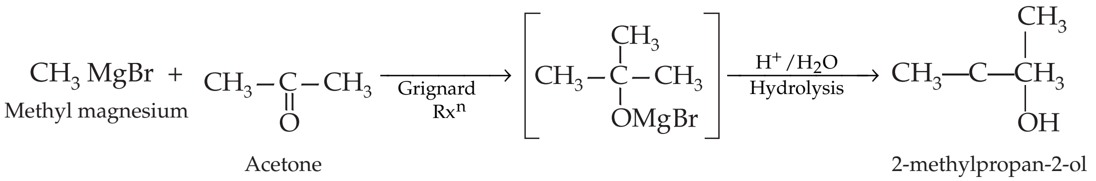
Resonance leads to lowering of energy and hence greater stability. On the other hand, no such resonance is possible in haloalkanes. Halogens directly attached to benzene ring are *o*, *p*-directing in electrophilic subsitution reactions. This is due to greater electron density at these positions in resonance.

23. (*i*) $XeF_6 + NaF \longrightarrow Na^+[XeF_7]^-$ (*ii*) $2NaN_3 \longrightarrow 2Na + 3N_2$

24. (*i*) Benzyl chloride to benzyl alcohol



(*ii*) Methyl magnesium bromide to 2-methylpropan-2-ol



$$\underset{\text{Methyl magnesium}}{CH_3MgBr} + \underset{\text{Acetone}}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3} \xrightarrow[\text{Rx}^n]{\text{Grignard}} \left[CH_3-\underset{OMgBr}{\overset{CH_3}{C}}-CH_3\right] \xrightarrow[\text{Hydrolysis}]{H^+/H_2O} \underset{\text{2-methylpropan-2-ol}}{CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3}$$

25. For the bcc structure, Z = 2

$$\text{Density, } \rho = \frac{Z \times M}{a^3 \times N_o}$$

$$7.2\ \text{g cm}^{-3} = \frac{2 \times M}{(288 \times 10^{-10}\ \text{cm})^3 \times (6.022 \times 10^{23})\ \text{mol}^{-1}}$$

or $M = 51.8\ \text{g mol}^{-1}$

By mole concept:

51.8 g of the element contains 6.022×10^{23} atoms

$\therefore$ 208 g of the element will contain = $\dfrac{6.022 \times 10^{23} \times 208}{51.8}$ = $\mathbf{24.17 \times 10^{23}}$ **atoms**

SECTION – C

26. **(*a*)** Scandium (Sc) **(*b*)** Potassium permangnate ($KMnO_4$)

(*c*) Cerium (Ce)

Or

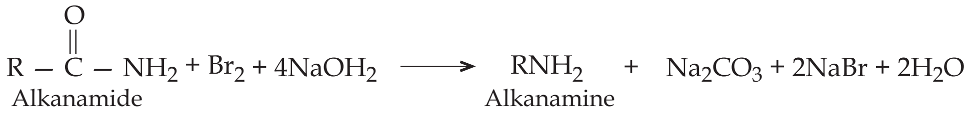
(*i*) **(*a*)** Cr^{3+}/Cr^{2+} has a negative reduction potential. Hence Cr^{3+} cannot be reduced to Cr^{2+}. Cr^{3+} is most stable. Mn^{3+}/Mn^{2+} has large positive E° values. Hence Mn^{3+} can be easily reduced to Mn^{2+}. Thus Mn^{3+} is least stable. Fe^{3+}/Fe^{2+} couple has a positive E° value but small. Thus the stability of Fe^{3+} is more than Mn^{3+} but less stable than Cr^{3+}.

(*b*) If we compare the reduction potential values, Mn^{2+}/Mn has the most negative value, *i.e.*, its oxidation potential value is most positive. Thus it is most easily oxidised. Thus the decreasing order for their ease of oxidation is Mn > Cr > Fe.

(*ii*) $K_4[Mn(CN)_6]$

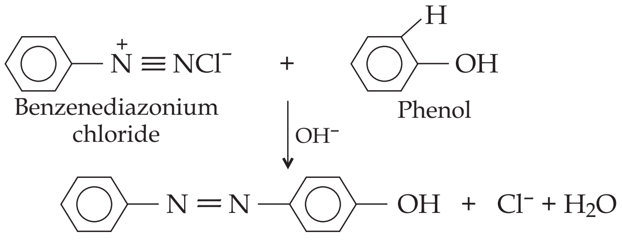
Mn is in +2 oxidation state. Magnetic moment 2.2 indicates that it has one unpaired electron and hence forms inner d-orbital or low spin complex. Hence, we can say that CN^- is a strong field ligand that causes the pairing of electrons. In presence of CN^- a strong ligand, hybridisation involved is d^2sp^3 (octahedral complex).

27. **(*i*)** **(*a*)** ***Hoffmann Bromamide Reaction:***



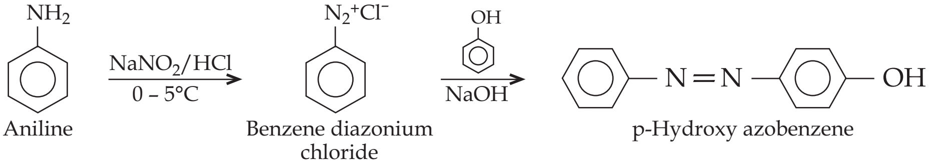
$$\underset{\text{Alkanamide}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + Br_2 + 4NaOH_2 \longrightarrow \underset{\text{Alkanamine}}{RNH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

(*b*) ***Coupling Reaction:***



4-Hydroxy azobenzene

(*ii*) Only Aniline, *i.e.*, a primary aromatic amine gives positive test for coupling reaction while ethylamine does not. Aniline reacts with benzene diazonium chloride in basic medium to give p-aminoazobenzene which is yellow in colour.

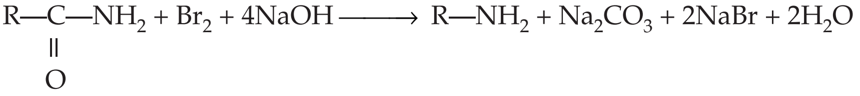


Or

(*a*) (*i*) Ortho-toludine is more basic than aniline due to the presence of electron releasing methyl group (+I effect) by which electron density at nitrogen of NH_2 in O-toludine increases.

(*ii*) Due to the absence of replaceable hydrogen atom at nitrogen, tertiary amines do not undergo acetylation reaction.

(*b*) **Hoffmann bromamide degradation reaction:**



$$R-\underset{\underset{\displaystyle O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

28. **Given:** $a = 5\ \text{Å} = 5 \times 10^{-8}$ cm, $M = 75$, $\rho = 2$ g/cc

For bcc: $r = \frac{\sqrt{3}}{2}a$

$$\rho = \frac{Z \times M}{a^3 \times N_A} \qquad \therefore\ Z = \frac{2 \times 6 \times 10^{23} \times (5 \times 10^{-8})^3}{75} = 2 \qquad \ldots[\because N_A = 6 \times 10^{23}$$

Therefore metal crystallises in bcc structure and for a bcc lattice, $r = \frac{\sqrt{3}}{4}a$

$\Rightarrow \quad r = \frac{\sqrt{3}}{4} \times 5 = \mathbf{2.165\ Å}$

29. (*i*) α helix-intramolecular H bonding.
β pleated-intermolecular H bonding.

(*ii*) Amylose is a straight chain polymer of D-glucose whereas amylopectin is a branched polymer of D-glucose.

30. (*i*) (*a*) $NH_4Cl\ (aq.) + NaNO_2\ (aq.) \longrightarrow N_2\ (g) + 2H_2O\ (l) + NaCl\ (aq)$

(*b*) $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$

(*ii*) Ka_1 is when H_2SO_4 gives HSO_4^- and H^+.
Ka_2 is when HSO_4^- gives SO_4^{2-} and H^+.
It is much easier for a neutral H_2SO_4 to release H^+ than a negatively charged HSO_4^-. Hence Ka_2 is much lesser than Ka_1.

SECTION D

31. (*a*) (*i*) F is more electronegative than Cl.
The difference in the electronegativity between N and F is much more than the difference between electronegativity of N and Cl. So there is need of much more energy to break the N–F bond.

(*ii*) Because of the low bond dissociation energy F_2 readily dissociates into atoms and reacts with other substances readily.

(*b*) (*i*) $C + 2H_2SO_4\ (\text{conc.}) \longrightarrow CO_2 + 2SO_2 + 2H_2O$

(*ii*) $Cl_2 + \underset{(\text{excess})}{3F_2} \longrightarrow 2ClF_3$

Or

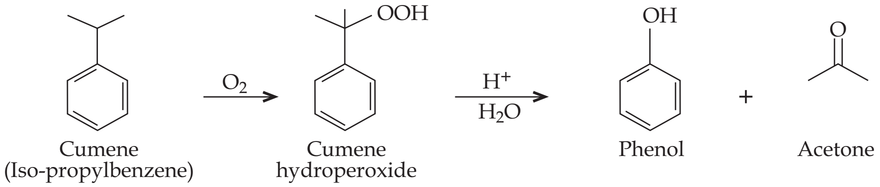
(*a*) (*i*) Because of decrease in electronegativity from chlorine to phosphorous, the bond dissociation enthalpy from HCl to H–P increases and their tendency to release H^+ decreases and thus acidic strength decreases.

(*ii*) Down the group, the tendency of next 's' orbital's electron to jump to previous 'd' orbital decreases very much due to inert pair effect.

(*b*) (*i*) $XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$

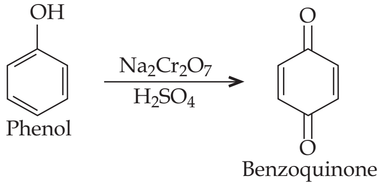
(*ii*) $I_2 + \underset{(\text{conc})}{10HNO_3} \longrightarrow 2HIO_3 + \underset{\text{Iodine to Iodic acid}}{10NO_2} + 4H_2O$

32. (*a*)



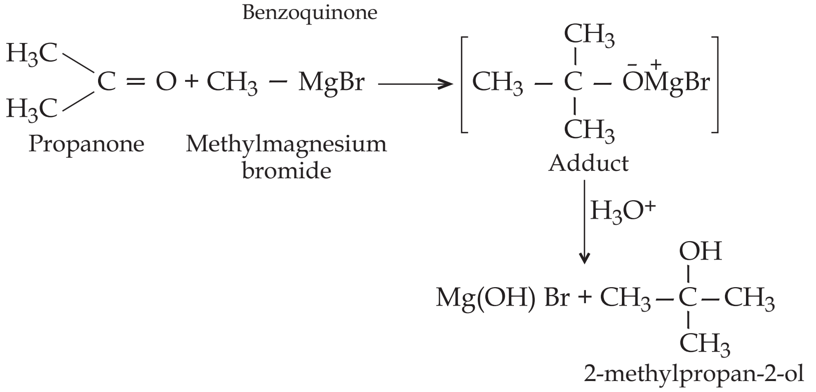
(*b*) Due to the presence of an alkyl group higher electron density is found in alkoxide ion.

(*c*) (*i*)



Phenol Benzoquinone

(*ii*)



$$\begin{array}{l}H_3C\\H_3C\end{array}\!\!>C=O+CH_3-MgBr\longrightarrow\left[CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-\overset{-}{O}\overset{+}{M}gBr\right]\xrightarrow{H_3O^+}Mg(OH)\,Br+CH_3-\underset{CH_3}{\overset{OH}{\overset{|}{\underset{|}{C}}}}-CH_3$$

Propanone Methylmagnesium bromide Adduct 2-methylpropan-2-ol

(*iii*) $CH_3-CH=CH_2\xrightarrow[\text{Ani-Markovnikov addition}]{\text{HBr/Peroxide}}CH_3-CH_2-CH_2-Br$

Propene 1-Bromopropane

$$\downarrow \text{(Nucleophilic substitution)} \quad \text{Aq. KOH/}\Delta$$

$CH_3-CH_2-CH_2-OH$

Propan–1–ol

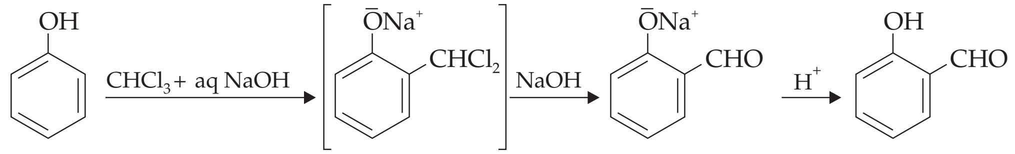
Or

(*a*) 1-Methylcyclohexene

(*b*) $C_6H_6\xrightarrow{\text{conc. }H_2SO_4,\,\Delta}C_6H_5SO_3H\xrightarrow{\text{NaOH, fuse, 575 K}}C_6H_5ONa\xrightarrow{\text{dil. HCl}}C_6H_5OH$

Benzene Benzene Sulphonic acid Sodium phenoxide Phenol

(*c*) (***i***) Reimer-Timman reaction—



(*ii*) Williamsons synthesis of an ether : The reaction involves the nucleophilic substitution of the halide ion from the alkyl halide by the alkoxide ion by S_N2 mechanism.

Example :

$$CH_3CH_2—O—Na^+ + \overset{\delta+}{C}H_3CH_2—\overset{\delta-}{Br}\xrightarrow[S_N2]{330\text{ K}}CH_3CH_2—O—CH_2—CH_3+NaBr$$

Sod. ethoxide Ethyl bromide Diethyl ether

33. (*a*) **Kohlrausch law of independent migration of ions.** This law states that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anions and cations of the electrolyte.

(*b*) $\Lambda^0_m\,(CaSO_4) = \lambda^0_{Ca^{2+}} + \lambda^0_{SO_4{}^{2-}}$

$= 119.0\text{ S cm}^2\text{ mol}^{-1} + 160.0\text{ S cm}^2\text{ mol}^{-1}$

$= \mathbf{279.0\ S\ cm^2\ mol^{-1}}$

(*c*) $\frac{1}{R} \times \frac{1}{a}$ = Conductance (C) × Cell constant

Molar conductance : $(\Lambda_m) = \frac{K \times 1000}{C}$.

Or

(*a*) **Degree of dissociation :** It is the measure of the extent to which an electrolyte gets dissociated into its constitutent ions.
Thus higher the degree of dissociation, higher will be its molar conductance.
Mathematically it can be expressed as :

$$\alpha = \frac{\text{Molar conductance at given concentration}}{\text{Molar conductance at infinite dilution}} \Rightarrow \alpha = \frac{\Lambda_m}{\overset{\circ}{\Lambda}_m}$$

(*b*) $Ni_{(s)} \mid Ni^{2+}{}_{(aq)} \parallel Ag^{+}{}_{(aq)} \mid Ag_{(s)}$

Given : $E^{\circ}_{Ni^{2+}/Ni} = 0.25\ V,\ E^{\circ}_{Ag^{+}/Ag} = 0.80\ V$

$$Ni + 2Ag^{+} \longrightarrow Ni^{2+} + 2Ag$$

$$E^{\circ}_{Cell} = E^{\circ}_{Cathode} - E^{\circ}_{Anode} = 0.80\ V - 0.25\ V$$

$$\therefore \quad E^{\circ}_{Cell} = 0.55\ V$$

Using formula,

$$\log K_C = \frac{nE^{\circ}_{Cell}}{0.0591} \quad \Rightarrow \log K_C = \frac{2 \times 0.55}{0.059} \quad \Rightarrow \log K_C = 18.644 \text{ or } K_C = 4.406 \times 10^{18}$$

Maximum work done can be calculated as,

$\Delta G^{o} = -nF\ E^{\circ}_{Cell}$

$= -2 \times 96500\ C\ mol^{-1} \times 0.55\ V$
$= -106.150\ J\ mol^{-1}$

Maximum work = **106.150 KJ mol^{-1}**

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