SAMPLE QUESTION PAPER

BLUE PRINT

Time Allowed : 3 hours

Maximum Marks : 70

S. No.	Chapter	Passage based/ MCQs/A & R (1 mark)	SA-I (2 marks)	SA-II (3 marks)	LA (5 marks)	Total
1.	The Solid State	2(2)	1(2)	–	–	**11(23)**
2.	Solutions	1(1)	1(2)	–	–	
3.	Electrochemistry	1(4)	–	1(3)	–	
4.	Chemical Kinetics	1(1)	–	–	1(5)	
5.	Surface Chemistry	1(1)	1(2)	–	–	
6.	The *p*-Block Elements	1(1)	1(2)	–	1(5)	**9(19)**
7.	The *d*- and *f*-Block Elements	1(1)	1(2)	1(3)	–	
8.	Coordination Compounds	2(2)	–	1(3)	–	
9.	Haloalkanes and Haloarenes	1(1)	–	–	1(5)	**13(28)**
10.	Alcohols, Phenols and Ethers	1(4)	1(2)	1(3)	–	
11.	Aldehydes, Ketones and Carboxylic Acids	1(1)	2(4)	–	–	
12.	Amines	1(1)	–	1(3)	–	
13.	Biomolecules	2(2)	1(2)	–	–	
	Total	**16(22)**	**9(18)**	**5(15)**	**3(15)**	**33(70)**

Subject Code : **043**

CHEMISTRY

Time allowed : 3 hours **Maximum marks : 70**

General Instructions : Read the following instructions carefully.

(a) There are 33 questions in this question paper. All questions are compulsory.

(b) Section A : Q. No. 1 to 16 are objective type questions. Q. No. 1 and 2 are passage based questions carrying 4 marks each while Q. No. 3 to 16 carry 1 mark each.

(c) Section B : Q. No. 17 to 25 are short answer questions and carry 2 marks each.

(d) Section C : Q. No. 26 to 30 are short answer questions and carry 3 marks each.

(e) Section D : Q. No. 31 to 33 are long answer questions carrying 5 marks each.

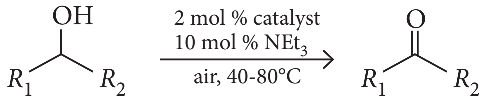
(f) There is no overall choice. However, internal choices have been provided.

(g) Use of calculators and log tables is not permitted.

SECTION - A (OBJECTIVE TYPE)

1. **Read the passage given below and answer the following questions :**

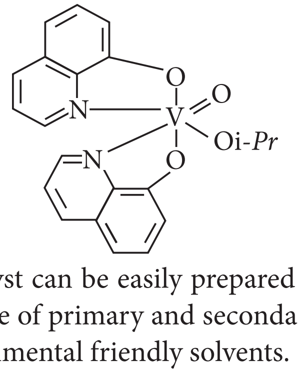
The oxidation of alcohols to carbonyl compounds is one of the most fundamental reactions in synthetic organic chemistry. An efficient vanadium-based catalyst has been discovered recently for the aerobic oxidation of benzylic, allylic and propargylic alcohols to their corresponding aldehydes or ketones in good yields.



where, R_1 = aryl, vinyl, alkynyl

R_2 = H, CH_3, aryl

Catalyst =



The catalyst can be easily prepared under air using commercially available reagents and is effective for a wide range of primary and secondary alcohols. Reactions proceed under mild conditions and in a variety of environmental friendly solvents.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) The vanadium-based catalyst mention in the study above can be used to convert

(a) acetone to *t*-butyl alcohol (b) benzyl alcohol to benzaldehyde

(c) 2-phenylpropan-2-ol to 2-phenylpropan-2-one (d) 1-methyl cyclopentene to 1-methyl cyclopentanol.

(ii) Which of the following is secondary allylic alcohol?

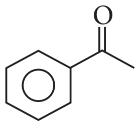
(a) 2-Methylbut-3-en-2-ol (b) Prop-2-enol

(c) 1-phenylbut-2-en-1-ol (d) 2-phenylbut-3-en- 2-ol

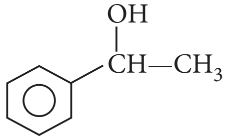
OR

An unknown organic compound, *X* having molecular formula, $C_8H_{10}O$ undergoes oxidation in presence of this vanadium-based catalyst and gives a compound, *Y*. Compound, *Y* on treatment with aq. Na_2CO_3 and I_2 solution gives yellow ppt. The compound, *Y* is

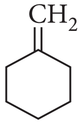
(a)



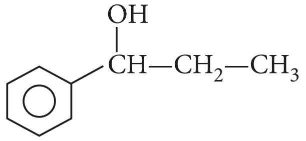
(b)



(c)



(d)



(iii) Primary alcohols can also be oxidised by using

(a) Al_2O_3 catalyst (b) Collins reagent (c) dil. H_2SO_4 (d) acetyl chloride.

(iv) Isopropyl alcohol is oxidised with this vanadium-based catalyst to give

(a) CH_3CHO (b) CH_3COCH_3 (c) $CH_3CH{=}CH_2$ (d) $CH_3CH_2CH_2COOH$

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

In an electrolytic cell, an electric current is passed from an electronic conductor through one, or several ionic conductors (electrolytes), bulk into a second electronic conductor. The circuit is closed outside of the cell through various electronic conductors. This typically includes a power supply and a current measuring device. The functions between the electronic and ionic conductors are called electrodes, namely cathodes and anodes. The difference between a cathode or an anode depends on the direction of current flow. At the cathode, electrons are transferred from the electronic conductor to some component of the electrolyte causing the discharge of some positive ion, or the generation of negative ion and also the reduction of some component of electrolyte.

As a common example, the transfer of electron from the cathode to a water molecule causes the formation of a OH^- ion and a hydrogen atom. Two of these hydrogen atoms will then combine to form a hydrogen molecule. The opposite occurs at anode. In a typical case, a chloride ion transfers its electron to anode and is converted to chlorine atom. It should be noted that anode and cathode indicate the direction of current flow and not the polarity.

In a cell that consumes electric power, such as in NaCl electrolysis, the anode is positive ; while in a cell that generates electric power, such as a fuel, it is negative.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(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 :** The products of electrolysis of water are hydrogen and oxygen.

Reason : In electrolysis process of water, hydrogen ions are attracted to anode and hydroxyl ions are attracted to cathode.

(ii) **Assertion :** In an electrolytic cell, anode and cathode are respectively negative and positive electrodes.

Reason : At anode oxidation takes place and at cathode reduction takes place.

(iii) **Assertion :** Cathode and anode indicate the polarity.
Reason : On passing electric current through the electrolytic solution, the ions are attracted by the oppositely charge electrodes and this movement of ions constitues flow of current through the solution.

OR

Assertion : The electrolysis of NaCl solution gives hydrogen at the cathode and chlorine at the anode.
Reason : Chlorine has higher oxidation potential than water.

(iv) **Assertion :** Input of energy is required by electrolytic cells.
Reason : Electrolytic cells have just one container.

The following questions (Q.No. 3-11) are multiple choice questions carrying 1 mark each :

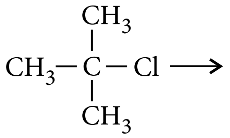
3. The pair in which both species have the same magnetic moment (spin only value) is
(a) $[Cr(H_2O)_6]^{2+}$, $[CoCl_4]^{2-}$
(b) $[Cr(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{2+}$
(c) $[Mn(H_2O)_6]^{2+}$, $[Cr(H_2O)_6]^{2+}$
(d) $[CoCl_4]^{2-}$, $[Fe(H_2O)_6]^{2+}$

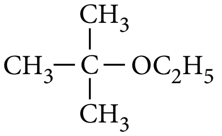
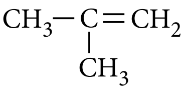
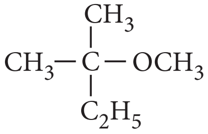
4. Two labels sticked upon the two bottles containing conc. H_2SO_4 are shown below :
A : Conc. H_2SO_4, (90% by volume), Density = 1.98 g/mL
B : Conc. H_2SO_4, (93% by volume), Density = 1.84 g/mL
Molalities of acids *A* and *B* respectively are
(a) 8.5, 10.4
(b) 10.4, 8.5
(c) 4.2, 5.2
(d) 5.2, 4.2

OR

Plot of $\frac{1}{X_A}$ vs $\frac{1}{Y_A}$ (X_A mole fraction of *A* in liquid and Y_A in vapour) is linear whose slope and intercept respectively are
(a) $p^\circ_B/p^\circ_A, \frac{p^\circ_B - p^\circ_A}{p^\circ_B}$
(b) $p^\circ_A - p^\circ_B, \frac{p^\circ_A - p^\circ_B}{p^\circ_B}$
(c) $p^\circ_A/p^\circ_B, \frac{p^\circ_B - p^\circ_A}{p^\circ_B}$
(d) $p^\circ_B - p^\circ_A, \frac{p^\circ_A - p^\circ_B}{p^\circ_B}$

5. An electric current is passed through an aqueous solution of a mixture of alanine (isoelectric point 6.0), glutamic acid (3.2) and arginine (10.7) buffered at pH 6. What is the fate of the three acids?
(a) Glutamic acid migrates to anode at pH 6. Arginine present as a cation and migrates to the cathode. Alanine as a dipolar ion remains uniformly distributed in solution.
(b) Glutamic acid migrates to cathode and others remain uniformly distributed in solution.
(c) All these remain uniformly distributed in solution.
(d) All three move to cathode.

6. Major product of the following reaction will be C_2H_5ONa +  $CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Cl \longrightarrow$

(a)  $CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OC_2H_5$
(b)  $CH_3-\underset{\displaystyle CH_3}{C}=CH_2$
(c) $CH_2=CH_2$
(d)  $CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle C_2H_5}{C}}-OCH_3$

7. Cl_2 and SO_2 are pollutants as well as bleaching agents. Their bleaching action is due to

	SO_2	**Cl_2**
(a)	Oxidation	Oxidation
(b)	Reduction	Reduction
(c)	Oxidation	Oxidation
(d)	Reduction	Oxidation

OR

During the formation of the N_2O_4 dimer from two molecules of NO_2, the odd electrons, one in each of the nitrogen atoms of the NO_2 molecules, get paired to form a

(a) weak N – N bond, two N – O bonds become equivalent and the other two N – O bonds become nonequivalent

(b) weak N – N bond and all the four N – O bonds become equivalent

(c) strong N – N bond and all the four N – O bonds become non-equivalent

(d) strong N – N bond and all the four N–O bonds become equivalent.

8. A compound of vanadium has a magnetic moment of 1.73 BM. Choose the correct electronic configuration of the vanadium ion in the compound.

(a) $1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^2$ (b) $1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^3$

(c) $1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^1$ (d) $1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^0$

9. The reaction, $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$ is a first order reaction with $k = 2.2 \times 10^{-5}\ s^{-1}$ at 320°C. The percentage of SO_2Cl_2 that is decomposed on heating after 30 minutes will be

(a) 3.8% (b) 65.4% (c) 39.5% (d) 48.5%

OR

$t_{1/2}$ for a first order reaction is 14.26 mins. The percentage of reactant decomposed after 50 s is

(a) 8% (b) 4% (c) 6% (d) 10.2%

10. If Al^{3+} ions replace Na^+ ions at the edge centres of NaCl lattice, then the number of vacancies in one mole of NaCl will be

(a) 3.01×10^{23} (b) 6.02×10^{23} (c) 9.03×10^{23} (d) 12.04×10^{23}

11. An optically active amine ($C_5H_{13}N$) on treatment with aq. $NaNO_2$/HCl forms an optically inactive alcohol ($C_5H_{12}O$) with evolution of N_2 gas. The amine is

(a) 1-pentanamine (b) 2-pentanamine

(c) 3-pentanamine (d) 2-methylbutanamine.

OR

Amongst the given set of reactants, the most appropriate for preparing 2° amine is

(a) $2°R\text{—Br} + NH_3$

(b) $2°R\text{—Br}$ + NaCN followed by H_2/Pt

(c) $1°R\text{—}NH_2 + R\text{CHO}$ followed by H_2/Pt

(d) $1°R\text{—Br}$ (2 mol) + potassium phthalimide followed by H_3O^+/heat.

In the following questions (Q. No. 12 - 16) 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.

12. **Assertion :** Due to Frenkel defect, there is no effect on the density of the crystalline solid.
Reason : In Frenkel defect, no cation or anion leaves the crystal.

13. **Assertion :** Aldol condensation can be catalysed both by acids and bases.
Reason : β-Hydroxyaldehydes or ketones readily undergo acid-catalysed dehydration.

14. **Assertion :** Colloidal solutions show colligative properties.
Reason : Colloidal particles are large in size than particles of true solution.

OR

Assertion : For the coagulation of sols carrying positive charge, PO_4^{3-} ions are more efficient than SO_4^{2-} or Cl^- ions.
Reason : This follows Hardy – Schulze rule.

15. **Assertion :** Glucose and fructose give the same osazone.
Reason : During osazone formation stereochemistry at C_1 and C_2 is destroyed and rest of the structure remains same.

16. **Assertion :** F^- ion is a weak ligand and forms outer orbital complex.
Reason : F^- ion cannot force the electrons of d_{z^2} and $d_{x^2-y^2}$ orbitals of the inner shell to occupy d_{xy}, d_{yz} and d_{zx} orbitals of the same shell.

SECTION - B

The following questions, Q.No. 17-25 are short answer type and carry 2 marks each.

17. Li crystallises in *bcc* structure. If the edge length of unit cell is 353 pm, calculate
   (i) radius of Li atom, (ii) packing efficiency of unit cell.

18. Give equations of the following reactions :
   (i) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution.
   (ii) Treating phenol with chloroform in the presence of aqueous NaOH followed by hydrolysis.

OR

Illustrate with examples the limitations of Williamson's synthesis for the preparation of certain types of ethers.

19. Assign a reason for each of the following observations :
   (i) The transition metals (with the exception of Zn, Cd and Hg) are hard and have high melting and boiling points.
   (ii) The ionisation enthalpies (first and second) in the first series of the transition elements are found to vary irregularly.

20. Write reactions stating conditions for the following conversions:
   (i) Benzene to acetophenone (ii) Ethanal to propanone.

21. 0.90 g of a non-electrolyte was dissolved in 87.90 g of benzene. This raised the boiling point of benzene by 0.25°C. If the molecular mass of the non-electrolyte is 103.0 g mol^{-1}. Calculate the molal elevation constant for benzene.

OR

What is the molar concentration of solute particle in human blood if the osmotic pressure is 7.2 atm at the body temperature of 37 °C? [$R = 0.0821$ L atm K^{-1}]

22. Give reasons : Describe the following about halogens (Group 17 elements):
   (a) Relative oxidising power of halogens. (b) Relative acidic strength of the hydrogen halides.

23. Explain the following observations :
   (i) Lyophilic colloid is more stable than lyophobic colloid.
   (ii) Sky appears blue in colour.

24. Give reasons for the following :
   (i) Carboxylic acids do not give characteristic reactions of carbonyl compound.
   (ii) Sodium bisulphite is used for the purification of aldehydes and ketones.

25. State differences between the reducing and non-reducing sugars.

OR

Enumerate the reactions of glucose which cannot be explained by its open chain structures.

SECTION - C

Q.No. 26-30 are short answer type II carrying 3 marks each.

26. Define conductivity and molar conductivity of a solution and explain their variation with change in concentration of solution for a weak and a strong electrolyte.

OR

(i) Equivalent conductance of a 0.0128 N solution of acetic acid is 1.4 mho cm^2 eq^{-1} and conductance at infinite dilution is 391 mho cm^2 eq^{-1}. Calculate degree of dissociation and dissociation constant of acetic acid.

(ii) The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}?

27. (a) Give reasons :

(i) Nitrobenzene does not undergo Friedel—Crafts alkylation.

(ii) Silver chloride dissolves in methylamine solution.

(b) Write the chemical reaction for the reduction of nitroethane by $LiAlH_4$.

28. Assign reasons for the following :

(i) Unlike Cr^{3+}, Mn^{2+}, Fe^{3+} and the subsequent other M^{2+} ions of the 3*d* series of elements, the 4*d* and the 5*d* series metals generally do not form stable cationic species.

(ii) Transition metals generally form coloured compounds.

(iii) Among lanthanoids, Ln(III) compounds are predominant. However, occasionally in solutions or in solid compounds, +2 and +4 ions are also obtained.

OR

(i) Explain the following observations :

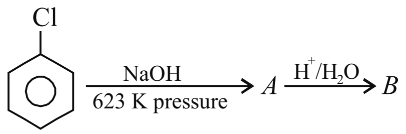
(a) The metal-metal bonding is more frequent for the second and third series of transition elements than that for the first series.

(b) The higher oxidation states are usually exhibited by members in the middle of a series of transition elements.

(ii) Compare the nature of oxides of 3*d*-series of transition elements.

29. (a) Identify *A* and *B* in each of the following sequence :

(i) $CH_3-CH=CH_2 \xrightarrow{HBr} A \xrightarrow{\text{alk. KOH}} B$

(ii) 

(b) Explain, why is *ortho*-nitrophenol more acidic than *ortho*-methoxyphenol?

30. (a) On the basis of crystal field theory, write the electronic configuration of d^4 in terms of t_{2g} and e_g in an octahedral field when $\Delta_o > P$.

(b) Explain the following giving appropriate reasons :

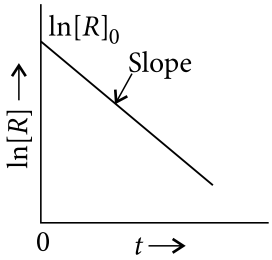
(i) Nickel does not form low spin octahedral complexes.

(ii) Co^{2+} is easily oxidised to Co^{3+} in the presence of a strong field ligand.

SECTION - D

Q. No. 31-33 are long answer type carrying 5 marks each.

31. (a) For a certain chemical reaction variation of $\ln[R]$ *vs*. time (s) plot is given below :



(i) Predict the order of the given reaction.
(ii) What does the slope of the line and intercept indicate?
(iii) What is the unit of rate constant k?

(b) A first order reaction takes 160 minutes time for 20% completion. Calculate time required for half completion of reaction.

OR

(a) The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume :

$SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$

Calculate the rate constant.

(Given : log 4 = 0.6021, log 2 = 0.3010)

Experiment	**Time/s**	**Total pressure/atm**
1	0	0.4
2	100	0.7

(b) The decomposition of NH_3 on platinum surface

$2NH_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3H_{2(g)}$

is a zero order reaction with $k = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}. What are the rates of production of N_2 and H_2?

32. (a) An optically active compound having molecular formula $C_7H_{15}Br$ reacts with aqueous KOH to give a racemic mixture of products. Write the mechanism involved for this reaction.

(b) When $CH_3-CH{=}CH-CH_2Cl$ reacts with alcoholic KCN, a mixture of isomeric products is obtained. Explain.

OR

(i) Give inorganic or organic reagents, needed to convert benzyl bromide into (a) benzyl iodide (b) benzyl ethyl ether (c) benzyl alcohol and (d) benzyl cyanide.

(ii) Which halogen best delocalises electron density of the benzene ring and why?

33. (a) Arrange the following according to given property and explain them.
(i) HCl, HBr, HF, HI ⇒ increasing order of bond strength
(ii) HOCl, $HOClO_2$, $HOClO_3$, HOClO ⇒ increasing order of thermal stability.
(iii) IO_4^-, BrO_4^-, ClO_4^- ⇒ increasing order of oxidising power.

(b) Name the two most important allotropes of sulphur. Which one of the two is stable at room temperature? What happens when the stable form is heated about 370 K?

OR

(a) When ammonia is passed through Nessler's reagent a brown precipitate is formed. Explain the chemistry of the test.

(b) Explain the following :
(i) The electron gain enthalpy with negative sign is less for oxygen than for sulphur.
(ii) NF_3 is an exothermic compound but NCl_3 is an endothermic compound.
(iii) HI is stronger acid than HCl.
(iv) Explain why NH_3 is basic while BiH_3 is only feebly basic?

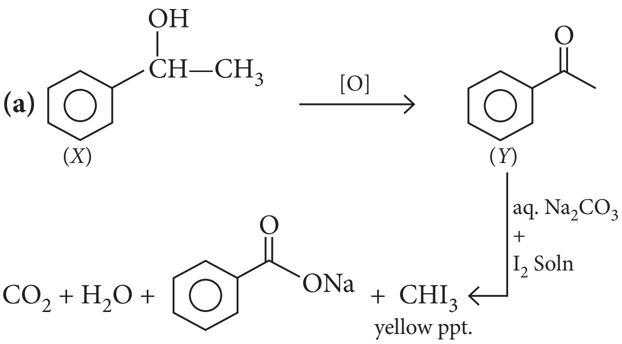
SOLUTIONS

1. (i) (b) : The vanadium-based catalyst is used for oxidation of primary and secondary alcohols only.

(ii) (c)

OR

(a)



(iii) (b)

(iv) (b)

2. (i) (c) : During the electrolysis of water, the electrolyte water dissociated in H^+ and OH^- ions which move to move to cathode and anode respectively, oxygen and hydrogen are produced.

(ii) (d) : Anode is positive electrode and cathode is negative electrode in electrolytic cell.

(iii) (d) : Cathode and anode indicate the direction of electric current not the polarity.

OR

(c) Chlorine has higher reduction potential than water.

(iv) (b) : Electrolytic cell is a device which converts electrical energy into chemical energy.

3. (b) : $[Cr(H_2O)_6]^{2+} = Cr^{2+}$; $3d^4$ = four unpaired electrons

$[Fe(H_2O)_6]^{2+} = Fe^{2+} = 3d^6$; four unpaired electrons

Hence, both the species have same magnetic moment.

4. (a) : For acid *A;*

$w_{acid} = 90$ g, $V_{solution} = 100$ mL,

$d = 1.98$ g/mL, $W_{solution} = 1.98 \times 100 = 198$ g

$$\therefore \quad m = \frac{w_{acid}}{M_{acid}} \times \frac{1000}{W_{water(g)}} = \frac{90}{98} \times \frac{1000}{(198-90)} = 8.50 \text{ m}$$

For acid *B* ;

$w_{acid} = 93$ g, $V_{solution} = 100$ mL,

$d = 1.84$ g/mL, $W_{solution} = 1.84 \times 100 = 184$ g

$$m = \frac{w_{acid}}{M_{acid}} \times \frac{1000}{W_{water(g)}} = \frac{93}{98} \times \frac{1000}{(184-93)} = 10.4 \text{ m}$$

OR

(c) : $p_A = p_A^\circ \times X_A$ = Total pressure $\times Y_A$

$p_B = p_B^\circ \times X_B$ = Total pressure $\times Y_B$

$$\therefore \quad \frac{p_B^\circ X_B}{p_A^\circ X_A} = \frac{Y_B}{Y_A}, \quad \frac{p_B^\circ(1-X_A)}{p_A^\circ X_A} = \frac{1-Y_A}{Y_A}$$

$$\frac{1}{X_A} - 1 = \frac{p_A^\circ}{p_B^\circ}\left(\frac{1}{Y_A} - 1\right) = \frac{p_A^\circ}{p_B^\circ}\frac{1}{Y_A} - \frac{p_A^\circ}{p_B^\circ}$$

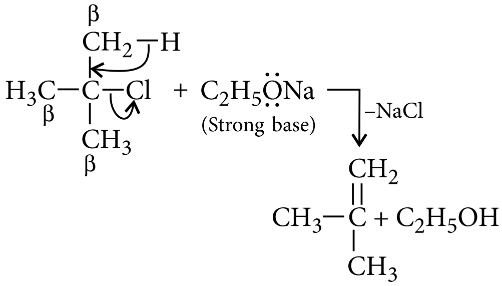
$$\text{or,} \quad \frac{1}{X_A} = \frac{p_A^\circ}{p_B^\circ}\cdot\frac{1}{Y_A} + \left(1 - \frac{p_A^\circ}{p_B^\circ}\right) = \frac{p_A^\circ}{p_B^\circ}\cdot\frac{1}{Y_A} + \frac{p_B^\circ - p_A^\circ}{p_B^\circ}$$

This is equation of straight line.

Slope $= \dfrac{p_A^\circ}{p_B^\circ}$, Intercept $= \dfrac{p_B^\circ - p_A^\circ}{p_B^\circ}$

5. (a) : At pH = 6, glutamic acid exists as a dianionic species and migrates to anode while arginine exists as cationic species and moves to cathode. Alanine does not migrate to any electrode at its isoelectric point.

6. (b) : As sodium ethoxide is a very strong base, hence, elimination reaction predominates over substitution reaction. It is governed by the acidity of β-hydrogen to be eliminated (Hoffmann rule).



7. (d) : SO_2 in the presence of moisture release nascent hydrogen which acts as bleaching agent of flowers, textiles, etc.

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + \underset{\text{Bleaching agent}}{2H}$$

Cl_2 in the presence of moisture releases nascent oxygen which acts as bleaching agent.

$$Cl_2 + H_2O \longrightarrow 2HCl + \underset{\text{Bleaching agent}}{O}$$

OR

(b)

8. (c) : Magnetic moment (μ) = $\sqrt{n(n+2)}$ BM

(n = number of unpaired electrons)

Given that, $\mu = 1.73$ BM.

$\therefore\ 1.73 = \sqrt{n(n+2)}$

On solving this equation we get, $n = 1$

So, vanadium atom must have one unpaired electron and thus its configuration is

${}_{23}\mathrm{V}^{4+} : 1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^1$

9. (a) : $k = \frac{2.303}{t}\log\frac{a}{a-x}$

$$2.2\times10^{-5} = \frac{2.303}{30\times60}\log\frac{a}{a-x}$$

$$\log\frac{a}{a-x} = \frac{2.2\times10^{-5}\times1800}{2.303} = 0.01719$$

$$\frac{a}{a-x} = \text{antilog}\ (0.01719) = 1.040$$

$a = 1.040a - 1.040x$

$0.040a = 1.040\,x$

$$\frac{x}{a} = \frac{0.040}{1.040} = 0.038 = 3.8\%$$

OR

(b) : $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.26\times60}\ \mathrm{sec}^{-1}$

$k = \frac{2.303}{t}\log\frac{a}{a-x}$ (for first order reaction)

$$\frac{0.693}{14.26\times60} = \frac{2.303}{50}\log\frac{a}{a-x}$$

$$\log\frac{a}{a-x} = \frac{0.693\times50}{14.26\times60\times2.303} = 0.0175$$

$$\frac{a}{a-x} = 1.041 \text{ or } \frac{a-x}{a} = 0.96 \text{ or } 1-\frac{x}{a} = 0.96$$

$$\frac{x}{a} = 0.04 = 4\%$$

10. (a) : There are 12 edge centres.

Contribution of $\mathrm{Na^+}$ ions at edge centres $= 12\times\frac{1}{4} = 3$

Besides, there is one $\mathrm{Na^+}$ ion at body centre.

Thus, there are four $\mathrm{Na^+}$ ions per unit cell.

$\frac{3}{4}$ are replaced by $\mathrm{Al^{3+}}$ ions.

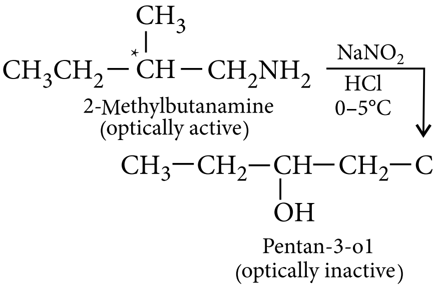
Total $\mathrm{Na^+}$ ions in 1 mole of NaCl $= 6.023\times10^{23}$

$\mathrm{Na^+}$ ion replaced by $\mathrm{Al^{3+}} = 3/4\times6.023\times10^{23}$

1 $\mathrm{Al^{3+}}$ replaces 3 $\mathrm{Na^+}$ ions, thereby creating 2 vacancies.

$$\therefore\ \text{No. of vacancies created} = \frac{2}{3}\times\left(\frac{3}{4}\times6.023\times10^{23}\right) = 3.01\times10^{23}$$

11. (d) : Since the amine ($C_5H_{13}N$) on treatment with aq. $NaNO_2/HCl$ evolves N_2 gas, it must be a 1° amine. Since, the amine is optically active, the $-NH_2$ group cannot be attached to a chiral centre because it will rapidly undergo racemisation due to nitrogen inversion. Therefore, the carbon skeleton must contain a chiral centre. In other words, the amine is 2-methylbutanamine. The reaction looks like,



$$\underset{\substack{\text{2-Methylbutanamine}\\ \text{(optically active)}}}{CH_3CH_2-\overset{\overset{CH_3}{|}}{\overset{*}{C}H}-CH_2NH_2} \xrightarrow[\text{HCl, 0–5°C}]{NaNO_2} \underset{\substack{\text{Pentan-3-o1}\\ \text{(optically inactive)}}}{CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3} + N_2\uparrow$$

OR

(c) : $R-NH_2 + RCHO \xrightarrow[\text{amination}]{\text{Reductive}} [R-N=CHR] \xrightarrow{H_2/Pt} \underset{\text{2° Amine}}{R-NH-CH_2R}$

12. (a) : In a Frenkel defect, an ion leaves its position in the lattice and occupies normally vacant interstitial position. Hence, density remains the same.

13. (b) : Both carbanion (formed in presence of a base) and enol form (formed in presence of an acid) act as nucleophiles and hence, react with the carbonyl group of aldehydes and ketones to give aldols. These, aldols are further dehydrated in presence of an acid to give α, β-unsaturated aldehydes or ketones.

14. (b)

OR

(a) : According to Hardy–Schulze rule, greater the valency of the flocculating ion added, greater is its power to cause precipitation.

15. (a) **16. (a)**

17. Given : structure = *bcc*, $a = 353$ pm, $r = ?$

(i) For *bcc* structure

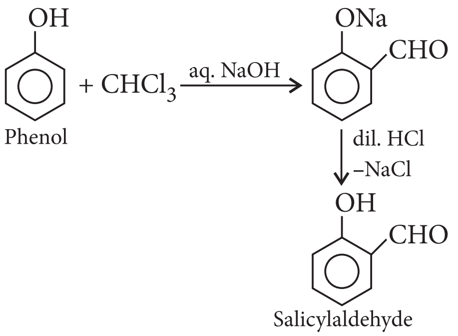
$$r = \frac{\sqrt{3}a}{4} = \frac{1.732\times353\ \text{pm}}{4} = 152.85\ \text{pm}$$

(ii) Packing efficiency of *bcc* unit cell $= \frac{Z\times\frac{4}{3}\pi r^3}{a^3}$

$$= \frac{2\times\frac{4}{3}\times3.14\times(152.85\times10^{-12}\ \text{m})^3}{(353\times10^{-12}\ \text{m})^3} = 0.68 = 68\%$$

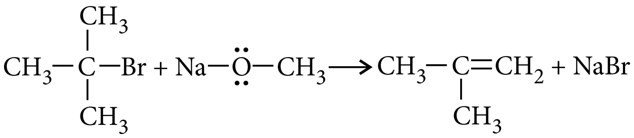
18. (i) $\underset{\text{Propan-1-ol}}{CH_3-CH_2-CH_2OH} \xrightarrow{\text{alk. }KMnO_4} \underset{\text{Propanoic acid}}{CH_3CH_2COOH} + H_2O$

(ii)



OR

Williamson's synthesis cannot be employed for tertiary alkyl halides as they yield alkenes instead of ethers. The reaction of CH_3ONa with $(CH_3)_3CBr$ gives exclusively 2-methylpropene.



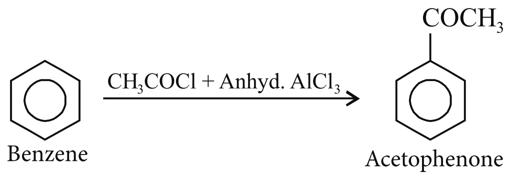
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + Na-\ddot{\underset{\cdot\cdot}{O}}-CH_3 \longrightarrow CH_3-\underset{CH_3}{C}=CH_2 + NaBr$$

Aryl halides and vinyl halides cannot be used as substrates because of their low reactivity in nucleophilic substitution reactions.

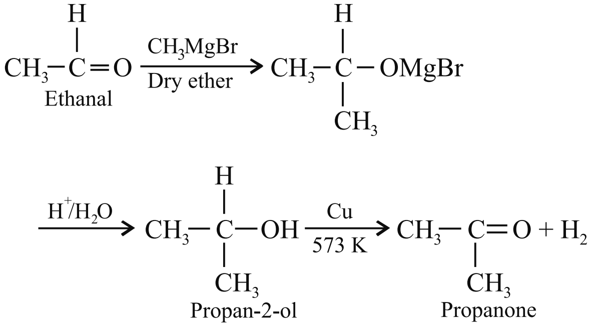
19. (i) Hardness and high melting and boiling points of these metals are attributed to the involvement of greater number of electrons from $(n - 1)d$ in addition to the ns electrons in the interatomic metallic bonding.

(ii) Irregular variation of ionisation enthalpies is mainly attributed to varying degree of stability of different $3d$-configurations (*e.g.*, d^0, d^5, d^{10} are exceptionally stable).

20. (i)



(ii)



$$\underset{\text{Ethanal}}{CH_3-\overset{H}{\overset{|}{C}}=O} \xrightarrow[\text{Dry ether}]{CH_3MgBr} CH_3-\underset{CH_3}{\overset{H}{C}}-OMgBr$$

$$\xrightarrow{H^+/H_2O} \underset{\text{Propan-2-ol}}{CH_3-\underset{CH_3}{\overset{H}{C}}-OH} \xrightarrow[573\text{ K}]{Cu} \underset{\text{Propanone}}{CH_3-\underset{CH_3}{C}=O} + H_2$$

21. $w_1 = 0.90$ g, $w_2 = 87.90$ g, $\Delta T_b = 0.25$°C

$M_1 = 103$ g mol^{-1}, $\Delta T_b = K_b m$

$$\Delta T_b = K_b \times \frac{w_1}{M_1} \times \frac{1000}{w_2},\ K_b = \frac{\Delta T_b \times M_1 \times w_2}{w_1 \times 1000}$$

$$\Rightarrow K_b = \frac{0.25 \times 103 \times 87.90}{0.90 \times 1000} \Rightarrow K_b = \frac{2263.42}{900}$$

$$\Rightarrow K_b = 2.5149 = 2.515 \text{ K kg mol}^{-1}$$

OR

Given, $\pi = 7.2$ atm, $R = 0.0821$ L atm K^{-1}

$T = 37°C = 273 + 37 = 310$ K

$$\pi = \frac{n}{V}RT$$

$$\Rightarrow \pi = CRT \qquad \left[C = \frac{n}{V}\right]$$

$$\Rightarrow 7.2 = C \times 0.0821 \times 310$$

$$\Rightarrow C = \frac{7.2}{0.0821 \times 310} \Rightarrow C = \frac{7.2}{25.451}$$

$C = 0.283$ mol L^{-1}

22. (a) From top to bottom in group-17 oxidising power of halogens decreases.

$F_2 > Cl_2 > Br_2 > I_2$.

(b) The acidic strength of the hydrohalic acids increases in the order : HF < HCl < HBr < HI

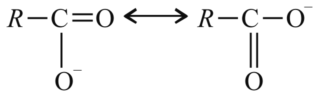
This order is a result of bond dissociation enthalpies of H — *X* bond, which decreases from H — F to H — I as the size of halogen atom increases.

23. (i) A lyophilic colloid is stable due to the charge as well as solvation of the sol particles. Such a solution can only be coagulated by adding an electrolyte and by adding a suitable solvent which can dehydrate the dispersed phase.

On the other hand, a lyophobic sol is stable due to charge only and hence can be easily coagulated by adding small amount of an electrolyte.

(ii) The atmospheric particles of colloidal range scatter blue component of the white sunlight preferentially. That is why sky appears blue.

24. (i) The carbonyl group in —COOH is inert and does not show nucleophilic addition reaction like carbonyl compound. It is due to resonance stabilisation of carboxylate ions :



$$R-\underset{O^-}{\underset{|}{C}}=O \longleftrightarrow R-\underset{O}{\underset{\|}{C}}-O^-$$

(ii) Sodium bisulphite reacts with aldehydes and ketones to form insoluble, crystalline addition products. These products can be easily separated in pure state. These products can be decomposed by dilute mineral acid or alkali to give back original aldehyde or ketone.

Hence, it can be used for purification of aldehydes and ketones.

25. Those carbohydrates which reduce Fehling's solution and Tollens' reagent due to presence of free aldehydic or ketonic group are referred to as reducing sugars. All monosaccharides like glucose, fructose, galactose are reducing sugars.

Those carbohydrates which cannot reduce Fehlings' solution and Tollens' reagent because of bonded aldehydic or ketonic groups are known as non-reducing sugars. Disaccharides like sucrose is non-reducing sugar.

OR

The following reactions of *D*-glucose cannot be explained on the basis of its open chain structure :

(a) *D*-Glucose does not react with sodium bisulphite ($NaHSO_3$).

(b) It does not give 2, 4-DNP test and Schiff's test.

(c) The pentaacetate of *D*-glucose does not react with hydroxyl amine.

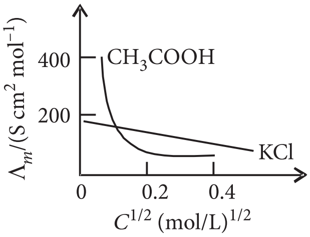
26. The reciprocal of resistivity is known as specific conductance or simply conductivity. It is denoted by κ (kappa).

$$\kappa = \frac{1}{\rho} \quad \text{or} \quad \kappa = G \times \frac{l}{a}$$

Hence, conductivity of a solution is defined as the conductance of a conductor of 1 cm length and having 1 sq. cm as the area of cross section. Alternatively, it may be defined as conductance of one centimetre cube of the solution of the electrolyte. Molar conductivity of a solution at a dilution V is the conductance of all the ions produced from 1 mole of the electrolyte dissolved in V cm^3 of the solution. It is represented by Λ_m.

$$\Lambda_m = \kappa V$$

Variation of conductivity and molar conductivity with concentration : Conductivity always decreases with decrease in concentration, for both weak and strong electrolytes. Because the number of ions per unit volume that carry the current in a solution decreases on dilution.



Molar conductivity *vs* $C^{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions

Molar conductivity increases with decrease in concentration. Because the total volume, V, of solution containing one mole of electrolyte also increases. It has been found that decrease in κ on dilution of a solution is more than compensated by increase in its volume.

OR

(i) Given : $\Lambda_e = 1.4$ mho cm^2 eq^{-1}, $\Lambda_e^\circ = 391$ mho cm^2 eq^{-1}, $\alpha = ?$ $K_a = ?$

Using formula $$\alpha = \frac{\Lambda_e}{\Lambda_e^o} = \frac{1.4 \text{ mho cm}^2 \text{ eq}^{-1}}{391 \text{ mho cm}^2 \text{ eq}^{-1}} = 0.00358$$

Again $$K_a = \frac{\alpha^2 C}{1-\alpha} = \frac{(0.00358)^2 \times 0.0128}{1 - 0.00358} = \frac{0.00000016}{0.99642} = 1.6 \times 10^{-7}$$

(ii) Here, conductivity (κ) = 0.146×10^{-3} S cm^{-1}, resistance (R) = 1500 Ω

$$\text{Cell constant} = \frac{\text{Conductivity}}{\text{Conductance}}$$

= Conductivity × Resistance

$$= \kappa \times R \qquad \left[\because \text{conductance} = \frac{1}{\text{resistance}}\right]$$

$= 0.146 \times 10^{-3} \times 1500 = 0.219$ cm^{-1}

27. (a) (i) Due to strong electron withdrawing effect of $-NO_2$ group, the benzene ring in nitrobenzene is deactivated towards Friedel—Crafts reaction.

(ii) Amines form soluble co-ordination compounds with Ag^+ ions. Therefore white ppt. of silver chloride is dissolved in methylamine solution.

$$\underset{\substack{\text{Silver chloride}\\ \text{(insoluble)}}}{AgCl} + 2CH_3{-}\ddot{N}H_2 \longrightarrow [(CH_3NH_2)_2Ag]Cl$$

(b) $$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} + 6[H] \xrightarrow[\text{ether}]{LiAlH_4} CH_3CH_2NH_2 + 2H_2O$$

28. (i) This is because due to lanthanoid contraction the expected increase in size does not occur hence, they have very high value of ionisation enthalpy.

(ii) This is due to *d*-*d* transition. When visible (white) light falls on transition metal compounds, they absorb certain radiation of visible light for transition of electrons from lower *d* level to higher *d* level and transmit the remaining ones. The colour observed corresponds to complementary colour of the light absorbed.

(iii) Lanthanum and all the lanthanoids predominantly show +3 oxidation state. However, some of the lanthanoids also show +2 and +4 oxidation states in solution or in solid compounds. This irregularity arises mainly due to attainment of stable empty ($4f^0$), half-filled ($4f^7$) and fully filled ($4f^{14}$) sub shell.

e.g. $Ce^{4+} : 4f^0$, $Eu^{2+} : 4f^7$
$Tb^{4+} : 4f^7$, $Yb^{2+} : 4f^{14}$

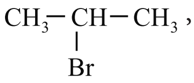
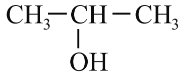
OR

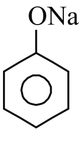
(i) (a) Nearly all the transition metals have the simple *hcp*, *ccp* or *bcc* lattice characteristics of true metals in which atoms are held together by strong metal-metal bonding. As we go down the group, electrons of elements of second and third series are available more easily as compared to first series hence, metal-metal bonding is more frequent in 4*d* and 5*d*-series of elements.

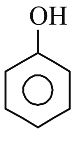
(b) The lesser number of oxidation states on the extreme ends of the series can be due to the presence of too few electrons or due to the presence of too many electrons and thus, fewer empty orbitals to share electrons with the ligands. In the middle of the series, *ns* and (*n* – 1)*d* electrons are involved hence, higher oxidation states are exhibited by them.

(ii) While moving along a period from Sc to Zn, basic nature decreases and acidic nature increases.

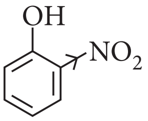
Also, with increase in the oxidation state of a given transition metal, the covalent character of its compound increases and thus, acidic character also increases.

29. (a) (i) *A* is 
$CH_3-\underset{|\atop Br}{CH}-CH_3$, *B* is 
$CH_3-\underset{|\atop OH}{CH}-CH_3$

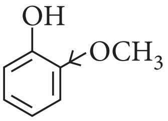
(ii) *A* is 

and *B* is 

(b) As we know that the electron withdrawing groups enhance the acidic character of phenols because they help in the stabilisation of phenoxide ion. Nitro group is an electron withdrawing group whereas methoxy group is an electron releasing group, so *o*-nitrophenol is more acidic than *o*-methoxyphenol.



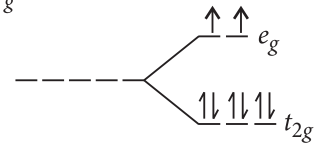
o-Nitrophenols



o-Methoxyphenol

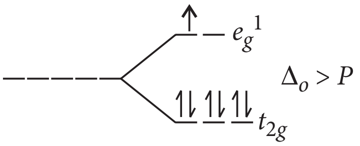
30. (a) : When $\Delta_o > P$, $t_{2g}^4 e_g^0$

(b) (i) Nickel forms octahedral complexes mainly in +2 oxidation state which has d^8 configuration. In presence of strong field ligand also it has two unpaired electrons in e_g orbital



Hence it does not form low spin octahedral complexes.

(ii) In presence of strong field ligand Co(II) has electronic configuration, $t_{2g}^6 e_g^1$.



It can easily lose only electron of e_g orbital to give stable t_{2g}^6 configuration. This is why Co^{2+} is easily oxidised to Co^{3+} in the presence of strong field ligand.

31. (a) (i) First order

(ii) $\ln[R] = -kt + \ln[R]_0$

Comparing this equation with $y = mx + c$, if we plot $\ln[R]$ *vs* t, we get a straight line with slope = $-k$ and intercept = $\ln[R]_0$

(iii) For first order reaction, unit of $k = s^{-1}$

(b) Given : $[R]_0 = 1$, $[R] = 0.80$, $t = 160$ min

$t_{1/2} = ?$

For first order reaction $k = \dfrac{2.303}{t}\log_{10}\dfrac{[R]_0}{[R]}$

or, $k = \dfrac{2.303}{160 \text{ min}}\log_{10}\dfrac{1}{0.8}$

or, $k = \dfrac{2.303}{160 \text{ min}} \times \log 1.25$

or, $k = \dfrac{2.303 \times 0.0969}{160 \text{ min}} = 1.39 \times 10^{-3} \text{ min}^{-1}$

Again $t_{1/2} = \dfrac{0.693}{k} = \dfrac{0.693}{1.39 \times 10^{-3}} \text{ min} = 497 \text{ min}$

OR

(a) The given reaction is

	$SO_2Cl_{2(g)} \longrightarrow$	$SO_{2(g)}$ +	$Cl_{2(g)}$
At $t = 0$	0.4 atm	0	0
At time t	$(0.4 - x)$ atm	x atm	x atm

Total pressure at time t will be

$P_T = (0.4 - x) + x + x = 0.4 + x$

$x = (P_T - 0.4)$

Pressure of SO_2Cl_2 at time t will be

$p_{SO_2Cl_2} = 0.4 - x = 0.4 - (P_T - 0.4) = 0.8 - P_T$

At time $t = 100$ s, $P_T = 0.7$ atm

$\therefore\ p_{SO_2Cl_2} = 0.8 - 0.7 = 0.1$ atm

According to first order kinetic equation

$$k = \frac{2.303}{t}\log\frac{p_{SO_2Cl_2}(\text{initial})}{p_{SO_2Cl_2}(\text{after reaction})}$$

$$= \frac{2.303}{100}\log\left(\frac{0.4}{0.1}\right) = 1.3 \times 10^{-2} \text{ s}^{-1}$$

(b) $2NH_{3(g)} \xrightleftharpoons{Pt} N_{2(g)} + 3H_{2(g)}$

$k = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}

The order of reaction is zero *i.e.*,

Rate = k [Reactant]^0

Rate = $2.5 \times 10^{-4} \times 1$

$= 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}

$$\therefore \text{ Rate of reaction} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt}$$

The rate of formation of N_2

$= 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}

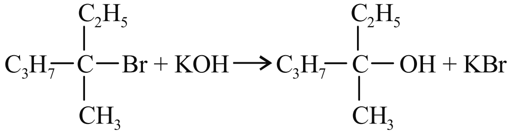
$$\text{Again, } 2.5 \times 10^{-4} = \frac{1}{3}\frac{d[H_2]}{dt}$$

$$\therefore \frac{d[H_2]}{dt} = 7.5 \times 10^{-4} \text{ mol L}^{-1}\text{ s}^{-1}$$

Therefore, rate of formation of H_2

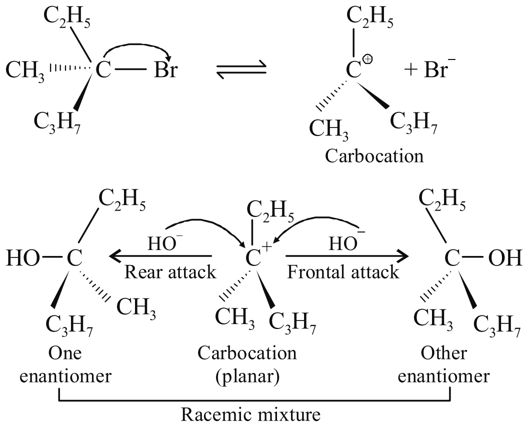
$= 7.5 \times 10^{-4}$ mol L^{-1} s^{-1}

32. (a) Clearly $C_7H_{15}Br$ is a tertiary halide.

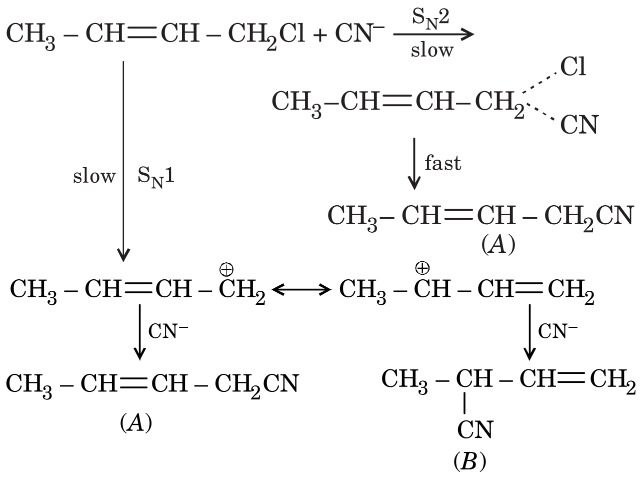


$$C_3H_7-\overset{C_2H_5}{\underset{CH_3}{C}}-Br + KOH \longrightarrow C_3H_7-\overset{C_2H_5}{\underset{CH_3}{C}}-OH + KBr$$

Mechanism :



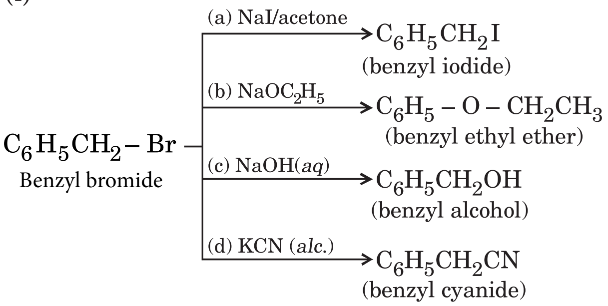
(b) It can undergo S_N1 and S_N2 reaction. By S_N2 reaction only one product is formed. But by S_N1 reaction, intermediate is carbonium ion.



Thus, we get two isomeric products by S_N1 reaction.

OR

(i)



(ii) Smaller the size of the halogen, more effective is the overlapping by *p-p* orbitals and thus more effective is the delocalisation.

Fluorine is the smallest halogen, the order of effective delocalisation is : F > Cl > Br > I.

33. (a) (i) HI < HBr < HCl < HF

The strength of H — *X* bond decreases as we move down the group. On moving down the group, the atomic size increases so H — *X* bond length increases. Larger the H — *X* bond length, lower is the bond energy and so lesser is the bond strength.

(ii) HOCl < HOClO < $HOClO_2$ < $HOClO_3$

As the oxidation state of Cl increases (or the number of oxygen atoms increases), the –ve charge dispersal becomes more and more from Cl atom due to higher electronegativity value of oxygen. Lesser the charge on Cl atom more is the stability.

(iii) Their oxidising power decreases in the order :

$BrO_4^- > IO_4^- > ClO_4^-$

This order can be explained on the basis of their electrode potentials for the following reactions, *i.e.*

$BrO_4^- + 2H^+ + 2e^- \longrightarrow BrO_3^- + H_2O$; $E° = 1.74$ V

$IO_4^- + 2H^+ + 2e^- \longrightarrow IO_3^- + H_2O$; $E° = 1.65$ V

$ClO_4^- + 2H^+ + 2e^- \longrightarrow ClO_3^- + H_2O$; $E° = 1.19$ V

Although among perhalates, BrO_4^- is the strongest oxidising agent, yet it is a weaker oxidising agent than F_2. It is because of this reason that perbromates and perbromic acid can be obtained by oxidation of bromates (BrO_3^-) by F_2 in alkaline solution.

$BrO_3^- + F_2 + 2OH^- \longrightarrow BrO_4^- + 2F^- + H_2O$

(b) Sulphur exists in numerous allotropes of which yellow, rhombic (α-sulphur) and monoclinic (β-sulphur) are most important. The stable form is rhombic, which transforms to monoclinic sulphur, when heated around 370 K.

OR

(a) On reaction with Nessler's reagent (alkaline K_2HgI_4), ammonia gives a brown precipitate called iodide of Millon's base.

$$NH_3 + 3KOH + 2K_2HgI_4 \rightarrow \underset{\text{Brown ppt.}}{H_2N.HgO.HgI} + 7KI + 2H_2O$$

(b) (i) The size of O atom is smaller than that of S. Thus, when an electron is added to neutral gaseous atom, the electron-electron repulsions experienced in the smaller 2*p*-subshell of O are comparatively larger than those encountered in the bigger 3*p*-subshell of S. As a result, more energy is released in case of S than

$O_{(g)} + e^- \rightarrow O^-_{(g)}; \Delta_{eg} = -141 \text{ kJ mol}^{-1}$

$S_{(g)} + e^- \rightarrow S^-_{(g)}; \Delta_{eg} = -200 \text{ kJ mol}^{-1}$

in case of O. In other words, negative electron gain enthalpy of S is higher than that of O.

(ii) In case of nitrogen, only NF_3 is known to be stable. N–F bond strength is greater than F–F bond strength, therefore, formation of NF_3 is spontaneous. In case of NCl_3, N—Cl bond strength is lesser than Cl—Cl bond strength. Thus, energy has to be supplied during the formation of NCl_3.

(iii) The acid strength depends upon the bond strength of H*X* and acid strength is more if the bond is weaker. As the size of atom *X* increases bond length increases. Longer the bond length, weaker is the acid. Hence, HI is stronger acid than HCl.

(iv) The central atoms in both NH_3 and BiH_3 contain a lone pair of electrons and thus, both should behave as Lewis bases. But the size of Bi atom is much larger than the nitrogen atom. The electron density on nitrogen atom is much higher in comparison to Bi atom. Consequently, the tendency to donate the electron pair by N in NH_3 is much higher than the tendency of Bi in BiH_3. Therefore, NH_3 is basic while BiH_3 is feebly basic.

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