तत् त्वं पूषन् अपावृणु
केन्द्रीय विद्यालय संगठन

Session : 2022-23

Class-XII

CHEMISTRY

KENDRIYA VIDYALAYA SANGATHAN

CHENNAI REGION

OUR PATRONS

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3		Mrs.S.Sobhana Kumari	KV Nagercoil	Chemical Kinetics
4		Smt V.Gowri	KV NO.1 Narimedu, Madurai	sample question paper 1 along with scoring key
5	Smt.Joan Santhi Joseph	Shri.V.Ganesa Ramachanran	AFS Sulur	d -and f -Block Elements
6		Smt.Nandhini	KV NO.1 AFS Tambaram	Coordination Compounds
7		Mrs. Hemathilaga	KV Minambakkam	Biomolecules
8		Smt.Joan Santhi Joseph	KV DGQA	sample question paper 2 along with scoring key
9	Smt. Ruby Simon	Shri.R.Lakshmanan	No.II, Tiruchirappalli	Haloalkanes and Haloarenes
10		Smt.Kavita	KV No.1, Kalpakkam	Alcohols, Phenols and Ethers
11		Smt.Janahi Vijayakumar	No.2, Pondicherry	Aldehydes, Ketones and Carboxylic Acids
12		Smt A Bharathi	KV AFS Avadi	Amines
13		Smt. Ruby Simon	KV CLRI	sample question paper 3 along with scoring key

SUBJECT CO-ORDINATOR

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KENDRIYA VIDYALAYA SANGATHAN, CHENNAI REGION
CLASS XII CHEMISTRY

COURSE STRUCTURE
CLASS XII (2022-23) (THEORY)

Time: 3 Hours **70 Marks**

S.No.	Title	No. of Periods	Marks
1	Solutions	15	7
2	Electrochemistry	18	9
3	Chemical Kinetics	15	7
4	d -and f -Block Elements	18	7
5	Coordination Compounds	18	7
6	Haloalkanes and Haloarenes	15	6
7	Alcohols, Phenols and Ethers	14	6
8	Aldehydes, Ketones and Carboxylic Acids	15	8
9	Amines	14	6
10	Biomolecules	18	7
	Total	**160**	**70**

Unit II: Solutions 15 Periods

Types of solutions, expression of concentration of solutions of solids in liquids, solubility of gases in liquids, solid solutions, Raoult's law, colligative properties - relative lowering of vapour pressure, elevation of boiling point, depression of freezing point, osmotic pressure, determination of molecular masses using colligative properties, abnormal molecular mass, Van't Hoff factor.

Unit III: Electrochemistry 18 Periods

Redox reactions, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibbs energy change and EMF of a cell, conductance in electrolytic solutions, specific and molar conductivity, variations of conductivity with concentration, Kohlrausch's Law, electrolysis and law of electrolysis (elementary idea), dry cell-electrolytic cells and Galvanic cells, lead accumulator, fuel cells, corrosion.

Unit IV: Chemical Kinetics **15 Periods**

Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst; order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half-life (only for zero and first order reactions), concept of collision theory (elementary idea, no mathematical treatment), activation energy, Arrhenius equation.

Unit VIII: d and f Block Elements **18 Periods**

General introduction, electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first-row transition metals – metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation, preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$.

Lanthanoids –

Electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction and its consequences.

Actinoids - Electronic configuration, oxidation states and comparison with lanthanoids.

Unit IX: Coordination Compounds **18 Periods**

Coordination compounds - Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT; structure and stereoisomerism, the importanceof coordination compounds (in qualitative analysis, extraction of metals and biological system).

Unit X: Haloalkanes and Haloarenes. **15 Periods**

Haloalkanes: Nomenclature, nature of C–X bond, physical and chemical properties, optical rotation mechanism of substitution reactions.

Haloarenes: Nature of C–X bond, substitution reactions (Directive influence of halogen inmonosubstituted compounds only). Uses and environmental effects of - dichloromethane,trichloromethane, tetrachloromethane, iodoform, freons, DDT.

Unit XI: Alcohols, Phenols and Ethers 14 Periods

Alcohols: Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration, uses with special reference to methanol and ethanol.

Phenols: Nomenclature, methods of preparation, physical and chemical properties, acidicnature of phenol, electrophilic substitution reactions, uses of phenols.

Ethers: Nomenclature, methods of preparation, physical and chemical properties, uses.

Unit XII: Aldehydes, Ketones and Carboxylic Acids 15 Periods

Aldehydes and Ketones: Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties, mechanism of nucleophilic addition, reactivity of alpha hydrogen in aldehydes, uses.

Carboxylic Acids: Nomenclature, acidic nature, methods of preparation, physical and chemical properties; uses.

Unit XIII: Amines 14 Periods

Amines: Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.

Diazonium salts: Preparation, chemical reactions and importance in synthetic organicchemistry.

Unit XIV: Biomolecules 18 Periods

Carbohydrates - Classification (aldoses and ketoses), monosaccharides (glucose and fructose), D-L configuration oligosaccharides (sucrose, lactose, maltose), polysaccharides(starch, cellulose, glycogen); Importance of carbohydrates.

Proteins -Elementary idea of - amino acids, peptide bond, polypeptides, proteins, structure of proteins - primary, secondary, tertiary structure and quaternary structures (qualitative idea only), denaturation of proteins; enzymes. Hormones - Elementary idea excluding structure.

Vitamins - Classification and functions.
Nucleic Acids: DNA and RNA.

SAMPLE PAPER (2022-23)

CHEMISTRY THEORY(043)

MM:70 **Time: 3 hours**

General Instructions:

Read the following instructions carefully.

a) There are **35** questions in this question paper with internal choice.
b) SECTION A consists of 18 multiple-choice questions carrying 1 mark each.
c) SECTION B consists of 7 very short answer questions carrying 2 marks each.
d) SECTION C consists of 5 short answer questions carrying 3 marks each.
e) SECTION D consists of 2 case- based questions carrying 4 marks each.
f) SECTION E consists of 3 long answer questions carrying 5 marks each.
g) **All questions are compulsory.**
h) **Use of log tables and calculators is not allowed**

SECTION A

The following questions are multiple-choice questions with one correct answer. Eachquestion carries 1 mark. There is no internal choice in this section.

1. The major product of acid catalysed dehydration of 1-methylcyclohexanol is:
   a. 1-methylcyclohexane
   b. 1-methylcyclohexene
   c. 1-cyclohexylmethanol
   d. 1-methylenecyclohexane

2. Which one of the following compounds is more reactive towards SN1 reaction?

   a. $CH_2=CHCH_2Br$
   b. $C_6H_5CH_2Br$

c. $C_6H_5CH\ (C_6H_5)Br$
d. $C_6H_5CH(CH_3)\ Br$

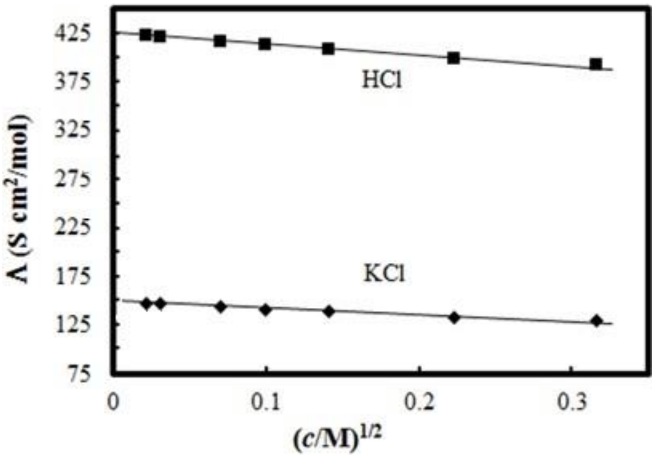
3. $KMnO_4$ is coloured due to:

a. d-d transitions
b. charge transfer from ligand to metal
c. unpaired electrons in d orbital of Mn
d. charge transfer from metal to ligand

4. Which radioactive isotope would have the longer half- life ^{15}O or ^{19}O? (Given rateconstants for ^{15}O and ^{19}O are $5.63 x\ 10^{-3}\ s^{-1}$ and $k = 2.38\ x\ 10^{-2} s^{-1}$ respectively.)

a. ^{15}O
b. ^{19}O
c. Both will have the same half-life
d. None of the above, information given is insufficient

5. The molar conductivity of CH_3COOH at infinite dilution is 390 Scm^2/mol. Using thegraph and given information, the molar conductivity of CH_3COOK will be:



a. 100 Scm^2/mol
b. 115 Scm^2/mol
c. 150 Scm^2/mol
d. 125 Scm^2/mol

***FOR VISUALLY CHALLENGED LEARNERS**

*5. What is the molar conductance at infinite dilution for sodium chloride if the molarconductance at infinite dilution of Na^+ and Cl^- ions are $51.12 \times 10^{-}$

^{4} Scm^2/mol and 73.54×10^{-4} Scm^2/mol respectively?

a. 124.66 Scm^2/mol
b. 22.42 Scm^2/mol
c. 198.20Scm^2/mol
d. 175.78 Scm^2/mol

6. For the reaction, $A + 2B \rightarrow AB_2$, the order w.r.t. reactant A is 2 and w.r.t. reactant B.What will be change in rate of reaction if the concentration of A is doubled and B is halved?

a. increases four times
b. decreases four times
c. increases two times
d. no change

7. Arrange the following in the increasing order of their boiling points:

A : Butanamine, B: N,N-Dimethylethanamine, C: N- Ethylethanaminamine

a. C<B<A
b. A<B<C
c. A<C<B
d. B<C<A

8. The CFSE of $[CoCl_6]^{3-}$ is 18000 cm^{-1} the CFSE for

$[CoCl_4]^-$ will be:a.18000 cm^{-1}
b. 8000cm^{-1}
c. 2000 cm^{-1}
d. 16000 cm^{-1}

9. What would be the major product of the following reaction?

$$C_6H_5\text{-}CH_2\text{-}OC_6H_5 + HBr \rightarrow A + B$$

a. A= $C_6H_5CH_2OH$, B= C_6H_6
b. A=$C_6H_5CH_2OH$,B= C_6H_5Br
c. A=$C_6H_5CH_3$,B= C_6H_5Br
d. A=$C_6H_5CH_2Br$, B= C_6H_5OH

10. Which of the following statements is not correct for amines?

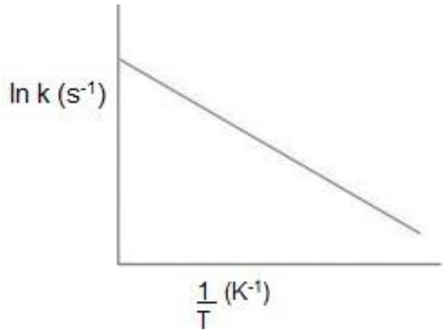
a. Most alkyl amines are more basic than ammonia solution.
b. pKb value of ethylamine is lower than benzylamine.

c. CH_3NH_2 on reaction with nitrous acid releases NO_2 gas.
d. Hinsberg's reagent reacts with secondary amines to form sulphonamides.

11. Which of the following tests/ reactions is given by aldehydes as well as ketones?

a. Fehling's test
b. Tollen's test
c. 2,4 DNP test
d. Cannizzaro reaction

12. Arrhenius equation can be represented graphically as follows:



The (i) intercept and (ii) slope of the graph are:

a. (i) ln A (ii) Ea/R
b. (i) A (ii) Ea
c. (i)ln A (ii) - Ea/R
d. (i) A (ii) -Ea

***FOR VISUALLY CHALLENGED LEARNERS**

*12. The unit of rate constant for the reaction 2A + 2B → A_2B_2 which has rate = k $[A]_2$ [B] is: a. mol $L^{-1}s^{-1}$ b. s^{-1} c. mol L^{-1} d. mol^{-2} L^{2} s^{-1}

13. The oxidation of toluene to benzaldehyde by chromyl chloride is called

a. Etard reaction
b. Riemer-Tiemann reaction
c. Stephen's reaction
d. Cannizzaro's reaction

14. For the reaction, A +2B → AB_2, the order w.r.t. reactant A is 2 and w.r.t. reactant B. What will be change in rate of reaction if the concentration of A is doubled and B is halved?

a. increases four times
b. decreases four times
c. increases two times

d. no change

15. Givn below are two statements labelled as Assertion (A) and Reason (R)

Assertion (A): An ether is more volatile than an alcohol of comparable molecularmass.
Reason (R): Ethers are polar in nature.
Select the most appropriate answer from the options given below:

a. Both A and R are true and R is the correct explanation of A
b. Both A and R are true but R is not the correct explanation of A.
c. A is true but R is false.
d. A is false but R is true.

16. Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion (A): Proteins are found to have two different types of secondary structures viz alpha-helix and beta-pleated sheet structure.
Reason (R): The secondary structure of proteins is stabilized by hydrogen bonding.
Select the most appropriate answer from the options given below:

a. Both A and R are true and R is the correct explanation of A
b. Both A and R are true but R is not the correct explanation of A.
c. A is true but R is false.
d. A is false but R is true.

17. Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion : Magnetic moment values of actinides are lesser than the theoretically predicted values.
Reason : Actinide elements are strongly paramagnetic.
Select the most appropriate answer from the options given below:

a. Both A and R are true and R is the correct explanation of A
b. Both A and R are true but R is not the correct explanation of A.
c. A is true but R is false.
d. A is false but R is true.

18. Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion (A): Tertiary amines are more basic than corresponding secondary and primary amines in gaseous state.
Reason (R): Tertiary amines have three alkyl groups which cause +I effect.
Select the most appropriate answer from the options given below:

a. Both A and R are true and R is the correct explanation of A
b. Both A and R are true but R is not the correct explanation of A.
c. A is true but R is false.
d. A is false but R is true.

SECTION B

This section contains 7 questions with internal choice in two questions. The followingquestions are very short answer type and carry 2 marks each.

19. A first-order reaction takes 69.3 min for 50% completion. What is the time needed for80% of the reaction to get completed?
(Given: log 5 =0.6990, log 8 = 0.9030, log 2 = 0.3010)

20. Account for the following:
    a. There are 5 OH groups in glucose
    b. Glucose is a reducing sugar

OR

What happens when D – glucose is treated with the following reagents
- a. Bromine water
- b. HNO3

21. Give reason for the following:
    a. During the electrophilic substitution reaction of haloarenes, parasubstituted derivative is the major product.
    b. The product formed during SN^1 reaction is a racemic mixture.

OR

- a. Name the suitable alcohol and reagent, from which 2-Chloro-2-methylpropane can be prepared.
- b. Out of the Chloromethane and Fluoromethane , which one is has higherdipole moment and why?

22. The formula $Co(NH_3)_5CO_3Cl$ could represent a carbonate or a chloride. Write thestructures and names of possible isomers.

23. Corrosion is an electrochemical phenomenon. The oxygen in moist air reacts asfollows:

$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-{}_{(aq)}$.

Write down the possible reactions for corrosion of zinc occurring at anode, cathode, andoverall reaction to form a white layer of zinc hydroxide.

24. Explain how and why will the rate of reaction for a given reaction be affected when
    a. a catalyst is added
    b. the temperature at which the reaction was taking place is decreased

25. Write the reaction and IUPAC name of the product formed when 2-Methylpropanal(isobutyraldehyde) is treated with ethyl magnesium bromide followed by hydrolysis.

SECTION C

This section contains 5 questions with internal choice in two questions. The followingquestions are short answer type and carry 3 marks each.

26. Write the equations for the following reaction:
    a. Salicylic acid is treated with acetic anhydride in the presence of conc.H_2SO_4
    b. Tert butyl chloride is treated with sodium ethoxide.
    c. Phenol is treated with chloroform in the presence of NaOH

27. Using Valence bond theory, explain the following in relation to the paramagneticcomplex $[Mn(CN)_6]^{3-}$
    a. type of hybridization
    b. magnetic moment value
    c. type of complex – inner, outer orbital complex

28. Answer the following questions:
    a. State Henry's law and explain why are the tanks used by scuba diversfilled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen)?
    b. Assume that argon exerts a partial pressure of 6 bar. Calculate the solubility of argon gas in water. (Given Henry's law constant for argondissolved in water, KH = 40kbar)

29. Give reasons for **any 3** of the following observations:
    a. Aniline is acetylated before nitration reaction.
    b. pK_b of aniline is lower than the m-nitroaniline.
    c. Primary amine on treatment with benzenesulphonyl chloride forms a product which is soluble in NaOH however secondary amine gives productwhich is insoluble in NaOH.
    d. Aniline does not react with methyl chloride in the presence of anhydrous $AlCl_3$ catalyst.

30. a. Identify the major product formed when 2-

cyclohexylchloroethane undergoes a dehydrohalogenation reaction. Name the reagent which isused to carry out the reaction.

b. Why are haloalkanes more reactive towards nucleophilic substitutionreactions than haloarenes and vinylic halides?

OR

a. Name the possible alkenes which will yield 1-chloro-1-methylcyclohexaneon their reaction with HCl. Write the reactions involved.

b. Allyl chloride is hydrolysed more readily than n-propyl chloride. Why?

SECTION D

The following questions are case-based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer thequestions that follow.

31. Strengthening the Foundation: Chargaff Formulates His "Rules"

Many people believe that James Watson and Francis Crick discovered DNA in the 1950s. In reality, this is not the case. Rather, DNA was first identified in the late 1860s by Swiss chemist Friedrich Miescher. Then, in the decades following Miescher's discovery, other scientists--notably, Phoebus Levene and Erwin Chargaff--carried out a series of research efforts that revealed additional details about the DNA molecule, including its primary chemical components and the waysin which they joined with one another. Without the scientific foundation provided by these pioneers, Watson and Crick may never have reached their groundbreaking conclusion of 1953: that the DNA molecule exists in the form of athree-dimensional double helix.

Chargaff, an Austrian biochemist, as his first step in this DNA research, set out to see whether there were any differences in DNA among different species. After developing a new paper chromatography method for separating and identifying small amounts of organic material, Chargaff reached two major conclusions:

(i) the nucleotide composition of DNA varies among species.

(ii) Almost all DNA, no matter what organism or tissue type it comes from maintainscertain properties, even as its composition varies. In particular, the amount of adenine (A) is similar to the amount of thymine (T), and the amount of guanine (G)approximates the amount of cytosine (C). In other words, the total amount of purines (A + G) and the total amount of pyrimidines (C + T) are usually nearly equal. This conclusion is now known as "Chargaff's rule."

Chargaff's rule is not obeyed in some viruses. These either have single- stranded DNA or RNA as their genetic material.

Answer the following questions:

a. A segment of DNA has 100 adenine and 150 cytosine bases. What is the total number of nucleotides present in this segment of DNA?
b. A sample of hair and blood was found at two sites. Scientists claim that thesamples belong to same species. How did the scientists arrive at this conclusion?
c. The sample of a virus was tested and it was found to contain 20% adenine,20% thymine, 20 % guanine and the rest cytosine. Is the genetic materialof this virus (a) DNA- double helix (b) DNA-single helix (c) RNA? What do you infer from this data?

OR

How can Chargaff's rule be used to infer that the genetic material of an organism is double- helix or single- helix?

32. Henna is investigating the melting point of different salt solutions.
She makes a salt solution using 10 mL of water with a known mass of NaCl salt.
She puts the salt solution into a freezer and leaves it to freeze.
She takes the frozen salt solution out of the freezer and measures thetemperature when the frozen salt solution melts. She repeats each experiment.

S.No	Mass of the salt used in g	Melting point in ^0C	
		Readings Set 1	Reading Set 2
1	0.3	-1.9	-1.9
2	0.4	-2.5	-2.6
3	0.5	-3.0	-5.5
4	0.6	-3.8	-3.8
5	0.8	-5.1	-5.0
6	1.0	-6.4	-6.3

Assuming the melting point of pure water as 0^oC, answer the following

questions:

a. One temperature in the second set of results does not fit the pattern. Which temperature is that? Justify your answer.
b. Why did Henna collect two sets of results?
c. In place of NaCl, if Henna had used glucose, what would have been the melting point of the solution with 0.6 g glucose in it?

OR

What is the predicted melting point if 1.2 g of salt is added to 10 mL of water? Justify your answer.

SECTION E

The following questions are long answer type and carry 5 marks each. Two questions have an internal choice.

33. a. Why does the cell voltage of a mercury cell remain constant during its lifetime?

b. Write the reaction occurring at anode and cathode and the products of electrolysis of aq KCl.

c. What is the pH of HCl solution when the hydrogen gas electrode shows a potential of -0.59 V at standard temperature and pressure?

35. Answer the following:

a. Why are all copper halides known except that copper iodide?
b. Why is the $E^{o}(V^{3+}/V^{2+})$ value for vanadium comparatively low?
c. Why HCl should not be used for potassium permanganate titrations?
d. Explain the observation, at the end of each period, there is a slight increase in the atomic radius of d block elements.
e. What is the effect of pH on dichromate ion solution?

MARKING SCHEME SECTION A

Q1 to 18 each correct answer 1 mark

1. b. 1-methylcyclohexene

According to Saytzeff rule i.e highly substituted alkene is major product. Heredehydration reaction takes place, alkene is formed due to the removal of a water molecule.

2. c $C_6H_5CH\ (C_6H_5)Br$
$C_6H_5CH\ (C_6H_5)+$ carbocation formed is more stable

3. b. charge transfer from ligand to metal
The Mn atom in $KMnO_4$ has +7 oxidation state with electron configuration $[Ar]3d^{0}4s^{0}$ Since no unpaired electrons are present, d−d transitions are notpossible. The molecule should, therefore, be colourless. Its intense purple due to L→M (ligand to metal) charge transfer 2p(L) of O to3d(M) of Mn.

4. a. ^{15}O

The rate constant for the decay of O-15 is less than that for O-19 . Therefore ,the rate of decay of O-15 will be slower and will have a longer half life .

5. b. 115 Scm^2/mol
$\Lambda^{O}CH3COOK = \Lambda^{O}\ CH3COOH + \Lambda^{O}KCl - \Lambda^{O}HCl = 390 + 150 - 425 = 115\ Scm^2/mol$

5* (For visually challenged learners)a. $124.66 \times 10^{-4}\ Sm^2mol^{-1}$

Molar conductance of NaCl = $\lambda^{+}Na + \lambda^{+}Cl$

$= 51.12 \times 10^{-4} + 73.54 \times 10^{-4}$

$= 124.66 \times 10^{-4}\ Sm^2mol^{-1}$

6. a. increases 4 times

Rate = $[A]^2$
If [A] is doubled then Rate’ = $[2A]^2 = 4\ [A]^2 = 4$ Rate

7. d. B<C<A
In primary amine intermolecular association due to H-bonding is maximumwhile in tertiary it is minimum.

8. b. 8000 cm^{-1}

$\Delta t = (4/9) \times 18000 cm^{-1} = 8000\ cm^{-1}$

9. d. A.=$C_6H_5CH_2Br$, B = C_6H_5OH,

$C_6H_5CH_2OC_6H_5$ H^+

$C_6H_5CH_2OC_6H_5$

10. c. CH_3NH_2 on reaction with nitrous acid releases NO_2 gas Wrong statement . The evolution of nitrogen gas takes place.

11. c. 2,4 DNP test
Fehling's, Tollen's and Cannizzao reaction is shown by alcohols only.

12. c.(i)ln A (ii) - Ea/R

12* (For visually challenged learners)

d. $mol^{-2}\ L^{2}\ s^{-1}$ since the order of reaction is 3.

13. c. 5
$1Fe^{2+}$, 2 SO_4^{2-} and 2 NH_4^{+} ions

14. A Etard reaction

15. b Both A and R are true but R is not the correct explanation of A.A and R are two different statements about ethers
The correct reason is that hydrogen bonding does not exist amongst ether molecules.

16. b Both A and R are true but R is not the correct explanation of A.

17. b Both A and R are true but R is not the correct explanation of A.
The magnetic moment is less as the 5f electrons of actinides are less effectively shielded which results in quenching of orbital contributions , theyare strongly paramagnetic due to presence of unpaired electrons

18. a Both A and R are true and R is the correct explanation of A.

SECTION B

19. Half life t1/2 = 0.693 /k
k= 0.693/69.3 = 1/100 = 0.01 min^{-1} (1/2)
For first order reaction

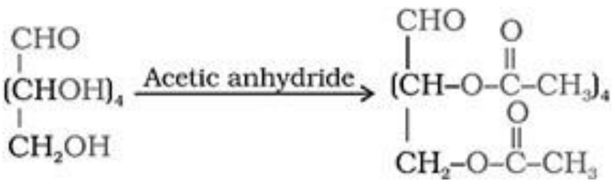
$$k = \frac{2.303}{t} \log \frac{[Ro]}{[R]}$$ (1)

$$t = \frac{2.303}{0.01} \log \frac{100}{20}$$

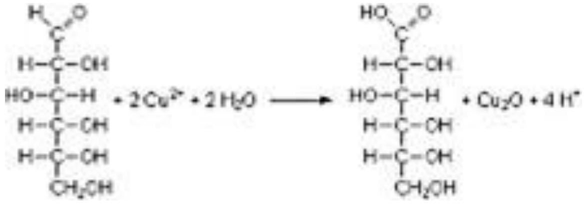
t = 230.3 log 5 (log 5 =0.6990)

t= 160.9 min (1/2)

20. a. Acetylation of glucose with acetic anhydride gives glucose pentaacetate which confirms the presence of five –OH groups. Since it exists as a stable compound, five –OH groups should be attached to different carbon atoms (1)



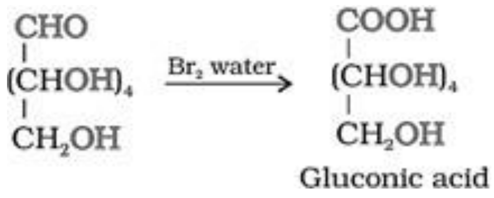
b. Glucose reduces Fehlings reagent



(1)

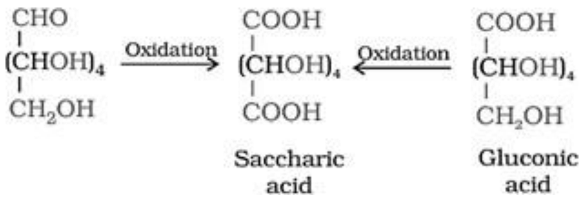
OR

a.



(1)

b.



(1)

21.

a. At the ortho position, higher steric hindrance is there, hence para isomer is usuallypredominate and is obtained in the major amount. (1)

b.During the SN^1 mechanism, intermediate carbocation formed is sp^2 hybridized and planar in nature. This allows the attack of nucleophile from either side of the plane resulting in a racemic mixture. (1)

OR

a. Tert butyl alcohol or 2-methyl propan-2-ol using Lucas reagent , mixture of concHCl and ZnCl2 the reaction will follow the SN^1 pathway.

(1)b.Chloromethane is having higher dipole moment . Due to smaller size of fluorine the dipole moment of flouromethane is comparatively lesser. (1)

22. [Co(NH3)5CO3]Cl and [Co(NH3)5Cl]CO3 (1/2+1/2)

Pentaaminecarbonatocobalt(III)chloride (1/2)

Pentaaminechloridocobalt(III)carbonate (1/2)

23. Anode: Zn (s) □ Zn^{2+} (aq) + 2 e- (1/2)

Cathode: O2(g) + 2H2O(l) + $4e^-$ → $4OH^-$ (aq). (1/2)

Overall: 2 Zn (s) + O2(g) + 2H2O(l) □ 2 Zn^{2+} (aq) + $4OH^-$ (aq)

2 Zn (s) + O2(g) + 2H2O(l) □ 2 Zn(OH)2 (ppt) (1)

24. The rate of reaction will increase. The catalyst decreases the activation energy of the reaction therefore the reaction becomes faster.

(1/2+1/2)b.The rate of reaction will decrease. At lower temperatures the kinetic energy of molecules decreases thereby the collisions decrease resulting in a lowering of rate of reaction.

(1/2+1/2)

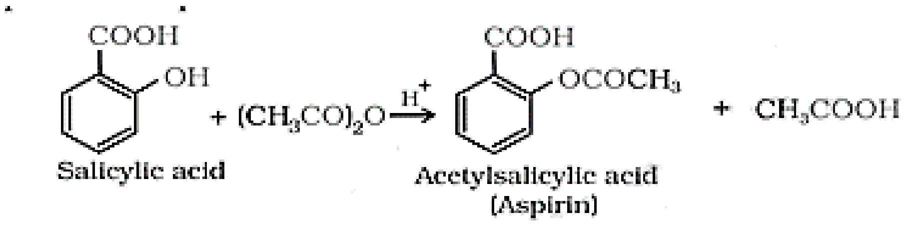
25. $(CH_3)_2CHCHO + C_2H_5MgBr \xrightarrow{\text{dry ether}} (CH_3)_2CHCH(C_2H_5)(OMgBr)$

$(CH_3)_2CHCH(C_2H_5)(OMgBr) \xrightarrow{H^+/H_2O} (CH_3)_2CHCH(C_2H_5)(OH)$ (1)

2-Methylpentan-3-ol

SECTION C

26. (i) Aspirin is formed

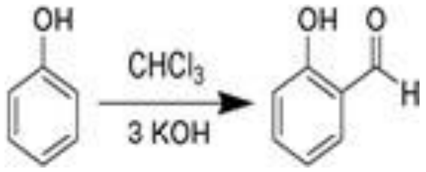


(1)

(ii) $(CH_3)_3CCl \xrightarrow{\text{sodium ethoxide}} (CH_3)_2C{=}CH_2$

2methylpropene (1)

(iii) o-hydroxybezaldehyde will be formed



(1)

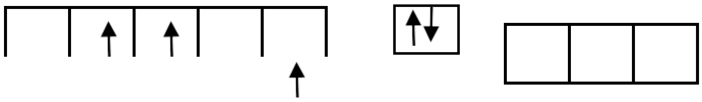
27. $[Mn(CN)6]^{3-}$

Mn = [Ar]

$3d^5 4s^2$ Mn^{3+}

= [Ar] $3d^4$

Mn (ground state)



Mn in +3 state

Mn in $[Mn(CN)_6]^{3-}$

d^2sp^3 hybridisation

xx are electrons donated by ligand CN^-

Type of hybridization – d^2sp^3 (1)

Magnetic moment value – $\surd n(n+2) = \surd(2(2+2)) = 2.87$ BM

(n= no. of unpaired electrons) (1)

Type of complex – inner orbital (1)

28. a. Henry's law: the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution. (1)

The pressure underwater is high, so the solubility of gases in blood increases. Whenthe diver comes to surface the pressure decreases so does the solubility causing bubbles of nitrogen in blood, to avoid this situation and maintain the same partial pressure of nitrogen underwater too, the dilution is done. (1)

b. $p = KH\ x$

mole fraction of argon in water $x = p/k = 6/ 40 \times 10^3 = 1.5 \times 10^{-4}$ (1)

29. (any 3)

a. Aniline is acetylated, before nitration reaction in order to avoid formation of tarry oxidation products and protecting the amino group, so that p -nitro derivativecan be obtained as major product. (1)

b.pKb of aniline is lower than the m-nitro aniline.The basic strength of aniline ismore that m-nitroaniline . pkb value is inversely proportional to basic strength. Presence of Electron withdrawing group decrease basic strength. (1)

c. Due to the presence of acidic hydrogen in the N-alkylbenzenesulphonamide formed by the treatment of primary amines. (1)

d. Aniline does not react with methylchloride in the presence of $AlCl_3$ catalyst , because aniline is a base and $AlCl_3$ is Lewis acid which lead to formation of salt.

(1)

30.

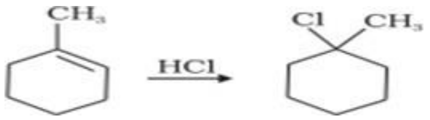
a. The major product formed when 2-cyclohexylchloroethane undergoes dehydrohalogenation reaction is 1- cyclohexylethene. The reagent which is usedto carry out the reaction is ethanolic KOH. (1+1)

b. Haloalkanes are more reactive than haloarenes and vinylic halides because of the presence of partial double bond character C-X bond in haloarenes and vinylic halides. Hence they do not undergo nucleophilic reactions easily. (1)

OR

a. Methylenecyclohexane

1-Methylcyclohexene (1/2+1/2)



(1/2+1/2)

b. Allyl chloride shows high reactivity as the carbocation formed in the first step isstabilised by resonance while no such stabilisation of carbocation exists in the case ofn-propyl chloride. (1)

SECTION D

31. a. A = 100 so T = 100

C=150 so G = 150

Total nucleotides = 100+100+150+150 =500 (1)

b. They studied the nucleotide composition of DNA. It was the same so they concluded that the samples belong to same species. (1)

c. A = T = 20%

But G is not equal to C so double helix is ruled out. (1/2)
The bases pairs are ATGC and not AUGC so it is not RNA (1/2)
The virus is a single helix DNA virus (1)

OR

According to Charagraff rule, all double helix DNA will have the same amount ofA and T as well as C will be same amount as G. If this is not the case then the helix is single stranded. (2)

32. The melting point of ice is the freezing point of water. We can use the depressionin freezing point property in this case.

a. 3rd reading for 0.5 g there has to be an increase in depression of freezing pointand therefore decrease in freezing point so also decrease in melting point when amount of salt is increased but the trend is not followed on this case. (1)

b.two sets of reading help to avoid error in data collection and give more objective data. (1)

c. ΔTf (glucose) = $1 \times Kf \times \frac{0.6 \times 1000}{180 \times 10}$ (1/2)

ΔTf (NaCl) = $2 \times Kf \times \frac{0.6 \times 1000}{58.5 \times 10}$ (1/2)

$3.8 = 2 \times Kf \times \frac{0.6 \times 1000}{58.5 \times 10}$

Divide equation 1 by

2 $\underline{\Delta Tf\ (glucose)}$ =

$\underline{58.}$

$\underline{5}$

3.8 2x 180 (1/2)

ΔTf (glucose = 0.62 Freezing point or Melting point = - 0.62 ^{o}C (1/2)

OR

depression in freezing point is directly proportional to molality (mass of solute whenthe amount of solvent remains same) (1)

0.3 g depression is 1.9 ^{O}C

0.6 g depression is 3.8 ^{O}C

1.2 g depression will be 3.8 x2 = 7.6 ^{O}C (1)

SECTION E

33. The cell potential remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.(1)

b. KCl (aq) à K^+ (aq) + Cl^- (aq)

cathode: H_2O(l) + e- à ½ H_2 (g) + OH^- (aq) (1/2)

anode: Cl- (aq) à ½ Cl_2 (aq) + e- (1/2)

net reaction:

KCl (aq) + H_2O (l) à K^+ (aq) +OH^- (aq) + ½ H_2 (g) + ½ Cl_2 (g) (1)

c. Given, potential of hydrogen gas electrode = –0.59 V

Electrode reaction: $H^+ + e^- \rightarrow 0.5\ H_2$

Applying Nernst equation,

$$E\,(H^+/H_2) = E^o\,(H^+/H_2) - \frac{0.059}{n} \log \frac{[H_2]^{1/2}}{[H^+]}$$ (1)

E^o (H^+/H_2) = 0 V

E (H^+/H_2) = -0.59 V

n = 1

$[H_2]$ =1 bar

$-0.59 = 0 - 0.059\ (- \log\ [H^+])$ (1/2)

$-0.59 = -0.059$pH

∴ pH = 10 (1/2)

OR

a. “A” is copper, metals are conductors thus have high value of conductivity. (1)

b. Mg^{2+} + $2e^-$ à Mg

1 mole of magnesium ions gains two moles of electrons or 2F to form 1 mole of Mg24 g Mg requires 2 F electricity

4.8 g Mg requires 2 x4.8/24 = 0.4 F = 0.4 x96500 = 38600C (1)

Ca^{2+} + $2e^-$ □Ca

2 F electricity is required to produce 1 mole =40 g Ca

0.4 F electricity will produce 8 g Ca (1)

c. F = 96500C, n=2,

Sn^{2+} (aq) + $2e^- \rightarrow$ Sn(s) –0.14V

$Cu^{2+}(aq) + e^{-}$ □ $Cu^{+}(aq)$ 0.15

$VE^{o}cell = E^{o}cathode – E^{o}$ anode

$= 0.15 – (-0.14) = 0.29V$ (1)

$\Delta G^{o} = -nFE^{o}cell$

$= -2 \times 96500 \times 0.29 = 55970$ J/mol (1)

34. A is an alkene

B is an aldehyde with –CH3

groupC is a methyl ketone

$CH_3CHO + [Ag(NH_3)_2]^{+} + OH^{-} \longrightarrow CH_3COO^{-} + Ag + NH_3 + H_2O$ (1/2)

$CH_3COCH_3 + NaOH + I_2 \longrightarrow CHI_3 + CH_3COONa$ (1/2)

A : $CH(CH_3)=C(CH_3)_2$ B: CH_3CHO

C: O=C(CH3)2 (1.5 = 1/2 each)

$CH_3COCH_3 + CH_3CHO$

$\downarrow Ba(OH)_2$

$(CH_3)_2C(OH)CH_2COCH_3 + CH_3CH(OH)CH_2CHO + (CH_3)_2C(OH)CH_2CHO + CH_3CH(OH)CH_2COCH_3$

$\downarrow$ heat

$(CH_3)_2C=CHCOCH_3 + CH_3CH=CHCHO + (CH_3)_2C=CHCHO + CH_3CH=CHCOCH_3$ (2.5 = 1/2 mark for each product, ½ for the reaction)

OR

a. (A): CCl_3COOH
b. (B): CH_3COOH (1)

c. $CH_3COOH \xrightarrow{\text{(i)Red P / Cl2}} CCl_3COOH$, Hell Volhard Zelinsky reaction (1/2

+1/2)(ii)H_2O

d. $CH_3COCl \xrightarrow{H_2O} CH_3COOH$ (1)

e. A will be more acidic due to presence of 3 Cl groups (electron withdrawing groups)which increase acidity of carboxylic acid. (1)

f. $CH_3COOH \xrightarrow{\text{(i)NaOH, CaO (ii) heat}} CH_4 + Na_2CO_3$ (1)

35. a. Cu^{2+} oxidizes iodide ion to iodine. (1)
   b. The low value for V is related to the stability of V^{2+} (half-filled t2g level) (1)
   c. Permanganate titrations in presence of hydrochloric acid are unsatisfactorysince hydrochloric acid is oxidised to chlorine.
   d. The d orbital is full with ten electrons and shield the electrons present in thehigher s-orbital to a greater extent resulting in increase in size.
   e. The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. Increasing the pH (in basic solution)of dichromate ions a colour change from orange to yellow is observed as dichromate ions change to chromate ions.

CHAPTER 1 SOLUTIONS

KEY POINTS

- Molarity (M) is the number of moles of solute present in 1L of solution.
- Molality (m) is the number of moles of solute present in 1kg of solvent.
- Normality (N) is the number of gram equivalents of solute dissolved per litre of solution.
- Mass %, ppm, mole fraction and molality are independent of temperature, whereas normality and molarity are function of temperature. This is because volume depends on temperature and mass does not.
- Mass by volume percentage (w/v): Mass of the solute dissolved in 100 mL of solution.
- **Parts Per Million (ppm):**

  When a solute is present in very minute amounts (trace quantities), the concentration is expressed in parts per million abbreviated as ppm.

  It is the parts of a component per million parts of the solution. It is expressed as

  $$ppm = \frac{\text{Number of parts of component}}{\text{Total number of parts of all components of solution}} X\ 10^6$$

- **Mole fraction** :It is the ratio of number of moles of one component to the total number of moles (solute and solvent) present in the solution.

  $$\text{Mole fraction of component} = \frac{\text{Moles of component}}{\text{Total number of moles of all the component}}$$

  A solution contains n_A moles of solute and n_B moles of the solvent. Then

$$\text{Mole fraction of A} = x_A = \frac{n_A}{n_A + n_B}$$

$$\text{Mole fraction of B} = x_B = \frac{n_B}{n_A + n_B}$$

The sum of mole fractions of all the components in solution is always equal to one.

$$\boldsymbol{\chi_A + \chi_B = 1}$$

- **Mole Fraction in the vapour phase**

  If $y_1$and y_2 are the mole fractions of components 1 and 2 in the vapour phase, then:

  $p_1=y_1.p_{total}$; $p_2=y_2.p_{total}$

  Generally, $\mathbf{p_i=y_i.p_{total}}$

- **Henry's Law**: It states that "At a constant temperature the solubility of gas in a liquid is directly proportional to the pressure of gas". In other words, "the partial pressure of gas in vapour phase is proportional to the mole fraction of the gas in the solution".

  Mathematically, $p = K_H \varkappa$ where p is the partial pressure of the gas; and $\varkappa$ is the mole fraction of the gas in the solution and K_H is Henry's Law constant.

- According to Raoult's Law, the vapour pressure of a solution containing a non-volatile solute is directly proportional to the mole fraction of the solvent ($\varkappa_A$). The proportionality constant is the vapour pressure of the pure solvent ($p°_A$)

  $$p_A = p°_A \, \varkappa_A$$

- A solution which obeys Raoult’s Law at all concentrations and temperatures is known as an ideal solution.

- **Characteristics of an ideal solution**:

The solutions that obey Raoult’s Law over the entire range of concentrations are known as ideal solutions.

$\Delta_{mix}H = 0$ and $\Delta_{mix}V = 0$

The intermolecular attractive forces between solute molecules and solvent molecules are nearly equal to those present between solute and solvent molecules i.e. A-A and B-B interactions are nearly equal to those between A-B.

- **Non-ideal solutions:**

When a solution does not obey Raoult’s Law over the entire range of concentration, then it is called non-ideal solution.

$\Delta_{mix}H \neq 0$ and $\Delta_{mix}V \neq 0$

The intermolecular attractive forces between solute molecules and solvent molecules are not equal to those present between solute and solvent molecules i.e. A-A and B-B interactions are not equal to those between A-B

- **Positive deviation**

The vapour pressure of a solution is higher than that predicted by Raoult’s Law.

The intermolecular attractive forces between solute-solvent molecules are weaker than those between solute-solute and solvent-solvent molecules i.e., A-B < A-A and B-B interactions.

$\Delta H_{mix} > 0$, $\Delta V_{mix} > 0$

Examples: Ethanol with acetone, carbon disulphide and acetone.

- **Negative deviation**

The vapour pressure of a solution is lower than that predicted by Raoult's Law.

The intermolecular attractive forces between solute-solvent molecules are stronger than those between solute-solute and solvent-solvent molecules i.e. A-B > A-A and B-B interactions.

$\Delta H_{mix}<0$, $\Delta V_{mix}<0$

Examples : phenol and aniline, chloroform and acetone

- Azeotopes: These are binary mixtures having same composition in liquid and vapour phase and boil at constant temperature. Liquids forming azeotrope cannot be separated by fractional distillation.
- Types of azeotropes: There are two types of azeotropes namely,
    - Minimum boiling azeotrope
    - Maximum boiling azeotrope

The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition.

The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition.

- Colligative properties: The properties of solution which depends only on the number of solute particles but not on the nature of solute are called colligative properties.
- Types of colligative properties: There are four colligative properties namely,

Relative lowering of vapour pressure
Elevation of boiling point
Depression of freezing point
Osmotic pressure

- Osmosis: The phenomenon of flow of solvent molecules through a semi permeable membrane from pure solvent to solution is called osmosis.
- Semipermeable membrane **:** The membrane which allows the solvent molecules, but not the solute molecules, to pass through it is called

semipermeable membrane(SPM). Parchment membrane, cellulose nitrate, animal bladder, etc can be used as semipermeable membranes.

- Osmotic pressure: The excess pressure that must be applied on the solution side to prevent the passage of solvent into solution through a semipermeable membrane is called osmotic pressure.

  Osmotic pressure can also be used to determine the molar mass of solute using the equation :

  $$M_2 = \frac{w_2RT}{\pi V}$$

- Isotonic solution: Two solutions having same osmotic pressure at a given temperature are called isotonic solution.
- Hypertonic solution: If a solution has more osmotic pressure than other solution it is called hypertonic solution.
- Hypotonic solution: If a solution has less osmotic pressure than other solution it is called hypotonic solution.
- Reverse osmosis: The process of movement of solvent through a semipermeable membrane from the solution to the pure solvent by applying excess pressure on the solution side is called reverse osmosis.
- Abnormal molar mass: Molar mass that is either lower or higher than expected or normal molar mass is called as abnormal molar mass.
- Van’t Hoff factor:Van’t Hoff factor(i)accounts for the extent of dissociation or association $i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$

  $$= \frac{\text{Total number of moles of particles after association / dissociation}}{\text{Total number of moles of particles before association / dissociation}}$$

  Value of i is less than unity in case solute undergo association and the value of i is greater than unity in case solute undergo dissociation.

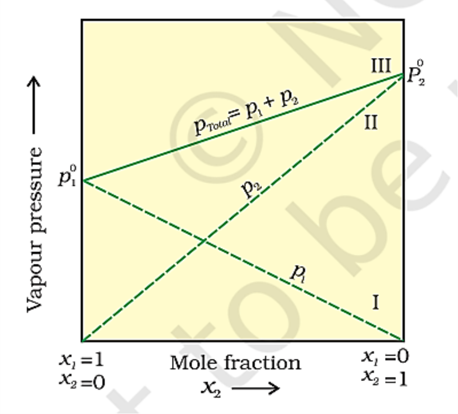
- **Degree of dissociation:** It is defined as the fraction of total substance that undergoes dissociation into ions, i.e.

Degree of dissociation = No. of moles of the substance dissociated / Total number of moles of the substance taken

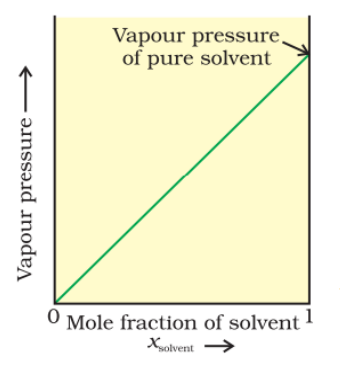
- **Degree of association:** It is defined as the fraction of total number of molecules which combine to form associated molecules, i.e.

Degree of association = No. of moles of the substance associated / Total number of moles of substance taken

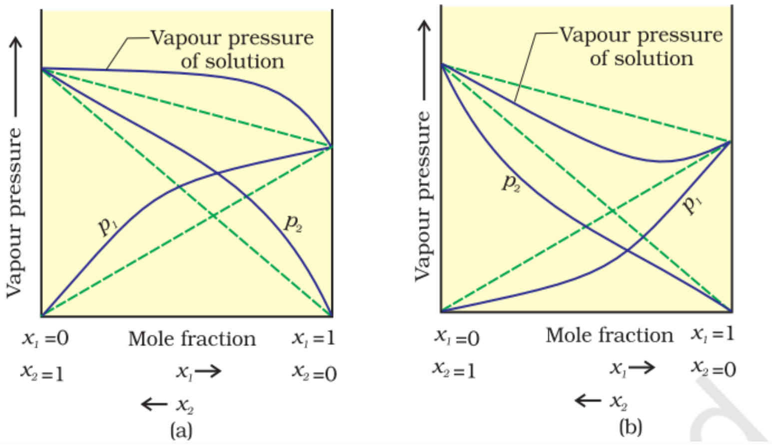
GRAPHS/DIAGRAMS



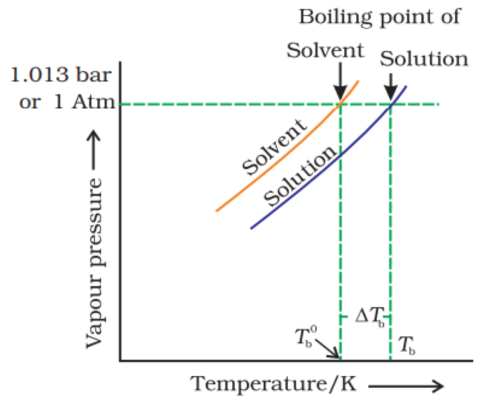
[Ideal solution]



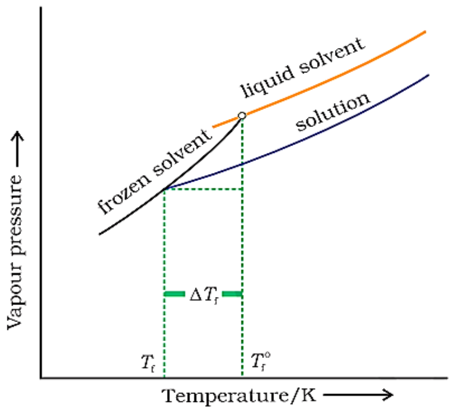
[*If a solution obeys Raoult's law for all concentrations, its vapour pressure would vary linearly from zero to the vapour pressure of the pure solvent*]



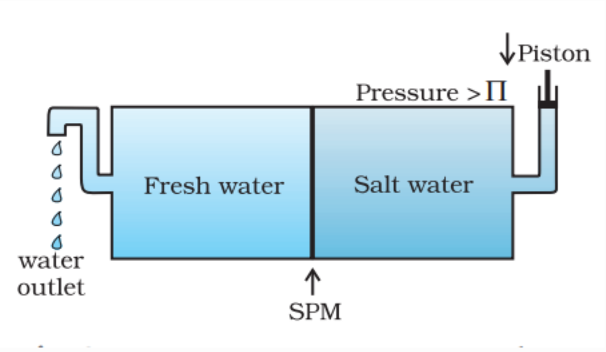
[(a) a solution that shows positive deviation from Raoult's law and (b) a solution that shows negative deviation from Raoult's law]



[The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that ΔT_b denotes the elevation of boiling point of a solvent in solution.]



[Diagram showing ΔT_f, depression of the freezing point of a solvent in a solution].



- ***[Reverse osmosis occurs when a pressure more than the osmotic pressure is applied to the solution]***

IMPORTANT FORMULAE

$$Molality = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kilograms}}$$

$$Molarity = \frac{\text{Number of moles of solute}}{\text{Volume of solution in litres}}$$

The difference in boiling points of solution T_b and pure solvent T_b^0 is called elevation in boiling point $\Delta T = T_b - T_b^0$

$$\Delta T_b = \frac{k_b \text{ x } 1000 \text{ x } w_2}{M_2 \text{ x } w_1}$$

$$\Delta T_f = \frac{k_f \text{ x } 1000 \text{ x } w_2}{M_2 \text{ x } w_1}$$

$$\frac{p_1^0 - p}{p_1^0} = i.\frac{n_2}{n_1}$$

$$\Delta T_b = i.\frac{k_b \text{ x } 1000 \text{ x } w_2}{M_2 \text{ x } w_1}$$

$\pi = i\, cRT$

$$\Delta T_f = i.\frac{k_f \text{ x } 1000 \text{ x } w_2}{M_2 \text{ x } w_1}$$

FOR DISSOCIATION

α =(i-1) /(n -1)

n is the number of ions after dissociation

α is the degree of dissociation

FOR ASSOCIATION

α =(i-1) /(1/n -1)

n is the number of simple molecules which combine to give associated molecule

α is the degree of association

MULTIPLE CHOICE QUESTIONS

1.The system that forms maximum boiling azeotrope is

(a) Acetone-chloroform

(b) ethanol-acetone

(c) n-hexane-n-heptane

(d) carbon disulphide-acetone

Answer: (a) Acetone-chloroform

2.For carrying reverse osmosis for desalination of water the material used for making semipermeable membrane is

(a) potassium nitrate

(b) parchment membrane

(c) cellulose acetate

(d) cell membrane

Answer: (c) cellulose acetate

3.The relative lowering in vapour pressure is proportional to the ratio of number of

(a) solute molecules to solvent molecules

(b) solvent molecules to solute molecules

(c) solute molecules to the total number of molecules in solution

(d) solvent molecules to the total number of molecules in solution

Answer: (c) solute molecules to the total number of molecules in solution

4.Sprinkling of salt helps in clearing the snow covered roads in hills. The phenomenon involved in the process is

(a) lowering in vapour pressure of snow

(b) depression in freezing point of snow

(c) melting of ice due to increase in temperature by putting salt

(d) increase in freezing point of snow

Answer: (b) depression in freezing point of snow

5.A plant cell shrinks when it is kept in a

(a) hypotonic solution

(b) hypertonic solution

(c) isotonic solution

(d) pure water

Answer: (b) hypertonic solution

6.The value of Henry's constant K_H _.

(a) increases with increase in temperature.

(b) decreases with increase in temperature.

(c) remains constant.

(d) first increases then decreases.

Answer: (a) increases with increase in temperature.

7. The Van't Hoff factor (i) accounts for

(a) degree of association of solvent

(b) the extent of dissociation of solute.

(c) the extent of dissolution of solute.

(d) the degree of decomposition of solution.

Answer: (b) the extent of dissociation of solute.

8.People add sodium chloride to water while boiling eggs. This is to

(a) decrease the boiling point.

(b) increase the boiling point.

(c) prevent the breaking of eggs.

(d) make eggs tasty.

Answer: (b) increase the boiling point.

9.Which has the lowest boiling point at 1 atm pressure?

(a) 0.1 M KCl

(b) 0.1 M Urea

(c) 0.1 M $CaCl_2$

(d) 0.1 M $A1Cl_3$

Answer:(b) 0.1 M Urea

10.An unripe mango placed in a concentrated salt solution to prepare pickle, shrivels because
(a) it gains water due to osmosis
(b) it loses water due to reverse osmosis
(c) it gains water due to reverse osmosis
(d) it loses water due to osmosis
Answer:(d) it loses water due to osmosis

11.The value of Van’t Hoff factors for KCl, NaCl and K_2SO_4, respectively are
(a) 2, 2 and 2
(b) 2, 2 and 3
(c) 1, 1, and 2
(d) 1, 1 and 1
Answer: (b) 2, 2 and 3

12.H_2S is a toxic gas used in qualitative analysis. If solubility of H_2S in water at STP is 0.195 m. what is the value of K_H?

(a) 0.0263 bar

(b) 69.16 bar

(c) 192 bar

(d) 282 bar

Answer:(d) 282 bar

13.A 5% solution of cane-sugar (molecular weight = 342) is isotonic with 1% solution of substance A. The molecular weight of X is

(a) 342

(b) 171.2

(c) 68.4

(d) 136.8

Answer:(c) 68.4

14.Which of the following 0.1 M aqueous solutions will have the lowest freezing point?

(a) potassium sulphate

(b) sodium chloride

(c) urea

(d) glucose

Answer:(a) potassium sulphate

15.Which of the following salt will have same value of Vant Hoff's factor (i) as that of

$K_4[Fe\ (CN)_6]$

(a) $Al_2(SO_4)_3$

(b) NaCl

(c) $Al(NO_3)_3$

(d) Na_2SO_4

Answer:(a) $Al_2(SO_4)_3$

16..Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixture will show a positive deviation from Raoulf s law?
(a) Methanol and acetone

(b) Chloroform and acetone
(c) Nitric acid and water

(d) Phenol and aniline

Answer:(a) Methanol and acetone

17.At a given temperature, osmotic pressure of a concentrated solution of a substance

(a) is higher than that of a dilute solution

(b) is lower than that of a dilute solution

(c) is same as that of a dilute solution

(d) cannot be compared with osmotic pressure of dilute solution

Solution:(a) is higher than that of a dilute solution

ASSERTION-REASON QUESTIONS

Given below are two statements labelled as Assertion (A) and Reason (R). Select the most appropriate answer from the options given below :

a. Both A and R are true and R is the correct explanation of A

b. Both A and R are true but R is not the correct explanation of A.

c. A is true but R is false.

d. A is false but R is true.

1. Assertion : When a solution is separated from the pure solvent by a semi-permeable membrane, the solvent molecules pass through it from pure solvent side to the solution side

Reason : Movement of solvent from a region of high concentration to a region of low concentration.

Answer : (c)

2.Assertion : Molarity of a solution changes with temperature.
Reason : The volume of a solution changes with change in temperature.

Answer : (a)

3. Assertion : Azeotropic mixtures are formed only by non-ideal solutions and they may have boiling points either greater than both the components or less than both the components.
Reason : The composition of the vapour phase is same as that of the liquid phase of an azeotropic mixture.

Answer : (b)

4. Assertion : If one component of a solution obeys Raoult's law over a certain range of composition, the other component will not obey Henry's law in that range.
Reason : Raoult's law is a special case of Henry's law.

Answer:(b)

5. Assertion: 1 M solution of KCl has greater osmotic pressure than 1 M solution of glucose at the same temperature.
Reason: In solution, KCl dissociates to produce more number of particles.
Answer:(a)

6. Assertion : When NaCl is added to water a depression in freezing point is observed.

Reason : The lowering of vapour pressure of a solution causes depression in the freezing point.

Answer(a)

7. Assertion: Two liquids nitric acid and water form a maximum boiling azeotrope when mixed in the ratio of 68% and 32% respectively.

Reason: Interaction between nitric acid and water are stronger than nitric acid – nitric acid interactions and water-water interactions.

Answer: (a)

8. Assertion: The addition of ethylene glycol (non–volatile) to water lowers the freezing point of water hence used as antifreeze

Reason: Heat must be removed from the water to make it freeze.

Answer:(c)

9. Assertion: On adding NaCl to water its vapour pressure increases.

Reason: The addition of non-volatile solute decreases the vapour pressure.

Answer:(d)

10. Assertion: Lowering of vapour pressure is not dependent on the number of species present in the solution.

Reason: The relative lowering of vapour pressure is a colligative property.

Answer: (d)

11. Assertion: The molecular weight of acetic acid determined by the depression in the freezing point method in benzene and water was found to be different.

Reason: Water is polar and benzene is non-polar

Answer: (a)

1 MARK QUESTIONS

1.Explain why on addition of 1 mol of glucose to 1 litre of water, the boiling point of water increases.

Answer: Glucose is a non-volatile solute, therefore, addition of glucose to water lowers the vapour pressure of water as a result of which boiling point of water increases.

2. Which of the following solutions has lower freezing point?

0.05 M $Al_2(SO_4)_3$, 0.05 M $K_3[Fe(CN)_6]$

Answer:0.05 M $Al_2(SO_4)_3$ has lower freezing point.

3.Why is osmotic pressure of 1 M KCl higher than 1 M urea solution?

Answer: On dissolving in water KCl dissociates into K^+ and Cl^- ions but urea does not dissociate into ions.

4.A person suffering from high blood pressure is advised to take less amount of table salt.Why?

Answer**:** The intake of NaCl can result in increasing the number of solutes in the body fluids. If the solute concentration is increased, the osmotic pressure increase can rupture the blood cells.

5. When fruits and vegetables that have been dried are placed in water, they slowly swell and return to original form**.** Why?

Answer: The drying of fruits or vegetables causes them to become more concentrated. When these are placed in water, the phenomenon of osmosis takes place resulting in the original form of those fruits and vegetables.

6.To avoid bends scuba divers use air diluted with helium. Why?

Answer: The bends during scuba diving is a condition which is very painful and dangerous for life. Thus, divers use helium as a dissolved gas in the air due to its low solubility in human blood.

2 MARKS QUESTIONS

1.Define the terms, ‘osmosis’ and ‘osmotic pressure’. What is the advantage of using osmotic pressure as compared to other colligative properties for the determination of molar masses of solutes in solutions?

Answer:

Osmosis: The net spontaneous flow of the solvent molecules from the solvent to the solution or from a less concentrated solution to a more concentrated solution through a semi-permeable membrane is called Osmosis.

Osmotic pressure: The external pressure that must be applied to the solution side to stop the passage of solvent into the solution through a semi-permeable membrane is known as osmotic Pressure.

The osmotic pressure method has the advantage over other method as pressure measurement is around the room temperature and molarity of the solution is used instead of molality. As compared to other colligative properties, its magnitude is large even for every dilute solution.

2.Blood cells are isotonic with 0.9% sodium chloride solution. What happens if we place blood cells in a solution containing

(i) 1.2% sodium chloride solution?

(ii) 0.4% sodium chloride solution?

Answer:

(i) 1.2% sodium chloride solution is hypertonic with respect to 0.9% sodium chloride solution or blood cells. When blood cells are placed in this solution, water flows out of the cells and they shrink due to loss of water by osmosis.

(ii) 0.4% sodium chloride solution is hypotonic with respect to 0.9% sodium chloride solution or blood cells. When blood cells are placed in this solution, water flows into the cells and they swell.

3.a) What are the units of ebullioscopic constant ?
Solution: K kg mol^{-1}

b)On mixing liquid X and liquid Y, volume of the resulting solution decreases. What type of deviation from Raoult's law is shown by the resulting solution?

Answer:The volume of the resulting solution decreases on mixing liquids X and Y. It shows negative deviation .

3 MARKS QUESTIONS

1.State Henry's law and mention two of its important applications.
Answer:
Henry's law : Henry's law states that "The partial pressure of the gas in vapour phase is proportional to the mole fraction of the gas in the solution ".

Applications of Henry's law :

i)To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

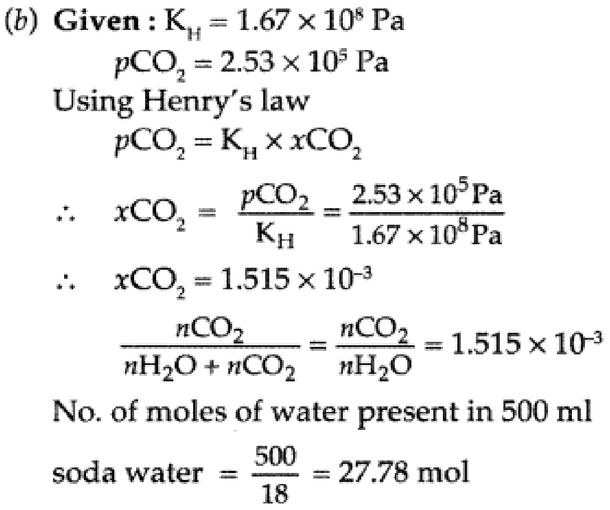
ii)To avoid a dangerous medical condition called bends, scuba divers use oxygen diluted with less soluble helium gas.

2. (a) Out of 1 M glucose and 2 M glucose, which one has a higher boiling point and why?

(b) Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298 K. Calculate the number of moles of CO_2 in 500 ml of soda water when packed under 2.53×10^5 Pa at the same temperature.

Answer:

(a) 2M glucose will have a higher boiling point than 1M glucose because elevation in boiling point is a colligative property which depends upon the number of particles in the solution which is more in the case of 2M glucose solution.



(*b*) **Given :** $K_H = 1.67 \times 10^8$ Pa

$pCO_2 = 2.53 \times 10^5$ Pa

Using Henry's law

$pCO_2 = K_H \times xCO_2$

$$\therefore \quad xCO_2 = \frac{pCO_2}{K_H} = \frac{2.53 \times 10^5 \text{Pa}}{1.67 \times 10^8 \text{Pa}}$$

$$\therefore \quad xCO_2 = 1.515 \times 10^{-3}$$

$$\frac{nCO_2}{nH_2O + nCO_2} = \frac{nCO_2}{nH_2O} = 1.515 \times 10^{-3}$$

No. of moles of water present in 500 ml

$$\text{soda water} = \frac{500}{18} = 27.78 \text{ mol}$$

i.e. $nH_2O = 27.78$ mol

$nCO_2/27.78 = 1.515 \times 10^{-3}$

i.e. $nCO_2 = 42.08 \times 10^{-3}$ moles = 0.042 mol

5 MARKS QUESTIONS

1.(a) A 10% solution (by mass) of sucrose in water has a freezing point of 269.15 K. Calculate the freezing point of 10% glucose in water if the freezing point of pure water is 273.15 K.

Given: (Molar mass of sucrose = 342 g mol^{-1}) (Molar mass of glucose = 180 g mol^{-1})

(b) Define the following terms:

(i) Molality (m)

(ii) Abnormal molar mass

Answer:

(a) Given:

Molar mass of sucrose

$= C_{12}H_{22}O_{11} = 12 \times 12 + 22 + 11 \times 16 = 342$

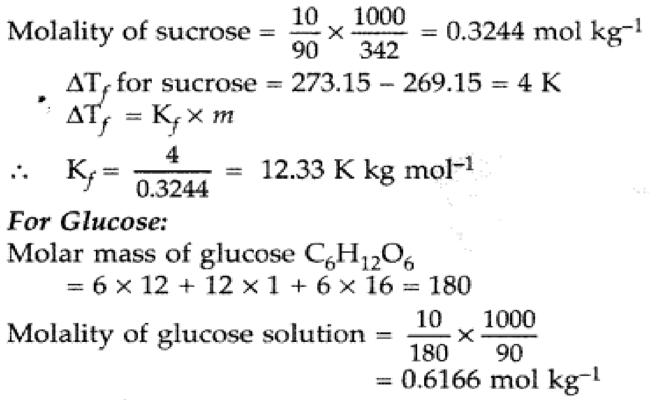
10% solution (by mass) of sucrose in water means 10 g of sucrose is present in

(100 – 10)

= 90 g of water

10% solution of sucrose means, w = 10 g

Mass of water, W = 90 g



$$\text{Molality of sucrose} = \frac{10}{90} \times \frac{1000}{342} = 0.3244 \text{ mol kg}^{-1}$$

$$\Delta T_f \text{ for sucrose} = 273.15 - 269.15 = 4 \text{ K}$$

$$\Delta T_f = K_f \times m$$

$$\therefore \quad K_f = \frac{4}{0.3244} = 12.33 \text{ K kg mol}^{-1}$$

For Glucose:

Molar mass of glucose $C_6H_{12}O_6$

$= 6 \times 12 + 12 \times 1 + 6 \times 16 = 180$

$$\text{Molality of glucose solution} = \frac{10}{180} \times \frac{1000}{90} = 0.6166 \text{ mol kg}^{-1}$$

$\therefore$ ΔT_f for glucose = 12.33 × 0.6166 = 7.60 K (approx.)

$\therefore$ Freezing point of 10% glucose solution

= (273.15 – 7.60) K = 265.55 K

(b) (i) Molality (m): Number of moles of solute dissolved per kg of the solvent.

(ii) Abnormal molar mass: If the molar mass calculated by using any of the colligative properties comes to be different than theoretically expected molar mass.

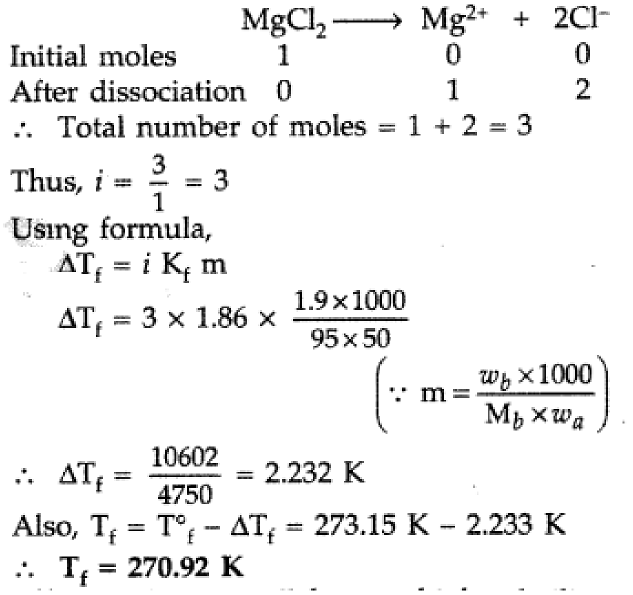
2.(a)Calculate the freezing point of solution when 1.9 g of $MgCl_2$ ($M = 95$ g mol^{-1}) was dissolved in 50 g of water, assuming $MgCl_2$ undergoes complete ionization. (K_f for water = 1.86 K kg mol^{-1})

(b) What is the significance of Henry’s Law constant K_H ?

(c) What happens when the external pressure applied becomes more than the osmotic pressure of solution?

Answer:

(a) Since $MgCl_2$ is an ionic compound, so it undergoes complete dissociation.



$$\begin{array}{lccc} & MgCl_2 \longrightarrow & Mg^{2+} & + \ 2Cl^- \\ \text{Initial moles} & 1 & 0 & 0 \\ \text{After dissociation} & 0 & 1 & 2 \end{array}$$

$\therefore$ Total number of moles $= 1 + 2 = 3$

Thus, $i = \frac{3}{1} = 3$

Using formula,

$$\Delta T_f = i \, K_f \, m$$

$$\Delta T_f = 3 \times 1.86 \times \frac{1.9 \times 1000}{95 \times 50}$$

$$\left(\because \ m = \frac{w_b \times 1000}{M_b \times w_a} \right)$$

$$\therefore \ \Delta T_f = \frac{10602}{4750} = 2.232 \text{ K}$$

Also, $T_f = T^\circ_f - \Delta T_f = 273.15 \text{ K} - 2.233 \text{ K}$

$\therefore$ $\mathbf{T_f = 270.92 \ K}$

(b)Solution: Henry's Law constant (K_H) helps in comparing the relative solubilities of different gases in the same solvent (e.g. water). In general, the lesser the value of K_H, the more the solubility of a gas.

(c) When the external pressure applied becomes more than the osmotic pressure of the solution, then the solvent will flow from the solution into the pure solvent through the semi-permeable membrane. The process is called reverse osmosis (RO).

NUMERICALS

1.Calculate the mass of ascorbic acid (vitamin C, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1·5°C. (K_f for CH_3COOH) = 3·9 K kg mol^{-1})

Solution:

$$W_B = \frac{M_B \times \Delta T_f \times W_A}{K_f}$$

Mass of acetic acid (W_A) = 75 g = 0·075 kg.
Depression in freeing point (ΔT_f) = 1·5°C = 1·5 K
Molar mass of ascorbic acid (M_B) = $6 \times 12 + 8 \times 1 + 6 \times 16 = 176\ \text{g mol}^{-1}$
Molal depression constant (K_f) = $3{\cdot}9\ \text{K kg mol}^{-1}$

$$W_B = \frac{(176\,\text{g mol}^{-1}) \times (1{\cdot}5\,\text{K}) \times (0{\cdot}075\,\text{kg})}{(3{\cdot}9\,\text{K kg mol}^{-1})} = \mathbf{5{\cdot}08\ g}$$

2.Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 mL of water at 37°C.

Solution:

Given: $V = 450\,\text{mL} = 0.45\,\text{L}$
$T = 37°\text{C} = 310\,\text{K}$
$R = 8.314\,\text{kPa L K}^{-1}\,\text{mol}^{-1}$

To find: $\pi = ?$

Solution: Applying the formula,

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

$$n = \frac{1.0\text{g}}{185{,}000\text{g mol}^{-1}}$$

$$\therefore P = \frac{1}{185{,}000} \times \frac{1}{0.45} \times 8.314 \times 10^3\ \text{Pa LK}^{-1}\ \text{mol}^{-1} \times 310\text{K}$$
$$= 30.96\,\text{Pa}$$

3. Assuming complete dissociation, calculate the expected freezing point of a solution prepared by dissolving 6.00 g of Glauber's salt, $Na_2SO_4.10H_2O$ in 0.100 kg of water. (K_f for water = 1.86 K kg mol^{-1}, Atomic masses : Na = 23, S = 32, O = 16, H = 1)

Since $Na_2SO_4.10H_2O$ is an ionic compound, it undergoes complete dissociation.

$$\begin{array}{lccc} & Na_2SO_4 \longrightarrow & 2Na^+ \; + & SO_4^{2-} \\ \text{Initial moles} & 1 & 0 & 0 \\ \text{After dissociation} & 0 & 2 & 1 \end{array}$$

Total number of moles = 2 + 1 = 3

Thus, $i = \frac{3}{1} = 3$

Using the formula :

$$\Delta T_f = i\, K_f\, m \qquad T_f^0 - T_f = i\, K_f\, m$$

$$\text{or} \quad 0°C - T_f = 3 \times 1.86 \times \frac{6}{322} \times \frac{1}{0.100}$$

$$\text{or} \quad -T_f = \frac{33.480}{32.2} \quad \therefore \; T_f = \mathbf{-1.04°}$$

4.Two elements A and B form compounds having formula AB_2 and AB_4. When dissolved in 20g of benzene (C_6H_6), 1 g of AB_2 lowers the freezing point by 2.3 K whereas 1.0 g of AB_4 lowers it by 1.3 K. The molar depression constant for benzene is 5.1 K kg mol^{-1}. Calculate atomic masses of A and B.

Solution:

Using the relation, $M_2 = \frac{1000 \times k_f \times w_2}{w_1 \times \Delta T_f}$

$$\therefore \quad M_{AB_2} = \frac{1000 \times 5{\cdot}1 \times 1}{20 \times 2{\cdot}3} = 110{\cdot}87 \text{ g mol}^{-1}$$

$$M_{AB_4} = \frac{1000 \times 5{\cdot}1 \times 1}{20 \times 1{\cdot}3} = 196{\cdot}15 \text{ g mol}^{-1}$$

Let the atomic masses of *A* and *B* are 'p' and 'q' respectively.

Then molar mass of

$AB_2 = p + 2q = 110{\cdot}87 \text{ g mol}^{-1}$ ...(*i*)

And molar mass of

$AB_4 = p + 4q = 196{\cdot}15 \text{ g mol}^{-1}$ ...(*ii*)

Substracting equation (*ii*) from equation (*i*), we get $2q = 85.28 \Rightarrow q = 42.64$

Putting $q = 42.64$ **in equ. (*i*), we get**

$p = 110.87 - 85.28$

$p = 25.59$

Thus, atomic mass of *A* = 25.59 g mol^{-1} and atomic mass of *B* = 42.64 g mol^{-1}

5.Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing 250 mL of 0·15 M solution in methanol.

Solution:

$$\begin{aligned}
\text{Molarity (M)} &= \frac{\text{Mass of solute/molar mass}}{\text{Volume of solution in litres}} \\
\text{M} &= 0{\cdot}15\ \text{M} = 0{\cdot}15\ \text{mol L}^{-1}\ ; \\
\text{Molar mass of solute} &= 7 \times 12 + 6 \times 1 \times 2 \times 16 = 122\ \text{g mol}^{-1}; \\
\text{Volume of solution} &= 250\ \text{mL} = 0{\cdot}25\ \text{L.} \\
(0{\cdot}15\ \text{mol L}^{-1}) &= \frac{\text{Mass of solute}}{(122\ \text{g mol}^{-1}) \times (0{\cdot}25\text{L})} \\
\text{Mass of solute} &= (0{\cdot}15\ \text{mol L}^{-1}) \times (122\ \text{g mol}^{-1}) \times (0{\cdot}25\ \text{L}) = \mathbf{4{\cdot}575\ g}
\end{aligned}$$

6.A solution of glycerol ($C_3H_8O_3$; molar mass = 92 g mol^{-1}) in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42 °C. What mass of glycerol was dissolved to make this solution? K_b for water = 0.512 K kg mol^{-1}.

Solution:

Given : M_2 = 92 g mol^{-1} w_1 = 500g

ΔT_b = 100.42°C – 100°C = 0.42°C

K_b = 0.512 K kg mol^{-1}

Substituting above values in the formula

$$\Delta T_b = \frac{1000\, K_b\, w_2}{w_1 \times M_2}$$

$$\therefore \quad w_2 = \frac{w_1\, M_2\, \Delta T_b}{1000\, K_b} = \frac{500 \times 92 \times 0.42}{1000 \times 0.512}$$

$$= \frac{19320}{512} = \mathbf{37.73\ g}$$

7. 3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression in freezing point of 1.62 K. Calculate the Van’t Hoff factor and predict the nature of solute (associated or dissociated).

(Given : Molar mass of benzoic acid = 122 g mol^{-1}, K_f for benzene = 4.9 K kg mol^{-1})

Solution:

$\Delta T_f = iK_f \times m$

$$\Delta T_f = iK_f \times \frac{w_b \times 1000}{m_b \times w_a}$$

$$1.62 = i \times 4.9 \times \frac{3.9}{122} \times \frac{1000}{49}$$

$$i = \frac{1.62 \times 122 \times 49}{4.9 \times 3.9 \times 1000}$$

$$i = \frac{9684.36}{19110} = 0.506$$

As $i < 1$, therefore solute gets associated

8.A 5 percent solution (by mass) of cane-sugar (M.W. 342) is isotonic with 0.877% solution of substance X. Find the molecular weight of X.

Solution:

Given : W (mass) of cane-sugar = 5% means 5 g

Molar mass of cane-sugar (M) = 342 g mol^{-1}

Mass of isotonic substance X

= 0.877% means 0.877 g

Molar mass of X = ?

Using formula,

W canesugar x M cane sugar =W X M_X

5 x 342 =0.877 x M_X

or M_x = 0.877g×342gmol/ 5

⇒299.934/5

∴ M_x = 59.9 ≈ 60 g mol^{-1}

9. 18 g of glucose, $C_6H_{12}O_6$ (Molar mass – 180 g mol^{-1}) is dissolved in 1 kg of water in a sauce pan. At what temperature will this solution boil? (K_b for water = 0.52 K kg mol^{-1}, boiling point of pure water = 373.15 K)

Solution:

Given: W_B = 18 g

M_B = 180g/mol

Wt. of solvent = 1 kg or 1000 g,

$K_b = 0.52$ K kg mol^{-1}

Elevation of boiling point $\Delta T_b = W_B x1000xKb / M_B x W_A$

Hence, ΔT_b = 18x0.52x1000 /180x1000 = 0.52 K

∴B.P of the solution = 373.15 + 0.052

= 373.202 K

10.When 2.56 g of sulphur was dissolved in 100 g of CS_2, the freezing point lowered by 0.383 K. Calculate the formula of sulphur (S_x).

(K_f for CS_2 = 3.83 K kg mol^{-1}, Atomic mass of Sulphur = 32 g mol^{-1})

Answer:

(a) Given: w_b = 2.56 g w_a = 100 g = 0.1 kg

ΔT_f = 0.383 K K_f= 3.83 K kg mol^{-1}

Atomic mass of sulphur = 32 g mol^{-1}

M_b = ?

Using formula,

$$M_b = \frac{K_f \times w_b}{\Delta T_f \times w_a} = \frac{3.83 \times 2.56}{0.383 \times 0.1}$$

$$\left[\because \ \Delta T_f = \frac{K_f \times w_b}{M_b \times w_a} \times 1000\right]$$

∴ M_b = 256 g mol^{-1}

Hence the no. of atoms present in one molecule of sulphur = 256/32 = 8

∴ the formula is S_8.

11. Calculate the boiling point elevation for a solution prepared by adding 10 g $CaCl_2$ to 200 g of water, assuming that $CaCl_2$ is completely dissociated.

(K_b) for water = 0.512 K kg mol^{-1}; Molar mass of $CaCl_2$ = 111 g mol^{-1})

Given : $w_2 = 10$ g, $w_1 = 200$ g,

$K_b = 0.512$ K kg mol^{-1}, $M_2 = 111$ g mol^{-1}

Using formula :

$$\Delta T_b = iK_b\, m, \text{ Here } m = \frac{w_2 \times 1000}{M_2 \times w_1}$$

$$\therefore \quad \Delta T_b = \frac{1000\, K_b w_2}{w_1 M_2} \times i$$

$$\Delta T_b = \frac{1000 \times 0.512 \times 10 \times 3}{200 \times 111} = \frac{5120 \times 3}{22,200}$$

$$\therefore \quad \Delta T_b = \mathbf{0.69\ K}$$

HOTS

1. 19.5g of CH_2FCOOH is dissolved in 500g of water. The depression in the freezing point of water observed is 1.0°C. Calculate the van's Hoff factor and dissociation constant of fluoroacetic acid.

Solution:

Calculation of Van't Hoff factor (i)

Given, $w_1 = 500$ g $= 0.5$ kg, $w_2 = 19.5$ g, $K_f = 1.86$ K kg mol^{-1}, $\Delta T_f = 1$ K

Molar mass of CH_2FCOOH (M_2)

$= 2 \times 12 + 3 \times 1 + 1 \times 19 + 2 \times 16$

$= 24 + 3 + 19 + 32$

$= 78$ g mol^{-1}

$\Delta T_f = i\ K_f\ m$

$$i = \frac{\Delta T_f}{K_f m} \qquad \text{...(i)}$$

$$\begin{aligned} m &= \frac{w_2}{M_2 \times w_1} \\ &= \frac{19.5\ \text{g}}{(78\ \text{g mol}^{-1}) \times (0.5\ \text{kg})} \\ &= 0.5\ \text{mol kg}^{-1} \qquad \text{...(ii)} \end{aligned}$$

From eq. (i), we get

$$\begin{aligned} i &= \frac{1}{(1.86\ \text{K kg mol}^{-1}) \times (0.5\ \text{mol kg}^{-1})} \\ &= 1.0753 \end{aligned}$$

Calculation of dissociation constant, K_a

Let α be the degree of dissociation of CH_2FCOOH then

$$CH_2FCOOH \rightleftharpoons CH_2FCOO^- + H^+$$

	CH_2FCOOH	CH_2FCOO^-	H^+
Initial conc.	C mol L^{-1}	0	0
At equilibrium	$C(1-\alpha)$	$C\alpha$	$C\alpha$

Total $= C(1+\alpha)$

$$\therefore \quad i = \frac{C(1+\alpha)}{C}$$

$$\Rightarrow \quad i = 1 + \alpha$$

$$\begin{aligned} \Rightarrow \quad \alpha &= i - 1 \\ &= 1.0753 - 1 \\ &= 0.0753 \end{aligned}$$

Now,
$$\begin{aligned} K_a &= \frac{[CH_2FCOO^-][H^+]}{[CH_2FCOOH]} \\ &= \frac{C\alpha . C\alpha}{C(1-\alpha)} \\ &= \frac{C\alpha^2}{1-\alpha} \end{aligned}$$

Taking the volume of the solution as 500 mL, we have the concentration :

$$\begin{aligned} C &= \frac{\frac{19.5}{78}}{500} \times 1000\ \text{M} \\ &= 0.5\ \text{M} \end{aligned}$$

Therefore,
$$\begin{aligned} K_a &= \frac{C\alpha^2}{1-\alpha} \\ &= \frac{0.5 \times (0.0753)^2}{1 - 0.0753} \\ &= \frac{0.5 \times 0.00567}{0.9247} \\ &= 0.00307 \\ &= 3.07 \times 10^{-3} \end{aligned}$$

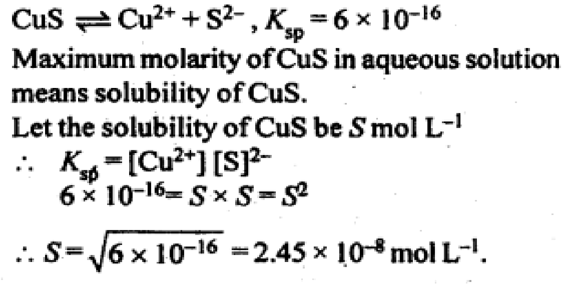
2.If the density of lake water is 1·25 g mL-1, and it contains 92 g of Na^+ ions per kg of water, calculate the molality of Na^+ ions in the lake.

Solution:

$$\begin{aligned} \text{Molality of } Na^+ \text{ ions } (m) &= \frac{\text{No. of moles of } Na^+ \text{ ions}}{\text{Mass of water in kg}} \\ &= \frac{(92\text{g}) / (23\text{g mol}^{-1})}{1\text{kg}} = 4\ \text{mol kg}^{-1} = \mathbf{4\ m} \end{aligned}$$

3. If the solubility product of CuS is 6 x 10^{-16}, calculate the maximum molarity of CuS in aqueous solution.

Solution:



$CuS \rightleftharpoons Cu^{2+} + S^{2-}$, $K_{sp} = 6 \times 10^{-16}$

Maximum molarity of CuS in aqueous solution means solubility of CuS.

Let the solubility of CuS be S mol L^{-1}

$\therefore \quad K_{sp} = [Cu^{2+}]\,[S]^{2-}$

$6 \times 10^{-16} = S \times S = S^2$

$\therefore S = \sqrt{6 \times 10^{-16}} = 2.45 \times 10^{-8}$ mol L^{-1}.

CASE BASED STUDY QUESTIONS

The following questions are case-based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow:

1.Osmosis is the movement of a solvent across a semipermeable membrane toward a higher concentration of solute. In biological systems, the solvent is typically water, but osmosis can occur in other liquids, supercritical liquids, and even gases. When a cell is submerged in water, the water molecules pass through the cell membrane from an area of low solute concentration to high solute concentration. For example, if the cell is submerged in saltwater, water molecules move out of the cell. If a cell is submerged in freshwater, water molecules move into the cell. When the membrane has a volume of pure water on both sides, water molecules pass in and out in each direction at exactly the same rate. There is no net flow of water through the membrane. Osmosis can be demonstrated when potato slices are added to a high salt solution. The water from inside the potato moves out to the solution, causing the potato to shrink and to lose its 'turgor pressure'. The more concentrated the salt solution, the bigger the loss in size and weight of the potato slice.

(a)How is osmotic pressure related to the concentration of a solute in a solution?

Answer: Osmotic pressure is directly proportional to the conentration of solute in solution $\pi \propto c$

(b) What is meant by reverse osmosis?

Answer:When the external pressure applied becomes more than the osmotic pressure of the solution, then the solvent molecules from the solution pass through the semipermeable membrane to the solvent side. This process is called reverse osmosis.

(c) (i)Give one practical use of the reverse osmosis

Answer: This can be used for desalination of water.

(ii) Name one SPM which can be used in reverse osmosis plant.

Answer: Film of cellulose acetate

(or)

(c)A solution containing 15 g urea (molar mass = 60 g mol^{-1}) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass = 180 g mol^{-1}) in water. Calculate the mass of glucose present in one litre of its solution.

For urea, concentration = 15/60 moles/lt.

For glucose, concentration = w/180 moles/lt.

∵ Solutions are isotonic

$\therefore w/180=15/60 \therefore w = 15\times180/60 = 45$ g

2.The **Van 't Hoff factor *i*** (named after Dutch chemist Jacobus Henricus Van 't Hoff) is a measure of the effect of a solute on colligative properties such as osmotic pressure, relative lowering in vapour pressure, boiling-point elevation and freezing-point depression. The Van 't Hoff factor is the ratio between the actual concentration of particles produced when the substance is dissolved and the concentration of a substance as calculated from its mass. For most non-electrolytes dissolved in water, the Van 't Hoff factor is essentially 1.

For most ionic compounds dissolved in water, the Van 't Hoff factor is equal to the number of discrete ions in a formula unit of the substance. This is true for ideal solutions only, as occasionally ion pairing occurs in solution. At a given instant a small percentage of the ions are paired and count as a single particle. Ion pairing occurs to some extent in all electrolyte solutions. This causes the measured Van 't Hoff factor to be less than that predicted in an ideal solution. The deviation for the Van 't Hoff factor tends to be greatest where the ions have multiple charges

a)Write the colligative property which is used to find the molecular mass of macromolecules.

Answer: Osmotic pressure

(b) In non-ideal solution, what type of deviation shows the formation of minimum boiling azeotropes?

Answer: Minimum boiling azeotropes show positive deviation from Raoult's law.

(c) Out of 0.1 molal aqueous solution of glucose and 0.1 molal aqueous solution of KCl, which one will have higher boiling point and why?

Answer:0.1 m KCl solution will have higher boiling point. This is because KCl dissociates in water to give two ions (K^+ and Cl^-) whereas glucose does not dissociate. Therefore, number of solute particles is greater in 0.1 m KCl as compared to 0.1 m glucose.

(or)

(c) Predict whether Van't Hoff factor is less than one or greater than one in the following:

(i) CH_3COOH dissolved in water

(ii) CH_3COOH dissolved in benzene

Answer:

(i) $i > 1$ because CH_3COOH dissociates in water.

(ii) $i < 1$ because CH_3COOH associates in benzene.

CHAPTER 2: ELECTROCHEMISTRY

BASIC CONCEPTS AND FORMULAE

KEY POINTS

1. Oxidation is defined as a loss of electrons while reduction is defined as a gain of electrons.
2. In a redox reaction, both oxidation and reduction reaction take place simultaneously
3. The device which converts chemical energy into electrical energy is known as an electrochemical cell.
4. In an electrochemical cell:

   a. The half-cell in which oxidation takes place is known as oxidation half-cell

   b. The half-cell in which reduction takes place is known as reduction half-cell.

   c. Oxidation takes place at anode which is negatively charged and reduction takes place at cathode which is positively charged. (In electrochemical cell)

   d. Transfer of electrons takes place from anode to cathode while electric current flows in the opposite direction.

   e. An electrode is made by dipping the metal plate into the electrolytic solution of its soluble salt.

   f. A salt bridge is a U-shaped tube containing an inert electrolyte in agar-agar and gelatine
5. A salt bridge maintains electrical neutrality and allows the flow of electric current by completing the electrical circuit.
6. When the concentration of all the species involved in a half cell is unity, then the electrode potential is known as standard electrode potential. It is denoted as E^{Θ}.
7. Oxidation potential is the tendency of an electrode to lose electrons or get oxidized.

8. Reduction potential is the tendency of an electrode to gain electrons or get reduced.
9. The electrode having a higher reduction potential has a higher tendency to gain electrons. So, it acts as a cathode. The electrode having a lower reduction potential acts as an anode and vice versa
10. According to convention, the Standard Hydrogen Electrode is taken as a reference electrode and it is assigned a zero potential at all temperatures.
11. In the electrochemical series, various elements are arranged as per their standard reduction potential values.
12. The potential difference between the two electrodes of a galvanic cell is called cell potential and is measured in Volts. The cell potential is the difference between the reduction potential of cathode and anode.

    $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$
13. Cell potential is called the electromotive force of the cell (EMF) when no current is drawn through the cell.
14. Nernst formulated a relationship between standard electrode potential $E^{\ominus}$ and electrode potential E.

$$E_{(M^{n+}/M)} = E^{\ominus}_{(M^{n+}/M)} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$$

15. Electrode potential increases with increase in the concentration of the electrolyte and decrease in temperature.
16. Nernst equation when applied to a cell:

$$aA + bB \longrightarrow cC + dD$$

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303RT}{nF} \log \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

.

17. Relationship between equilibrium constant Kc and standard cell potential

$$E^{\theta}_{cell} = \frac{2.303RT}{nF}\log K_c = \frac{0.059}{n}\log K_c$$

18. Work done by an electrochemical cell is equal to the decrease in Gibbs energy

    $\Delta G° = - nFE°_{cell}$

19. Every conducting material offers some obstruction to the flow of electricity which is called resistance. It is denoted by R and is measured in ohm. (Ω)

    The resistance of any object is directly proportional to its length l and inversely proportional to its area of cross section A.

    $R = \rho \times l / A$

    p is called specific resistance or resistivity. Its SI unit is ohm metre.

20. The inverse of resistance is known as conductance,

    $G = 1 / R = A / \rho \times l$

    Unit of conductance is ohm^{-1} or mho. It is also expressed in Siemens denoted by S.

21. The inverse of resistivity is known as conductivity. It is represented by the symbol κ. The SI unit of conductivity is Sm^1. But it is also expressed in Scm^1

    $k = \frac{1}{R}\frac{l}{a}$

    So, conductivity = Conductance x Cell constant

22. A conductivity cell consists of two Pt electrodes coated with Platinum black. They have area of cross section A and are separated by a distance l. Resistance of such a column of solution is given by the equation:

    $R = p\ \ l/A = 1/\kappa \times l/A$

    l/A is called cell constant and is denoted by the symbol G*

23. Molar conductivity of a solution is defined as the conducting power of the ions produced by dissolving 1 mole of an electrolyte in solution.

    Unit of Molar conductivity is $Scm^2\ mol^{-1}$

24. **Kohlrausch's Law of independent migration of ions**: According to this law, molar conductivity of an electrolyte, at infinite dilution, can be expressed as the sum of individual contributions from its individual ions. If the limiting molar conductivity of

the cation is denoted by $\lambda°_+$ and that of the anions by $\lambda°_-$,then the limiting molar conductivity of electrolyte is:

$\Lambda_m^0 = v_+\lambda°_+ + v_-\lambda°_-$

Where v_+ and v- are the number of cations and anions per formula of electrolyte.

25. Application of Kohlrausch law

*To calculate λ_m^∞ of a weak electrolyte

*To determine the degree of dissociation of weak electrolyte

*To determine the K_a of weak electrolyte

26. Degree of dissociation: It is ratio of molar conductivity at a specific concentration 'c' to the molar conductivity at infinite dilution, it is denoted by α

$$\alpha = \frac{\Lambda^c_m}{\Lambda^°_m} =$$

$Ka = \frac{C\alpha^2}{1-\alpha}$ where K_a is acid dissociation constant, 'c' is concentration of electrolyte, α is degree of ionization.

27. The nature of the product obtained at cathode or anode depends upon E° value of given chemical species. The chemical species which has higher E° will form product at cathode and The chemical species which has lower E° will form product at anode. Inert electrodes do not take part in chemical reactions

28.

Faraday's First Law of electrolysis	The amount of a substance deposited or liberated at an electrode is directly proportional to the quantity of electricity passed through the electrolyte.
Faraday's Second Law electrolysis	When the same quantity of electricity is passed through solutions of different electrolytes, the weight of different substances deposited or liberated at the respective electrodes are proportional to their chemical equivalent weights.

Product of Electrolysis

NaCl (molten)	Cathode : Na(s) Anode : Cl_2

NaCl (aq)	Cathode : $H_2(g)$ Anode : $Cl_2(g)$
H_2SO_4(dil)	Cathode : H_2 Anode: $O_2(g)$
(H_2SO_4conc)	Cathode : H_2 Anode: $H_2S_2O_8$ Peroxydisulphuric acid
$AgNO_3$(aq)-Ag electrodes	Cathode : Ag(s) Anode: $Ag^+(aq)$
$AgNO_3$(aq)- Pt electrodes	Cathode : Ag(s) Anode: $O_2(g)$
$CuCl_2$(aq)- Pt electrodes	Cathode : Cu(s) Anode: $O_2(g)$

29. **Differences between electrochemical reaction and electrolysis.**

Electrochemical reaction	**Electrolysis.**
Chemical reaction produce electricity	Electrical energy is used to carry out chemical reaction.
It is spontaneous, ΔG is -ve	It is non-spontaneous, ΔG is +ve

30. **Functions of Salt Bridge**

1. Salt Bridge maintains electrical neutrality in solutions.
2. It completes circuit internally

31. * Applications of electrochemical series

i) **To compare the relative oxidizing and reducing powers-** A chemical species with higher value of E° will be stronger oxidizing agent and a chemical species with more –ve E° will be stronger reducing agent

ii) **To compare the relative activities of metals-**A metal with more –ve E°value will be more reactive

iii) **To calculate the E°_{cell} of given cell-**

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

or

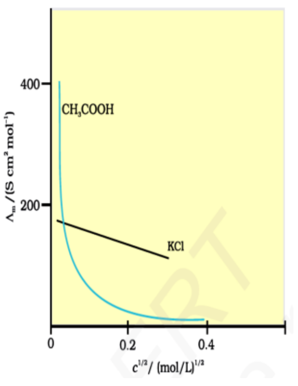
$E^\circ_{cell} = E^\circ_{RHS} - E^\circ_{LHS}$

NOTE: E° for SHE is taken 0 (Zero)

iv) To predict whether a metal will displace hydrogen from its compound or not- All the chemical species which have –ve E° value will displace hydrogen from its compounds

$M \rightarrow M^{n+} + ne^-$ **(electron lost is gained by H^+ ion to undergo reduction and H_2 is formed)**

32. **Molar Conductivity-** It the conductance due to all the ion produced from 1 mole of an electrolyte in $V cm^3$ of the solution. It is represented by $\lambda^c{}_m$ at conc. ‘C’ and $\lambda^\infty{}_m$ at infinite dilution.

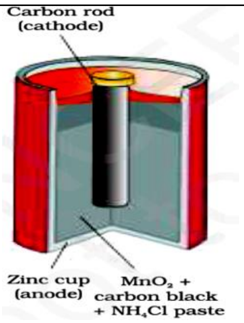
	Λ_m for strong electrolyte increases constantly on dilution. can be calculated on extrapolating the curve.
	Λ_m for weak electrolyte steeply (sharply) on dilution. $\lambda^\infty{}_m$ be calculated on extrapolation of the curve. It is determine using Kohlrausch’s law.

33. Advantages of fuel cell---long lasting, more efficient, eco friendly, give useful by products

Commercial cells- These are of 4 types

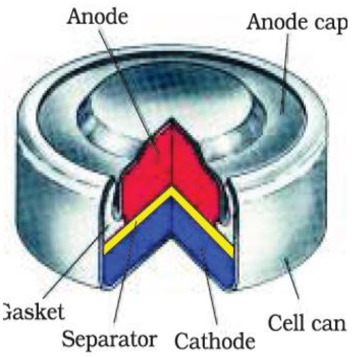
1) Dry cell (primary cell) – It is a Non rechargeable cell. Used in Torch, Wall clock etc.

	The following reaction takes place at Anode and Cathode i the Dry cell :

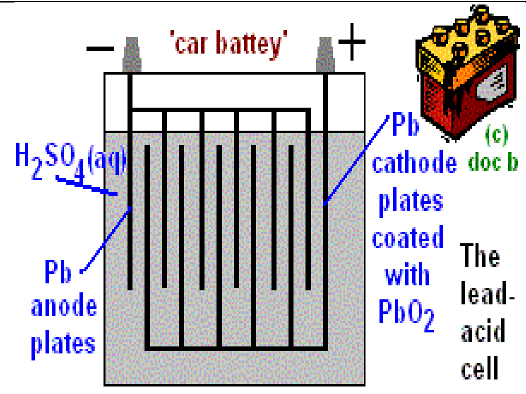
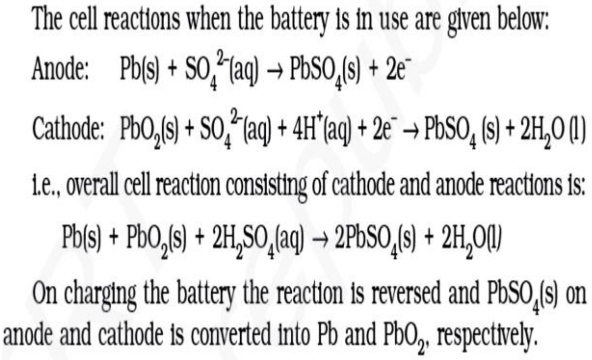
	Anode: $Zn(s) \longrightarrow Zn^{2+} + 2e^-$ The above reaction takes place at anode i.e. **Zn plate**
	Cathode: $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$ The above reaction takes place at cathode i.e. **Carbon rod**

34. Mercury cell/Button Cell – It is used in hearing aids and watches etc.

The cell gives constant voltage through out its life because there is no ions involved in the overall reaction.

	The following reaction takes place at Anode and Cathoc the Mercury cell/Button Cell :
	Anode: $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$ The above reaction takes place at anode i.e. **Zn containe**
	Cathode: $HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$ The above reaction takes place at cathode i.e. **Carbon rc**

35. Lead storage battery – It is a Rechargeable battery. Used in automobiles and inverters, Rechargeable batteries used in house hold appliances etc.

	 The cell reactions when the battery is in use are given below: Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$ Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$ i.e., overall cell reaction consisting of cathode and anode reactions is: $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$ On charging the battery the reaction is reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb and PbO_2, respectively.

36. <u>**Fuel cell**</u>: This cell is based on the combustion of fuels like Hydrogen by oxygen:

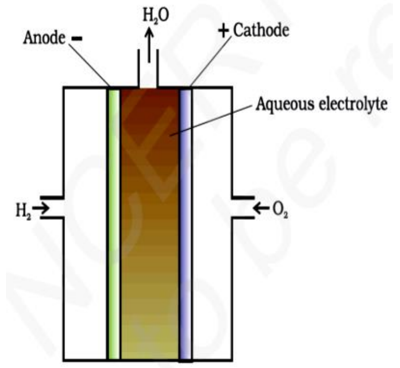
<u>**Advantages of Fuel Cells**</u> :

1. It can be controlled by the supply Hydrogen & oxygen gas

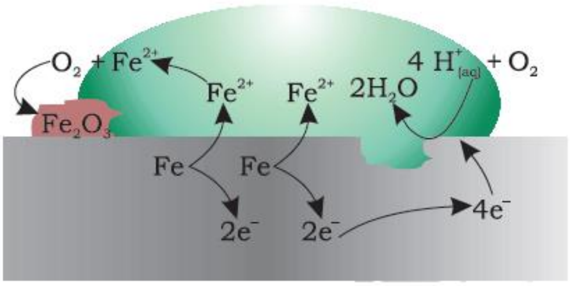
2.It causes no pollution

3. Its efficiency is 70%

4. Its by product (Water) is also useful.

	The following reaction takes place at Anode and Cathode in the fuel cell.
	Cathode: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
	Anode: $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$
	Overall reaction being: $2H_2(g) + O_2(g) \longrightarrow 2\ H_2O(l)$

37.Corrosion- In this process metal surface reacts with atmospheric oxygen in presence of moisture to form a layer of oxide. It is an electrochemical reaction.



The following reaction takes place during rusting :

]

Oxidation: $Fe\ (s) \rightarrow Fe^{2+}\ (aq) + 2e^-$

Reduction: $O_2\ (g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

Atomospheric oxidation: $2Fe^{2+}(aq) + 2H_2O(l) + ½O_2(g) \rightarrow Fe_2O_3(s) + 4H^+(aq)$

Anodic Reaction

Cathodic Reaction

Over all Reaction

IMPORTANT FORMULAE

S	Formula	What to calculate

N		
1	$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode}$	Cell potential of a cell can be calculated by this equation
2	$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n} \log \frac{1}{Mn+}$ At T=298K	Half Cell potential of a half-cell can be calculated by this expression
3	$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n} \log \frac{[P]}{[R]}$ At T=298K	Cell potential of a cell can be calculated by this expression
4	$E^{o}_{cell} = \frac{0.0591}{n} \log K_c$ At T=298K	To calculate cell potential from K_c and vice versa
5	$\Delta G^{\circ} = -nFE^{o}_{(cell)}$	To calculate cell potential from free energy change and vice versa
6.	$R = \rho \frac{l}{A}$	Resistance of a metallic conductor that obeys ohm's Law.
7.	$G^{*} = R\,\acute{K}$	Cell constant with respect to resistance and conductivity.
8.	$\lambda_m^{\infty} = \frac{K \times 1000}{M}$	Molar conductivity of an electrolyte at infinite dilution.
9.	$\acute{K} = \frac{l}{A} \times \frac{1}{R}$ (or) $\lambda_m^{\infty} = \frac{K \times A}{l}$	Conductivity as dimensions of a conductor
10.	$W = Z \times I \times t$ $Z = E/96500$	Amount of a substance produced at any electrode
11.	$\frac{W1}{E1} = \frac{W2}{E2}$	Amount of a substance produced at an electrode of different cells connected in a series
12	$E_{cell}^{\circ} = \frac{0.0591}{n} \log \frac{1}{[H+]}$	To calculate cell potential from pH and

.		vice-versa
13 .	$\alpha = \Lambda_m / \Lambda^{\infty}{}_m$	To calculate the degree of dissociation of weak electrolyte
14	$Ka = c\alpha^2 / (1-\alpha)$	To calculate the dissociation constant of a weak electrolyte from the ratio of molar conductivity and limiting molar conductivity.

MULTIPLE CHOICE QUESTIONS(MCQ)

Qn	QUESTION	ANSWER
1	The limiting molar conductivity for NaCI, KBr and KCI are 126,152 and150 Scm^2mol^{-1}, the limiting molar Conductivity of NaBr is: a)278 Scm^2mol^{-1} b)176 Scm^2mol^{-1} c) 128 Scm^2mol^{-1} d) 302 Scm^2mol^{-1}	Ans-c
2	Limiting molar conductivity of NH_4OH is equal to -: a)$\Lambda^o{}_mNH_4Cl + \Lambda^o{}_mNaCl + \Lambda^o{}_mNaOH$ b)$\Lambda^o{}_mNaOH + \Lambda^o{}_mNaCl - \Lambda^o{}_mNH_4Cl$ c)$\Lambda^o{}_mNaOH - \Lambda^o{}_mNH_4Cl - \Lambda^o{}_mHCl$ d)$\Lambda^o{}_mNH_4Cl + \Lambda^o{}_mNaOH - \Lambda^o{}_mNaCl$	Ans-d

3	Which cell will measure standard electrode potential of copper electrode? (i) Pt (s) | H2 (g, **0.**1 bar) | H^{+} (aq. , 1 M) || Cu^{2+}(aq.,1M) | Cu (ii) Pt(s) | H2 (g, 1 bar) | H^{+} (aq. , 1 M) || Cu^{2+} (aq., 2 M) | Cu (iii) Pt(s)| H2 (g, 1 bar) | H^{+} (aq. , 1 M) || Cu^{2+} (aq.,1 M) | Cu (iv) Pt(s) | H2 (g, 1 bar) | H^{+} (aq.,0.1 **M**) || Cu^{2+} (aq.,1 M) | Cu	Ans-c
4	How is electrical conductance of a conductor related with length and area of cross-section of the conductor **i) G = *l* . a.k**$^{-1}$ **ii) G =k. *l*.a**$^{-1}$ iii)**G = k.a .*l***$^{-1}$ **iv) G = k. *l*.a**$^{-2}$	Ans-c
5	The potential of a hydrogen electrode at pH = 10 is a. 0.591 V b. 0.00V c. – 0.591 V d. -0.059 V	Ans-c
6	The standard oxidation potentials (E°) for Zn and Fe are as: Zn → Zn^{2+} + 2e^{-}; E° = +0.76 V Fe → Fe^{2+} + 2e^{-}; E° = +0.44 V The standard cell potential for the cell reaction	Ans-c

	$Fe^{2+} + Zn \rightarrow Zn^{2+} + Fe$ is ------------- a) +0.32 V b) +1.2 V c) -0.32 V d) -1.2 V	
7.	Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100 Ω. The conductivity of this solution is $1.29 Sm^{-1}$. Resistance of the same cell when filled with 0.2 M of the same solution is 520Ω. The molar conductivity of 0.02 M solution of the electrolyte will be: a) 124×10^{-4} S m^2 mol^{-1} b) 1.24×10^{-4} S m^2 mol^{-1} c) 1240×10^{-4} S m^2 mol^{-1} d) 12.4×10^{-4} S m^2 mol^{-1}	Ans-a
8.	The standard reduction potentials at 25^oC of Li^+|Li, Ba^{2+}|Ba, Na^+|Na and Mg^{2+}|Mg are -3.05, -2.73, -2.71 and -2.37 V respectively. Which is strongest reducing agent? a)Mg b) Na c) Li d) Ba	Ans-c
9.	The standard EMF of a cell involving one electron change is found to be 0.591 V at 25^oC. The equilibrium constant of the reaction is:	Ans-a

	a) 10^{10} b) 10^{5} c) 10^{1} d) 10^{30}	
10.	The factors which influence the conductance of solution: a)solute-solvent interaction b) solute-solute interaction c) all of these d) temperature	Ans-c
11.	The ionic mobility of alkali metal ions in aqueous solution is maximum for: a) K^+ b) Li^+ c) Na^+ d) Rb^+	Ans-d
12.	Which of the following is/are the same for a Zn-Cu Daniel cell and a dry cell? a) Oxidation half reaction b) Both the electrodes c) Overall cell reaction d) Reduction half reaction	Ans-a
13.	During the electrolysis of molten sodium chloride, the time required to produce 0.10 mol of chlorine gas using a current of 3 ampere is: a)220 minute b) 110 minute c) 330 minute d) 55 minute	Ans-b
14.	The term infinite dilution refers when: a)$\alpha = 1$, for weak electrolytes b) an electrolyte is 100% dissociated c) all inter-ionic effects disappears d) all of these	Ans-d

ASSERTION AND REASONING TYPE QUESTIONS

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

a) Both assertion and reason are true and the reason is the correct explanation ofassertion.

b) Both assertion and reason are true and the reason is not the correct explanation of assertion.

c) Assertion is true but the reason is false.

d) Assertion is false but reason is true.

QUESTION	ANSWER
1. Assertion: Cu is less reactive than hydrogen. **Reason :** $E^{\circ}_{Cu^{2+}/Cu}$ is positive	Ans- a
2. Assertion: E^{o} cell should have a positive value for the cell to function. **Reason :** $E_{cathode} < E_{anode}$	Ans-c
3. Assertion: Conductivity of all electrolytes decreases on dilution. **Reason :** On dilution number of ions per unit volume decreases	Ans-a
4. Assertion: Λ_m for weak electrolytes shows a Sharp increase when the electrolyticsolution is diluted. **Reason :** For weak electrolytes degree of dissociation increases with dilution of solution	Ans-a

5. Assertion: Mercury cell does not give a steady potential. **Reason :** In the cell reaction, ions are not involved	Ans-d
6. Assertion: Electrolysis of NaCl aqueous solution gives chlorine at anode instead of O_2. **Reason :** Formation of oxygen at anode requires overvoltage	Ans-a
7. Assertion: For measuring resistance of an ionic solution an AC source is used. **Reason :** Concentration of ionic solution will change if DC source is used	Ans-a
8.Assertion : Current stops flowing when $E_{Cell} = 0$. **Reason :** Equilibrium of the cell reaction is attained.	Ans-a
9.Assertion : $E_{Ag+/Ag}$ increases with increase in concentration of Ag^+ ions. **Reason :** $E_{Ag+/Ag}$ has a positive value.	Ans-d
10.Assertion : Copper sulphate can not be stored in zinc vessel. **Reason :** Zinc is less reactive than copper	Ans-c
11.Assertion: Cu dissolves in HNO_3 **Reason**: In nitric acid it is oxidised by nitrate ion and not by hydrogen ion	Ans-a
12. Assertion: Metals like platinum or gold are used as inert electrodes. **Reason**: They do not participate in the reaction but provide their surface for reactions and for the conduction of electrons.	Ans-a

IMPORTANT TWO MARK QUESTIONS

Q1. What is the effect of temperature on the electrical conduction of i) Metallic conductor. ii) Electrolytic conductor?

Ans. With increase of temperature the electrical conduction of metals decreases whereas that of electrolytic conduction increases.

Q2. What is the reference electrode in determining the standard electrode potential?

Ans. Normal hydrogen electrode (NHE).

Q3. What are the units of specific conductance?

Ans: $\text{ohm}^{-1}\ \text{cm}^{-1}$ or Scm^{-1} .

Q4What is the effect of the decreasing concentration on the molar conductivity of a weak electrolyte?

Ans. Molar conductance of a weak electrolyte increase with decrease of theconcentration.

Q5. Arrange the following metals in order of their increasing reducing power.

$K^+/K = -2.93V$, $Ag^+/Ag = 0.80V$, $Hg^{2+}/Hg = 0.79\ V$, $Mg^{2+}/Mg = -2.37\ V$ $Cr^{3+}/Cr = -0.74V$.

Ans.Lower the reduction potential, easily if gets oxidized hence greater is the reducing power, therefore the increasing order of reducing power is Ag <Hg<Cr<mg<K.

Q6.The conductivity of 0.20M solution of KCl at 298 K is $0.0248\ \text{Scm}^{-1}$. Calculate its molar conductivity.

Ans.: $\Lambda m = \frac{K \times 1000}{M} = \frac{0.0248 \times 1000}{0.20} = 124\ \text{Scm}^2\ \text{mol}^{-1}$

Q7.How much Faraday is required to produce 40gm Al from Al_2O_3?

Ans: $Al^{3+} + 3e^- \rightarrow Al\ (27g)$

27g Al is deposited by 3F

40g Al will be deposited by = $\frac{3 \times 40}{27} = 4.44\ F$

Q8.Predict if the reaction between the following is feasible? Fe^{3+} and Br^-.

Ans : $Fe^{3+} + Br^- \rightarrow Fe^{2+} + \frac{1}{2} Br_2$

E°cell = 0.77V – 1.09V = -0.32V not feasible

Q9.Calculate EMF of the following cell

$Cd/Cd^{2+}\ (0.10\ M)//H^+\ (0.20\ M)/H_2\ (0.5\ atm)/Pt$

[Given E° for Cd^{2+} /Cd =-0.403 V]

Ans: $E_{cell} = E°_{cell} – [\underline{0.059}1/n] \log [Cd^{2+}]/ [H^{+}]^{2}$

$E°_{cell}= 0 – (–.403V) =0.403V$

$=0.0403 –[0.0591/2] \log (0.10)X0.5/(0.2)^{2} \quad = 0.400V$

Q10.Calculate EMF of the following cell at 298K

$Zn/Zn^{2+}(10^{-4}M)|| Cu^{2+}(10^{-2}M)/Cu$

Ans: Given $E^{0}_{Zn / Zn^{2+}} = - 0.76$

$E^{0}_{Cu^{2+}/Cu} = + 0.34V$

Cell reaction is as follows. $Zn(s)+Cu^{2+}(aq)\rightarrow Zn^{2+}(aq)+Cu(s)$ n=2 ,T=298K

$E^{0}_{cell} = E_{cathode} – E_{anode} = 1.1V$

$E_{cell} = 1.1 V - 0.0295 \log \frac{10^{-14}}{10^{-2}}$

$=1.10 –[0.02955 \times \log 10^{-2}]$

$=1.10 + (2 \times 0.02955)$

$=1.10V + 0.0591 V \qquad =1.1591V$

Q11What happens when a piece of copper is added to

(a)an aqueous solution of $FeSO_4$

(b)an aqueous solution of $FeCl_3$?

Ans a. Nothing will happen when the piece of copper is added to $FeSO_4$ Because reduction potential $E^{0}_{Cu^{2+}/Cu}$ (0.34v) is more than the reduction potential $E^{0}_{Fe2+/Fe}$ is 0.44 V

b. Copper will dissolve in an aqueous solution of $FeCl_3$because reduction potential $E^{0}_{Fe^{3+}/Fe^{2+}}$ 0.77 V is more than the reduction potential of $E^{0}_{Cu^{2+}/Cu}$ (0.34V)

$Cu(s)+2FeCl_3(aq) \longrightarrow Cu^{2+} + 2 FeCl_2$

THREE MARK QUESTIONS

Q1.For the standard cell

$Cu(s)/Cu^{2+}(aq) \| Ag^{+}(aq) /Ag(s)$

$E^{o}_{(Cu^{2+}/Cu)} = +0.34\ V$

$E^{0}_{Ag^{+}/Ag} = +0.80\ V$

i. Identify the cathode and the anode as the current is drawn from the cell.

ii. Write the reaction taking place at the electrodes.

iii. Calculate the standard cell potential.

Ans:i. From the cell representation Ag/Ag^{+} electrode is cathode and Cu/Cu^{+} electrode is anode .

ii. **At anode :**

$Cu(s) \longrightarrow Cu^{2+}(aq)+2e$

At Cathode

$Ag^{+} + 1e \longrightarrow Ag$

Over all reaction is $Cu(s)+ Ag^{+}(aq) \rightarrow Cu^{2+}(aq)+2\ Ag(s)$

iii. $E^{0}_{cell}=E^{0}_{cathode}-E^{0}_{anode}$

$=E^{0}_{Ag+/Ag}-E^{0}_{Cu2+/Cu}$

$=+.80\ V - (+0.34V)$

$=+0.80V-0.34V$

$=0.46V$

Q2.Can we store copper sulphate in (i) Zinc vessel (ii) Silver vessel? Give reasons**.**

Given $E^{0}_{Cu^{2+}/Cu}= +0.34V$, $E^{0}_{Zn^{2+}/Zn}= -0.76V$, $E^{0}_{Ag^{+}/Ag} = +0.80V$

Ans:(i) A metal having lower reduction potential can displace a metal having higher reduction potential from solution of its salt. .Since standard reduction potential of Zinc ($E^{0}Zn^{2+}/Zn=-0.76V$) is less than the standard reduction potential of Copper ($E^{0}Cu^{2+}/Cu=+0.34V$), Zn can displace copper from copper sulphate solution. Thus, $CuSO_4$solution cannot be stored in zinc vessel.

(ii) Standard reduction potential of silver , ie. $E^0 Ag^+/Ag=+0.80$ V is more than the Standard reduction potential of copper E^0 ($Cu^{2+}/Cu = + 0.34$ V), silver cannot displace copper from copper sulphate solution. Hence copper sulphate can be stored in silver vessel.

Q3.How many grams of chlorine can be produced by the electrolysis of molten NaCl with a current of 1.02 A for 15 min?

Ans: $2NaCl_{(l)} \longrightarrow 2Na^+_{(l)} + 2Cl^-_{(l)}$

$2Cl^- \longrightarrow Cl_{2\,(g)} + 2e^-$

2mole 1mol

Q= n F

Q=2 x 96500 C/mol= 1.93 x 10^5C

Quantity of electricity used = It

=1.02 A X (15 x 60) sec

=900C

Molar mass of Cl_2 = 2 X 35.5 = 71 $gmol^{-1}$X10^5C

Mass of Chlorine produced by 1.93X 10^5C of charge = 71gm

Mass of Chlorine produced by 900C of charge = $(71 \text{ x } 900)/(1.93X10\text{^}5)$

=0.331 gm

Q4.Determine the values of equilibrium constant (Kc) and ΔG° for the following reaction:

$Ni(s) + 2Ag+ (aq) \rightarrow Ni^{2+} (aq) + 2Ag (s)$,

E° = 1.05 V (1F = 96500 C mol-1)

Answer:

According to the formula

$\Delta G° = -nFE° = -2 \times 96500 \times 1.05$

or $\Delta G° = -202650 \text{ J mol}^{-1} = -202.65 \text{ KJ mol}^{-1}$

Now $\Delta G° \Rightarrow -202650 \text{ J Mol}^{-1}$

$R = 8.314$ J/Mol/K, $T = 298$ K

$$\log K = \frac{\Delta G°}{2.303\,RT}$$

$$\text{or } \log K = \frac{-202650}{2.303 \times 8.314 \times 298}$$

$$\log K = \frac{-202650}{5705.84831} = 35.52$$

$$K = \text{Antilog of } 35.52 \quad \therefore\ K = 0.35 \times 10^{7}$$

Q5.The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol^{-1}. Calculate the conductivity of this solution.

Answer:

$C = 1.5$ M, $\Lambda_m = 138.9$ S cm^2 mol^{-1}

$\Lambda_m = K \times 1000/c$

$\therefore K = \Lambda_m \times C/1000 = 138.9 \times 1.5/1000 = 0.20835$ S cm^{-1}

Q6.Write the reactions taking place at cathode and anode in lead storage battery when the battery is in use. What happens on charging the battery?

Answer:

At Anode: $Pb + SO_4^{-2} \rightarrow PbSO_4 + 2e-$

At Cathode : $PbO_2 + SO_4^{-2} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$

On charging the battery, the reaction is reversed and $PbSO_4$ on anode and cathode is converted into Pb and PbO_2 respectively.

Q 7. The standard electrode potential for Daniel cell is 1.1 V. Calculate the standard Gibbs energy for the cell reaction. (F = 96,500 C mol-1)

Answer:

Given : E° = 1.1V, F = 96,500 C mol-5, n = 2

Zn + Cu^{2+} ⇌ Cu + Zn^{2+}

Using ΔG° = -nFE° = -2 × 96500 × 1.1

= 212,300 CV mol^{-1}

Q8.From the given cells: Lead storage cell, Mercury cell, Fuel cell and Dry cell
Answer the following:

(i) Which cell is used in hearing aids?

(ii) Which cell was used in Apollo Space Programme?

(iii) Which cell is used in automobiles and inverters?

Answer:

(i) Mercury cell is used in hearing aids.

(ii) Fuel cell was used in the Apollo Space Programme.

(iii) Lead storage cell is used in automobiles and inverters.

Q9.Calculate the degree of dissociation (a) of acetic acid if its molar conductivity (Λm) is 39.05 S cm2 mol^{-1}.

Given: λ°(H+) = 349.6 S cm2 mol-1 and λ°(CH3COO–) = 40.9 S cm^2 mol^{-1}

Answer:

$\Lambda°m(HAC) = \lambda°H^+ + \lambda°AC^-$

$= \lambda°CH_3COOH = \lambda°H+ + \lambda°CH_3COO–$

= 349.6 S cm2 mol-1 + 40.9 S cm2 mol-1

= 390.5 S cm2 mol-1

Q10.Write the name of the cell which is generally used in transistors. Write the reactions taking place at the anode and the cathode of this cell.

Answer: Leclanche cells (Dry cell) is used in transistors.

Reaction at Anode:

$Zn(s) \rightarrow Zn^{2+} + 2e^–$

At Cathode:

$MnO_2 + NH_4^+ + e^– \rightarrow MnO(OH) + NH_3$

FIVE MARKS QUESTIONS

Q1.a)Explain the electrochemical theory of rusting of iron .

Ans: The water layer present on the surface of iron (especially in the rainy season) dissolves acidic oxides of air like CO_2 ,SO_2 etc. to from acids which dissociate to give H^+ ions:

$H_2O + CO_2 \rightarrow H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$

In the presence of H^+ ions iron starts losing electrons at some spot to form ferrous ions, i.e. its oxidation takes place. Hence, this spot acts as the anode:

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

The electrons this released through the metal to reach another spot where H^+ ions and the dissolved oxygen takes up these electrons and reduction reaction takes place. Hence, this spot acts as the cathode:

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

The overall reaction is :

$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$

Ferrous ions are further oxidized by the atmospheric oxygen to ferric ions which combine with water molecules to form hydrated ferric oxide, $Fe_2O_3.xH_2O$ which is rust

b)A strip of nickel metal is placed in a 1-molar solution of Ni $(NO_3)_2$ and a strip of silver metal is placed in a 1-molar solution of $AgNO_3$. An electrochemical cell is created when

the two solutions are connected by a salt bridge and the two strips are connected by wires to a voltmeter. Write the balanced equations for the overall reaction occurring in the cell and calculate the cell potential.

Ans Reactions involved for the electrochemical cells are

At anode:

$$Ni(s) \rightarrow Ni^{2+}(1M) + 2e^-$$

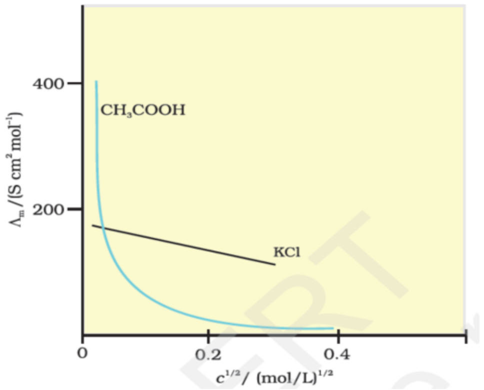
At Cathode:

$$Ag^+(1M) + 2e^- \rightarrow 2Ag(s)$$

Net cell reaction:

$$Ni(s) + 2Ag^+(aq) \rightarrow Ni^{2+}(aq) + 2Ag(s)$$

Q2. a)The following curve is obtained when molar conductivity, Λ_m is plotted against the square root of concentration, $C^{1/2}$ along y and x-axis respectively for the two electrolytes X and Y.



$Y = CH_3COOH$

$X = KCl$

i) What can you say about the nature of these two electrolytes?

ii) How do you account for the increase in Λ_m for the electrolytes X and Y with dilution?

iii) How can you determine Λ^∞ for these electrolytes?

Ans.i. Electrolyte X is a strong electrolyte and Y is a weak electrolyte.

ii. Molar conductivity,Λ_m of X (strong electrolysis) increases slowly with dilution. This is because interionic forces of attraction decreases on dilution, although the number of ions remain the same. As a result ions move freely and hence Λ_m increases with dilution. On the other hand, for Y (weak electrolyte) Λ_m increases sharply with dilution. This is because degree of dissociation increases on dilution resulting in greater number of ions on dilution. Hence Λ_m increases

iii. For X electrolyte Λ^∞ can be obtained by extrapolation to zero concentration

CASE –BASED QUESTIONS :

Q1.**Read the text carefully and answer the questions:**

A Lead storage battery is the most important type of secondary cell having a lead anode and a grid of lead packed with PbO_2 as a cathode. A 38% solution of sulphuric acid is used as the electrolyte (Density = 1.294 g mL^{-1}). The battery holds 3.5 L of the acid. During the discharge of the battery, the density of H_2SO_4 falls to 1.139 g mL^{-1}. (20% H_2SO_4 by mass) a)Write the reaction taking place at the cathode when the battery is in use.

Ans:Reaction taking place at cathode when the battery is in use:

$PbO_2(s) + (aq) + 4H^+(aq) + 2e- \rightarrow PbSO_4(s) + 2H_2O(l)$

b) Lead storage battery is considered a secondary cell. Why?

Ans:It can be recharged after use.

c)What is the Molarity of sulphuric acid before discharge?

Ans:Molarity = 38 x1.294 x1000/ 98X100 = 5.02M

(or)

c)Write the products of electrolysis when dilute sulphuric acid is electrolyzed using Platinum electrodes.

Ans:At anode: O_2 (g)

At cathode: H_2 (g)

Q2.Read the text carefully and answer the questions:

Conductors allow the passage of electric current through them. Metallic and electrolytic are the two types of conductors. Current carriers in metallic and electrolytic conductors are free electrons and free ions respectively. Specific conductance or conductivity of the electrolyte solution is given by the relation: Ꝃ= c x l/A where c = $1/R$ is the conductance and l/A is the cell constant. Molar conductance of strong electrolyte depends on concentration:

$\Lambda_m = \Lambda^0_m - b\sqrt{c}$

Λm = molar conductance at infinite dilution ,c= concentration of the solution ,b = constant

The degrees of dissociation of weak electrolytes are calculated as:

$\alpha = \lambda m/\lambda m^\infty$

a)Out of specific conductance and molar conductance, which one of the following decreases on dilution of electrolyte solution?

Ans. Specific conductance decreases on dilution of electrolyte solution.

b) What is the correct order of equivalent conductance at infinite dilution for LiCl, NaCl and KCl?

Ans. The correct order of equivalent conductance at infinite dilution is KCl > NaCl > LiCl.

c) Out of $BaCl_2$ and KCl for which electrolyte solutions Λ_m and Λ_e are equal?

Ans. In KCl electrolyte solution λ^m and λ^0 are equal

(or)

c) What is equal to the cell constant of the conductivity cell when the conductance of a solution of an electrolyte is equal to that of its specific conductance?

Ans. The conductance of a solution of an electrolyte is equal to that of its specific conductance. The cell constant of the conductivity cell is equal to the unity.

Q3.Read the text carefully and answer the questions:

The driving force ΔG diminishes to zero on the way to equilibrium, just as in any other spontaneous process.Both ΔG and the corresponding cell potential ($\Delta E = \Delta G/nF$) are zero when the redox reaction comes to equilibrium. The Nernst equation for the redox process of the cell may be given as:

$$E = E° - 0.0591/n \log_{10} Q$$

The key to the relationship is the standard cell potential $E°_{cell}$ derived from the standard free energy change as:

$$\Delta E^0 = - \Delta G^0 / nF$$

At equilibrium, the Nernst equation is given as:

$$E = E° - 0.0591/n \log_{10} K$$

a)When does the equilibrium constant K_C will be equal to Q?

Ans. When E = O; then $K_c = Q$

b) On the basis of information available for a reaction:

$4/3\ Al + O_2 \longrightarrow 2/3\ Al_2O_3$; $\Delta G = -827$ kJ/mol of O_2

What is the minimum EMF required to carry out electrolysis of Al_2O_3?

Ans

$\Delta G = -nFE_{cell}$

-827 kJ/mol = $- 4 \times 96500$ C x E_{cell}

$E_{cell} = 2.14$ V

c) Why is the equilibrium constant k related to only $E°_{cell}$ and not E_{cell} ?

The equilibrium constant k related to only E^0_{cell} and not E cell because at equilibrium, $E_{cell} = 0$.

(or)

c) Calculate the EMF of the cell, containing Ni and Cu electrodes.

Given

E^0 (Ni^{2+}/Ni) = - 0.25 V and E^0 (Cu^{2+}/Cu) = + 0.34 V

EMF of cell = E^0 cathode - E^0 anode

= E^0 (Cu^{2+}/Cu) - E^0 (Ni^{2+}/Ni)

= + 0.34 V - (-0.25 V)

= 0.59V

HOTS QUESTION

Q1.A current of 5 ampere is flowing through a wire for 193 seconds. Calculate number of electrons flowing through cross section of wire for 193 seconds.

Ans- Q = I x t = 5x193= 965C

96500C is equivalent to flow of 6.022×10^{23} electrons

∴ 965C will be equivalent to flow of electrons = $6.022 \times 10^{23} \times 965/96500 = 6.022 \times 10^{23}$ electron.

Q2. Calculate $\Lambda°$ m NH_4OH from the following values.

$\Lambda°$ m for $Ba(OH)_2$, $BaCl_2$, NH_4Cl are 257.6, 240.6, 129.8 $Scm^2\ mol^{-1}$ respectively.

Ans- $\Lambda°$ m $(NH_4OH) = \Lambda°\ NH_4^+ + \Lambda°OH^-$

$= (\Lambda°\ NH_4^+ + \Lambda°Cl^-) + ½\ (\Lambda°Ba^{++} + 2\Lambda°OH^-)$

$= -1/2\ (\Lambda°Ba^{++} + 2\Lambda°Cl^-)$

$= 129.8 + ½ \times 457.6 - ½\ 240.6$

$= 238.3\ Scm^2\ mol^{-1}$

Q3.The EMF of following reaction is 0.28V at 25º C

$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$ (1 atm) E°cell = 0.76 V

Calculate pH of solution at hydrogen electrode.

Ans- $E_{cell} = E°_{cell} - 0.0591/n \times \log [Zn^{2+}]/ [H^+]^2$

$= 0.76 - .0591/2 \log [0.1]/ [H^+]^2$

$0.28 = 0.76 - .02955 (-1+ 2pH)$

$2\ pH - 1 = 16.244$

pH = 8.62

CHAPTER -3 CHEMICAL KINETICS

1. **Chemical kinetics: -** The branch of chemistry, which deals with the study of reaction rates and their mechanisms is called Chemical kinetics.

2. **Rate of a Chemical Reaction :-**
   The speed of a reaction or the rate of a reaction can be defined as the change in

concentration of a reactant or product in unit time.
Consider a hypothetical reaction, assuming that the volume of the system remains constant.

$$R \rightarrow P$$

Rate of disappearance of R

$$= \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = -\frac{\Delta [R]}{\Delta t}$$

Rate of appearance of P

$$= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = +\frac{\Delta [P]}{\Delta t}$$

[Since Δ[R] is a negative quantity (as concentration of reactants is decreasing), it is multiplied with –1 to make the rate of the reaction a positive quantity.]

Unit of rate of reaction: a) $molL^{-1}s^{-1}$ b) $atms^{-1}$

3. **Types of rate of reaction** :

Average Rate	**Instantaneous Rate**
It is the change in concentration of reactants in a given interval of time.	It is the change in concentration of reactants at instantaneous time.
$r_{av} = - \Delta[R] / \Delta t = + \Delta[P] / \Delta t$	**$r_{inst} = - d[R] /dt = + d[P] / dt$**

4. **For the reaction, $2HI \longrightarrow H_2 + I_2$**
Rate of reaction $= -\frac{1\Delta[H_2]}{2\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$

5. **Factors affecting the Rate of a Chemical Reaction:-**
1- Nature of reactant :Ionic substances react much faster than covalent substances.
2-Concencentration of Reactants: Rate of reaction is directly proportional to Concentration of reactants (partial pressure in case of gaseous - phase reactions).
3-Temperature : Rate of reaction increases with increase in temperature.
4-Presence of Catalyst : A catalyst increases the speed of a reaction without itself being consumed in the reaction.
5-Surface Area of the Reactants: Rate of reaction ∝ surface area.
6- Presence of light: Some reactions take place in presence of light are called photochemical reactions.In case of photochemical reactions, the rate of reaction increases with increasing the intensity of light.

6. **Rate Law Expression**: It is a mathematical expression in which rate of reaction is expressed in terms of molar concentration of reactants with each term raised to some power, which may or may not be equal to the stoichiometric coefficient of the reacting species in a balanced chemical equation.
Consider a general reaction: $a A + b B \rightarrow c C + d D$, then Rate Law $= k [A]^x [B]^y$,

where, ‘x’ may/ may not be equal to ‘a’ and ‘y’ may/ may not be equal to ‘b’.

7. **Rate Constant:** For a general reaction
$aA + bB \rightarrow cC + dD$
Rate of reaction = $k[A]^x[B]^y$
Where k is known as rate constant
When [A] = [B] = 1 mol/L, then Rate of reaction = k
Thus rate constant of a chemical reaction may be defined as the reaction rate when the concentration of each reactant is unity.
   - The value of rate constant is definite and constant for a particular reaction at given temperature.
   - Rate constant is independent of concentration of reactants it depends only upon temperature and presence of catalyst.

8. **Order of a Reaction**: The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.
Consider a general reaction: $aA + bB \rightarrow cC + dD$, then Rate Law = $k[A]^x[B]^y$,
Here, x = order of reaction w.r.t. A
y = order of reaction w.r.t. B
Overall order of reaction(n) = x + y

Order of a reaction can be 0, 1, 2, 3 and even a fraction. A zero order reaction means that the rate of reaction is independent of the concentration of reactants.

9. Units of rate constant (k) :
= **$(\text{conc})^{1-n}\ \text{time}^{-1}$**

REACTION	ORDER	UNITS OF RATE CONSTANT
Zero order reaction	0	$\text{mol L}^{-1}\text{S}^{-1}$
First order reaction	1	S^{-1}
Second order reaction	2	$\text{mol}^{-1}\text{ L S}^{-1}$

[NOTE: To know the order of reaction when unit of rate constant is given, then just add 1 to the number given in power of litre factor.]

10. Some Examples of Reactions of Different Orders:-
a)Zero order –
i)Decomposition of ammonia on a hot platinum surface at high pressure.
Rate = $k[NH_3]^0$
In this reaction, platinum metal acts as a catalyst. At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration.
ii) Decomposition of HI on gold surface.
Rate = $k[HI]^0$

b) First order – Natural and artificial decay of unstable nuclei.

c) Second order-

$2HI \longrightarrow H_2 + I_2$ Rate = k$[HI]^2$

d) Third order- $2NO + O_2 \longrightarrow 2NO_2$

Rate = k $[NO]^2 [O_2]$

e) Fractional order – $H_2 + Br_2 \longrightarrow 2HBr$

Rate = k $[H_2] [Br_2]^{1/2}$, order = 11/2

11. **Molecularity of a Reaction**: The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

$NH_4NO_2 \longrightarrow N_2 + 2H_2O$ (unimolecular)

12. **Difference between order of reaction and molecularity of reaction:**

Order	Molecularity
1.It is the sum of powers of concentrations of reactants expressed in rate law.	The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction
2. Order of a reaction is an experimental quantity.	Molecularity of a reaction is a theoretical quantity.
3. It can be a whole number, zero and even fractional.	Molecularity is always a whole number.
4. Order is applicable to elementary as well as complex reactions.	Molecularity is applicable only for elementary reactions.

13. **Integrated Rate Equations:**

a) Zero Order Reactions:

Consider zero order reaction R → products

Let [R]o be the initial concentration of reactant and [R] be the final concentration at time‘t’. For zero order reaction, the rate of the reaction is proportional to zero power of the concentration of reactants. Rate = $-\,d[R]$ = k $[R\,]^0$

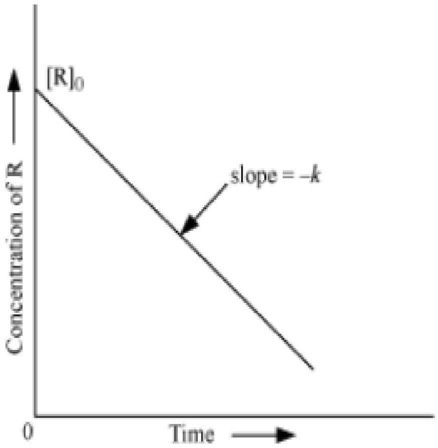
$$-\frac{d[R]}{dt} = k\,[R\,]^0$$

$$d[R] = -\,k\,dt$$

Integrating on both sides $[R] = -\,k\,t + I$, where, I is the constant of integration. when t = 0, the concentration of the reactant R becomes $[R]_0$, where $[R]_0$ is initial concentration of the reactant. $[R]_0 = -k \times 0 + I$ $\Rightarrow [R]_0 = I$

$\therefore\ [R] = -kt + [R]_0$

$$k = \frac{[R]_0 - [R]}{t}$$



Some enzyme catalysed reactions and reactions which occur on metal surfaces are a few examples.

b)First Order Reactions:

Consider first order reaction $R \rightarrow P$

Let $[R]_0$ be the initial concentration of reactant and [R] be the final concentration at time'‘t’. For first order reaction, the rate of the reaction is proportional to the first power of the concentration of the reactant R.

Rate $= -\frac{d[R]}{dt} = k R \Rightarrow \frac{d[R]}{R} = -kdt$

Integrating on both sides, $\ln [R] = -kt + I$, I is the constant of integration.

When t = 0, R becomes $[R]_0$, where $[R]_0$ is the initial concentration of the reactant.

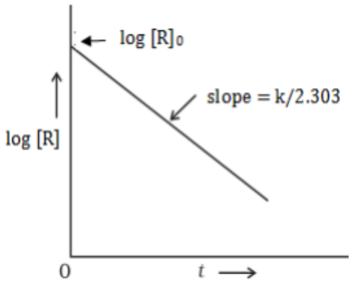
Therefore, $\ln [R]_0 = -k \times 0 + I \Rightarrow \ln [R]_0 = I$

Substituting the value of I, $\ln[R] = -kt + \ln[R]_0$

Rearranging this equation, $\ln \frac{[R]}{[R]o} = kt$

Or, $k = \frac{1}{t} \ln \frac{[R]o}{R} \Rightarrow k = \frac{2.303}{t} \log \frac{[R]o}{R}$

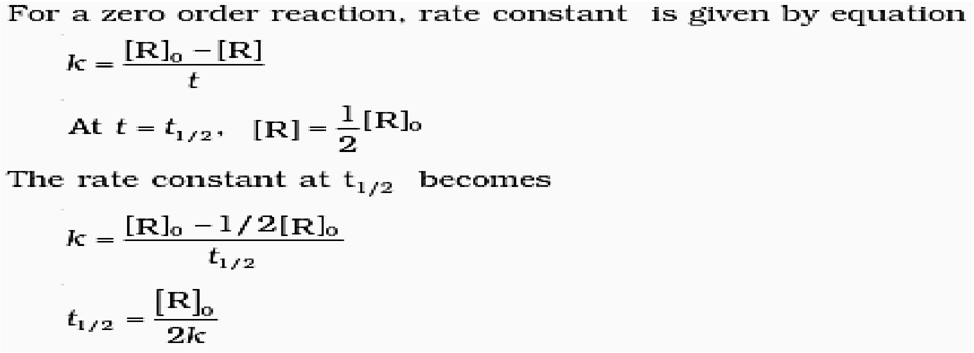
A graph is drawn between log [R] against ‘t’ gives a straight line with slope = –k and intercept equal to log $[R]_0$



14. Half-Life of a Reaction:

It is the time required to reduce the concentration of reactant to one half of its initial concentration. It is represented as $t_{1/2}$.

Case 1: Zero order reaction.



For a zero order reaction, rate constant is given by equation

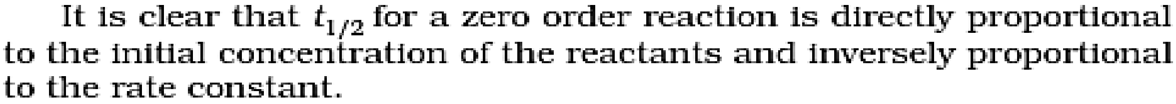
$$k = \frac{[R]_0 - [R]}{t}$$

At $t = t_{1/2}$, $[R] = \frac{1}{2}[R]_0$

The rate constant at $t_{1/2}$ becomes

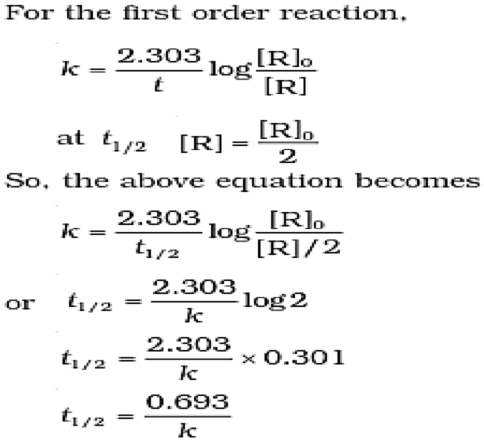
$$k = \frac{[R]_0 - 1/2[R]_0}{t_{1/2}}$$

$$t_{1/2} = \frac{[R]_0}{2k}$$



It is clear that $t_{1/2}$ for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

Case 2. First order reaction



For the first order reaction,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

at $t_{1/2}$ $[R] = \frac{[R]_0}{2}$

So, the above equation becomes

$$k = \frac{2.303}{t_{1/2}} \log \frac{[R]_0}{[R]/2}$$

or $t_{1/2} = \frac{2.303}{k} \log 2$

$$t_{1/2} = \frac{2.303}{k} \times 0.301$$

$$t_{1/2} = \frac{0.693}{k}$$

Thus for a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of the reacting species.

15. **Elementary reactions:** The reactions taking place in single step without the formation of any intermediate are called elementary reactions.

Complex reactions: These reactions proceed in more than one step and involve mechanism. In these reactions, the sequence of elementary reactions give the products through a suitable mechanism.

Rate determining step: The different elementary reactions of a complex reaction do not take place at the same rate. The slowest step determine the overall rate of a reaction and is known as rate determining step.

First order gas phase reaction:

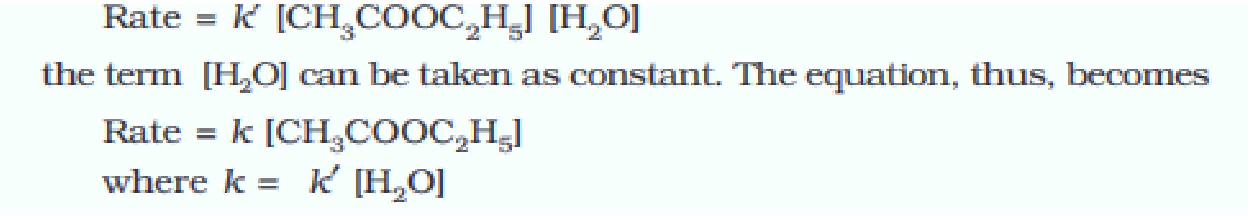
$$K = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)}$$

16. **Pseudo First Order Reaction:**

A reaction which appears to follow higher order but follows first order kinetics.

In bimolecular reactions, one reactant is present in large excess and rate of reaction is independent of its concentration.

$$\mathbf{CH_3COOC_2H_5 + H_2O \rightarrow \quad CH_3COOH + C_2H_5OH}$$



$$\text{Rate} = k' \, [CH_3COOC_2H_5] \, [H_2O]$$

the term $[H_2O]$ can be taken as constant. The equation, thus, becomes

$$\text{Rate} = k \, [CH_3COOC_2H_5]$$

$$\text{where } k = k' \, [H_2O]$$

17. **Dependence of temperature on rate of a reaction–Arrhenius Equation**

$$\mathbf{K = Ae^{-Ea/RT}}$$

$\mathbf{e^{-Ea/RT}}$ represents the fraction of molecules with energies equal to or greater than Ea

where A is the Arrhenius factor or the frequency factor (or pre-exponential factor, a constant specific to aparticular reaction. The number of collisions per second per unit volume of the reaction mixture is known as collision frequency) .R is gas constant and Ea is activation energy measured in $Jmol^{-1}$.

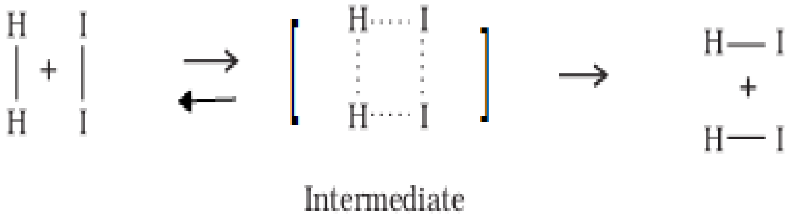
$$\log k = \frac{-Ea}{2.303\,RT} + \log A$$

$$\log \frac{k_2}{k_1} = \frac{Ea}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

18. **Activated complex (Transition State theory)**:

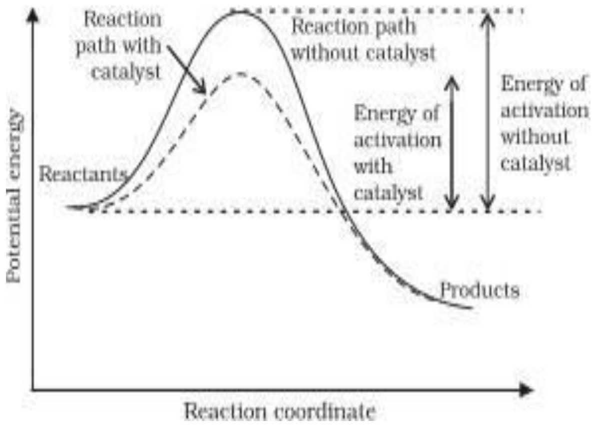
Activated complex state is highly energy state and hence it is highly unstable state. It is always reversible state.

Consider areaction: **$H2(g)+I2(g) \rightarrow 2HI(g)$**



If the total energy of reacting species are equal or higher than threshold energy then the reaction proceed in forward direction and hence gives the products otherwise it retains as reactants only**.**

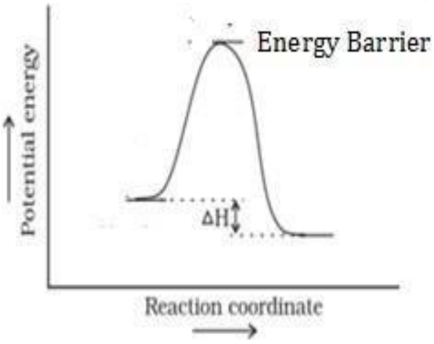
19. **Effect of Catalyst:** A catalystis a substance which alters the rate of a reaction without itself undergoing any permanent chemical change.



Catalyst help to increase the rate of chemical reaction. The presence of catalyst lowers the potential energy barrier and the reaction follows a new alternate pathway which requires less activation energy.

20. **CollisionTheory**:

1. A reaction is possible when all reacting molecules come closer to each other and then collide.
2. All collisions may not result into products. Only those collisions which result into products are called ‘**effective collisions’ or ‘fruitful collisions’.**
3. In a reaction, all colliding molecules must have minimum energy called ‘**Threshold Energy’**(It is the minimum energy required by the reacting molecules to get the products).
4. Most of the reacting molecules have energy less than Threshold energy. Therefore, additional energy required by the reacting molecules to attain Threshold energy is called **Activation energy.**
   Activation Energy =Threshold Energy–Average energy of reacting molecules
5. For effective collisions, all reacting molecules must be **properly oriented.**

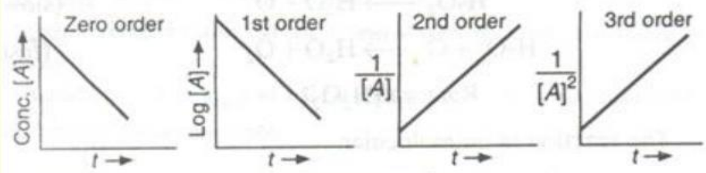


To get the products, all reacting molecules have to cross over the energy barrier. Only those reactingmolecules whose total energy is equal or greater than Threshold energy can only cross over the energybarrierandhencegives theproduct.
According to this theory reaction occurs only when the collisions are effective. The number of collisions that takes place per second per unit volume of the reaction mixture is called **collision frequency.**
For a reaction $A + B \rightarrow$ Products, if Z_{AB} is the collision frequency and f is

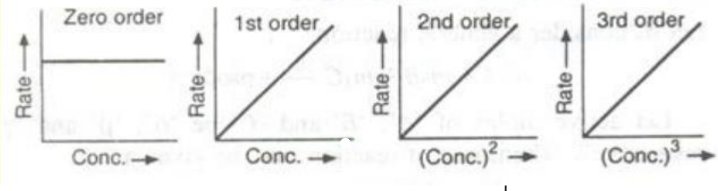
the fraction of molecules whose collisions are effective , then Rate of reaction = Z_{AB} x f

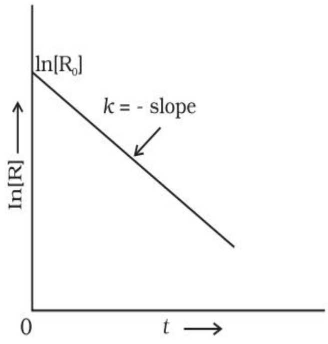
f = $e^{-Ea/RT}$ then Rate = $Z_{AB}\, e^{-Ea/RT}$
As the reaction is directly related to rate constant, we can write k = $Z\, e^{-Ea/RT}$
Colliding molecules must have proper orientation. If the orientation factor P is introduced , then k = $PZ\, e^{-Ea/RT}$.

GRAPHS

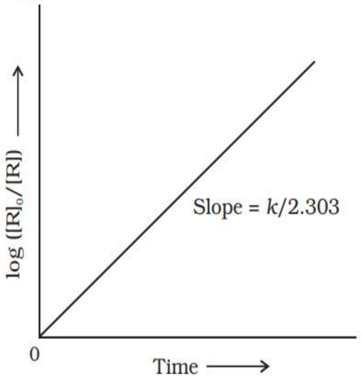


(b) Plots from integrated rate equations:





A plot between ln[R] and t for a first order reaction



Plot of log $[R]_0/[R]$ vs time for a first order reaction

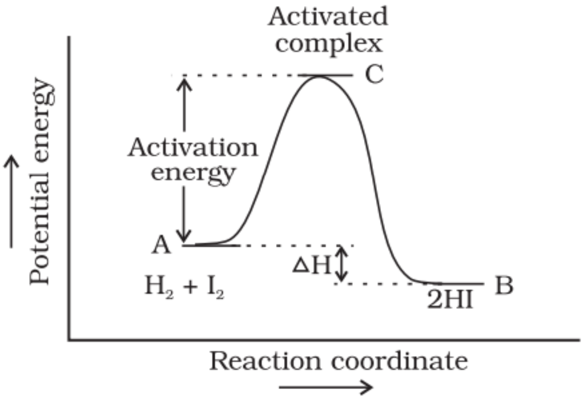
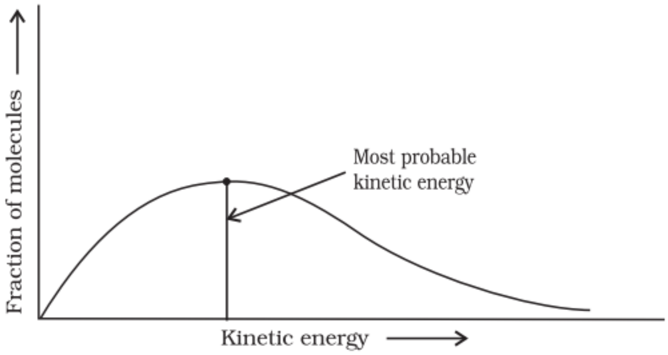
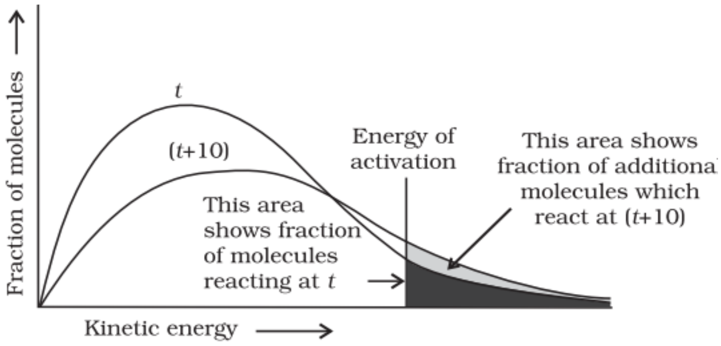


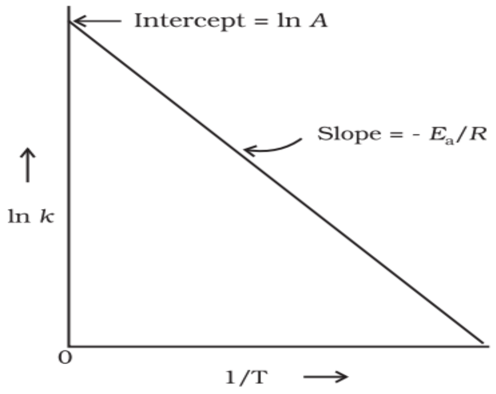
Diagram showing plot of potential energy vs reaction coordinate.



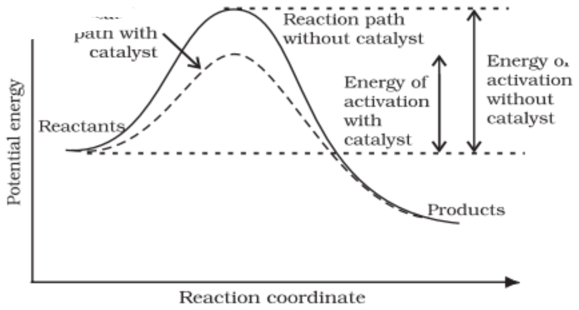
Distribution curve showing energies among gaseous molecules



Distribution curve showing temperature dependence of rate of a reaction



A plot between ln k and 1/T



Effect of catalyst on activation energy

MULTIPLE CHOICE QUESTIONS

1. The unit of the rate of reaction is the same as that of the rate constant for a –
 (a) Zero order reaction
 (b) Second order reaction
 (c) first order reaction
 (d) half order reaction
2. The unit for the rate constant of the second order reaction –
 (a) mol^{-1} litre s^{-1}
 (b) mol $litre^{-1}$ s^{-1}
 (c) mol $litre^{-2}$ s^{-1}
 (d) s^{-1}
3. If the rate of reaction between A and B is expressed as $k[A][B]^2$,the reaction is:
 (a) First order in A
 (b) Second order in B
 (c) Overall third order
 (d) All are correct
4. The rate constant of a reaction is 1.2×10^{-2} s^{-1} , the order of reaction is:
 (a) 0
 (b) 1

(c) 0.5

d) 2

5. In a reaction,2X→Y,the concentration of X decreases from 0.50M to 0.38M in10min.What is the rate of reaction inMs^{-1}during this interval?

(a) 2×10^{-4}

(b)4×10^{-2}
(c) 2×10^{-2}
(d)1×10^{-2}

6. The decomposition of dimethyl ether is a fractional order reaction. The rate is given by

rate =$\mathbf{k(P_{CH_3OCH_3})^{3/2}}$.

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constant?

(a) bar min^{-1}, $bar^2 min^{-1}$
(b) barmin^{-1}, $bar^{-1/2} min^{-1}$
(c) $bar^{1/2} min^{-1}$, $bar^2 min^{-1}$
(d) bar min^{-1}, $bar^{1/2} min^{-1}$

7. A first order reaction has a rate constant$1.15\times10^{-3} s^{-1}$.How long time will 5g of this reactant take to reduce to3g?

(a)444s
(b) 400s
(c) 528s
(d) 669s

8. For a reaction x+ y → z the rate of reaction becomes twenty seven times when the concentration of X is increased three times. What is the order of the reaction?
(a) 2
(b) 1
(c) 3
(d) 0

9. The role of a catalyst is to change ______________.
(a) Gibbs energy of reaction.

(b) Enthalpy of reaction.
(c) Activation energy of reaction.
(d)Equilibrium constant.

10. Which of the following statements is incorrect about the collision theory of chemical reaction?
(a)It considers reacting molecules or atoms to be hard spheres and ignores their structural
features.
(b) Number of effective collisions determines the rate of reaction.
(c)Collision of atoms or molecules possessing sufficient threshold energy results into the
product formation.
(d) Molecules should collide with sufficient threshold energy and proper orientation for the
collision to be effective.

11. The half-life of the first order reaction having rate constant K =1.7x$10^{-5}s^{-1}$is:
a)12.1hb) 9.7h
c)11.3h
d)1.8h

12. If the initial concentration of reactant is doubled, **t1/2** is also doubled, the order of reaction is…
(a)Zero (b)1 (c) 2 (d) 3

13. If the concentration of a reactant A is doubled and the rate of its reaction increased by a factor of 2,the order of reaction with respect to A is...
(a)first (b) zero (c) third (d) second

14. The half – life of a substance in a certain enzyme- catalysed reaction is 138s. The time required for the concentration of the substance to fall from 1.28mg L^{-1} to 0.04mg L^{-1}, is
(a) 414s
(b) 552 s
(c) 690 s
(d) 276 s

15. The time taken for 10% completion of a first order reaction is 20 minutes. Then for 19% completion, the reaction will take…..
(a) 40 mins.
(b) 60mins.
(c) 30 mins
(d) 50mins.

16. For an endothermic reaction, where ΔH represents the enthalpy of the reaction in kJ/mol, the minimum value for the energy of activation will be…

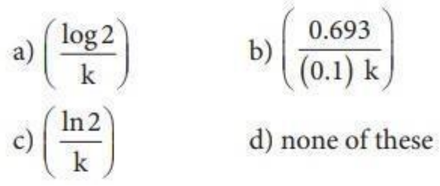
(a) Less than ΔH
(b) zero
(c) more than ΔH
(d) equal to ΔH

17. According to Maxwell Boltzmann distribution of energy,
    (a) The fraction of molecules with most probable kinetic energy does not change at higher temperatures.
    (b) The fraction of molecules with most probable kinetic energy increases at higher temperatures.
    (c) Most probable kinetic energy increases at higher temperatures.
    (d) Most probable kinetic energy decreases at higher temperatures.

18. For there action N2O5(g)→2NO_2(g)+½O_2(g),the value of rate of disappearance of N_2O_5 is given as 6.5×10^{-3}mol$L^{-1}s^{-1}$.The rate of formation of NO_2 andO_2isgiven respectively as…

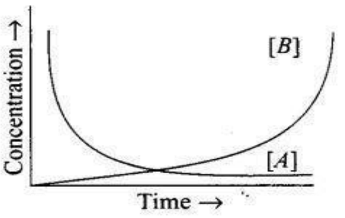
a)(3.25×10^{-2}mol$L^{-1}s^{-1}$)and($1.3\times10-^{2}$mol$L^{-1}s^{-1}$)
b)($1.3\times10-^{2}$mol$L-^{1}s-^{1}$)and($3.25\times10-^{2}$mol$L^{-1}s^{-1}$)
c)(1.3×10^{-2}mol$L^{-1}s^{-1}$)and($3.25\times10-^{3}$mol$L^{-1}s^{-1}$)
d)None of these

19 In a first order reaction $x \rightarrow y$; if k is the rate constant and the initial concentration of the reactant x is0.1M, then, the half life is…..

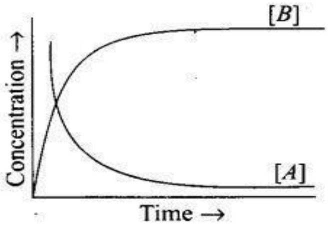

a) $\left(\frac{\log 2}{k}\right)$ b) $\left(\frac{0.693}{(0.1)\,k}\right)$
c) $\left(\frac{\ln 2}{k}\right)$ d) none of these

20. Consider the reaction A—>B. The concentration of both the reactants and the products varies exponentially with time. Which of the following figures correctly describes the change in concentration of reactants and products with time?

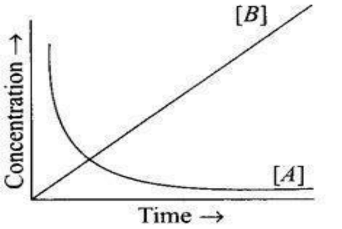
(a)



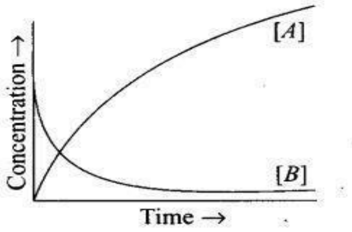
(b)



(c)



(d)



ANSWER KEY:

1.a	2.a	3.d	4. b	5. a
6.b	7.a	8.c	9.c	10.d
11.c	12.a	13.a	14.c	15.a
16. c	17. c	18.c	19.c	20.b

ASSERTION – REASON TYPE QUESTIONS

A statement of assertion is followed by a statement of reason. Mark the correct choice from the options given below:

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

(b) Both assertion and reason are true and reason is not the correct explanation of assertion.

(c) Assertion is true but reason is false.

(d) Assertion is false but reason is true.

1. Assertion: Complex reaction takes place in different steps and the slowest step is the rate determining step.

   Reason: Order and molecularity of a reaction are always equal.

2. Assertion: Rate of reaction increases with increase in temperature.

   Reason: Number of effective collisions increase with increase in temperature.

3. Assertion: Order of a reaction with respect to any reactant or product can be zero, whole number and fractional.

   Reason: Rate of a reaction cannot decrease with increase in concentration of a reactant or product.

4. Assertion: The rate of a reaction sometimes does not depend on concentration.
Reason : Lower the activation energy, faster is the reaction.

5. Assertion: For a certain reaction, a large fraction of molecules may have energy more than the threshold energy , still the reaction is very slow.
Reason: The colloiding molecules must not be properly oriented for effective collisions.

6. Assertion: Hydrolysis of methyl ethanoate is a pseudo first order reaction.
Reason: Water is present in large excess and therefore its concentration remained constant throughout the reaction.

7. Assertion: Increase in concentration of reactant will not change the rate for a zero-order reaction.
Reason: Rate constant for a zero-order reaction is a constant for a particular initial .concentration.

8. Assertion: Diamond shall be convert to graphite.
Reason: The rate is so slow that the change is not perceptible at all.

9. Assertion: The thermal decomposition of HI on gold is a zero-order reaction.
Reason: The thermal decomposition of HI on gold depends on the initial concentration.

10 Assertion: The rate of a reaction quadrupled when concentration is doubled.
Reason: It is second order reaction.

11. Assertion: Half-life of a reaction can be used to predict order of a reaction.
Reason: The relationship between half-life and initial concentration of the reactant is dependent on order

12. Assertion: For the reaction RCl + NaOH(aq) → ROH + NaCl, the rate of reaction is reduced to half on reducing the concentration of RCl to half.
Reason: The rate of the reaction is represented by k[RCl], ie., it is a first order reaction.

13. Assertion: The molecularity of the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr\ (g)$ is 2.
Reason : The order of the reaction is 3/2.

14. Assertion: All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.
Reason: In a first order reaction half-life is independent of initial concentration**.**

ANSWER KEY

1.c	**2.a**	**3.c**	**4.b**	**5.a**
6.a	**7.b**	**8.b**	**9.c**	**10.a**
11.a	**12.c**	**13.b**	**14.b**	

1 MARK QUESTIONS.

1. How is rate constant related to concentration of the reactants?

   Ans: The rate constant is equal to the rate of the reaction when concentration of reactants is unity. Thus, rate constant does not depend upon the concentration of reactants.

2. Why is the probability of reaction with molecularity higher than three very rare?

   Ans: This is because the probability of more than three molecules to collide simultaneously is very small

3. For a reaction: A+B→P, the rate law is given by, $r= k[A]^{1/2}[B]^2$. What is the order of reaction?

   Ans: Order= 1/2+2=5/2=2.5

4. The rate constant of a reaction is $3x10^2 \text{ min}^{-1}$. What is the order of reaction?

   Ans: Given unit of rate constant is min^{-1}. So order of the reaction is one.

5. What is the molecularity of the reaction? $Cl \rightarrow 1/2\, Cl_2(g)$

   Ans: Molecularity=1

6. A reaction is found to be zero order. Will its molecularity be zero?

   Ans: Molecularity of a reaction cannot be zero so even if order=0 ; molecularity is not equal to zero.

7. Write the rate equation for the reaction 2A + B → C if the order of the reaction is zero.

   Ans: Rate = $k\,[A]^0\,[B]^0$ or Rate = k

8. For which type of reactions, order and molecularity have the same value?

   Ans: If the reaction is an elementary reaction, order is same as molecularity.

9. In a reaction if the concentration of reactant A is tripled, the rate of reaction becomes twenty seven times. What is the order of the reaction?

   Ans: Three, because rate = $k\,[A]^3$

10. What will be the effect of temperature on rate constant?

    Ans: Rate constant of a reaction is doubled for every $10^{\mathbf{0}}$ rise in temperature.

11. Why can't molecularity of any reaction be equal to zero?
Ans: Molecularity is the number of molecules taking part in an elementary step. For this we require at least a single molecule leading to the value of minimum molecularity of one.

12. The conversion of molecule X to Y follows second order kinetics. If conc. of X is increased to 3 times, how will it affect the rate of formation of Y ?
Ans: $X \longrightarrow Y$ follows second order kinetics.
Rate = $\mathbf{k[X]^2}$
when conc. of X increased three times the rate $= k[3X]^2 = 9$ times.

13. Mention the factors that affect the rate of a chemical reaction.
Ans: Nature of the reactants, Temperature, catalyst, surface area of the reactants, concentration of the reactants, presence of light.

14. Calculate the half-life of a first order reaction if it's rate constant is 350 s^{-1}.
Ans: $\mathbf{t_{1/2} = 0.693/k = 0.693/350 = 1.98 \times 10^{-3}\ s}$

15 What is the shape of graph between log k vs 1/T .What is the relationship between its slope and activation energy (Ea)?
Ans: It is straight line whose slope is – Ea / 2.303R

16. The rate constant of a first order reaction is $60s^{-1}$. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value?

Ans. $\mathbf{t = \frac{2.303}{k} \log \frac{a}{a/16} = \frac{2.303}{60s^{-1}} \log 16 = 4.62 \times 10^{-2}}$

17. The half life period of a first order reaction is 60 minutes. What percentage will be left after 240 minutes?
Amount of substance left after n half lives = $\mathbf{[R]_0/2^n}$
Ans: No. of half lives = 240/60 , n=4
Amount left after 4 half- lives $= \frac{[R]_0}{2^4} = 0.0625$ of $R_0 = 6.25\%$

2 MARK QUESTIONS

1. Consider the decomposition of hydrogen peroxide in alkaline medium which is catalysed by iodide ions.

$$2H_2O_2 \xrightarrow{I^- /\ \text{alkaline medium}} 2H_2O + O_2$$

Thisreaction takesplace in twostepsasgivenbelow:

$H_2O_2 + I^- \longrightarrow H_2O + OI^-$ (slow)

$H_2O_2 + OI^- \longrightarrow H_2O + O_2 + I^-$ (fast)

(i) Write the rate law expression and determine the order of reaction w.r.t. H_2O_2.

(ii) What is the molecularity of each individual step?

Ans:

(i) Rate =k$[H_2O_2][I^-]$

Orderw.r.t.$_{H_2O_2}$=1

(ii) Molecularity: Step I=2, StepII=2

2. A reaction is first order w.r.t. reactant A as well as w.r.t .reactant B.

Give the rate law. Also give one point of difference between average

rate and instantaneous rate.

Ans.Rate=k[A][B]

Average rate- Rate of a reaction for a particular period or interval of time.

Instantaneous rate–Rate of a reaction at a particular instant of time

3. Define pseudo first order reaction.Give an example**.**

Ans: Chemical reactions which are not first order but behave as first order reaction under suitable conditions are called pseudo first order Reactions.

Ex: Inversion of cane sugar. C12H22O11+H2O >C6H12O6+C6H12O6

4. The half-life for decay of radioactive 14C is 5730 years. An archaeological artifact containing wood has only 80% of the 14C activity as found in living trees. Calculate the age of the artifact.

Let $[A]_0 = 100$

$\therefore \quad [A] = 100 \times 80\% = 80$

Decay constant $(k) = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730}$

$$t = \frac{2.303}{k}\log\frac{[A]_0}{[A]} = \frac{2.303}{0.693/5730}\log\frac{100}{80}$$

$$= \frac{2.303\times5730}{0.693}\times\log 1.25 = \frac{2.303\times5730}{0.693}\times 0.0969$$

$$= \frac{1278.7108}{0.693} = 1845.18 \approx 1845\,\text{years}$$

5. **Differentiate between Rate of reaction and reaction rate constant.**

Rate of reaction	**Rate constant (K)**
Change in concentration of any one of the reactants/products per unit time	Rate constant when concentrations of all reactants are unity. It is independent of the initial

It is dependent on the initial concentrations of the reactant. Unit: mol L^{-1} s^{-1} or atm s^{-1} .	concentrations of the reactant. Unit: depends on the order of reaction.

6. A reaction is second order in A and first order in B. (i) Write the differential rate equation. (ii) How is the rate affected on increasing the concentration of A three times? (iii) How is the rate affected when the concentration of both A and B are doubled?

(i) Differential rate equation is
Rate = $k[A]^2[B]$
(ii) The new concentration of $A = [3A]$
$\therefore$ New rate = $k[3A]^2[B] = 9k[A]^2[B]$
$\therefore$ New rate = 9 times of the original rate
(iii) New concentration of $A = [2A]$
New concentration of $B = [2B]$
$\therefore$ New rate = $k[2A]^2[2B] = 8k[A]^2[B]$
$\therefore$ New rate = 8 times of the original rate.

3 MARKS QUESTIONS

1. The rate of a reaction becomes 4 times when the temperature changes from 293K to 313K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

$$\log\frac{k2}{k1} = \frac{Ea}{2.303R}\left(\frac{T2-T1}{T1T2}\right)$$

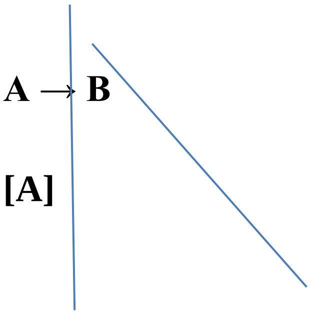
$$\text{Log } 4 = \frac{Ea}{2.303X\ 8.314}\left(\frac{313-293}{293\ X313}\right)$$

$$0.6021 = \frac{Ea}{19.147}\left(\frac{20}{91709}\right)$$

$$Ea = \frac{0.6021 \times 19.147 \times 91709}{20}$$

$$= 52862.94 \text{ Jmol}^{-1}$$

2. For a general reaction A → B, plot of concentration of A vs time is given in Fig. Answer the following question on the basis of this graph. (i) What is the order of the reaction? (ii) What is the slope of the curve? (iii) What are the units of rate constant?



Ans: (i) Zero

(ii) –k

(iii) mol L^{-1} s^{-1}

3. i) What is a temperature coefficient?

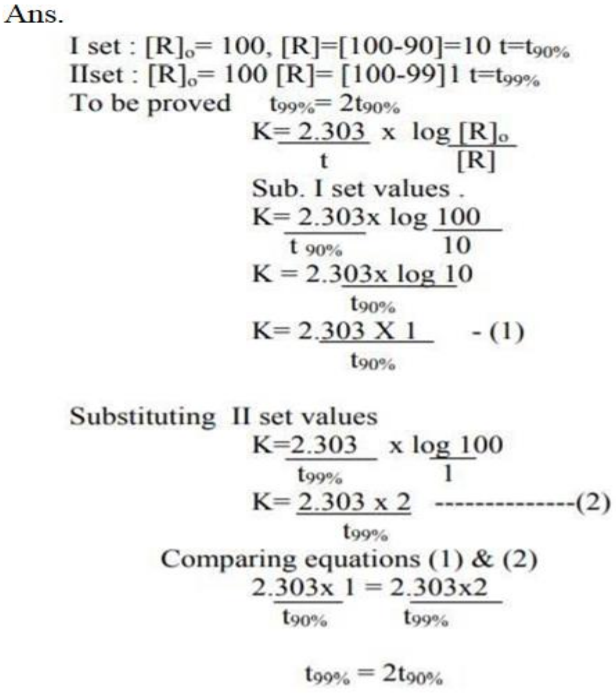
ii)Why is the rate of reaction does not remain constant throughout the course of the reaction? iii)In which order of reaction ,rate of reaction becomes equal to specific reaction rate?

Ans: i) ratio of rate constant of two temperatures differing by 10^{o} C.

ii) rate of reaction is dependent on concentration of reactants and concentration gradually decreases with time.

iii) zero order reaction

4. Show that the time required for 99% completion of a first order reaction is twice the time required for the completionof 90% of reaction.



Ans.

I set : $[R]_o = 100$, $[R] = [100-90] = 10$ $t = t_{90\%}$

IIset : $[R]_o = 100$ $[R] = [100-99] 1$ $t = t_{99\%}$

To be proved $t_{99\%} = 2t_{90\%}$

$$K = \frac{2.303}{t} \times \log \frac{[R]_o}{[R]}$$

Sub. I set values .

$$K = \frac{2.303}{t_{90\%}} \times \log \frac{100}{10}$$

$$K = \frac{2.303 \times \log 10}{t_{90\%}}$$

$$K = \frac{2.303 \times 1}{t_{90\%}} \quad -(1)$$

Substituting II set values

$$K = \frac{2.303}{t_{99\%}} \times \log \frac{100}{1}$$

$$K = \frac{2.303 \times 2}{t_{99\%}} \quad \text{--------------}(2)$$

Comparing equations (1) & (2)

$$\frac{2.303 \times 1}{t_{90\%}} = \frac{2.303 \times 2}{t_{99\%}}$$

$$t_{99\%} = 2t_{90\%}$$

5. Rate constant k for a first order reaction has been found to be 2.54×10^{-3} sec^{-1}. Calculate its 3/4th life. (log 4 = 0.6020)

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$k = \frac{2.303}{t} \log \frac{a}{a - \frac{3}{4}a}$$

$$k = \frac{2.303}{t} \log \frac{a}{0.25a}$$

$$t_{3/4} = \frac{2.303}{2.54 \times 10^{-3}\ \text{sec}^{-1}} \times \log \frac{1}{0.25}$$

$$t_{3/4} = 546\ \text{s}$$

Therefore, the 3/4th life of the reaction is 546 seconds.

6. The decomposition of NH_3 on platinum surface : $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$ 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?

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

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

The order of reaction is 0 *i.e.*,

Rate = k $[\text{Reactant}]^0$

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

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

The rate of formation of $N_2 = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}

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

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

Therefore, rate of formation of H_2

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

7. If the concentration is expressed in mol/L units and time in seconds what would be units of k for (i) zero order (ii)first (iii) second

Ans: (i) mol L-1 S -1 (ii)s -1 (iii) Lmol-1 s -1

8. The decomposition of phosphine, $4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$ has the rate law, Rate = $k[PH_3]$. The rate constant is $6.0 \times 10^{-4} s^{-1}$ at 300 K and activation energy is 3.05×10^5 J mol^{-1}. Calculate the value of rate constant at 310 K. [Given : R = 8.314 J $K^{-1}mol^{-1}$]

Ans:

Using Arrhenius equation,

$$\log\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$$\text{or, }\log\frac{k_2}{k_1}=\frac{3.05\times10^5\ \text{J mol}^{-1}}{2.303\times8.314\ \text{JK}^{-1}\ \text{mol}^{-1}}\times\left[\frac{310-300}{300\times310}\right]$$

$$\log\frac{k_2}{k_1}=\frac{3.05\times10^5\text{J mol}^{-1}\times10\ \text{K}}{1780684.2\ \text{JK}^{\ 1}\text{mol}^{\ 1}}$$

$$\log\frac{k_2}{k_1}=1.71\ \Rightarrow\ \frac{k_2}{k_1}=\text{antilog}(1.71)$$

$$\frac{k_2}{6\times10^{-4}}=51.28$$

$$k_2=3.07\times10^{-2}\ \text{s}^{-1}$$

5 MARK QUESTIONS

1. a)The rate constant for a reaction is $1.5\times 10^7\ s^{-1}$ at 50^0C and $4.5\times 10^7\ s^{-1}$at 100^0C.

Calculate the value of activation energy for the reaction R=8.314 $JK^{-1}\ mol^{-1}$?

Ans:

$$\log\frac{k_2}{k_1}=\frac{Ea}{2.303R}\left(\frac{T_2-T_1}{T_1T_2}\right)$$

$$\log\frac{4.5\times10^7}{1.5\times10^7}=\frac{Ea}{2.303\times3.314}\left(\frac{373-323}{}\right)$$

$$\log1.5=\frac{Ea}{2.303\times3.314}\left(\frac{50}{373\times323}\right)$$

$$Ea=\left(\frac{2.303\times3.314\times373\times323}{50}\right)\times\log1.5$$

$$=22\ KJ/mol$$

b) For the reaction at 500K, NO_2 (g) + CO(g)→CO_2 (g) + NO(g), the proposed mechanism is as below:

$NO_2 + NO_2 \rightarrow NO + NO_3$ (slow)

$NO_3 + CO \rightarrow CO_2 + NO_2$ (fast)

What is the rate law for the reaction?

Ans: a) k $[NO_2]^{2}$

(c) From the rate expression of the given reaction, $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$

Rate = k $[CH_3CHO]^{3/2}$. Determine the dimensions of rate constant.

Ans: $L^{1/2}mol^{-1/2}s^{-1}$

CASE BASED QUESTION.

Read given passage and answer the questions that follow: Chemical kinetics deals with rate of chemical reactions, how fast reactants get used up or how fast products are formed in the reaction. Differed chemical reactions have different speed. Rate of reaction depends upon concentration of reactants, temperature, pressure especially in gaseous reactions and presence of catalyst. Chemical reaction takes place as a results of collision between reacting molecules. The rate of reaction does not depend upon total number of collisions rather it depends upon number of effective collisions. In a redox reaction, if E°cell is +ve, ΔG° will be –ve and 'K' equilibrium constant will be high i.e. products formed will be more than the reactants.

a) (Activation Energy) Ea and 'A' (Arrhenius constant) are

104.4 kJ mol^{-1} and $6.0 \times 10^{14}\ s^{-1}$respectively. What is value of 'k' when T → ∞?

a)Ans**:** Arrhenius constant $k = Ae^{-Ea/RT}$

$\Rightarrow k = Ae^{-Ea/\infty}$

$= Ae^{\circ} = A = 6.0 \times 10^{14}\ s^{-1}$.

b) In a reaction, 2A —-> Products, the concentration of A decreases from 0.5 mol L^{-1} to 0.4 $molL^{-1}$ in 10 minutes. Calculate the rate during this interval?

Ans.

$$\text{Average Rate} = \frac{-1}{2}\frac{\Delta[A]}{\Delta t} = \frac{-1}{2}\frac{[A]_2 - [A]_1}{t_2 - t_1}$$

$$= \frac{-1}{2}\frac{(0.4 - 0.5)}{10} = \frac{-1}{2}\frac{(-0.1)}{10}$$

$$= 5 \times 10^{-3}\ M\ min^{-1}$$

(c)What is meant by activation energy? What does $\mathbf{e}^{-Ea/RT}$ represent?

Ans**:** The extra energy which must be supplied to reactants in order to undergo effective

collision to form products. It represents fraction of molecules possessing activation energy (Ea) or more than Ea**.**

(or)

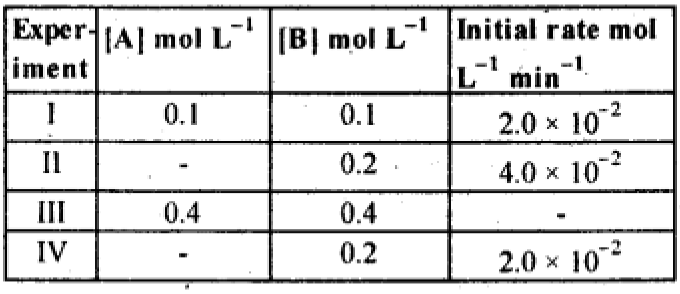
(c) If **Fe** $^{3+}$ **+ 2I** $^{-}$**→ Fe**$^{2+}$ + **I**$_2$ **has E°** = **0.24V,** what is the value of log K? What does value of 'K' indicate?

$$\log K = \frac{nE^0}{0.0591} = \frac{2 \times 0.24v}{0.0591} = 8.122$$

The value indicates that products are formed 10^8 times than reactants.

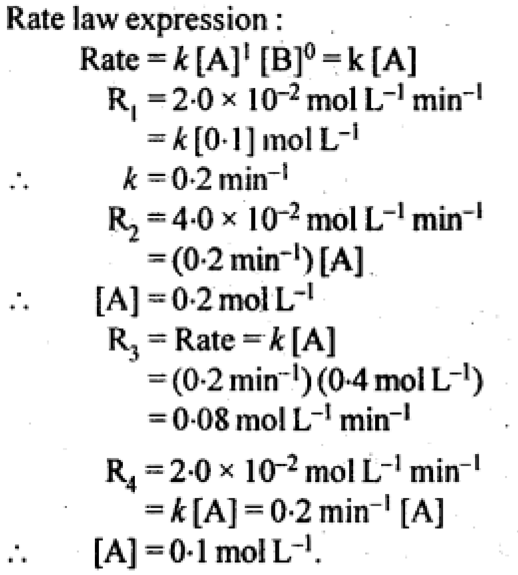
HOTS QUESTIONS

1.The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table:



Experiment	[A] mol L^{-1}	[B] mol L^{-1}	Initial rate mol L^{-1} min^{-1}
I	0.1	0.1	2.0×10^{-2}
II	-	0.2	4.0×10^{-2}
III	0.4	0.4	-
IV	-	0.2	2.0×10^{-2}

Sol:



Rate law expression :

$$\text{Rate} = k\,[A]^1\,[B]^0 = k\,[A]$$

$$R_1 = 2{\cdot}0 \times 10^{-2}\ \text{mol L}^{-1}\ \text{min}^{-1}$$

$$= k\,[0{\cdot}1]\ \text{mol L}^{-1}$$

$$\therefore \quad k = 0{\cdot}2\ \text{min}^{-1}$$

$$R_2 = 4{\cdot}0 \times 10^{-2}\ \text{mol L}^{-1}\ \text{min}^{-1}$$

$$= (0{\cdot}2\ \text{min}^{-1})\,[A]$$

$$\therefore \quad [A] = 0{\cdot}2\ \text{mol L}^{-1}$$

$$R_3 = \text{Rate} = k\,[A]$$

$$= (0{\cdot}2\ \text{min}^{-1})(0{\cdot}4\ \text{mol L}^{-1})$$

$$= 0{\cdot}08\ \text{mol L}^{-1}\ \text{min}^{-1}$$

$$R_4 = 2{\cdot}0 \times 10^{-2}\ \text{mol L}^{-1}\ \text{min}^{-1}$$

$$= k\,[A] = 0{\cdot}2\ \text{min}^{-1}\,[A]$$

$$\therefore \quad [A] = 0{\cdot}1\ \text{mol L}^{-1}.$$

2.During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If 1 µg of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically ?

Solution:

As radioactive disintegration follows first order kinetics. Hence

Decay constant of ^{90}Sr, $(\lambda) = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{28.1}$

$= 2.466 \times 10^{-2}\ yr^{-1}$

To calculate the amount left after 10 years

Given, $[R_0] = 1\ \mu g$, $t = 10$ years,

$k = 2.466 \times 10^{-2}\ yr^{-1}$, $[R] = ?$

Using formula, $\lambda = \dfrac{2.303}{t} \log \dfrac{[R_0]}{[R]}$

or $\quad 2.466 \times 10^{-2} = \dfrac{2.303}{10} \log \dfrac{1}{[R]}$

$\dfrac{2.466 \times 10^{-2} \times 10}{2.303} = -\log[R]$

or, $\quad \log [R] = -0.1071$

or, $\quad [R] = \text{Antilog } (-0.1071) = 0.7814\ \mu g$

To calculate the amount left after 60 years,

$t = 60$ years, $[R_0] = 1\ \mu g$, $[R] = ?$

or, $\quad 2.466 \times 10^{-2} = \dfrac{2.303}{60} \log \dfrac{1}{[R]}$

or, $\quad \dfrac{2.466 \times 10^{-2} \times 60}{2.303} = -\log [R]$

or, $\quad \log [R] = -0.6425$

or, $\quad [R] = \text{Antilog } (-0.6425) = 0.2278\ \mu g$

CHAPTER – 4

d AND f BLOCK ELEMENTS

_INTRODUCTION:

d block elements are present from fourth period onwards there are mainly three series of the transition metals, 3d series (Sc to Zn), 4d series (Y to Cd) and 5 d series (La to Hg omitting Ce to Lu). d block elements are also known as transition elements. Electronic configuration of the d block elements is $(n\text{-}1)d^{1\text{-}10}$ ns $^{1\text{-}2}$ but Zn, Cd, Hg are d block elements, but not transition metals because these have completely filled d orbitals in its atomic and ionic state.

GENERAL PROPERTIES OF THE TRANSITION ELEMENTS

1. ATOMIC AND IONIC RADII:

In transition metals, left to right net nuclear charge increases due to poor shielding effect. Due to this, the atomic and ionic radii for transition elements for a given series show a decreasing trend is between the s block and p block elements.Hf and Zr are having same size due to lanthanoid contraction.

2. ENTHALPIES OF ATOMISATION

Transition elements exhibit higher enthalpies of atomization because of large number of unpaired electrons in their atoms they have stronger interatomic interaction and hence stronger bond.

3. IONISATION ENTHALPIES

In a series from left to right, ionization enthalpy increases due to increase in nuclear charge. The irregular trend in the first ionization enthalpy of the 3d metals, through of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4s and 3d orbitals.

4. OXIDATION STATES

Transition metals shows variable oxidation state due to incomplete outermost shells. Only stable oxidation states of the first row transition metals are Sc(+3), Ti(+4), V(+5), Cr(+3,+6), Mn(+2,+7), Fe(+2,+3), Co(+2,+3)Ni(+2), Cu(+2) and Zn(+2).

The transition in their lower oxidation states (+2 & +3) usually forms ionic compounds. In higher oxidation state compounds are normally covalent.

Only Os and Ru show +8 oxidation states in their compounds.

Ni and Fe in Ni(CO)4 and Fe(CO)5 show zero oxidation state.

5. TRENDS IN THE STANDARD ELECTRODE POTENTIALS

The standard reduction potentials of divalent ions of 3d series generally becomes more and more positive from L to R. Variations occur at V2+,Mn2+ and Zn2+. This is due to less enthalpies of atomization of Mn and V and irregular variations of sum of first two ionization enthalpy terms. The unique behaviour of Cu, having a **positive E^o value** , accounts for its inability to liberate H2 from acids. Only oxidising acids (nitric and hot concentrated sulphuric) react with Cu, the acids being reduced. The high energy to transform Cu(s) to Cu2+(aq) is not balanced by its hydration enthalpy.

6. **TRENDS IN STABILITY OF HIGHER OXIDATION STATES:**The higher oxidation number are achieved in TiX_4, VF_5 and CrF_6. The +7 state for Mn is not represented in simple halides but MoO3F is known and beyond Mn no metal has a trihalide except FeX_3 and CoF_3. The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy and the ability of oxygen to form multiple bonds to metals Increasing order of **oxidizing power** in the series is $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$ which is due to the increasing stability of the lower species to which they are reduced.Copper (I) compounds are unstable in aqueous solution and undergo disproportionation. $2Cu^+ \rightarrow Cu^{2+} + Cu$. The stability of Cu2+ (aq) rather than Cu+ (aq) is due to the much more negative hydration enthalpy of Cu2+ (aq) than Cu+ , which more than compensates for the second ionisation enthalpy of Cu

7. **MAGNETIC PROPERTIES**

When a magnetic field is applied to substances, mainly two types of magnetic behavior are observed: diamagnetism and paramagnetism. Paramagnetism due to presence of unpaired electrons each such electron having a magnetic moment associated with its spin angular momentum.

The magnetic moment is determined by the number of unpaired electrons.

Magnetic moment (μ) = $\sqrt{n(n+2)}$ where n is the number of unpaired electrons. If all electrons are paired, substance will be diamagnetic and magnetic moment will be zero.

8. **FORMATION OF COLOURED IONS**

d block elements are coloured due the presence of unpaired electrons. When an electron from a lower energy d orbital is excited to a higher energy d orbital, the energy of required wavelength is absorbed and rest light is transmitted out. Therefore the colour observed corresponds to the complementary colour of the light absorbed. In V2O5 , V is in +5 oxidation state. It is coloured due to defects in crystal lattice.

9. **FORMATION OF COMPLEX COMPOUNDS**

Transition metals have small size, high nuclear charge and availability of incompletely filled d orbital which facilitates the acceptance of lone pair of electron from ligands.

10. **CATALYTIC PROPERTIES**

Transition metals have variable oxidation states and form intermediates with low activation energy, therefore used as a catalyst. Transition metals are small and also provide larger surface area for the reactant to be adsorbed.

11.FORMATION OF INTERSTITIAL COMPOUNDS

Small size of nonmetals (H,C,N) fit into the voids of crystalline solid of tranasition metals and form interstitial compounds. The principal physical and chemical characteristics of these compounds are as follows:

a. They have high melting points, higher than those of pure metals.
b. They are hard some borides approach diamond in hardness.
c. They retain metallic conductivity
d. They are chemically inert.

12.ALLOY FORMATION

Alloy is the homogenous mixture of two or more metals. Transition metals have approximate same size therefore, in molten form they can fit to each other crystalline structure and form homogenous mixture and form the alloy. Example brass (copper and zinc) and bronze (copper and tin) etc.,

SOME IMPORTANT COMPOUNDS OF TRANSITION ELEMENTS

POTASSIUM DICHROMATE

A. **ORE**: Ferrochrome or chromite ($FeO.Cr_2O_3$) or ($FeCr_2O_4$)

B. PREPARATION

$4FeO.Cr_2O_3 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

(Yellow)

$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

(Orange)

$Na_2Cr_2O_7 + 2KCI \rightarrow K2Cr_2O_7 + 2NaCI$

Sodium dichromate is more soluble than potassium dichrmoate and so , potassium dichrmoate can be prepared by treating the solution of sodium dichromate with potassium chloride.

C. PROPERTIES

Chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solutions.

$2\,CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H2O$

$Cr_2O_7^{2-} + 2\,OH^- \rightarrow 2\,CrO_4^{2-} + H2O$

Sodium and potassium dichromates are strong oxidising agents, thus acidified K2Cr2O7 will oxidise iodides to iodine, sulphides to sulphur, tin(II) ti tin(IV) and iron (II) salt to iron(III).

$Cr_2O_7^{2-} + 14H+ + 6I^- \rightarrow 2Cr3+ + 7H2O + 31_2$

$Cr_2O_7^{2-}$ + $3H_2S$ + 8 $H^+ \rightarrow 2Cr^{3+}$ + 3S + 7H2O

$Cr_2O_7^{2-}$ + $14H^+$ + $3Sn^{2+} \rightarrow 3Sn^{4+}$ $+2Cr^{3+}$ +7H2O

D. USES

- potassium dichromate is used as oxidizing agent in volumetric analysis.
- it is used in mordant dyes, leather industry, photography (for hardening of film)
- It is used in chromyl chloride test
- It is used in cleaning glassware.

POTASSIUM PERMANGANATE (KMnO4)

Ore pyrolusite (MnO2)

$2MnO_2$ + 4KOH +$O_2 \rightarrow 2K_2MnO_4$ + 2H2O

(Green)

$3MnO_4^{2-}$ + $4H^+ \rightarrow 2MnO_4^-$ + MnO_2 + 2H2O

(purple)

PROPERTIES

KMnO4 acts as strong oxidising agent.

A. In presence of dilute sulphuric acid potassium permanganate is reduced to manganous salt.

Acidified KMnO4 solution oxidises oxalates to CO_2 iron(II) to iron(III), nitrites to nitrates and iodides to iodine. The half reactions of reductants are

$C_2O_4^{2-}$ → CO_2 + 2e

Fe^{2+} → Fe^{3+} +e-

NO_2^- → NO_3^- + 2e-

$2I^-$ → I_2 + 2e-

To acidify $KMnO_4$ only sulphuric acid is used and not hydrochloric acid or nitric acid because hydrochloric acid reacts with $KMnO_4$ and produce chlorine while nitric acid itself acts as oxidizing agent.

B. In alkaline medium, $KMnO_4$ is reduced to insoulble MnO_2.

Alkaline or neutral $KMnO_4$ solution oxidises I- to IO_3^-, $S_2O_3^{2-}$ to $SO_4^{2-,}$ Mn^{2+} to MnO_2 ect

USES

- In laboratory preparation of chlorine
- $KMnO_4$ is used as oxidising agent, disinfectant
- In making Baeyers reagent

THE INNER TRANSITION ELEMENTS (F BLOCK)

The f block consists of the two series lanthanoids and actinoids. Lanthanoids are known as rare earth metals and actinoids are known as radioactive elements. (Th to Lr)

LANTHANOIDS

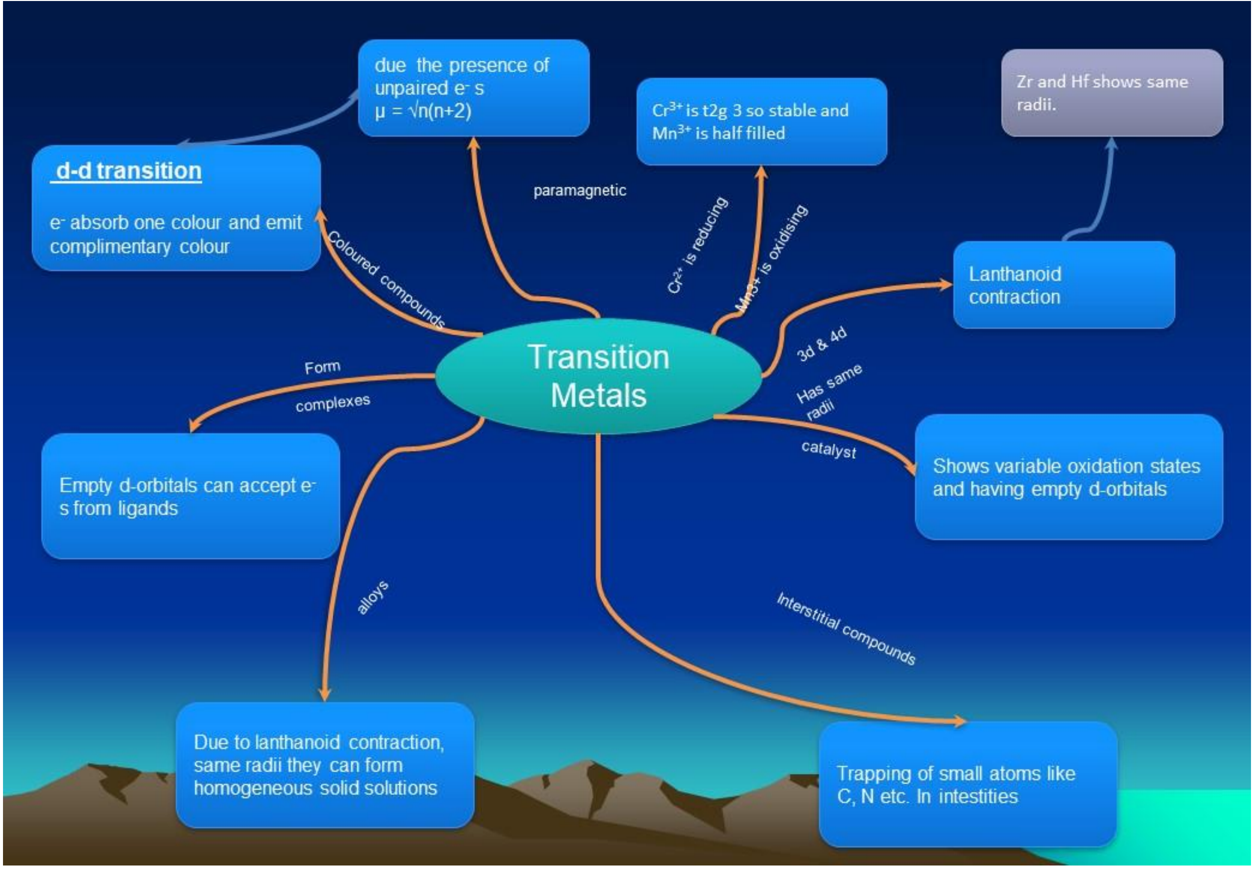
GENERAL CHARACTERISTICS

- General configuration (Xe) $4f^{1-14}$, $5d^{0-}1$, $6s^2$
- This is known as lanthanoid contraction
- All the lanthanoids are silvery white soft metals and tarnish rapidly in air.
- Many trivalent lanthanoid ions are coloured both in the soild state and in aqueous solutions. Neither La^{3+} nor Lu^{3+}ion shows any colour but the rest do so.
- The overall decrease in atomic and ionic radii from lanthanum to lutetium due to ineffective shielding of 4f orbital electron is known as **lanthanoid contraction**. The radii of the members of the third transition series to be very similar to those of the corresponding members of the second series. The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.
- Ion other the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism arises to maximum in neodynium.
- Oxidation states of Ce^{4+} is favoured by its noble gas configuration but it is a strong oxidant reverting to the common +3 state. The standard potential value for Ce^{4+}/Ce^{3+} is +1.74V the reaction rate is very slow and hence, Ce(IV) is a good analytical reagent, Pr, Nd,Tb and Dy also exhibit +4 state but only in oxides, Eu^{2+}
- is formed by losing the two s electrons and its f^7 configuration account for the formation of this ion. However Eu^{2+} is a strong reducing agent changing to the common +3 state. Similarly Yb^{2+} which has f^{14} configuration is a reductant. Tb^{4+} has half filled f orbitals and is an oxidant.
- Lanthanoid are very reactive metals like alkaline earth metals.
- Misch metals contain lanthanoids about 90-95% and 5% Fe and traces of S,C,Ca,Al. Mischmetall is used in Mg-based alloy to produce bullets, shell and lighter flint.

ACTINOIDS

- General configuration $[Rn]5f^{1-14}$, $6d^{0-2}$, $7s^2$
- Actinoids exhibit a range of oxidation states due to comparable energies of 5f,6d and 7s orbits. The general oxidation state of actinoids is +3.
- All the actinoids are strong reducing agents and very reactive.
- Actinoids also react with oxygen, halogen, hydrogen and sulphur etc., like lanthanoids.

- Actinoids are radioactive in nature in nature and therefore, it is difficult to study their chemical nature.



Transition Metals

d-d transition

e^- absorb one colour and emit complimentary colour

due the presence of unpaired e^- s
$\mu = \sqrt{n(n+2)}$

Cr^{3+} is t2g 3 so stable and Mn^{3+} is half filled

Zr and Hf shows same radii.

Lanthanoid contraction

Shows variable oxidation states and having empty d-orbitals

Empty d-orbitals can accept e^- s from ligands

Due to lanthanoid contraction, same radii they can form homogeneous solid solutions

Trapping of small atoms like C, N etc. In intestities

MULTIPLE CHOICE QUESTIONS AND ANSWERS:

1. The element of 3d series which forms a colorless 3+ ion is
a) Fe b) Co c) Mn d) Sc
Ans: d) Sc

2. Which among the following is not a transition element?
a) Mn b) V c) Cr d) Cd
Ans: d) Cd

3. Zn has lowest enthalpy of atomization among the 3d elements, because
a) It has high melting point
b) it has no unpaired electrons to participate in active inter-atomic metallic bonding
c) It has got incompletely filled d subshell
d) it is not a transition element
Ans: b) it has no unpaired electrons to participate in active inter-atomic metallic bonding

4. Among Zn^{2+}, Ni^{2+}, Cu^{2+} and Mn^{2+} the one with largest size is
a) Zn^{2+} b) Cu^{2+} c) Mn^{2+} d) Ni^{2+}
Ans: c) Mn^{2+}

5.The E^oM^{2+}/M reduction potentials of Cu^{2+}, Ni^{2+}, Zn^{2+} and V^{2+} are +0.34V, -0.25V

,-0.76V,-1.18V respectively. The pair of ions with least and highest oxidising power is

a) Ni^{2+} and Cu^{2+} b) V^{2+} and Cu^{2+} c) Cu^{2+} and Zn^{2+} d) Zn^{2+} and Ni^{2+}

Ans: b) V^{2+} and Cu^{2+}

6. Which among the following has similar atomic radii?

a) Sc and Y b) Nb and Ta c) Zr and Hf d) Ni and Pt

Ans: c) Zr and Hf

7. The stability of highest Oxidation state of transition elements down a group

a) decreases b) Increases c) remains same d) doesn't show any regular trend

Ans: b) Increases

8. The no. of oxidation states exhibited by a transition element is maximum in the middle of a Series. This is because of

a) the presence of more no. of electrons in d and s subshells
b) the presence of more no. of unpaired electrons in d subshell
c) Availability of empty orbitals in valence shell
d) All of these

Ans: d) All of these

9. Which has more ionisation enthalpy, Cr^+ or V^+ or Mn^+?

a) V^+ b) Cr^+ c) Mn^+ d) both Cr^+ and Mn^+

Ans: b) Cr^+

10. $E^o_{Mn3+/Mn2+}$ is more positive than those of Ti^{3+}/Ti^{2+} and V^{3+}/V^{2+}. This is because of

a) Change in d configuration from d^4 to d^5, the d^5 system being more stable by loss of energy through spin exchange
b) Change in d configuration from d^5 to d^4
c) Change in d configuration from d^4 to d^5, d^5 system being more stable due to symmetrical distribution of electron density
d) Both a and c

Ans: d) Both a and c

11. The lowest common oxidation state shown by 3d series elements is

a) +1 b) +2 c) +3 d) +4

Ans: b) +2

12. Cu^+ is less stable than Cu^{2+} in aqueous solution. This is because of

a) More negative Hydration enthalpy of Cu^+ ion
b) More negative Hydration enthalpy of Cu^{2+} ion
c) Less negative Hydration enthalpy of Cu^{2+} ion
d) Less enthalpy atomization of Cu

Ans: b) More negative Hydration enthalpy of Cu^{2+} ion

13. The ion that shows paramagnetic character is

a) Zn^{2+} b) Sc^{3+} c) Ti^{4+} d) Ti^{3+}

Ans: d) Ti^{3+}

14. A dipositive ion 3d series element has s spin only magnetic moment of 5.91 BM. The metal

Ion is

a) Co^{2+} b) Fe^{2+} c) Ni^{2+} d) Mn^{2+}

Ans: d) Mn^{2+}

15. Match the following:

ELEMENT	PROPERTY
A) Zinc	1) Stable +3 state
B) Copper	2) Lowest ΔHa
C) Manganese	3) Paramagnetic moment is 1.732 BM
D) Chromium	4)Shows maximum +4 with flourine and +7 oxidation state with oxygen

a) A-2: B-3 : C-4: D-1 b) A-1; B-2;C-3;C-4

c)A-4;B-2;C-3;D-1 d) A-4;B-3;C-2;D-1

Ans: a) A-2: B-3 : C-4: D-1

16. Mischmetall contains

a) a lanthanoid element and Zinc b) a lanthanoid element and Iron

c) an actinoid element and Mn d) an actinoid element and Mg

Ans: b) a lanthanoid element and Iron

17. Ti^{3+} ion forms a complex in aqueous solution and is purple colored . This is due to

a) d-d transition b) f-f transition c) L→M charge transfer d) M→L charge transfer

Ans: a) d-d transition

18. KMnO4 forms a purple colored solution with water. This is due to

a) d-d transition b) f-f transition c) L→M charge transfer d) M→L charge transfer

Ans: c) L→M charge transfer

19. Which of the following is most stable in aqueous solutions?

a) Mn^{2+} b) Cr^{3+} c) V^{3+} d) Ti^{3+}

Ans: b) Cr^{3+}

20. The oxidation state of Cr in the final product formed by the reaction of KI and acidified $K_2Cr_2O_7$ is

a) +4 b) +6 c) +2 d) +3

Ans: d) +3

21. The correct order of second Ionisation enthalpy of Ti,V,Cr and Mn is

a) V>Mn>Cr>Ti b) Mn>Cr>Ti>V c) Ti>V>Cr>Mn d) Cr>Mn>V>Ti

Ans: d) Cr>Mn>V>Ti

22. The heaviest transition element is

a) Zn b) Sc C) Ta d) Os

Ans: d) Os

23. Which of the following statements related to lanthanoids is incorrect?

a) Eu shows +2 oxidation state b) $Pr(OH)_3$ to $Lu(OH)_3$, basicity decreases

c) All lanthanoids are more reactive than Al d) Ce^{4+} is an oxidizing agent

Ans:c) All lanthanoids are more reactive than Al

24. Intersitial compounds are non-stoichiometric compounds formed by Transition elements when atoms like H,C,N are trapped in the interstitial sites of transition metal lattices.

Which of the following is not a property of interstitial compounds?

a) They are very hard b) They retain metallic conductivity

c) They have high melting points d) They are chemically very reactive

Ans: d) They are chemically very reactive

25. Ti^{3+} in aqueous solution forms a complex ion with water. The purple color of this complex is due to the d-d transition ie., the electronic transition from

a) t_{2g} to e_g b) e_g to t_{2g} c) t_2 to e_g d) e_g to t_2

Ans: a) t_{2g} to e_g

26. Which among the following oxides of Vanadium is amphoteric

a) V_2O_5 b) VO_2 c) V_2O_3 d) V_2O_4

Ans: a) V_2O_5

27. Which is most covalent Mn_2O_7 or MnO2 or MnO?

a) Mn_2O_7 b) MnO c) MnO_2 d) Both MnO and MnO_2

Ans:a) Mn_2O_7

ASSERTION AND REASONING QUESTIONS:

Note: 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) Both A and R are correct statements and R is the correct explanation of A

b) Both A and R are correct statements but R is not the correct explanation of A

c) Both A and R are false statements

d) A is true R is false.

1. Assertion : Cr^{2+} is a good reducing agent

Reason : Cr^{2+} donates one electron to become Cr^{3+} which in turn is a stable half filled t_{2g} system.

Ans: a

2. Assertion : Actinoid contraction is greater from element to element than Lanthanoid contraction

Reason: The shielding effect of 5f orbitals is poor in comparison to 4f orbitals

Ans; a

3. Assertion : The $E^0_{Ce4+/Ce3+}$ reduction potential is more positive

Reason : Ce $^{4+}$ can act as an analytical agent

Ans: b

4. Assertion: Cr in +6 oxidation state is a better oxidizing agent than Mo in +6 oxidation state

Reason : In transition elements, the stability of highest oxidation state increases down a group

Ans: a

5. Assertion: MnF_7 is unknown whereas KMnO4 is known
Reason: Oxygen, though being less electronegative than Fluorine, is versatile in stabilizing
Highest oxidation states of transition metals by forming multiple bonds with metal atom.
Ans:a

6. Assertion : Mn_2O_7 is more acidic than MnO

Reason : Higher the oxidation state of the metal less is the acidic character.

Ans: d

7. Assertion : Transition metals and their compounds can act as good catalysts

Reason: Transition metals can adopt multiple oxidation states.

Ans: a

8. Assertion : Transition metal ions can form complex compounds with ligands

Reason : Transition metal ions have large size, low charge and completely filled d orbitals

Ans: d

9. Assertion : Transition metals show variable oxidation states.

Reason : This is due to the incompletely filled d orbitals

Ans: a

2 MARKS QUESTIONS AND ANSWERS:

1) What are d and f block elements? Write their general electronic configurations.

The elements present in groups 3 to 12 and in the periods 4 to 7 of modern Periodic Table are called d and f block elements.

General electronic configuration of d block elements: $(n\text{-}1)d^{1\text{-}10}\ ns^{1,2}$ where n= 4,5,6,7

General electronic configurationof f block elements: $(n\text{-}2)f^{1\text{-}14}\ (n\text{-}1)d^{0,1}\ ns^2$ where n= 6,7

2) Group 12 elements are not considered as transition elements. Why?

Zn, Cd and Hg have completely filled d subshell in its atomic state as well as in its ionic

states. So they are not considered as Transition elements.

3) Sc is a transition element whereas Zn is not. Why?

Sc has incompletely filled d subshell (d^1) in its ground state where as Zn has got completely filled d subshell in both ground state as well as excited state (d^{10})

4) Silver atom has completely filled d orbitals in the ground state ($4d^{10}$). How can you say that it

is a transition element?

Though silver has $4d^{10}$ configuration in its ground state as well as +1 excited state, in its

+2 state it has a d^9 configuration. So it is considered as a transition element.

Note; A transition element should have incompletely filled d subshell either in its atomic state or

in one of its ionic states.

5) In 3d series, the melting point and enthalpy of atomisation of Manganese is less compared to

those of its immediate neighbors. Why?

Mn has a half filled d subshell(d^5) which is stable. Therefore the willingness of electrons in

d5 system to actively participate in inter atomic metallic bonding will be less.

6) What is Lanthanide contraction? What is its consequence?

The gradual decrease in atomic and Ionic sizes of lanthanoid elements(from L to R in 4f

series) due to imperfect shielding of 4f orbitals is called Lanthanoid contraction.

Consequence: 1.4d and 5d series elements will have similar atomic/ionic sizes. Physical

separation of 4d and 5d series elements from each other becomes difficult as the sizes are

similar.

Eg: Zr and Hf have similar atomic radii and their physical separation from each other is difficult

2.Basic character of lanthanum hydroxide decreases from La to Lu

7) Why do transition elements show variable oxidation states?

This is due to incompletely filled d orbitals and the participation of both (n-1)d and ns

electrons in the bonding process as they have comparable energies.

8) Why is Cr^{2+} reducing whereas Mn^{3+} oxidizing when both have d^4 configuration?

Cr^{2+} is a reducing agent because it donates one electron to become Cr^{3+} which in turn is

characterized by half filled t_{2g} orbitals,(a stable system).

On other hand, Mn^{3+} is an oxidizing agent because it accepts one electron to become Mn^{2+}

which is characterized by a stable half filled d subshell ie., d^5.

9) The $E^o_{M2+/M}$ reduction potential of Cu^{2+} reduction is most positive (+0.34V) among

$E^o_{M2+/M}$ reduction potential values of divalent ions in 3d series. Why?

The energy invested in creating +2 state of Cu (ΔHa + ΔHi(1) + ΔHi(2)) is more in comparison to the energy released during hydration of Cu2+ ion in water (Hydration enthalpy)

10) How would you account for the irregular variation of first ionisation enthalpies in the first series of the transition elements?

Irregular variation of ionisation enthalpies is mainly due to varying degree of stability of different 3d configurations (d^0 ,d^5 and d^{10} are exceptionally stable)

11) Which is a stronger reducing agent Cr^{2+} or Fe^{2+} and why?

Cr^{2+} is a stronger reducing agent than $Fe^{2+.}$ The E^o values are $E^o_{Cr3+/Cr2+}$ = 0.41V and

$E^o_{Fe3+/Fe2+}$ = 0.77V.

The transition $Cr^{2+} \rightarrow Cr^{3+} + e$ is easier as Cr^3+ is stable by the virtue of having having half filled t_{2g} orbitals.

The transition $Fe^{2+} \rightarrow Fe^{3+} + e$ is comparatively less because it involves losing of an electron from Fe2+ with EC d^6 to d^5 configuration.

12) Why is Cu+ unstable in aqueous solutions?

In aqueous solution, Cu+ undergoes disproportionation reaction.

$2Cu^+ \rightarrow Cu^{2+} + Cu$

The higher stability of Cu^{2+} (aq) is due to higher negative hydration enthalpy of Cu^{2+} in comparison to that of Cu+.

13) Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

In actinoids, the poor shielding effect of 5f orbitals cause more contraction in sizes of actinoids as we move from left to right across the 5f series. The 5f electrons have poor shielding effect as compared to 4f electrons.

14) How is the variability in oxidation states of transition metals different from that of non-transition elements?

In transition metals the oxidation state vary by unity (due to in completely filled d orbitals) In non- transition elements this variation is selective, differing by 2.

15)Why is the highest oxidation state of a metal exhibited in its oxide and fluoride only?

This is due to a) high electronegativities of Fluorine and Oxygen and ability of oxygen to form multiple bonds

b) high lattice energy as in the case of CoF_3 or high bond enthalpy terms in covalent fluorides like **VF_5 and CrF**

3 MARKS QUESTIONS AND ANSWERS

1. Give reasons:

Transition metals a) form complexes b) their compounds act as catalysts c) form coloured compounds

Ans: a) Transition metal ions have high charge, small size and availability of incomplete d orbitals b) Transition metals have variable oxidation states and form intermediates with low activation energy, therefore used as a catalyst. Transition metals are small and so provide larger surface area for the reactant to be adsorbed.

c) Transition metal ions have unpaired electron and undergo d-d transition.

2. Explain by giving reasons:

a) Transition metals and many of their compounds show paramagnetic behavior

b) The enthalpies of atomization of transition metals are high

c) Transition metals form alloys and Interstitial compounds

Ans: a) They have unpaired electrons and show paramagnetic behavior

b) Unpaired electrons in ultimate and penultimate shells actively participate in inter-atomic metallic bonding and due to strong M-M bonding the enthalpies of atomization of transition metals are high

c) Transition metal atomic sizes do not vary much. So alloys are easily formed among transition metals. They form interstitial compounds because the interstitial sites in transition metal lattices can accommodate smaller atoms like H,C,N etc

3. Suggest reasons:

a) The lowest oxide of transition metal is basic, the highest amphoteric or acidic

b) The highest oxidation state is exhibited in oxoanions of transition metal

c) For the 3d series elements the $E^o_{M2+/M}$ reduction potentials are irregular

Ans: a) In lowest oxide, the oxidation state of the transition metal is less and the metal can donate electrons as some electrons are not involved in bonding whereas in highest oxide the oxidation state is high as the electrons are involved in bonding and can’t be donated. So they are amphoteric. In some highest oxides the oxidation state is so high that the metal can receive electron density from other species and thus behaving like acidic oxides

b) Oxygen, the second most electronegative element and it can form multiple bonds with metal atom.

c) The reduction potentials are not regular which can be explained from the irregular variation of Ionisation enthalpies ($\Delta Hi(1) + \Delta Hi(2)$) and also the sublimation enthalpies which are relatively less for Mn and V.

4. List the differences between Lanthanoids and actinoids

LANTHANOIDS	ACTINOIDS
4f subshell gets progressively filled up with electrons and lanthanoid contraction takes place	5f sub shell progressively gets filled up with electrons and actinoid contraction takes place
Less reactive than actinoids	More reactive than lanthanoids
+3 state is more common along with +2 and +4	Can show O.S from +2 to +7 which are not uncommon

5. Explain the oxidizing action of acidified $K_2Cr_2O_7$ with a) Iodide ions b) H_2S c) Fe^{2+}

Ans: a) Dichromate ions oxidise Iodide ions to elemental Iodine

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

b) Dichromate ions in acidic conditions oxidize H_2S to elemental sulfur

$$Cr_2O_7^{2-} + 8H^+ + 3H_2S \rightarrow 2Cr^{3+} + 3S + 7H_2O$$

c) Ferrous ions are oxidized to Ferric ions by acidified $K_2Cr_2O_7$

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

6.What is meant by the term lanthanoid contraction? What is it due to and what consequences does it have on the chemistry of elements following lanthanoids in the periodic table?

Ans. Lanthanoid contraction: Steady decrease in the size of the lanthanoids ions with increase in the atomic number across the period. The electrons of 4f orbitals offer imperfect / poor shielding effect in the same subshell as we go from La to Lu.

Consequence:

i) Due to this 5d series elements have nearly same radii as that of 4d series.

ii) Decrease in the basic strength from La (OH)3 to Lu(OH)3.
iii) Due to similar atomic size there is difficulty in separation of lanthanides..

7.a.For the first row of transition metals the E^0 values are:-

E^0 values	V	Cr	Mn	Fe	Co	Ni	Cu
M2+/M	-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

Explain the irregularity in the above values

b. Transition elements show high melting points. Why?

c. Zinc is soft whereas Cr is hard. Why?

Answer

a. The Standard Electrode Potential E^0 values for M2+/M as depend on the thermochemical parameters such as enthalpies and ionization energies. There is no regular trend in the E^0 values of first transition element. It is because, their ionization enthalpies (IE1 + IE2) and sublimation enthalpies do not show any regular trend. The general trend towards less negative E0 values along the series is due to the general increase in the sum of first and second ionization enthalpies.

b. Due to strong metal-metal bonding

c. Zn has completely filled d-orbital; hence d orbital electrons are not involved in metallic bonds while Cr has half-filled d-orbital and can form metallic bonds. Since metallic bonds make a metal hard, Cr is hard and Zn is soft.

5 Marks Question

Q. 1- Assign reasons for the following:
a) The enthalpies of atomization of transition elements are high.
b) The transition metals and many of their compounds act as good catalysts.
c) There is a gradual decrease in the atomic sizes of transition elements in a series with increasing atomic number.
d) The transition elements have great tendency for complex formation.
e) Transition metals generally form coloured compounds.

Ans- a) This is because transition elements have strong metallic bonds as they have large number of unpaired electrons, therefore they have greater interatomic overlap.
b) The catalytic activity of transition metals is attributed to the following reasons
i) Because of their variable oxidation state, transition metals form unstable intermediate compounds and provide a new path with lower activation energy for the reaction.
ii) In some cases, the transitions metal provides a suitable large surface area with free valencies on which reactants are adsorbed.

c) There is a gradual decrease in the atomic sizes of transition elements in a series with increasing atomic numbers due to poor shielding effects of the d-electrons, the net electrostatic attraction between the nucleus and the outermost electrons increases.

d) Incompletely filled d orbitals of suitable energy, small size of cations and higher nuclear charge.

e) Due to presence of unpaired electrons in d-orbitals which undergoes d-d transition.

CASE BASED QUESTIONS:

1. Potassium dichromate is a very important chemical compound used in leather industry. It is used as an oxidant. It is also used in the preparation of many azo compounds. It is a crystalline ionic solid with bright color. It is not deliquescent in contrast to Sodium dichromate. The conversion of chromate ions to dichromate ions and vice versa is pH sensitive. Potassium dichromate in acidic condition is a milder oxidising agent than acidified Potassium permanganate. This fact is revealed by their corresponding standard reduction potential values which can be extracted from any chemical literature pertaining to Inorganic chemistry.

i) If the pH of the solution containing chromate ions is decreased, what is it converted to?

Ans: It is converted to dichromate ions.

$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$

ii) What is the oxidation state of Cr in $K_2Cr_2O_7$?

1) +2 2) +3 3) +4 4) +6

ANS: +6

iii) Write balanced chemical equations for the reaction of acidified Potassium dichromate reactions with a) KI b) Sn^{2+} ions

ANSWER:

a) $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I2 + 7H2O$

b) $Cr_2O_7^{2}- + 14H^+ + 3Sn^{2+} \rightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$

2) Potassium permanganate is an inorganic crystalline salt with purplish black color that dissolves in water to produce K+ and MnO_4- ions.The aqueous solution is intensely pink to purple in color. Potassium permanganate is a powerful oxidizing agent in acidic and basic conditions. As a strong oxidant that does not generate toxic by products , Potassium permanganate has many niche uses. It is used in the treatment of Dermatitis and in treatment of water. It is also called as Bayer's reagent.

i) Alkaline oxidative fusion of MnO_2 gives ---------

1) MnO_4^- 2) MnO_4^{2-} 3) MnO d) Mn_2O_7

Ans: MnO_4^{2-} (Manganate ion)

ii) Assertion: $KMnO_4$ in acidic condition is a good oxidizing agent

Reason : It can oxidize Iodide ions to elemental Iodine

a) Both A and R are correct statements and R is the correct explanation of A

b) Both A and R are correct statements but R is not the correct explanation of A

c) Both A and R are false statements

d) A is true R is false.

Ans: b

iii) Write the balanced chemical equations for the reaction of acidified KMnO4 with 1) Fe^{2+} 2) $C_2O_4^{2-}$

Ans 1) $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

2) $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

HOTS QUESTIONS AND ANSWERS:

1. When a chromite ore (A) is fused with Sodium carbonate in free excess of air and the product Is dissolved in water, a yellow solution of the compound(B) is obtained. After treatment of this yellow solution with Sulfuric acid, compound (C) can be crystallized from the solution. When compound (C) is treated with KCl, orange crystals of compound(D) crystallize out. Identify A to D and also explain the reactions.

A= Fe_2CrO_4, B= Na_2CrO_4, C= $Na_2Cr_2O_7$, D= $K_2Cr_2O_7$

a) $4Fe_2CrO_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8 Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

b) $2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2 Na^+ + H_2O$

c) $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

2. When an oxides of Manganese (A) is fused with KOH in presence of an oxidizing agent and dissolved in water , it gives a dark green solution of compound (B). The compound (B) disproportionate in neutral or acidic solution to give purple compound(C). An alkaline solution of Compound (C) oxidizes KI solution to a compound (D) and compound (A) is also formed. Identify compounds A to D and also explain the reactions involved.

Ans: A= MnO_2, B= K_2MnO_4, C= KMnO4 and D = KIO_3

a) $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2 H_2O$

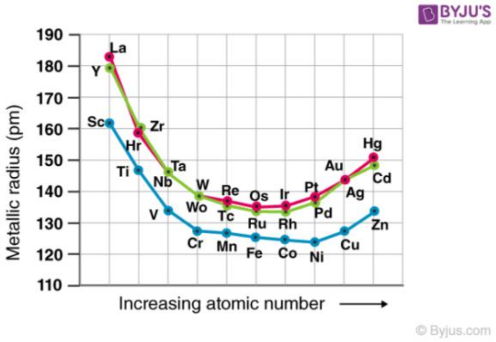
b) $3MnO_4^- + 4H^+ \rightarrow 2 MnO_4^- + MnO_2 + 2H_2O$

c) $2MnO_4^- + H_2O + KI \rightarrow 2MnO_2 + 2OH^- + KIO_3$

3. Why does Cu not displace Hydrogen from acid?

$E^{o}_{Cu2+/Cu}$ is more positive than $E^{0}_{H+/H2.}$

4.



a. In the above graph which all the transition series have same size. Why?

b. Although Zr belongs to 4d and Hf belongs to 5d transition series but it is quite difficult to separate them. Why?

c. Transition elements exhibit higher enthalpies of atomization. why

Answer

a. 4d and 5d series, due to Lanthanoid contraction

b. Due to Lanthanoid contraction the increase in size from second to third series vanishes.

So Zr and Hf have almost similar size and it is difficult to separate.

c. Due to the presence of unpaired electrons and d-d transition.

IMPORTANT CHEMICAL EQUATIONS:

1. $4FeCrO_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8 Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

$2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2 Na^+ + H_2O$

$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

2. $Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$ (oxidising action of dichromate in acidic medium)

3. $Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$

(Orange) (yellow)

4. $Cr_2O_7^{2-} + 8H^+ + 3\ NO_2^- \rightarrow 2Cr^{3+} + 3\ NO_3^- + 4H_2O$
5. $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$
6. $Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow 2Cr^{3+} + 3S + 7H_2O$
7. $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$
8. $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$
9. $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$
10. $2MnO_4^- + 10I^- + 16H^+ \rightarrow 2\ Mn^{2+} + 5I_2 + 8H_2O$
11. $2MnO_4^- + H_2O + I^- \rightarrow 2\ MnO_2 + 2OH^- + IO_3^-$
12. $2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5\ MnO_2 + 4H^+$
13. $2\ MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2\ Mn^{2+} + 8H_2O + 10CO_2$
14. $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$
15. 2KMnO4 → $K_2MnO_4 + MnO_2 + O_2$ (decomposition on heating)

CHAPTER 5 COORDINATION COMPOUNDS

	TERMS	DEFINITIONS WITH EXAMPLES
1	**DOUBLE SALTS**	i. They are formed from two or more salts mixed in stoichiometric proportions from their solution. ii. In aqueous solutions, they dissociate into simple ions. Eg. Mohr's salt
2	**COORDINATION COMPOUNDS**	i. **A chemical compound in which the central ion or atom is bound to a set number of atoms, molecules, or ions** with coordinate bonds is called a coordination compounds. ii. They do not lose their identity in the solid state as well in aqueous solutions. They give complex ion and counter ion in solution Eg. K4[Fe(CN)6] will give $4K^+$ ions and a complex ion $[Fe(CN)6]^{4-}$
3	**DENTICITY**	The number of ligating (donor) atoms present in a complex is called the denticity of ligand. Ligands may be unidentate, (containing only one donor atom)eg Cl^-,bidentate(containing two donor atoms.eg en),polydentate eg, EDTA(ethylene diamine tetra acetate ion) a hexadentate ligand
4	**AMBIDENTATE LIGAND**	Unidentate ligands containing more than one coordinating atoms are called ambidentate ligands . eg/NO2- can link through N or O
6	**CHELATING LIGAND**	If the ligand is able to form five or six membered ring with Central Metal ion eg,EDTA(ethylene diamine tetra acetate ion)
7	**COORDINATI**	The number of ligand donor atoms to which the metal is directly

	ON NUMBER	bonded is called coordination number
8	**COORDINATION SPHERE**	The central atom and the ligand attached to it are enclosed in the square brackets are collectively known as coordination sphere.
	COUNTER IONS	The ionisable groups written outside the brackets are called counter ions eg. K2[Pt Cl6] , 2K+ Counter ions. [Pt Cl6] $^{2-}$ Coordination sphere
10	**IUPAC NOMENCLATURE:**	**RULE 1:** In ionic complexes Cation should be named first followed by anions **Rule 2:** ligands are named in alphabetical order. **Rule3:** Anionic ligands ending with –ide (e is replaced by o).eg. chloride – chlorido, oxide – oxo, hydroxide- hydroxo, suphide- sulphido, amide- amido, nitride- nitride,Cyanide-cyanido Rule 4 : ligands whose name end in-ite, –ate will become–ito ,–ato. eg: carbonate- carbanato,oxalate- oxalate, sulphate- sulphato, nitrate-nitrato, nitrite (ONO- nitrito-O),NO_2^- Nitrito-N Neutral Ligands: **named as molecule** eg. Pyridine(py), O_2- dixoygen, $(CH_2 NH_2)_{2-}$ ethane 1,2-diamine , **which are not named as molecule:** **H_2O- aqua , CO- carbonyl, NH_3-ammine , NO-nitrosyl, CS- thiocarbonyl.** **RULE 4: a.If more ligands are of same type is present, then di-, tri-, tetra- should be added eg:** [Co**$(NH_3)_6$**]**Cl - hexa** ammine , [Co**$(NH_3)_4$**$Cl_2]^+$.- tetra ammine b. if the ligand already has di, tri then bis, tris is used. Eg: $Co(en)_2Cl_2$]cl- **bis** (ethane 1,2- **di** amine) **Rule : 5 Positive and neutral complex has no special ending.** [Fe**$(CO)_5$**] – pentacarbonyl iron(0) Anionic complexes always end in –ate. Eg: Pb- plumbate, Au- aurate, Zinc- Zincate, tin-stannate, silver- Argentate, Cobalt- cobaltate. Eg: **K_3** [Fe**$(CN)_6$**]- potassium hexacyanoferrate (III) Rule : 6: Ambidentate lignads (donor should be mentioned) **NH_3** [Cr**$(SCN)_6$**]- ammonium hexathiocyanato-S-chromate (III)

11	**HOMOLEPTIC AND HETERO LEPTIC COMPLEXES**	Complexes in which a metal is bound to only one type of donor groups are known as homoleptic eg. $[Co(NH_3)_6]^{3+}$, complexes in which a metal is bound to more than one kind of donor groups are known as heteroleptic eg. $[Co(NH_3)_4Cl_2]^{+}$.
STRUCTURAL ISOMERISM		
a.	**IONISATION ISOMERISM**	When two complexes with same composition give different ions in solution Eg,.$[CO(NH_3)Br]SO_4$ &$[CO(NH_3) SO_4]$ Br
b	**LINKAGE ISOMERISM**	When complexes differ only in the point of attachment of the ambidentate ligand with central metal atom eg.$Co[(NH_3)_5(ONO)]^{2+}$ and $Co[(NH_3)_5(NO_2)]^{2+}$
c	**COORDINATION ISOMERISM**	When the interchange of ligands take place between cationic and anionic entities of different metal ions present in a complex eg. [CO(en)3[Cr(CN)6] and [Cr(en)3][Co(CN)6]
d	**GEOMETRICAL ISOMERISM**	When similar groups are present in adjacent postion , it is **cis**. When they are present in opposite position it is **trans**. It occurs in square planar and octahedral complexes.
e	**OPTICAL ISOMERISM**	This is shown by complexes whose mirror images are non superimposable . Such complexes are called optical isomers. It is shown by the octahedral complexes and exists in two forms laevo and dextro. The isomer which rotates the plane polarized light towards right is called dextrorotatory (d-) and the other rotates towards left is called laevo rotatory.Only cis forms shows optical isomerism. and tetrahedral complexes do not show geometrical isomerism
11. BONDING AND STABILITY IN COORDIDNTION AND ORGANOMETALLIC COMPOUNDS		
	WERNER'S THEORY OF COORDINATON COMPOUNDS	Accodring to WERNER'S theory metal consist of two types of valencies called primary valency and secondary valency. **Primary valency**- is equal to oxidation state. **Secondary valency:**It is equal number of ligating atoms which is also known as coordination number
	VALENCE BOND	POSTULATES: Metal –ligand bond is formed by the donation of electron by ligand to metal Metal atom have vacant orbitals of equal energies, equal to the

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<td>THEORY</td>
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no of ligands to be attached

Sometimes unpaired (n-1)d electrons pairs up to create empty orbitals

Depending upon the type of hybridization **d^2sp^3,dsp^2,sp^3** the shapes of complex are octahedral , square planar and tetrahedral respectively

If paired electron is present, then complex is diamagnetic. If unpaired electrons are present, complex is paramagnetic

Strong field ligand forces the d-electrons of central metal are pair up against Hund’s rule.The strong field ligand which causes pairing are **CO,NO,CN-,NO^{2-},NH_3,en** (ethylene diamine).Some weak field ligands are H_2O,X^-,NO^{3-},ROH etc

If complex formed involves inner (n-1)d orbitals for hybridization (d^2SP^3) then it is called inner orbital. Eg.$[Ni(CN)_4]^{2-}$, whereas if complex formed involves outer ‘d orbitals for hybridisation(SP^3d^2 it is called outer orbital, complex$[Ni(H_2O)_6]^{2+}$ .Complexes with paired electron are called low spin or spin paired complex and with unpaired electron are called high spin or spin free complexes

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<td>BONDING IN $Ni(CN)_4]^{2-}$</td>
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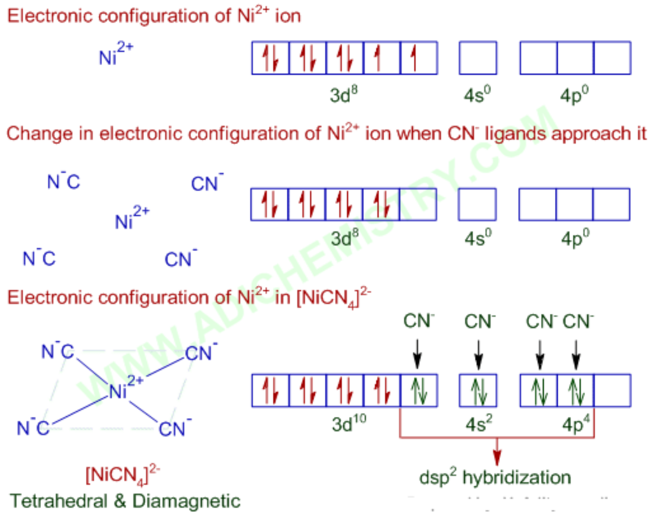
$Ni(CN)_4]^{2-}$



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<td>BONDING IN $[Ni(CO)_4]$</td>
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$[Ni(CO)_4]$ NOTE: The oxidation state of Ni is zero due to neutral ligand.

CO is a strong ligand and pairing takes place.

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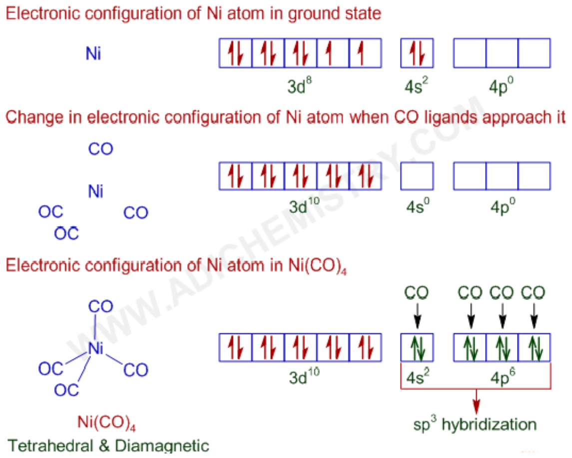
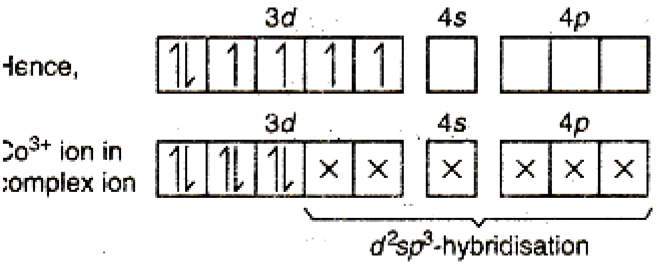
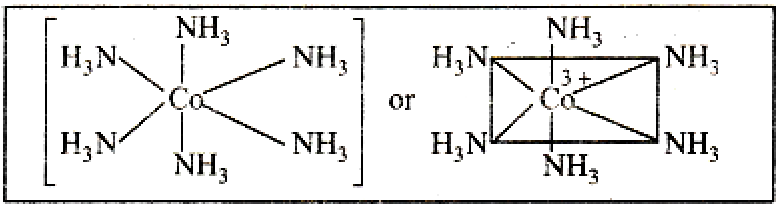
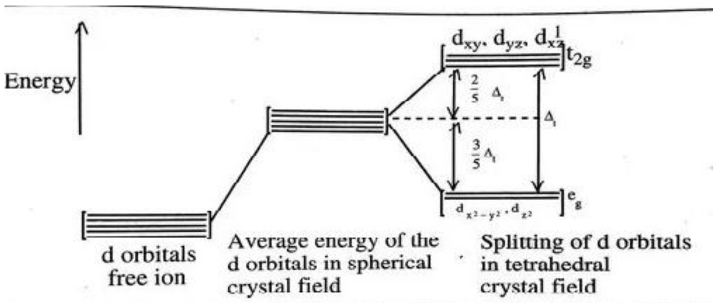
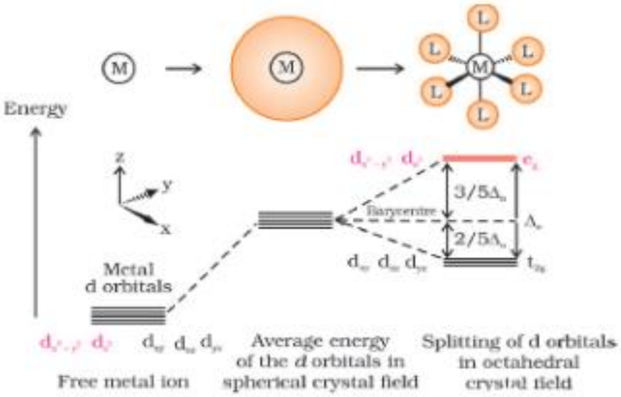
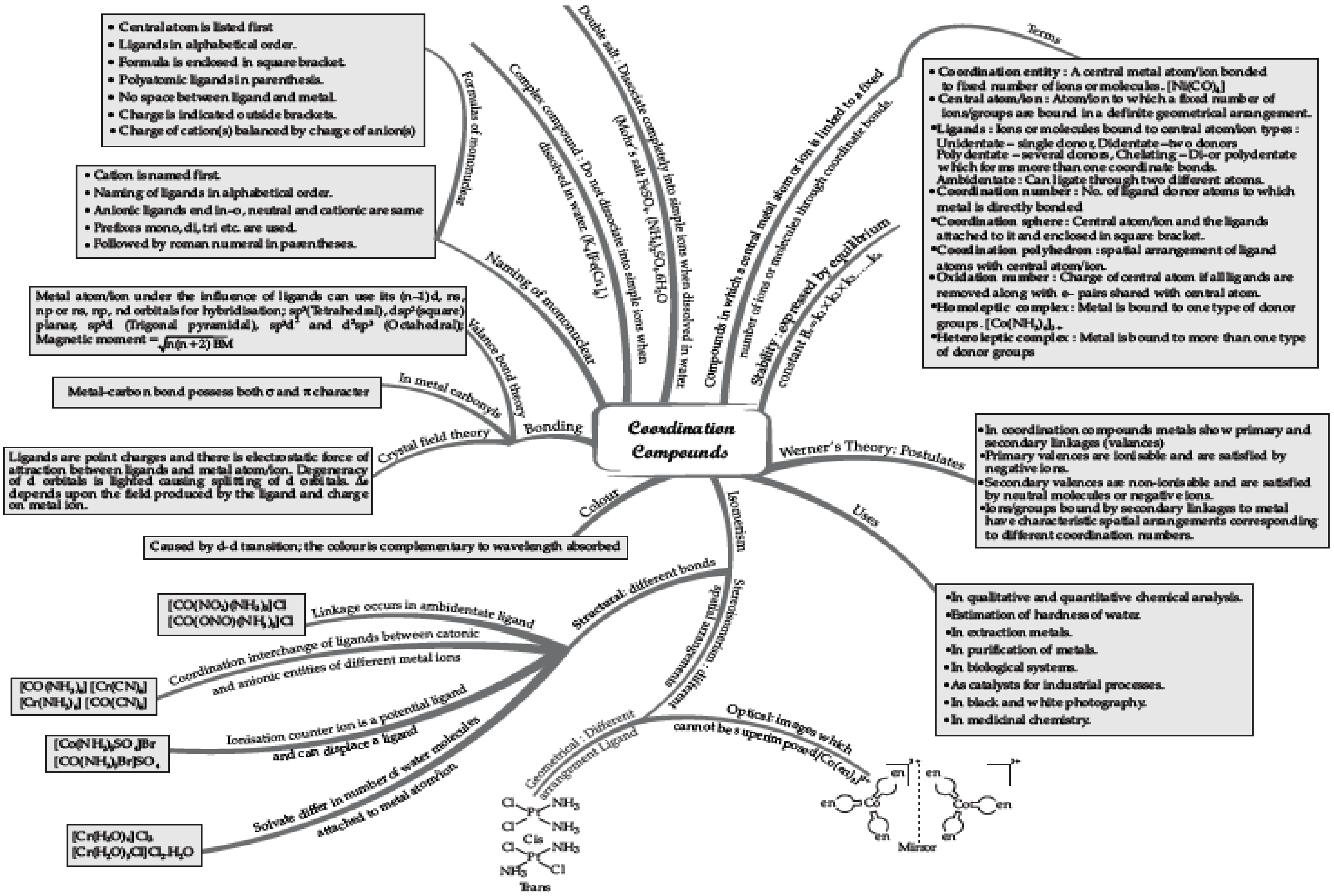
		
	BONDING IN $[CO(NH_3)_6]^{3+}$	$[CO(NH_3)_6]^{3+}$ (**NOTE**: Ammonia normally act as weak ligand, but in this complex, it acts as strong ligand) $_{27}Co = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^7, 4s^2$ $Co^{3+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6$   Structure of $[Co(NH_3)_6]^{3+}$ is octahedral.
	LIMITATIONS OF VBT:	- It does not distinguish between weak and strong ligands - It does not give any satisfactory explanation for the colour of the complexes, magnetic moment data. Thermodynamic or kinetic stabilities of coordination compounds - It fails to predict tetrahedral and square planar structures of some 4-coordinate complexes.
	CRYSTAL FIELD THEORY	According to CFT,under the influence of ligand field, degeneracy of the d-orbital is destroyed and it splits into two or more energy levels. The difference of energy between the two sets of d-orbital(in octahedral) is called CFSE or Δ_o (CRYSTAL FIELD

		SPLITTING ENERGY) N: in case of octahedral set eg. dx^2-y^2,dz^2 are of higher energy while in case of tetrahedral complexes t_{2g} set (dxy,dyz,dzx) has higher energy.
	FACTORS AFFECTING THE MAGNITUDE OF CFSE	**NATURE OF LIGANDS**: - The ligands with smaller size, large negative charge, with good σ donor and π acceptor properties will give large field splitting **<u>SPECTROCHEMICAL SERIES: -</u>** the increasing order of the value Δ_o is given below I^-<Br- <SCN^- < Cl^- <S^{2-} <F^- <OH^- <$C_2O_4^-$ <O^{2-} <H_2O <NCS^- <$EDTA^{4-}$ <NH_3 <en <NO_2- <CN^- <CO **<u>IN CASE OF d^4 IONS</u>** If $\Delta_o < P$ the fourth electron enters one of the eg. Orbitals giving the configuration $t_{2g}3eg^1$ and the ligands are weak. If $\Delta_o > P$, the fourth electron enters t2g orbital giving the configuration $t_{2g}4eg^0$, ligands are strong **OXIDATION STATE OF METAL ION**: All the five d-orbitals have the same energy which mean dxy,dyz,dzx ,dx^2-y^2,dz^2 are degenerate. Ligands approach the metal in sphereical structure, then repulsion takes place between the lone pair of electrons in ligands and the electron in Metal d orbital, again all the d orbitals energy will be raised (Average energy of the d orbitals in spherical crystal field). Since there is no difference in d orbitals, the **ligands approach the metal in between the axis** where the dxy, dzx, dyz (t2g) orbitals will experience repulsion and go to the higher energy in case of **Tetrahedral complex.** 

		the **ligands approach the metal in along the axis** where the **dx^2-y^2** & **$d_Z{}^2$** (eg) orbitals will experience more repulsion and go to higher energy in case of **Octahedral complex as shown below .**  *d orbital splitting in an octahedral crustal field*
	BONDING IN METAL CARBONYLS	Compounds which have at least one metal-carbon bond are called organo metallic bond are called organometallic compounds. The metal-carbon bond in metal carbonyls possesses both π and σ character. The metal-carbon(M-C) σ bond is formed by sharing of lone pair of electrons by the carbonyl carbon into a vacant orbital of the metal. The metal-carbon(M-C) π bond is formed by sharing of pair of electrons from a filled d-orbital of metal to vacant π* orbital of the carbonyl carbon. The metal to ligand bonding creates a synergic effect which strengthens the bond between the CO and the Metal . In these the oxidation state of metal is zero
	APPLICATIONS OF COORDINATION COMPOUNDS	Electroplating : In electroplating of silver K$_4$**[Ag(CN)$_6$], and in gold** K**[Au(CN)$_2$],** are used as electrolyte WATER TREATMENT: sodium salts of EDTA is effective in removing hardness from water caused by Ca $^{2+}$ and Mg^{2+} ions. MEDICINE: Vitamin B12 used to prevent anaemia is complex of cobalt. Chelating with EDTA is used to cure a person suffering from lead poisoning. Platinum complex, cis-platin inhibit the growth of cancer cells.

		Haemoglobin a complex of iron act as oxygen carrier in the body



Coordination Compounds

Terms

- Coordination entity : A central metal atom/ion bonded to fixed number of ions or molecules. $[Ni(CO)_4]$
- Central atom/ion : Atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement.
- Ligands : Ions or molecules bound to central atom/ion types : Unidentate – single donor, Didentate – two donors Polydentate – several donors, Chelating – Di-or polydentate which forms more than one coordinate bonds. Ambidentate : Can ligate through two different atoms.
- Coordination number : No. of ligand donor atoms to which metal is directly bonded
- Coordination sphere : Central atom/ion and the ligands attached to it and enclosed in square bracket.
- Coordination polyhedron : spatial arrangement of ligand atoms with central atom/ion.
- Oxidation number : Charge of central atom if all ligands are removed along with e– pairs shared with central atom.
- Homoleptic complex : Metal is bound to one type of donor groups. $[Co(NH_3)_6]^{3+}$
- Heteroleptic complex : Metal is bound to more than one type of donor groups

Compounds in which a central metal atom or ion is linked to a fixed number of ions or molecules through coordinate bonds.

Stability : expressed by equilibrium constant $\beta_n = k_1 \times k_2 \times k_3 \ldots\ldots k_n$

Double salt : Dissociate completely into simple ions when dissolved in water. (Mohr's salt $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$)

Complex compound : Do not dissociate into simple ions when dissolved in water. ($K_4[Fe(CN)_6]$)

Werner's Theory: Postulates

- In coordination compounds metals show primary and secondary linkages (valences)
- Primary valences are ionisable and are satisfied by negative ions.
- Secondary valences are non-ionisable and are satisfied by neutral molecules or negative ions.
- Ions/groups bound by secondary linkages to metal have characteristic spatial arrangements corresponding to different coordination numbers.

Uses

- In qualitative and quantitative chemical analysis.
- Estimation of hardness of water.
- In extraction metals.
- In purification of metals.
- In biological systems.
- As catalysts for industrial processes.
- In black and white photography.
- In medicinal chemistry.

Naming of mononuclear

- Cation is named first.
- Naming of ligands in alphabetical order.
- Anionic ligands end in -o, neutral and cationic are same
- Prefixes mono, di, tri etc. are used.
- Followed by roman numeral in parentheses.

Formulas of mononuclear

- Central atom is listed first
- Ligands in alphabetical order.
- Formula is enclosed in square bracket.
- Polyatomic ligands in parenthesis.
- No space between ligand and metal.
- Charge is indicated outside brackets.
- Charge of cation(s) balanced by charge of anion(s)

Bonding

Valence bond theory: Metal atom/ion under the influence of ligands can use its (n–1)d, ns, np or ns, np, nd orbitals for hybridisation; sp^3(Tetrahedral), dsp^2(square) planar, sp^3d (Trigonal pyramidal), sp^3d^2 and d^2sp^3 (Octahedral); Magnetic moment $= \sqrt{n(n+2)}$ BM

In metal carbonyls: Metal–carbon bond possess both σ and π character

Crystal field theory: Ligands are point charges and there is electrostatic force of attraction between ligands and metal atom/ion. Degeneracy of d orbitals is lighted causing splitting of d orbitals. Δ_o depends upon the field produced by the ligand and charge on metal ion.

Colour: Caused by d-d transition; the colour is complementary to wavelength absorbed

Isomerism

Structural: different bonds

- Linkage occurs in ambidentate ligand: $[CO(NO_2)(NH_3)_5]Cl$, $[CO(ONO)(NH_3)_5]Cl$
- Coordination interchange of ligands between cationic and anionic entities of different metal ions: $[CO(NH_3)_6][Cr(CN)_6]$, $[Cr(NH_3)_6][CO(CN)_6]$
- Ionisation counter ion is a potential ligand and can displace a ligand: $[Co(NH_3)_5SO_4]Br$, $[CO(NH_3)_5Br]SO_4$
- Solvate differ in number of water molecules attached to metal atom/ion: $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

Stereoisomerism : different spatial arrangements

- Geometrical : Different arrangement Ligand
- Optical: images which cannot be superimposed $[Co(en)_3]^{3+}$

MCQ:

1. The total number of possible isomers for the complex compound [Cu(NH3)4][PtIICl4]
   a. 3
   b. 6
   c. 5
   d. 4

   Correct Answer: d

2. The IUPAC name of : [Pt(NH3)3(Br)(NO2)Cl]Cl is
   a. Triamminechlorobromonitro platinum(IV)chloride
   b. Triamminebromonitrochloro platinum(IV)chloride
   c. Triamminebromochloronitro platinum(IV)chloride
   d. Triamminenitrochlorobromo platinum (IV)chloride

   Correct Answer: c.

3. A co-ordination complex compound of cobalt has the molecular formula containing five ammonia molecules, one nitro group and two chlorine for one cobalt atom. One mole of this compound produces three mole ions in an aqueous solution. On reacting this solution with excess of AgNO3 solution, we get two moles of AgCl precipitate.

   The formula for this complex would be
   a. [Co(NH3)4(NO2)Cl][(NH3Cl]
   b. [Co(NH3)Cl][Cl(NO2)]
   c. [Co(NH3)5(NO2)]Cl2
   d. [Co(NH3)5][(NO2)2Cl2]

   Correct Answer: c

4. Of the following complex ions, which is diamagnetic in nature?
   a. [Ni(CN)4]2−
   b. [CuCl4]2−
   c. [CoF6]3−
   d. [NiCl4]2−

   Correct Answer: c

5. A magnetic moment of 1.73 BM will be shown by one among the following
   a. [Cu(NH3)4] 2+
   b. [(NiCN)4] 2-
   c. TiCl4

   d. none of these

   Correct Answer: d

6. Which of the following complexes is used to be as an anticancer agent?
   a. mer−[Co(NH3)3Cl3]
   b. cis−[PtCl2(NH3)2]
   c. cis−K2[PtCl2Br2]
   d. Na2CoCl4

   Correct Answer: b

7. Cobalt (III) chloride forms several octahedral complexes with ammonia. Which of the following will not give test for chloride ions with silver nitrate at 25°C?
   a. CoCl3.3NH3
   b. CoCl3.4NH3
   c. CoCl3.5NH3
   d. CoCl3.6NH3

   Correct Answer: a
8. The hybridisation involved in complex [Ni(CN)4]2− Atomic number of Ni = 28) is
   a. dsp2
   b. sp3
   c. d2sp2
   d. d2sp3

   Correct Answer: a

9. Which of the following complex compounds will exhibit highest paramagnetic behaviour? (At.no.:Ti=22,Cr=24,Co=27,Zn=30)
   a. [Ti(NH3)6]3+
   b. [Cr(NH3)6]3+
   c. [Co(NH3)6]3+
   d. [Zn(NH3)6]2+

   Correct Answer: c

Assertion and Reasoning Questions

1. Assertion: Toxic metal ions are removed by the chelating ligands.
   Reason: Chelate complexes tend to be more stable.
   Answer: a

2. Assertion: Linkage isomerism arises in coordination compounds containing ambidentate ligand.

Reason: Ambidentate ligand has two different donor atoms.
Answer: a

3. Assertion: Complexes of MX6 and MX5L type (X and L are unidentate) do not show geometrical isomerism.
   Reason: Geometrical isomerism is not shown by complexes of coordination number 6.
   Answer: c

4. Assertion: $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.
   Reason: Because it has d^2sp^3 type hybridization.
   Answer: d

1 Mark Questions

10. Out of NH_3 and 'en', which ligand forms more stable complex with metal and why?
    Ans: en will form more stable complex because it is bidentate ligand

11. [NiCl4]2-is paramagnetic while $[Ni(CO)_4]$ is diamagnetic, though both are tetrahedral. Why? (Atomic number of Ni = 28)
    Ans: [NiCl4]2-has unpaired electron, whereas $[Ni(CO)_4]$ does not have unpaired electrons, therefore, diamagnetic

12. A $CuSO_4$ solution is mixed with $(NH_4)_2$ SO_4 solution in the ratio of 1 : 4 does not give test for Cu2+ ion, Why?
    Ans: $[CU(NH_3)_4]$ SO_4 is formed which does not have free Cu^{2+} ions.

13. Why is CO a stronger ligand than NH3 in complexes?
    Ans: It is because CO can form σ as well as πbonds, therefore, it is stronger ligand than NH_3 which can form only a-bond.

14. Give an example of the role of coordination compounds in biological systems.
    Ans Haemoglobin a complex of iron act as oxygen carrier in the body.

15. Co2+ is easily oxidised to Co3+ in presence of a strong ligand
    Ans Strong ligands provide energy which overcomes 3rd ionisation enthalpy and Co2+ gets oxidised to Co3+.

16. What do you understand by 'denticity of a ligand'?
    Ans: It is defined as the number of coordinate bonds formed by a ligand.

2 Marks Questions

1. What is meant by crystal field splitting energy? On the basis of crystal field theory, write the electronic configuration of d4 in terms of t2g and eg in an octahedral field when (i) $\Delta^0 > P$ (ii) $\Delta^0 < P$

   Ans: The difference between energies of two sets of d-orbitals t2g and e is called crystal field splitting energy (Δ^0).
   If $\Delta^0 > P$, the configuration will be $t2g^4$, eg^0. Ligands will produce strong field and pairing takes place.
   If $\Delta^0 < P$, the configuration will be $t2g^3$, eg^1 and it is in the case of weak field ligands and pairing will not take place

2.
   1. Nickel (II) does not form low spin octahedral complexes.
   2. $[Fe(CN)_6]^{4-}$ and $[Fe(H_20)_6]^{2+}$ are of different colours in dilute solutions.

   Ans:
   i. Ni^{2+} has unpaired electrons, therefore, forms high spin complex as pairing of electrons does not take place because after pairing only one d-orbital will be left which cannot be used in octahedral complex.
   (ii) They absorb different wavelengths from visible light, undergo d-d transitions and radiate complementary colour. CN- is stronger ligand than H2O.

3. Name the following coordination compounds according to IUPAC system of nomenclature.
   1. $[CO(NH_3)_2 (H_2O) Cl] Cl_2$
   2. $[Cr Cl_2(en)2] Cl$, (en = ethane-1,2-diamine)

   Answer:
   1. Tetraammineaquachlorido cobalt(III) chloride.
   2. Dichlorido bis(ethane 1, 2-diamine) chromium (III) chloride.

4. Describe the shape and magnetic behaviour of following complexes:
   $[CO(NH_3)_6]^{3+}$
   $[Ni(CN)_4]^{2-}$

Answer:
It is octahedral, d^2sp^3 hybridised, diamagnetic in nature.
It is square planar, dsp^2 hybridised, diamagnetic in nature.

3 Marks Questions

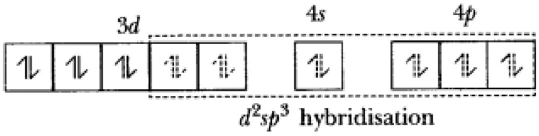
1. Give the formula of each of the following coordination entities:
    i. Co^{3+} ion is bound to one Cl-, one NH_3 molecule and two bidentate ethylene diamine (en) molecules.
    ii. Ni^{2+} ion is bound to two water molecules and two oxalate ions.

    Write the name and magnetic behaviour of each of the above coordination entities.

    Answer

    (*i*) $[CoNH_3Cl(en)_2]^{2+}$ amminechloridobis(ethane-1,2-diamine)cobalt (III) ion

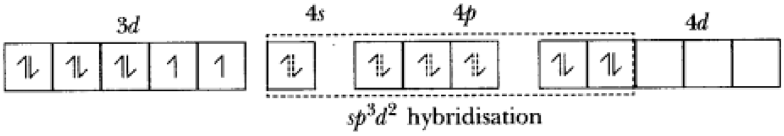
    Co^{3+} : $4s^0 3d^6$ diamagnetic



    (*ii*) $[Ni(H_2O)_2(ox)_2]^{2-}$

    diaquadioxalatonickelate (II) ion

    Ni^{2+} : $4s^0 3d^8$ paramagnetic



2. Write the name of the structure and the magnetic behaviour of each one of the following complexes (At. nos. Co = 27, Ni = 28, Pt = 78)

    i. $[Pt(NH_3)_2Cl(NO_2)]$
    ii. $[CO(NH_3)_4 Cl_2] Cl$
    iii. $Ni(CO)_4$

    Answer:
    i. Diammine chlorido nitrito-N-platinum(II). It is square planar and diamagnetic.
    ii. Tetraammine dichlorido cobalt(III) chloride. It is octahedral and diamagnetic.
    iii. Tetracarbonyl nickel(O). It is tetrahedral and diamagnetic complex.

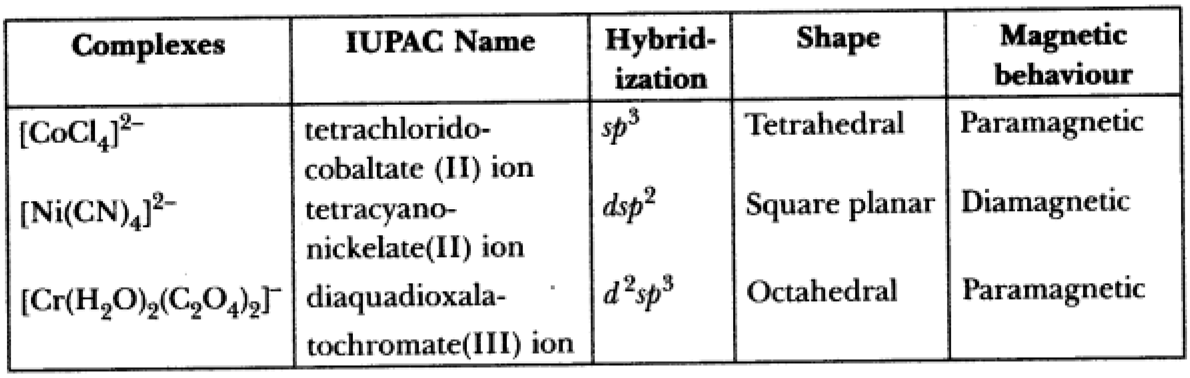
3. For the complex $[Fe(en)_2Cl_2]Cl$, identify the following:
    i. Oxidation number of iron.

ii. Hybrid orbitals and shape of the complex.
iii. Magnetic behaviour of the complex.
iv. Number of its geometrical isomers.
v. Whether there may be optical isomer also.
vi. Name of the complex.

Answer:

i. +3 (III)
ii. d_2sp_3, octahedral
iii. paramagnetic
iv. Two geometrical isomers
v. Yes, there may be optical isomer also due to presence of polydentate ligand.
vi. Dichlorido bis-(ethane 1, 2-diamine) Iron (III)

4. Write the name, the state of hybridization, the shape and the magnetic behaviour of the following complexes:$[CoCl_4]^{2-}$, $[Cr(H_2O)_2(C_2O_4)_2]^-$, $[Ni(CN)_{4]}^{2-}$
(At. No. : Co = 27, Ni = 28, Cr = 24)
Answer:

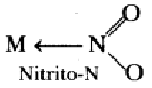


Complexes	IUPAC Name	Hybrid-ization	Shape	Magnetic behaviour
$[CoCl_4]^{2-}$	tetrachlorido-cobaltate (II) ion	sp^3	Tetrahedral	Paramagnetic
$[Ni(CN)_4]^{2-}$	tetracyano-nickelate(II) ion	dsp^2	Square planar	Diamagnetic
$[Cr(H_2O)_2(C_2O_4)_2]^-$	diaquadioxala-tochromate(III) ion	d^2sp^3	Octahedral	Paramagnetic

5. Explain the following terms giving a suitable example in each case:
i. Ambidentate ligand
ii. Denticity of a ligand
iii. Crystal field splitting in an octahedral field.

Answer:

(*i*) **Ambidentate ligand:** Ligands which can ligate (link) through two different atoms present in it are called *ambidentate ligands*, e.g. NO_2^-, SCN^-, CNO^- and CN^-. NO_2^- can link through 'N' as well as oxygen while SCN^- can link through 'S' as well as 'N' atoms.



$M \leftarrow O{-}N{=}O$

Nitrito-O

$M \leftarrow SCN$

Thiocyanato

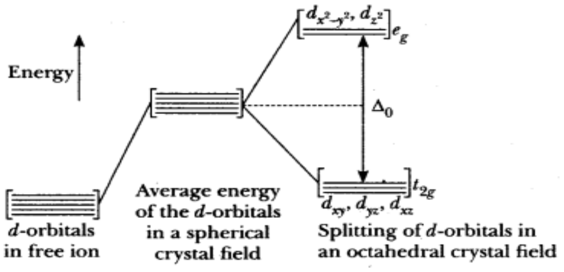
$M \leftarrow NCS$

Isothiocyanato

(*ii*) **Denticity:** The number of ligating (linking) atoms present in ligand is called *denticity* of ligand, e.g. CN^- has 1, $\begin{matrix}COO^- \\ | \\ COO^-\end{matrix}$ has 2, $H_2N{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}NH_2$ has 3, $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$ has 4, $[EDTA]^{3-}$ has 5 and $[EDTA]^{4-}$ has 6 denticity.

(*iii*) **Crystal field splitting in an octahedral coordination complexes:**

- All the six ligands are assumed to be positioned symmetrically along the axis with the metal atom at the origin.



d-orbital splitting in an octahedral crystal field

- As the ligand approaches, there is an increase in energies of all *d*-orbitals relative to that of free ion in spherical field. The orbitals $d_{x^2-y^2}$ and d_{z^2} lie on axis, therefore, their energy is raised. It is called e_g, the other orbitals d_{xy}, d_{yz}, d_{zx} have lower energy because they lie in between the axes are less repelled. These orbitals are t_{2g}.
- The difference in energy of these two set of orbitals is called energy of separation (Δ_o).

Case Based Questions

1. Complex compounds play an important role in our daily life. Werner's theory of complex compounds says every metal atom or ion has primary valency (oxidation state) which is satisfied by –vely charged ions, ionisable where secondary valency (coordination number) is non-ionisable, satisfied by ligands (+ve, –ve, neutral) but having lone pair. Primary valency is non-directional, secondary valency is directional. Complex compounds are name according to IUPAC system. Valence bond theory helps in determining shapes of complexes Based on hybridisation, magnetic properties, outer or inner orbital complex. Complex show ionisation, linkage, solvate and coordination isomerism also called structural isomerism. Some of them also show stereoisomerism i.e. geometrical and optical isomerism. Ambidentate ligand are essential to show linkage isomerism. Polydentate ligands form more stable complexes then unidentate ligands. There are called chelating agents. EDTA is used to treat lead

poisoning, cis-platin as anticancer agents. Vitamin B12 is complex of cobalt. Haemoglobin, oxygen carrier is complex of Fe^{2+} and chlorophyll essential for photosynthesis is complex of Mg^{2+}.

a. What is the oxidation state of Ni in [Ni(CO)4]?
Ans. Zero

b. Out Cis – $[Pt(en)_2 Cl_2]^{2+}$ and trans $(Pt(en)_2Cl_2)^{2+}$ which one shows optical isomerism?
Ans. Cis – $[Pt(en)_2 Cl_2]^{2+}$ shows optical isomerism.

c. What is hybridisation of $[CoF_6]^{3-}$? [Co = 27] Give its shape and magnetic properties.
Ans. sp^3d^2, octahedral, paramagnetic. It is outer orbital complex.

2. Transition metals form complex compounds which play a very important role in our daily life.
Complexes are also formed by other groups elements e.g. Chlorophyll is coordination compound of Mg. Organometallic compounds like Grignard reagent is most useful in organic chemistry. Complexes are used in medicines, analytical chemistry, qualitative analysis, electroplating, biological processes .Stability of complexes depends upon charge on central metal ion, strength of ligand. Counter ions outside the coordination entity are ionisable but inside the coordination sphere are not ionisable.

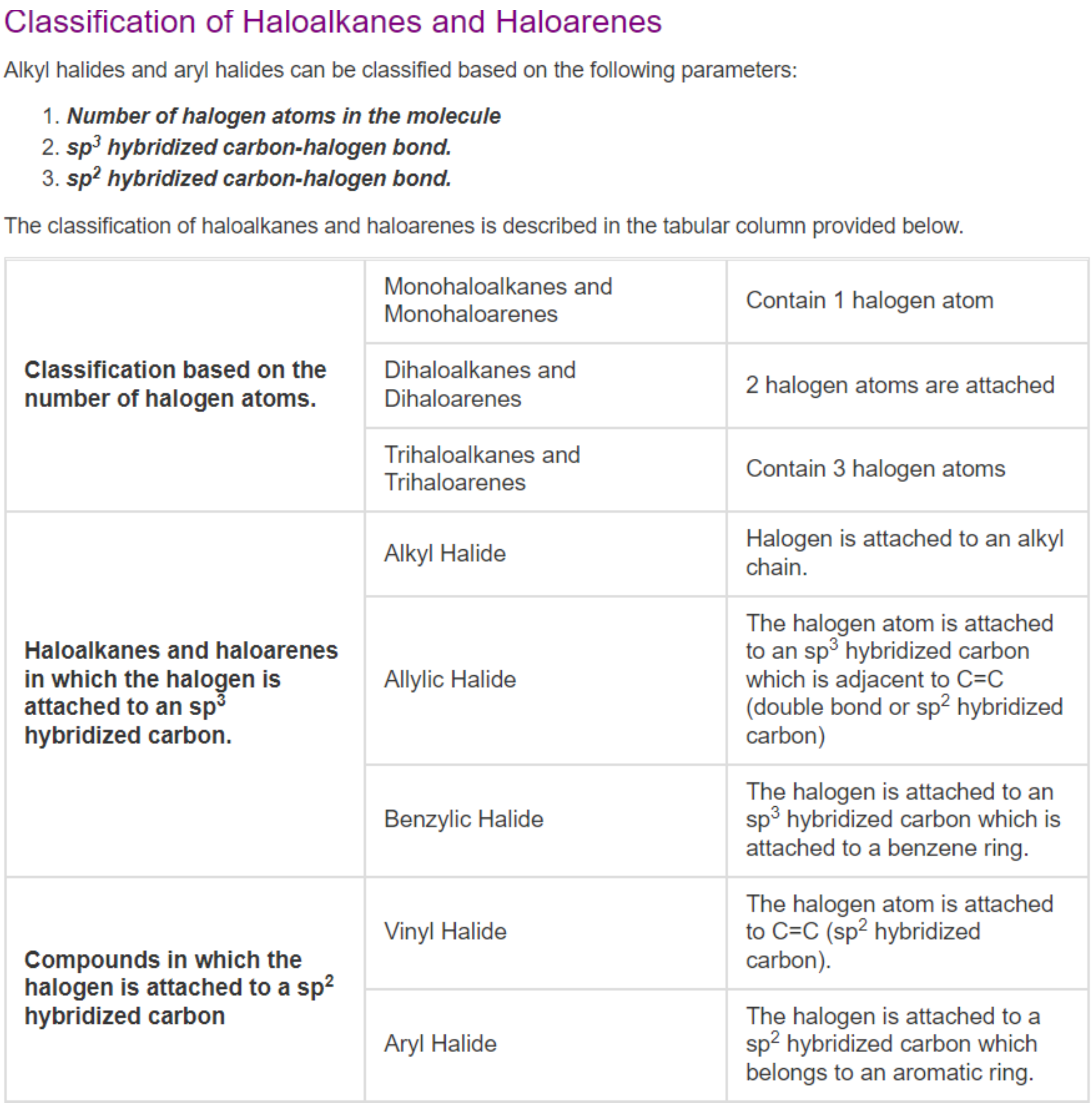
   a. Name a complex used as anticancer agent?
   Ans. Cis-platin

   b. What is coordination number of Co in$[Co(en)_3]^{3+}$ and why?
   Ans. Coordination number of Co is 6 because ‘en’(ethane 1, 2-diammine) is bidentate ligand.

   c. Name a complex used for determining hardness of water. What is its denticity?
   Ans. EDTA, it is hexadentate ligand, denticity 6

CHAPTER 6 . HALO ALKANES AND HALOARENES

KEY POINTS



Classification of Haloalkanes and Haloarenes

Alkyl halides and aryl halides can be classified based on the following parameters:

1. ***Number of halogen atoms in the molecule***
2. ***sp^3 hybridized carbon-halogen bond.***
3. ***sp^2 hybridized carbon-halogen bond.***

The classification of haloalkanes and haloarenes is described in the tabular column provided below.

Classification based on the number of halogen atoms.	Monohaloalkanes and Monohaloarenes	Contain 1 halogen atom
	Dihaloalkanes and Dihaloarenes	2 halogen atoms are attached
	Trihaloalkanes and Trihaloarenes	Contain 3 halogen atoms
Haloalkanes and haloarenes in which the halogen is attached to an sp^3 hybridized carbon.	Alkyl Halide	Halogen is attached to an alkyl chain.
	Allylic Halide	The halogen atom is attached to an sp^3 hybridized carbon which is adjacent to C=C (double bond or sp^2 hybridized carbon)
	Benzylic Halide	The halogen is attached to an sp^3 hybridized carbon which is attached to a benzene ring.
Compounds in which the halogen is attached to a sp^2 hybridized carbon	Vinyl Halide	The halogen atom is attached to C=C (sp^2 hybridized carbon).
	Aryl Halide	The halogen is attached to a sp^2 hybridized carbon which belongs to an aromatic ring.

Physical Properties of Halo alkanes:

Melting Point and Boiling Point of Haloalkanes

There is a large electronegativity difference between halogens and carbon resulting in highly polarised molecules. The higher molecular mass and greater polarity as compared to the parent hydrocarbon results in stronger intermolecular forces of attraction (dipole-dipole and van der Waals) in the halogen derivatives. The boiling Point depends upon the intermolecular forces of attraction and hence the boiling points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons of comparable molecular mass.

As we go down in homologous series of haloalkanes, the forces of attraction become stronger due to the increase in molecular size and mass, hence the boiling point increases down the homologous series. But the boiling point decreases with branching.

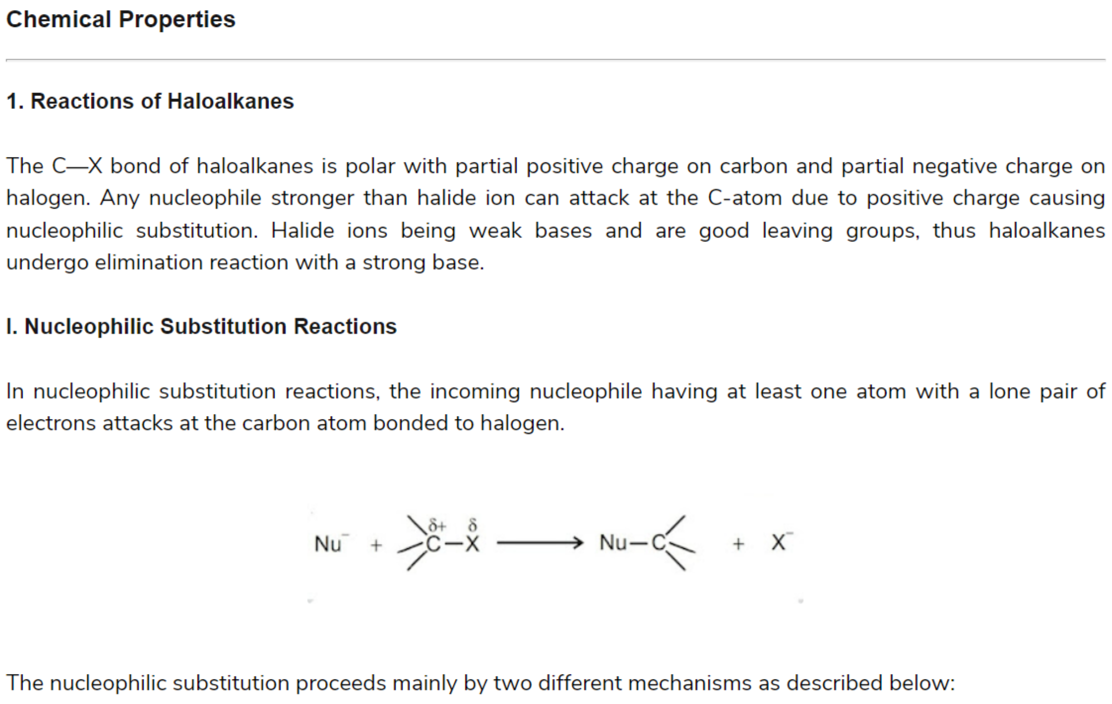
The melting point of a compound depends upon the strength of the lattice structure of a compound. The melting point also follows the same trend as the boiling point. An exception to this is para-isomers. The para-isomers have higher melting as compared to their ortho and meta-isomers. It is due to the symmetry of para-isomers that fits in the crystal lattice better as compared to ortho– and meta-isomers

Density of Haloalkanes

Density is directly proportional to the mass of the compound, hence down the homologous series, density increase due to increase in the mass, also fluoro derivatives are less dense than chloro derivatives; chloro derivatives are less dense than bromo derivatives and so on.

Solubility of Haloalkanes

Haloalkanes are slightly soluble in water. This is because of the relatively larger amount of energy required to break the bond between halogen and carbon and the smaller amount of energy released when the bond is formed after the dissolution of ion and water.



Chemical Properties

1. Reactions of Haloalkanes

The C—X bond of haloalkanes is polar with partial positive charge on carbon and partial negative charge on halogen. Any nucleophile stronger than halide ion can attack at the C-atom due to positive charge causing nucleophilic substitution. Halide ions being weak bases and are good leaving groups, thus haloalkanes undergo elimination reaction with a strong base.

I. Nucleophilic Substitution Reactions

In nucleophilic substitution reactions, the incoming nucleophile having at least one atom with a lone pair of electrons attacks at the carbon atom bonded to halogen.

The nucleophilic substitution proceeds mainly by two different mechanisms as described below:

Aryl halides are less reactive towards nucleophilic substitution reaction. Their low reactivity is attributed due to the following reasons:

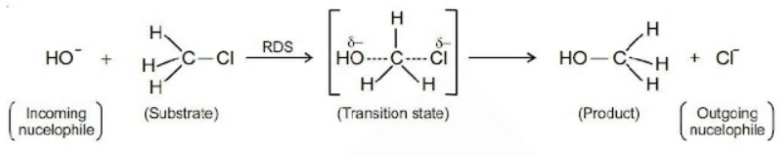
1. Due to resonance, C-X bond has partial double bond character.

2. Stabilisation of the molecule by delocalisation of electrons.

3. (Instability of phenyl carbocation.

(a) Substitution nucleophilic bimolecular (S_N2)

S_N2 is a single step bimolecular reaction in which the incoming nucleophile attacks the C–atom of substrate in a direction opposite to the outgoing nucleophile. The reaction passes through a transition state in which both the incoming and outgoing nucleophiles are bonded to the same C–atom.



(b) Substitution nucleophilic unimolecular (S_N1)

S_N1 is a two step unimolecular reaction. The first step is the slow ionisation of substrate and is the rate-determining step. The second step is the rapid reaction between the carbocation (formed in the first step) and the nucleophile. SN1 reactions generally proceed in polar protic solvents such as H_2O, CH_3OH, CH_3COOH etc.

$R—X \rightarrow R^+ + X^-$ (Step 1)

$R^+ + Nu^- \rightarrow R—Nu$ (Step 2)

MCQ QUESTIONS

1.Which of the following reaction will yield 2,2-Dibromopropane:

(i) CH3-C≡CH +2HBr → (ii) CH3-CH=CH-Br +HBr →

(iii) CH≡CH +2HBr → (iv) CH3-CH=CH2 +HBr →

Ans: (i) CH3-C≡CH +2HBr →

2. Fluorobenzene can be synthesized in laboratory

(i) by heating phenol with HF and KF (ii) by heating the diazonium salt with HBF_4

(iii) by direct fluorination of benzene with F_2 gas

(iv) by heating 1-Bromobenzene with NaF solution

Ans: (ii) by heating the diazonium salt with HBF_4

3. Toluene reacts with chlorine in the presence of iron (III) chloride gives X and in presence of light gives Y then X and Y are

(i) X= m-Chlorotoluene, Y= p-Chlorotoluene

(ii) X= o and p-Chlorotoluene, Y= Trichloromethyl benzene

(iii) X= Benzyl chloride, Y= m-Chlorotoluene

(iv) X= Benzyl chloride ,Y= o-Chlorotoluene

Ans: (ii) X= o and p-Chlorotoluene ,Y= Trichloromethylbenzene

4. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of AlCl3. Which of the following species attacks the benzene ring in this reaction?

(i) Cl^- (ii) Cl^+ (iii) $AlCl_3$ (iv) $[AlCl_4]$–

Ans: (ii) Cl^+

5. Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is

(i) Electrophilic elimination reaction	(ii) Electrophilic substitution reaction
(iii) Free radical addition reaction	(iv) Nucleophilic substitution reaction

Ans: (ii) Electrophilic substitution reaction

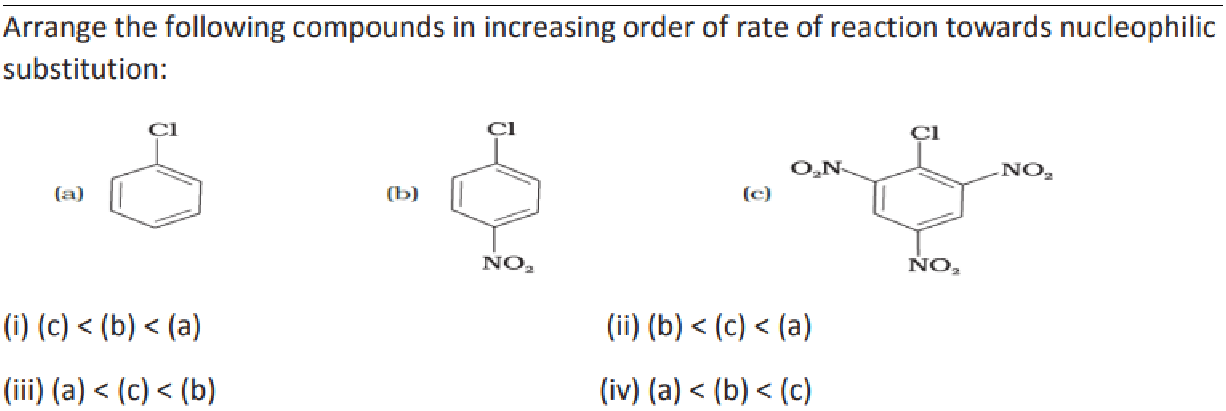
6 Which of the following is not chiral?

(i) 2-Hydroxypropanoic acid (ii) 2-Butanol

(iii) 2,3-Dibromobutane (iv) 3-Bromopentane

Ans: (iv) 3-Bromopentane

7.



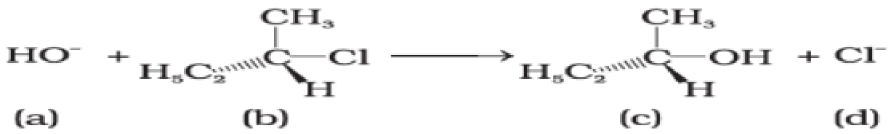
Arrange the following compounds in increasing order of rate of reaction towards nucleophilic substitution:

(i) (c) < (b) < (a) (ii) (b) < (c) < (a)

(iii) (a) < (c) < (b) (iv) (a) < (b) < (c)

Ans: (iv) (a) < (b) < (c)

8. Which of the following statements are correct about the mechanism of this reaction?



(i) A carbocation will be formed as an intermediate in the reaction.

(ii) OH– will attach the substrate (b) from one side and Cl– will leave it simultaneously from

other side.

(iii) An unstable intermediate will be formed in which OH– and Cl– will be attached by weak bonds

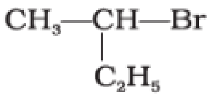
(iv) Reaction proceeds through SN^2 mechanism

Ans: (i) A carbocation will be formed as an intermediate in the reaction.

9.

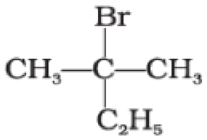
Which of the following compounds will give racemic mixture on nucleophilic substitution by OH– ion?

(a)



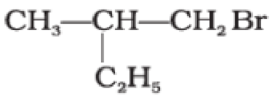
$CH_3-CH(C_2H_5)-Br$

(b)



$CH_3-C(Br)(C_2H_5)-CH_3$

(c)



$CH_3-CH(C_2H_5)-CH_2Br$

(i) (a)
(ii) (a), (b), (c)
(iii) (b), (c)
(iv) (a), (c)

Ans: (i) (a)

10. Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows:

(i) SN^1 mechanism (ii) SN^2 mechanism

(iii) Any of the above two depending upon the temperature of reaction

(iv) Saytzeff rule

Ans: (i) SN^1 mechanism

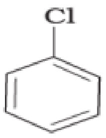
11. What is name of following reaction:

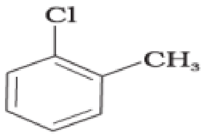
(i) Wurtz Reaction (ii) Fitting Reaction

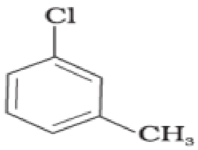
(iii) Wurtz- Fitting Reaction (iv) swartz reaction

Ans: (ii) Fitting Reaction

12. Arrange the following compounds in increasing order of rate of reaction towards nucleophilic substitution:

(a) 

(b) 

(c) 

(i) (a) < (b) < (c) (ii) (a) < (c) < (b) (iii) (c) < (b) < (a) (iv) (b) < (c) < (a)

13. Which one of the following compounds is more reactive towards SN1 reaction?

a. $CH_2=CHCH_2Br$ b. $C_6H_5CH_2Br$ c. $C_6H_5CH(C_6H_5)Br$ d. $C_6H_5CH(CH_3)Br$

Ans: c. $C_6H_5CH(C_6H_5)Br$

14. Which of the following isomer has the highest melting point:

(a) 1,2-dicholorbenzene (b) 1,3 -dichlorobenzene

(c) 1,4-dicholorbenzene (d) all isomers have same melting points

Ans: (c) 1,4-dicholorbenzene

15. Major product obtained on reaction of 3-Phenyl propene with HBr in presence of organic

peroxide

(a)3- Phenyl 1- bromopropane (b) 1 –Phenyl -3- bromopropane

(c) 1-Phenyl -2-bromopropane (d) 3-Phenyl -2- bromopropane

Ans: (b) 1 –Phenyl -3- bromopropane

16. . Which is the correct increasing order of boiling points of the following compounds?

1-Bromoethane, 1-Bromopropane, 1-Bromobutane, Bromobenzene

(a) Bromobenzene < 1-Bromobutane < 1-Bromopropane < 1-Bromoethane

(b) Bromobenzene < 1-Bromoethane < 1-Bromopropane < 1-Bromobutane

(c) 1-Bromopropane < 1-Bromobutane < 1-Bromoethane < Bromobenzene

(d) (d) 1-Bromoethane < 1-Bromopropane < 1-Bromobutane < Bromobenzene

Ans: 1-Bromoethane < 1-Bromopropane < 1-Bromobutane < Bromobenzene

17. Which of the following is a correct statement for C_2H_5Br?

(a) It reacts with metallic Na to give butane.

(b) It gives nitroethane on heating with aqueous solution of KNO_2

(c) It gives C_2H_5OH on boiling with alcoholic potash.

(d) It forms diethyl thioether on heating with alcoholic KSH

Ans: (a) It reacts with metallic Na to give butane.

18. Which of the following alkyl halides will undergo S_N1 reaction most readily?

(i) $(CH_3)_3C—F$ (ii) $(CH_3)_3C—Cl$ (iii) $(CH_3)_3C—Br$ (iv) $(CH_3)_3C—I$

Ans: (iv) $(CH_3)_3C—I$

19. The reagent for following conversion is (are) CH2Br-CH2Br → CH≡CH

(i) Alcoholic KOH (ii) Alcoholic KOH followed byNaNH2

(iii) Aqueous KOH followed by $NaNH_2$ (iv) Zn/methanol

Ans: (ii) Alcoholic KOH followed by$NaNH_2$

20. The organic choro compound, which shows complete stereo chemical inversion during a SN^2 reaction, is

(i) $(C_2H_5)_2CHCl$ (ii) $(CH_3)_3CCl$

(iii) $(CH_3)_2CHCl$ (iv) CH_3Cl

Ans: (iv) CH_3Cl

ASSERTION AND REASONING TYPE QUESTIONS

(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.

1. Assertion: Thionyl chloride are preferred over Phosphorus chlorides (tri and penta) for the preparation of alkyl chlorides from alcohols.

Reason: Phosphorus chlorides give pure alkyl halides.

Ans: (c) Assertion is correct statement but reason is wrong statement

2. Assertion: The boiling points of alkyl halides decrease in the order :

RI > RBr > RCl > RF

Reason : The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass.

Ans: (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion

3 Assertion: KCN reacts with methyl chloride to give methyl isocyanide

Reason: CN^- is an ambident nucleophile.

Ans: (d) Assertion is wrong statement but reason is correct statement.

4. Assertion : tert-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane.

Reason: In Wurtz reaction, alkyl halides react with sodium in dry ether to give hydrocarbon containing double the number of carbon atoms present in the halide.

Ans: (a) Assertion and reason both are correct statements and reason is correct explanation for assertion

5. Assertion: Presence of a nitro group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution.

Reason: Nitro group, being an electron withdrawing group decreases the electron density over the benzene ring.

Ans: (a) Assertion and reason both are correct statements and reason is correct explanation for assertion

6. Assertion: In monohaloarenes, further electrophilic substitution occurs at ortho and para positions.

Reason: Halogen atom is a ring deactivator.

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

7. Assertion: Aryl iodides can be prepared by reaction of arenes with iodine in the presence

of an oxidizing agent.

Reason: Oxidizing agent oxidizes I_2 into HI.

Ans: (iii) Assertion is correct but reason is wrong statement.

8. Assertion: It is difficult to replace chlorine by –OH in chlorobenzene in comparison to

that in chloroethane.

Reason: Chlorine-carbon (C—Cl) bond in chlorobenzene has a partial double bond

character due to resonance.

Ans: (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

9. Assertion: Hydrolysis of (–)-2-bromooctane proceeds with inversion of configuration.

Reason: This reaction proceeds through the formation of a carbocation.

Ans: c) Assertion is correct statement but reason is wrong statement

10. Assertion: Nitration of chlorobenzene leads to the formation of m-nitro chlorobenzene

Reason: —NO_2 group is a m-directing group.

Ans: (d) Assertion is wrong statement but reason is correct statement

TWO MARKS QUESTIONS:

1. Arrange each set of compounds in order of increasing boiling points.

(i) Bromomethane, Bromoform, Chloromethane, Di bromomethane.

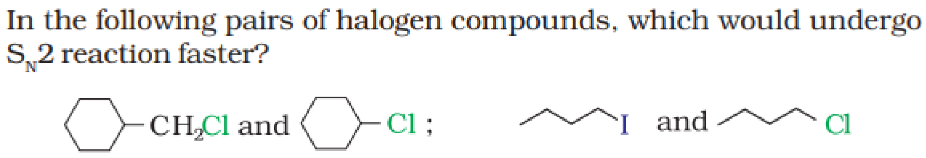
(ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

Ans:

(i) Chloroethane<Bromoethane <Dibromo ethane < Bromoform

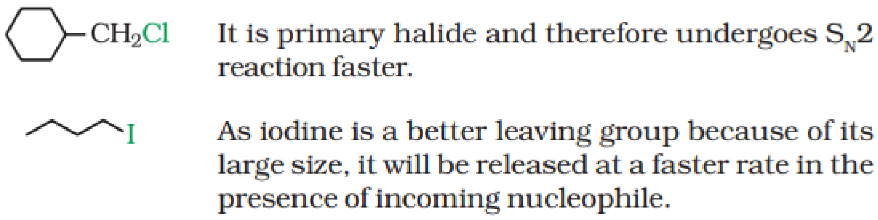
(ii) Isopropyl chloride < 1-chloropropane < 1- Chlorobutane

2.



In the following pairs of halogen compounds, which would undergo S_N2 reaction faster?

Ans:



It is primary halide and therefore undergoes S_N2 reaction faster.

As iodine is a better leaving group because of its large size, it will be released at a faster rate in the presence of incoming nucleophile.

3. (a) Why does p-dichlorobenzene have a higher m.p. than its o- and m-isomers?

(b) Why is (±)-Butan-2-ol optically inactive?

Answer:

(a) p-isomers are comparatively more symmetrical and fit closely in the crystal lattice, thus

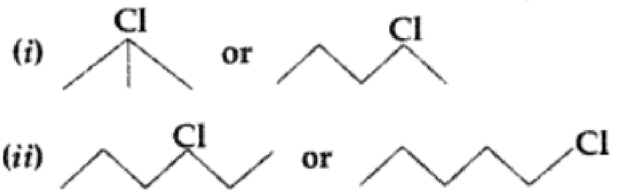
require more heat to break these strong forces of attraction. Therefore higher melting point

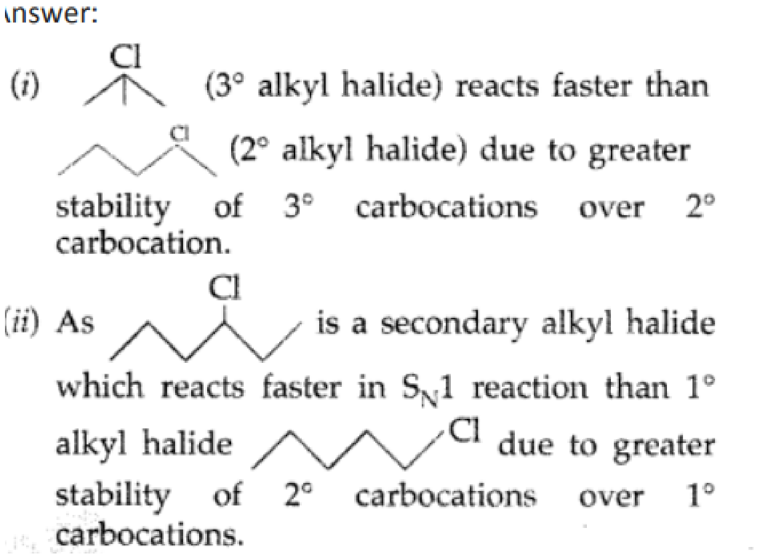
than o- and m-isomers.

(b) (±)-Butan-2-ol is optically inactive because in racemic mix one type of rotation is cancelled by other.

$CH_3CH(OH)CH_2CH_3$

4. Which one in the following pairs undergoes SN^1 substitution reaction faster and why?




nswer:

(i) (3° alkyl halide) reacts faster than (2° alkyl halide) due to greater stability of 3° carbocations over 2° carbocation.

(ii) As is a secondary alkyl halide which reacts faster in S_N1 reaction than 1° alkyl halide due to greater stability of 2° carbocations over 1° carbocations.

5. (1)Which compound in each of the following pairs will react faster in SN^2 reaction with —OH?

(i) CH_3Br or CH_3I (ii) $(CH_3)_3$ CCl or CH_3Cl

Answer:

(i) CH_3I: Because Iodide is better leaving group than bromide.

(ii) CH_3Cl : Carbon atom leaving group is less hindered.

6. Explain why:

(a) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(b) Alkyl halides, though polar, are immiscible with water.

Answer:

(a) Chlorobenzene has lower dipole moment than cyclohexyl chloride due to lower

magnitude of -ve charge on the Cl atom and shorter C – Cl distance. Due to greater S character, a sp^2 -hybrid carbon is more electronegative than a sp^3-hybrid carbon. Therefore, the sp^2 -hybrid carbon of C – Cl bond in chlorobenzene has less tendency to release electrons to Cl than a sp3 hybrid carbon of cyclohexyl chloride.
(b) Alkyl halides and polar molecules are held together by dipole-dipole interaction. The molecules of H_2O are held together by H- bonds. Since the new forces of attraction between water and alkyl halide molecules are weaker than the forces of

attraction already existing between alkyl halide-alkyl halide molecules and water-water molecules, therefore alkyl halides are immiscible (not soluble) with water.

7. Account for the following:

(i) The C – Cl bond length in chlorobenzene is shorter than that in $CH_3 – Cl$

(ii) Grignard reagent should be prepared under anhydrous conditions.

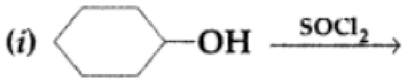
Answer:

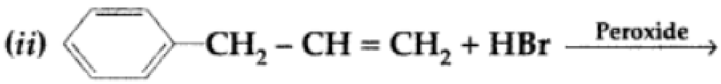
(i) In haloalkanes, the halogen atom is attached to sp3 -hybridized carbon while in haloarenes it is attached to sp^2 -hybridized carbon whose size is smaller than sp^3 orbital carbon. Therefore C – Cl bond in chloro-benzene is shorter than alkyl chloride.

(ii) Grignard reagents are very reactive. In the presence of moisture, they react to give alkanes. Therefore, Grignard reagents should be prepared under anhydrous conditions.

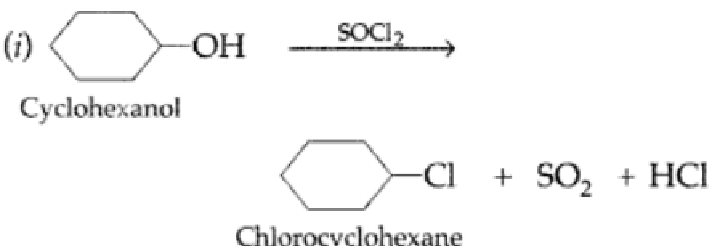
$RMgX + H_2O \rightarrow RH + Mg(OH)X$

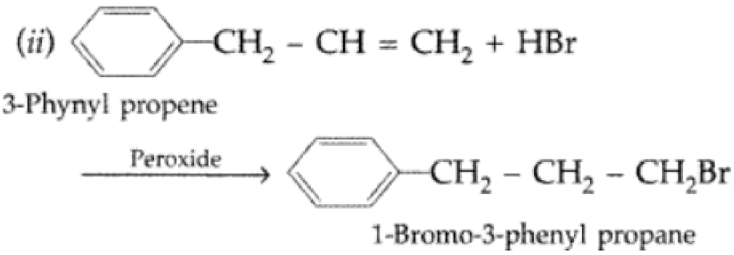
8. Draw the structure of major mono halo product in each of the following reactions:





Ans:

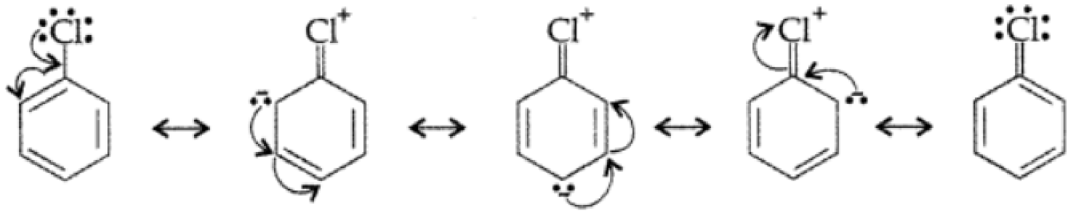




9.. Haloalkanes undergo nucleophilic substitution whereas haloarenes undergo electrophilic substitution. Explain.

Ans:

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 substitution reactions. This is due to greater electron density at these positions in resonance.

10(i). Give reason for the following:

a. During the electrophilic substitution reaction of haloarenes, para substituted derivative is the major product.

b. The product formed during S_N1reaction is a racemic mixture.
Answers:

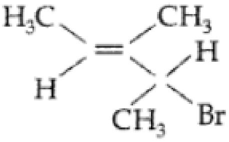
a. At the ortho position, higher steric hindrance is there, hence para isomer is usually predominate and is obtained in the major amount.

b.During the S_N1 mechanism, intermediate carbocation formed is sp2 hybridized and planar in nature. This allows the attack of nucleophile from either side of the plane resulting in a racemic mixture. (1)
11. Identify the major product formed when 2-cyclohexylchloroethane undergoes a dehydrohalogenation reaction. Name the reagent which is used to carry out the reaction.

Answer:

The major product formed when 2-cyclohexylchloroethane undergoes dehydrohalogenation reaction is 1- cyclohexylethene. The reagent which is used to carry out the reaction is ethanolic KOH.

12. (a) Give the IUPAC name of the following compound:



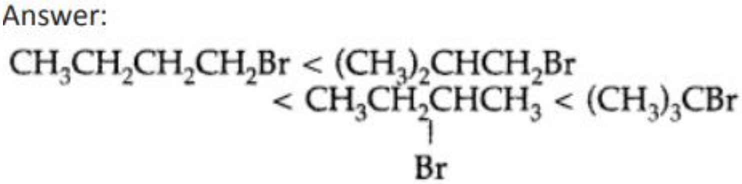
Ans: 2-Bromo 3-mehyl pentene

(b) Predict the order of reactivity of the following compounds in SN1 reaction :

$C_6H_5CH_2Br$, $C_6H_5C(CH_3)(C_6H_5)Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5CH(CH3)Br$

Answer: $C_6H_5C(CH_3)(C_6H_5)Br > C_6H_5CH(C_6H_5)Br > C_6H_5CH(CH_3)Br > C_6H_5CH_2Br$

13. (a) Predict the increase in order of reactivity of four isomeric bromobutanes in SN1 reaction.



Answer:

$$CH_3CH_2CH_2CH_2Br < (CH_3)_2CHCH_2Br < CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 < (CH_3)_3CBr$$

(b) Give chemical tests to distinguish between the following pairs of compound:

Benzyl chloride and Chlorobenzene

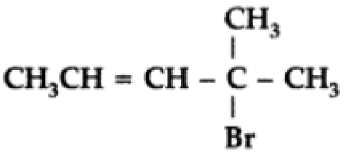
Ans: Benzyl chloride is more reactive than chlorobenzene towards nucleophillic substitution reactions, therefore, benzyl chloride on boiling with aqueous KOH produces benzyl alcohol and KCl. But chlorobenzene does not undergo hydrolysis under these mild conditions to give phenol and KCl.

13, (a) What happens when CH_3 — Br is treated with KCN?

Ans:

$$\underset{\text{Methyl bromide}}{CH_3-Br} + \underset{\text{Potassium cyanide}}{KCN} \longrightarrow \underset{\text{Methyl cyanide}}{CH_3CN} + \underset{\text{Potassium bromide}}{KBr}$$

(b) Write the IUPAC name of



$$CH_3CH=CH-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3$$

Ans: 4-bromo-4-methylpent-2-ene

Ans: 

(b) In the following pair of halogen compounds, which compound will react faster by SN1

mechanism? $(CH_3)_3C$-Cl and $CH_3\,CH_2\,CH(Cl)CH_3$

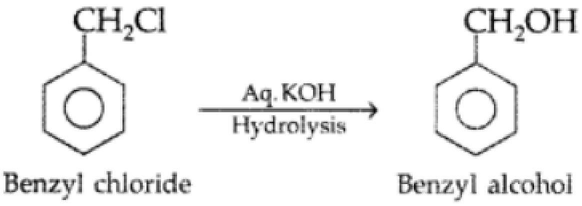
Ans: $(CH_3)_3C$-Cl

THREE MARKS QUESTIONS

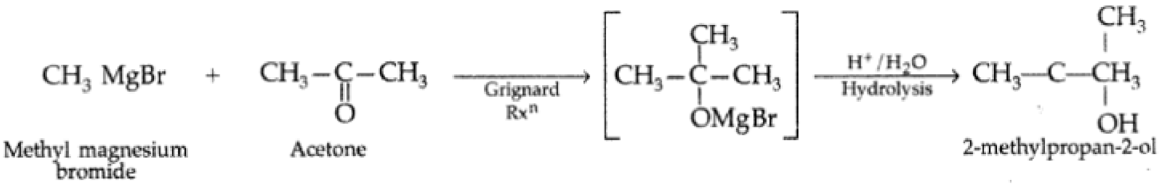
1. How are the following conversions carried out?
(i) Benzyl chloride to benzyl alcohol,
(ii) Methyl magnesium bromide to 2-methyl- propan-2-ol.
(iii) Chlorobenzene to Toluene

Answer:

(i) Benzyl chloride to benzyl alcohol

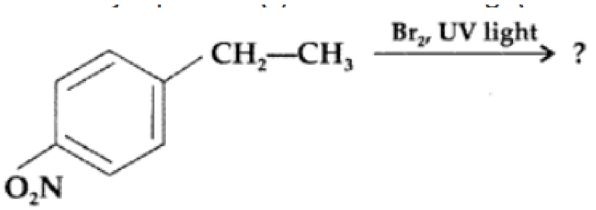


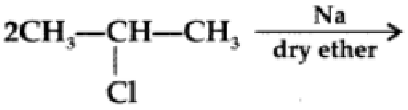
(ii) Methyl magnesium bromide to 2-methylpropan-2-ol



(iii) C_6H_5Cl +2Na + CH_3Cl → (in presence of dry ether) C_6H_5-CH_3

2. Write the major product(s) in the following:

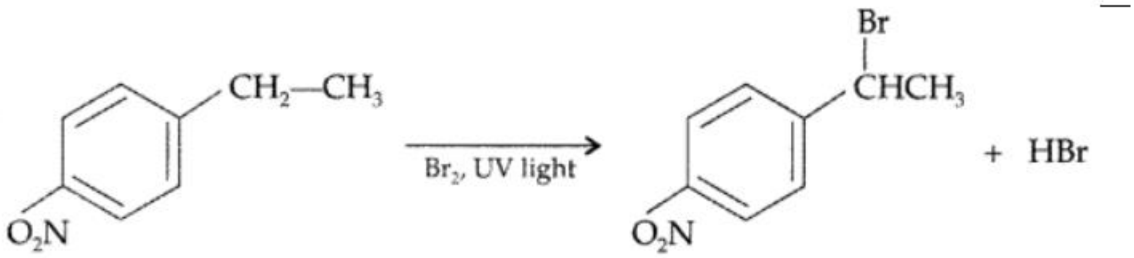
(i) 

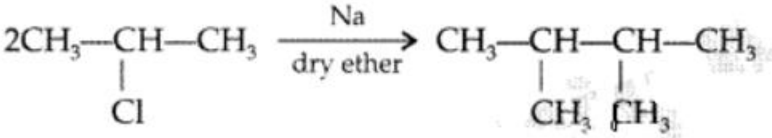
(ii) 

$$2CH_3\underset{\displaystyle Cl}{-\underset{|}{C}H-}CH_3 \xrightarrow[\text{dry ether}]{Na}$$

(iii) $CH_3—CH_2—Br \xrightarrow{AgCN}$

Answer:

(i) 

(ii) 

$$2CH_3-\underset{\displaystyle Cl}{\underset{|}{C}H}-CH_3 \xrightarrow[\text{dry ether}]{Na} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}H}-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3$$

2-chloropropane 2, 2-dimethylbutane

(iii) $CH_3CH_2—Br + AgCN(alc.) \longrightarrow CH_3CH_2N \rightleftarrows C + AgBr$

Bromoethane Ethylisocyanide

3. What happens when

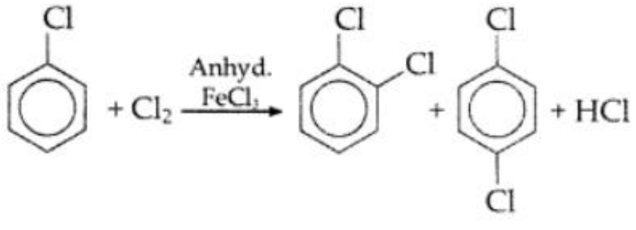
(i) Chlorobenzene is treated with $Cl_2/FeCl_3$,

(ii) Ethyl chloride is treated with $AgNO_2$,

(iii) 2-bromopentane is treated with alcoholic KOH?

Write the chemical equations in support of your answer.

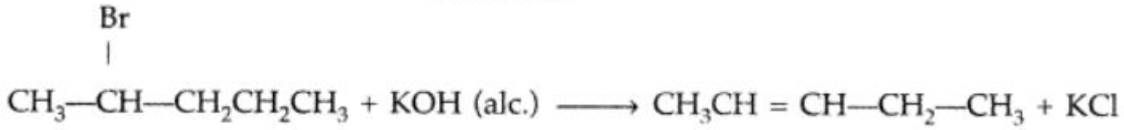
Answer:

(i) 

1,2-dichlorobenzene 1,4-dichlorobenzene

(ii) $CH_3CH_2Cl + AgNO_2 \longrightarrow CH_3CH_2NO_2 + AgCl$

Nitro ethane

(iii) 

$$CH_3-\overset{\displaystyle Br}{\overset{|}{C}H}-CH_2CH_2CH_3 + KOH\ (alc.) \longrightarrow CH_3CH = CH—CH_2—CH_3 + KCl$$

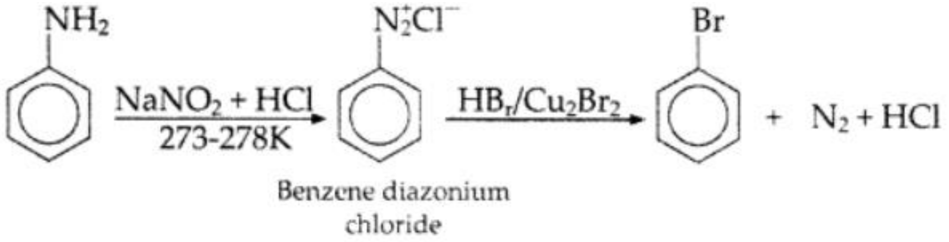
Pent-2-ene

4. How can the following conversions be carried out :

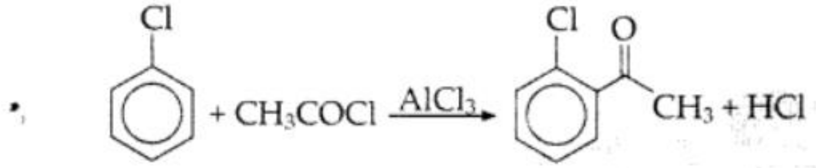
(i) Aniline to bromobenzene (ii) Chlorobenzene to 2-chloroacetophenone

(iii) Chloroethane to butane

Answers: (i) Aniline to Bromo benzene



***(ii)* Chlorobenzene to 2-chloroacetophenone**



***(iii)* Chloroethane to butane**

$$2CH_3CH_2Cl + 2Na \xrightarrow{\text{Dry ether}} CH_3CH_2\text{—}CH_2\text{—}CH_3 + 2NaCl$$

5. Give reasons :

(a) n-Butyl bromide has higher boiling point than t-butyl bromide.

(b) Racemic mixture is optically inactive.

(c) The presence of nitro group ($-NO_2$) at o/p positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.

Answer:

(a) n-Butyl bromide has higher boiling point than f-butyl bromide because it has larger surface area hence have more Van der Waals’ forces.

(b) Rotation due to one enantiomer is cancelled by another enantiomer.

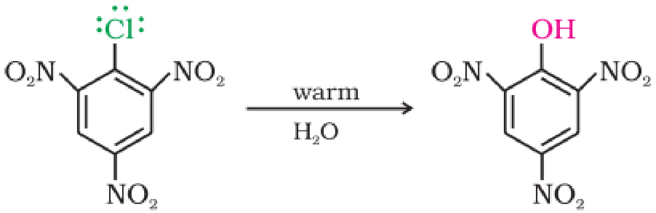
(c) The presence of nitro group ($-NO_2$) at ortho and para positions withdraws the electron density’ from benzene ring and thus facilitating the attack of nucleophile.

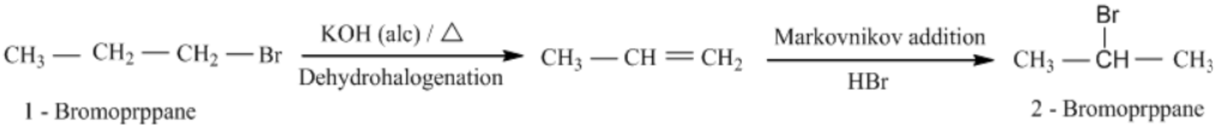
6.How are the following converted?

(a) 2, 4, 6 trinitro chlorobenzene to 2,4,6 trinitro phenol (Picric acid)

(b) 1- bromopropane to 2- bromo propane

(c) Bromo ethane to ethoxy ethane

Answer: 



(a)

(b) $C_2H_5Br + C_2H_5ONa \rightarrow C_2H_5O\ C_2H_5 + NaBr$

CASE STUDY QUESTION (4 MARKS)

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

Nucleophilic substitution reactions are of two types; substitution nucleophilic bimolecular (S_N2) and substitution nucleophilic unimolecular (S_N1) depending on molecules taking part in determining the rate of reaction. Reactivity of alkyl halide towards S_N1 and S_N2 reactions depends on various factors such as steric hindrance, stability of intermediate or transition state and polarity of solvent. S_N2 reaction mechanism is favoured mostly by primary alkyl halide or transition state and polarity of solvent, S_N2 reaction mechanism is favoured mostly by primary alkyl halide then secondary and then tertiary. This order is reversed in case of S_N1 reactions.

a. Name the possible alkenes which will yield 1-chloro-1-methylcyclohexane on their reaction with HCl. Write the reactions involved. (1+1)

b. Allyl chloride is hydrolysed more readily than n-propyl chloride. Why? (1)

c. Why are haloalkanes more reactive towards nucleophilic substitution reactions than haloarenes and vinylic halides? (1)

Answers:

a. Methylenecyclohexane

1-Methylcyclohexene (1/2+1/2)

(1/2+1/2)

b. Allyl chloride shows high reactivity as the carbocation formed in the first step is stabilised by resonance while no such stabilisation of carbocation exists in the case of n-propyl chloride. (1)

c. Haloalkanes are more reactive than haloarenes and vinylic halides because of the presence of partial double bond character C-X bond in haloarenes and vinylic halides. Hence they do not undergo nucleophilic reactions easily. (1)

FIVE MARKS QUESTIONS

1. What happens when

(A) n-butyl chloride is treated with alcoholic KOH,

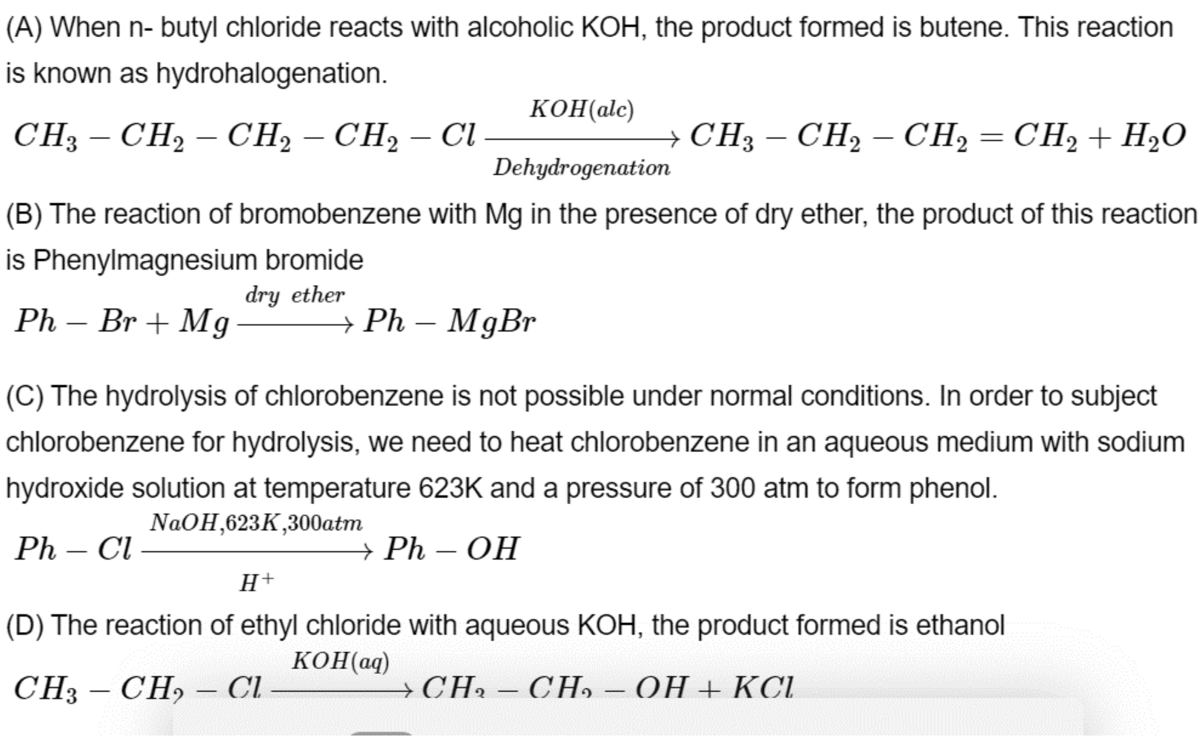
(B) bromobenzene is treated with Mg in the presence of dry ether,

(C) chlorobenzene is subjected to hydrolysis,

(D) ethyl chloride is treated with aqueous KOH,

(E) methyl chloride is treated with KCN

Answers:



(A) When n- butyl chloride reacts with alcoholic KOH, the product formed is butene. This reaction is known as hydrohalogenation.

$$CH_3-CH_2-CH_2-CH_2-Cl \xrightarrow[Dehydrogenation]{KOH(alc)} CH_3-CH_2-CH_2=CH_2+H_2O$$

(B) The reaction of bromobenzene with Mg in the presence of dry ether, the product of this reaction is Phenylmagnesium bromide

$$Ph-Br+Mg \xrightarrow{dry\ ether} Ph-MgBr$$

(C) The hydrolysis of chlorobenzene is not possible under normal conditions. In order to subject chlorobenzene for hydrolysis, we need to heat chlorobenzene in an aqueous medium with sodium hydroxide solution at temperature 623K and a pressure of 300 atm to form phenol.

$$Ph-Cl \xrightarrow[H^+]{NaOH,623K,300atm} Ph-OH$$

(D) The reaction of ethyl chloride with aqueous KOH, the product formed is ethanol

$$CH_3-CH_2-Cl \xrightarrow{KOH(aq)} CH_3-CH_2-OH+KCl$$

(E)

(F) The reaction of methyl chloride with KCN, the product formed is methyl cyanide. This reaction is a substitution reaction.

$$CH_3 - Cl + KCN \xrightarrow[\text{Nucleophilic substitution}]{} CH_3 - CN + KCl$$

2. (i) Write the products of the following reactions

a)$C_6H_5O_{Na}$ +C_2H_5Cl $\longrightarrow$

b)$CH_3CH_2CH_2OH$ +$SOCl_2$ $\longrightarrow$

c)$CH_3CH_2CH{=}CH_2$ +HBr $\longrightarrow$

Answers:

$$C_6H_5ONa + C_2H_5Cl \xrightarrow[\left(\text{Williamson synthesis}\right)]{} C_6H_5-O-C_2H_5 + NaCl$$

Sodium phenoxide Chloroethane Phenetole

$$CH_3CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2CH_2Cl + SO_2 + HCl$$

1 – Propanol 1 – Chloropropane

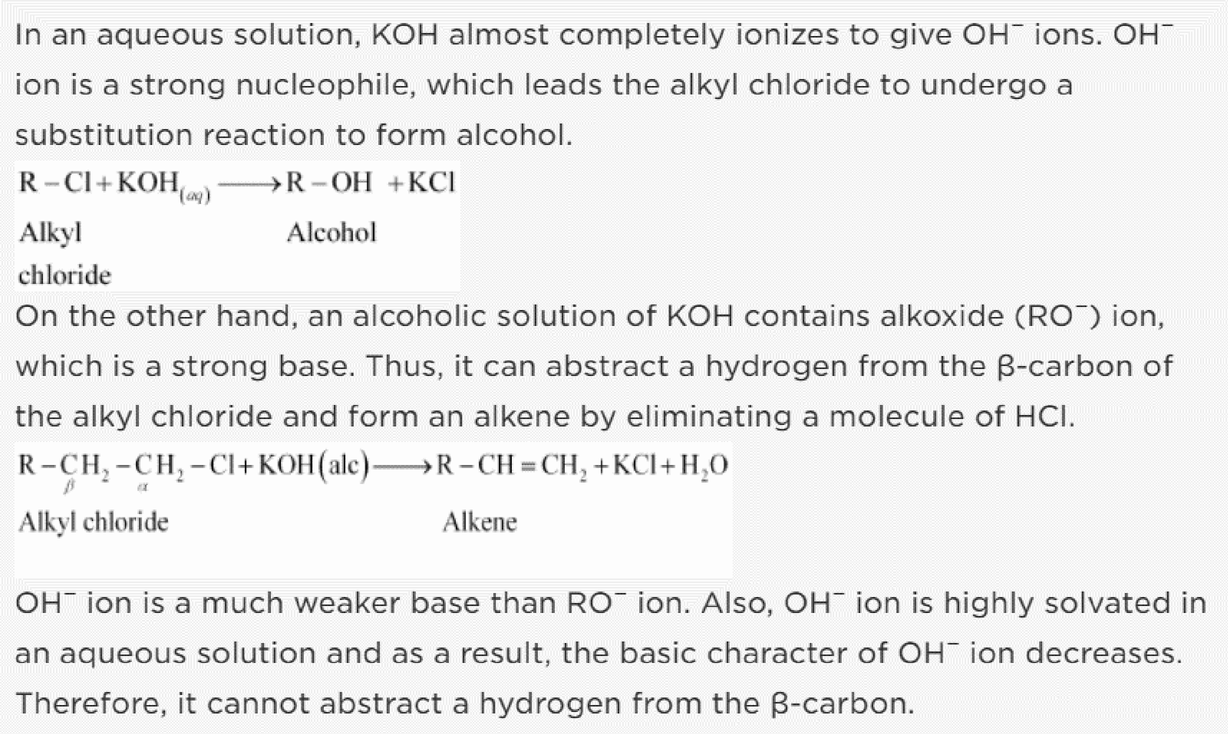
c)

$$CH_3CH_2CH = CH_2 + HBr \xrightarrow[\left(\text{Anti-Markovnikov's addition}\right)]{\text{Peroxide}} CH_3CH_2CH_2CH_2 - Br$$

But – 1 – ene 1 – Bromobutane

HOTS QUESTIONS AND ANSWERS

1. The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.
Answer:



In an aqueous solution, KOH almost completely ionizes to give OH^- ions. OH^- ion is a strong nucleophile, which leads the alkyl chloride to undergo a substitution reaction to form alcohol.

$$\underset{\text{Alkyl chloride}}{R-Cl}+KOH_{(aq)}\longrightarrow \underset{\text{Alcohol}}{R-OH}+KCl$$

On the other hand, an alcoholic solution of KOH contains alkoxide (RO^-) ion, which is a strong base. Thus, it can abstract a hydrogen from the β-carbon of the alkyl chloride and form an alkene by eliminating a molecule of HCl.

$$\underset{\text{Alkyl chloride}}{R-\underset{\beta}{C}H_2-\underset{\alpha}{C}H_2-Cl}+KOH(alc)\longrightarrow \underset{\text{Alkene}}{R-CH=CH_2}+KCl+H_2O$$

OH^- ion is a much weaker base than RO^- ion. Also, OH^- ion is highly solvated in an aqueous solution and as a result, the basic character of OH^- ion decreases. Therefore, it cannot abstract a hydrogen from the β-carbon.

2. Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.

Answer:

KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C—C bond is more stable than C—N bond. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product

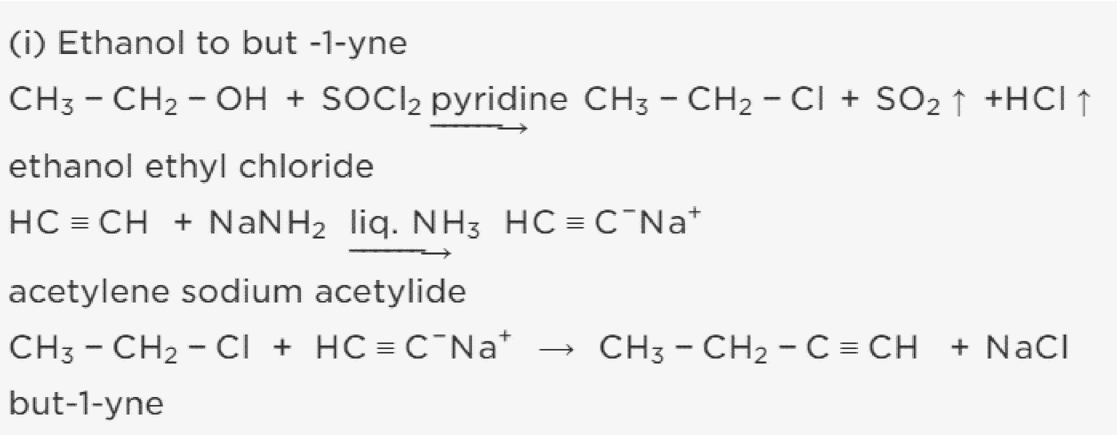
3. How will you bring about the following conversions?

(i) Ethanol to but-1-yne (ii) Ethane to bromoethene

(iii) Propene to 1-nitropropane (iv) Toluene to benzyl alcohol

(v) Propene to propyne

Answers:



(i) Ethanol to but -1-yne

$CH_3-CH_2-OH + SOCl_2 \xrightarrow{\text{pyridine}} CH_3-CH_2-Cl + SO_2\uparrow + HCl\uparrow$

ethanol ethyl chloride

$HC\equiv CH + NaNH_2 \xrightarrow{\text{liq. }NH_3} HC\equiv C^-Na^+$

acetylene sodium acetylide

$CH_3-CH_2-Cl + HC\equiv C^-Na^+ \longrightarrow CH_3-CH_2-C\equiv CH + NaCl$

but-1-yne

(ii) Ethane to bromoethane

$CH_3-CH_3 + Br_2 \xrightarrow{\text{UV light}} CH_3CH_2Br \xrightarrow{\text{alc. KOH}}$

ethane $CH_2=CH_2 \xrightarrow{Br_2} Br-CH_2CH_2-Br$

$Br-CH_2-CH_2-Br \xrightarrow{\text{alc. KOH}} CH_2=CHBr$

bromo ethene

(iii) Propene to 1 - nitropropane

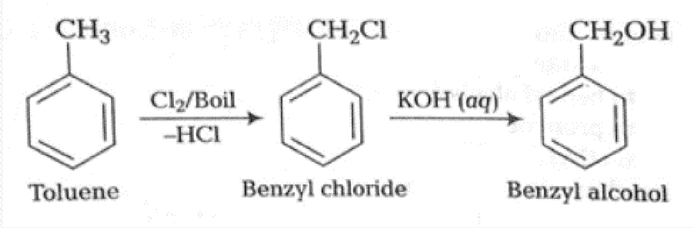
$CH_3CH=CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2Br \xrightarrow{AgNO_2} CH_3CH_2CH_2NO_2 + AgBr$

1-nitro propane

(iv) Toluene to benzyl alcohol

$C_6H_5-CH_3 + Cl_2 \xrightarrow{\text{UV light}} C_6H_5-CH_2Cl \xrightarrow{NaOH} C_6H_5-CH_2OH + NaCl$ toluene

benzyl alcohol

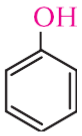


(v) Propene to propyne

$CH_3CH=CH_2 + Br_2 \xrightarrow{CCl_4} CH_3CH(Br)-CH_2(Br) \xrightarrow{NaNH_2} CH_3C\equiv CH$

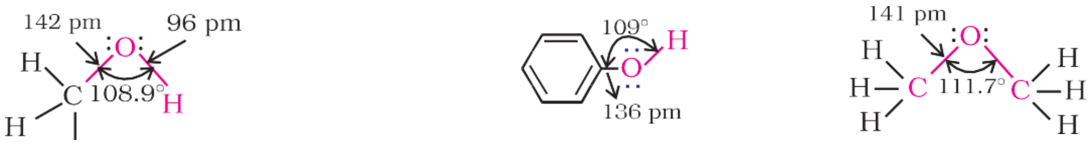
CHAPTER 7.

ALCOHOL PHENOLS AND ETHERS:



	R-OH		R-O-R'
	ALCOHOL	PHENOL	ETHER
IUPAC NAME:	ALKANOL	PHENOL	ALKOXYALKANE

STRUCTURE:



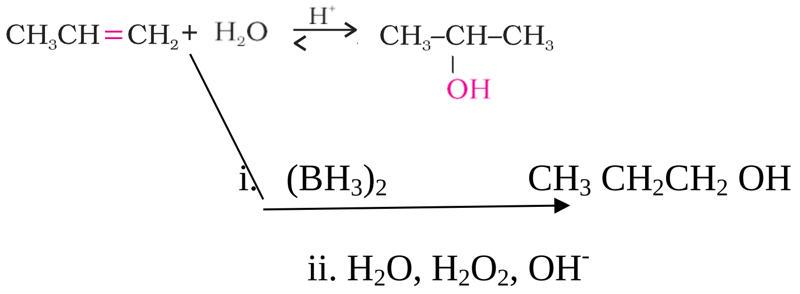
METHANOL PHENOL METHOXYMETHANE

Fig. Structures of methanol, phenol and methoxymethane

1. The bond angle in alcohols is less than tetrahedral angle ($109^0\ 28'$) due to lone pair- lone pair repulsion . However, in ether the bond angle is larger than tetrahedral angle due to repulsive interaction between two bulky groups.
2. The carbon in alcohol and ether attached by oxygen is sp^3 hybridised , however in phenol it is sp^2 hybridised.
3. The C-C bond length in phenols is less than C-C bond length in alcohols and ethers due to partial double bond character in phenols, due to conjugation of unshared e- pair of oxygen and due to sp^2 character of carbon in phenols.

Preparation of alcohols:

1. From Alkenes:

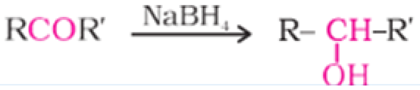


$$CH_3CH{=}CH_2 + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$$

$$CH_3CH{=}CH_2 \xrightarrow[\text{ii. } H_2O,\ H_2O_2,\ OH^-]{\text{i. } (BH_3)_2} CH_3\ CH_2CH_2\ OH$$

2. From Adehyde and ketones: Reducing reagent may be H_2 in presence of Ni, Pd or Pt, $NaBH_4$ or $LiAlH_4$.

$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH$$



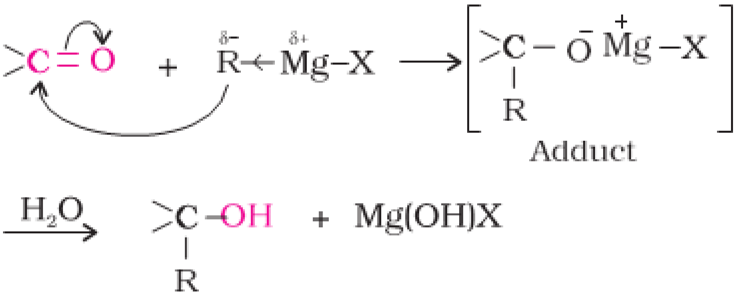
$$RCOR' \xrightarrow{NaBH_4} R-\underset{\displaystyle OH}{\underset{|}{CH}}-R'$$

3. From Carboxylic acid and Ester:

$$RCOOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} RCH_2OH$$

$$RCOOH \xrightarrow[H^+]{R'OH} RCOOR' \xrightarrow[\text{Catalyst}]{H_2} RCH_2OH + R'OH$$

4. From Grignard Reagent:



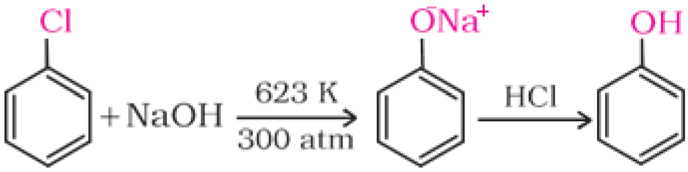
i. Formaldehyde produces primary alcohol.

ii. Any other aldehyde produces secondary alcohol.

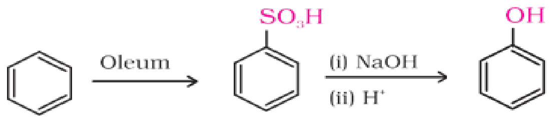
iii. Ketone produces tertiary alcohol.

Preparation Of Phenols:

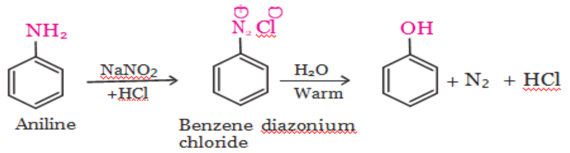
1. From Chlorobenzene



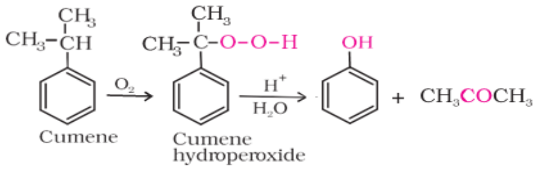
2. From Benzenesulphonic acid:



3. From Diazonium Salts:

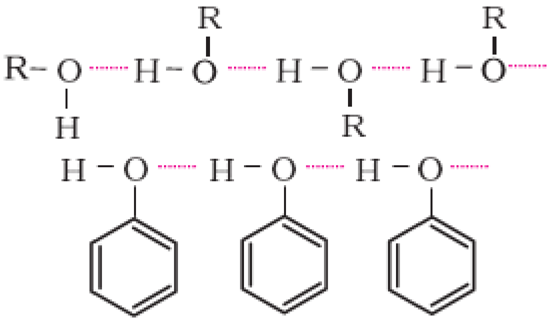


4. From Cumene: Industrial process.

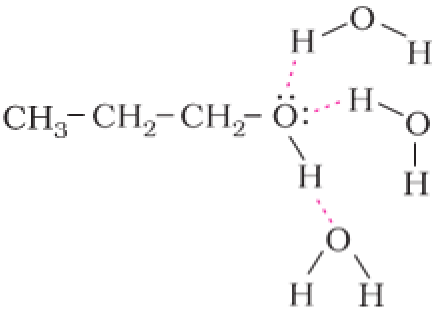


Physical Properties:

1. The boiling points of alcohols and phenols increase with increase in the number of carbon atoms (increase in van der Waals forces).
2. In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area).
3. Boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses due to the presence of intermolecular H- bonding.



4. Solubility: Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules as shown.



Chemical Reactions of Alcohols:

1. Acidic Behavior:

$$2R{-}O{-}H + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2R{-}O{-}Na} + H_2$$

2. Esterification:

$$Ar/RO{-}H + R'{-}COOH \xrightleftharpoons{H^+} Ar/ROCOR' + H_2O$$

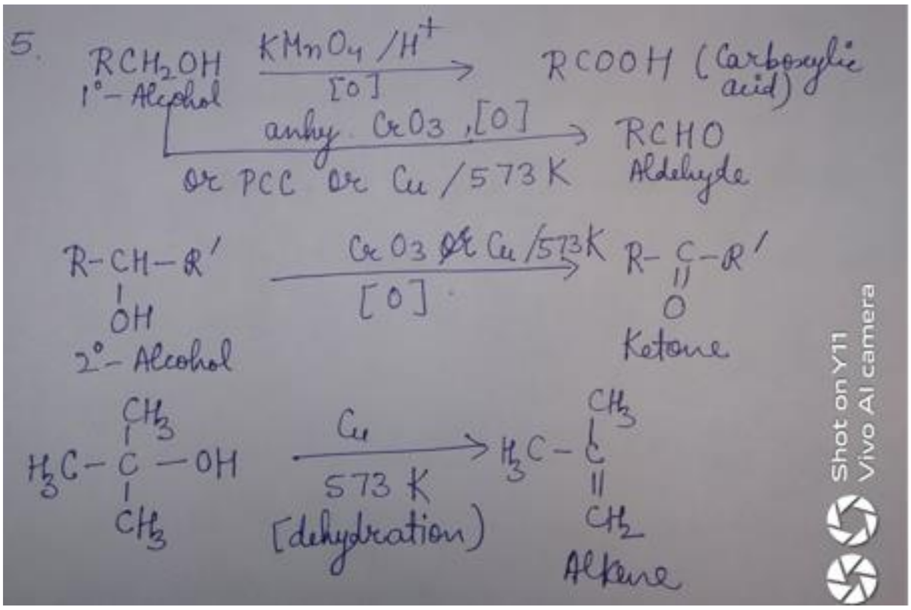
$$Ar/R\_OH + (RCO)_2O \xrightleftharpoons{H^+} Ar/ROCOR + RCOOH$$

$$R/ArOH + R'COCl \xrightarrow{\text{Pyridine}} R/ArOCOR' + HCl$$

3. Dehydration:

$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O$$

4. Oxidation:



5. $\underset{1°-\text{Alcohol}}{RCH_2OH} \xrightarrow[{[O]}]{KMnO_4/H^+} RCOOH$ (Carboxylic acid)

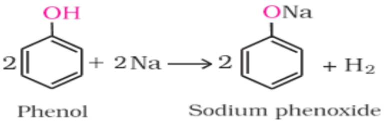
$\xrightarrow[\text{or PCC or Cu/573 K}]{\text{anhy. } CrO_3, [O]} \underset{\text{Aldehyde}}{RCHO}$

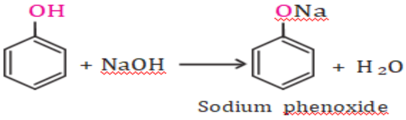
$\underset{2°-\text{Alcohol}}{R-\underset{OH}{\underset{|}{CH}}-R'} \xrightarrow[{[O]}]{CrO_3 \text{ or } Cu/573K} \underset{\text{Ketone}}{R-\underset{O}{\underset{||}{C}}-R'}$

$H_3C-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH \xrightarrow[\text{573 K (dehydration)}]{Cu} H_3C-\overset{CH_3}{\overset{|}{\underset{CH_2}{\underset{||}{C}}}}$ Alkene

Chemical Reaction Of Phenols:

1. Acidic Behaviour-





i. Phenols are more acidic than alcohol.

ii. The presence of e- withdrawing group such as nitro enhances the acidic strength of phenol, however presence of e- releasing group soch as methoxy decreases acidic behaviour. This effect is more pronounced when the substituent is present at ortho and para positions.

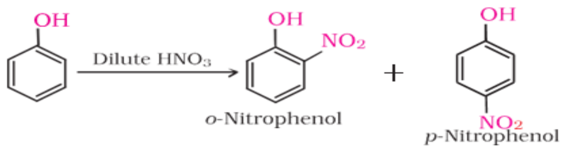
2. Esterification:

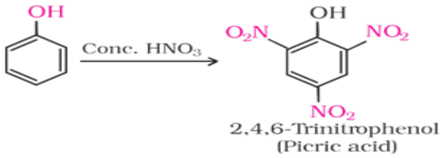
$$Ar/RO-H + R'-COOH \rightleftharpoons Ar/ROCOR' + H_2O$$

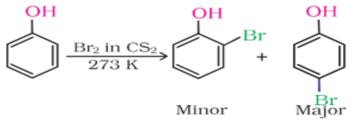
$$Ar/R\_OH + (RCO)_2O \underset{}{\overset{H^+}{\rightleftharpoons}} Ar/ROCOR + RCOOH$$

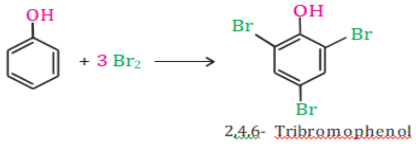
$$R/ArOH + R'COCl \xrightarrow{\text{Pyridine}} R/ArOCOR' + HCl$$

3. Electrophilic Aromatic Substitution: -OH group is o-,p- directing and ring activator.



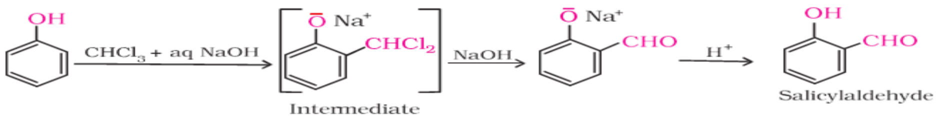




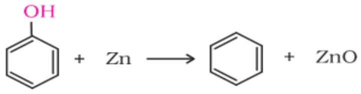


4. Kolbe's Reaction:

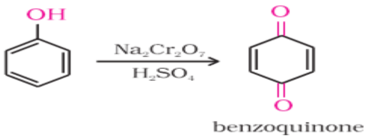
5. Reimer-Tiemann Reaction:



6. Reaction with Zn dust:



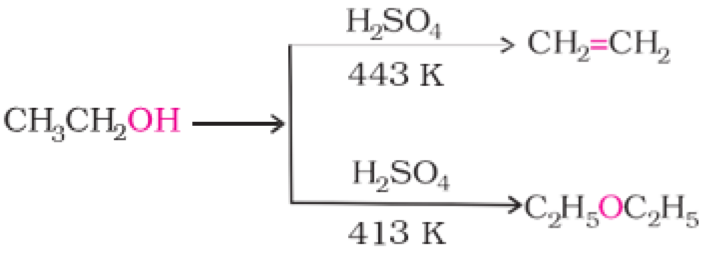
7. Oxidation:



Ethers:

Preparation Of Ethers:

1. By dehydration of Alcohols: Only symmetrical ethers can be prepared.

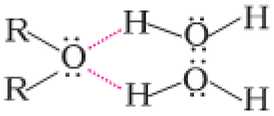


2. Williamson Synthesis: SN2 attack of alkoxide ion on 1° alkyl halide.

$$R{-}X + R'{-}\ddot{\underset{\cdot\cdot}{O}}\,Na \longrightarrow R{-}\ddot{\underset{\cdot\cdot}{O}}{-}R' + NaX$$

Physical Properties:

1. Ethers boiling point is comparable with alkanes having same molar mass but very less than alcohols. As ether can not form intermolecular H-bonding with themselves.
2. Ethers have almost same soluibility in water as alcohol of same molecular mass as they can form H- bonding with water molecule.



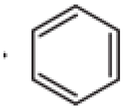
<u>Chemical Properties Of Ethers:</u> Least reactive functional group.

1. Reaction with HX: React with HI and HBr at high temperature.

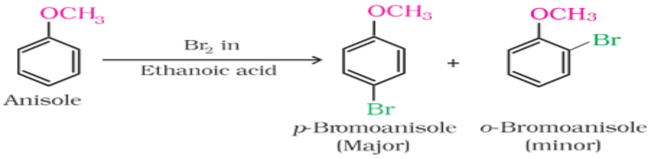
$$R{-}O{-}R + HX \longrightarrow RX + R{-}OH$$

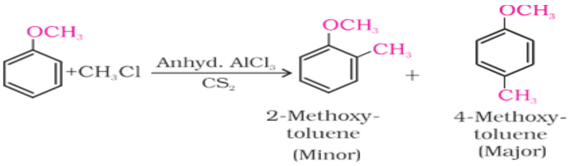
$$R{-}OH + HX \longrightarrow R{-}X + H_2O$$

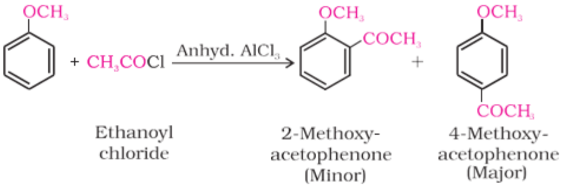
S. N.	R	R'	Product	Mechanism
1.	1° ($-CH_3$)	1° ($-C_2H_5$)	CH_3I (least hindered)	SN2
2.	1°	2°	1° alkyl halide	SN2

3.	1^o	3^o	3^o alkyl halide	SN1
4.	2^o	3^o	3^o alkyl halide	SN1
5.		R (alkyl)	R-X	

2. Electrophilic Substitution Reactions: Alkoxy group is o,p- directing and ring activator.

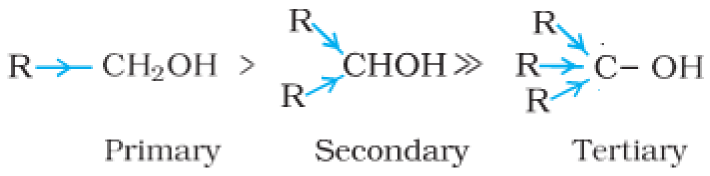






Important Points:

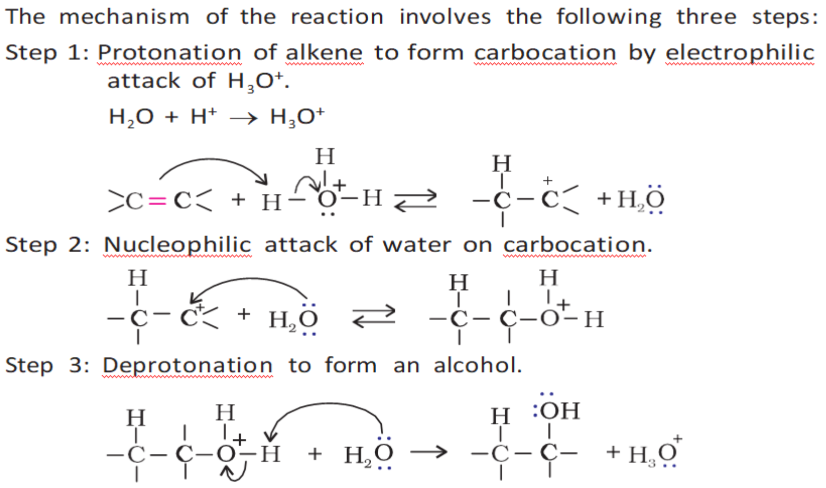
- 1^o, 2^o and 3^o – alcohols can be distinguished by Lucas reagent (conc. HCl + $ZnCl_2$). 3^o alcohol give the turbidity immediatedly as it is most reactive. 2^o – alcohols produces turbidity after 5 minutes, however 1^0- alcohol being least reactive does not produce turbidity at room temperature.
- Acidic Behaviour Of Alcohols: Due to +I effect of alkyl group:



- **Acidic Behaviour of Substituted Phenols :** The presence of e- withdrawing group such as nitro enhances the acidic strength of phenol, however presence of e- releasing group such as methoxy decreases acidic behaviour. This effect is more pronounced when the substituent is present at ortho and para positions.

- Write the mechanism (using curved arrow notation) of the following reaction:

$CH_2 = CH_2 \xrightarrow{H3O+} CH_3\text{-}CH_2OH + H_2O$


The mechanism of the reaction involves the following three steps:

Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+.

$H_2O + H^+ \rightarrow H_3O^+$

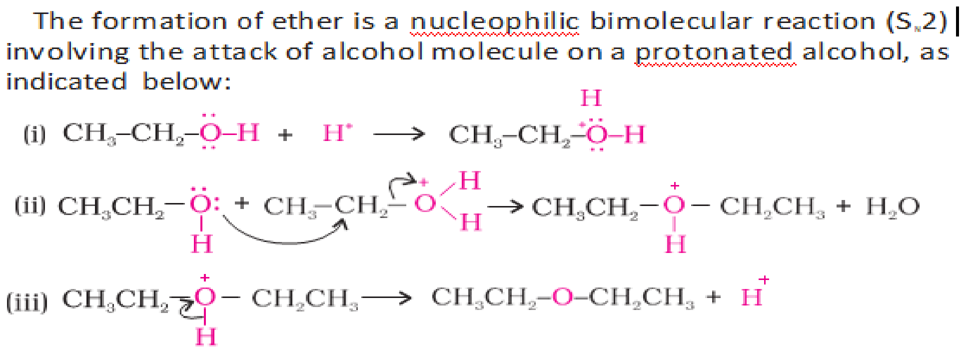
Step 2: Nucleophilic attack of water on carbocation.

Step 3: Deprotonation to form an alcohol.

- Write the mechanism of the following reaction:

$2CH_3CH_2OH \xrightarrow{\text{Conc. } H_2SO_4} CH_3CH_2\text{-}O\text{-}CH_2CH_3$

Mechanism:

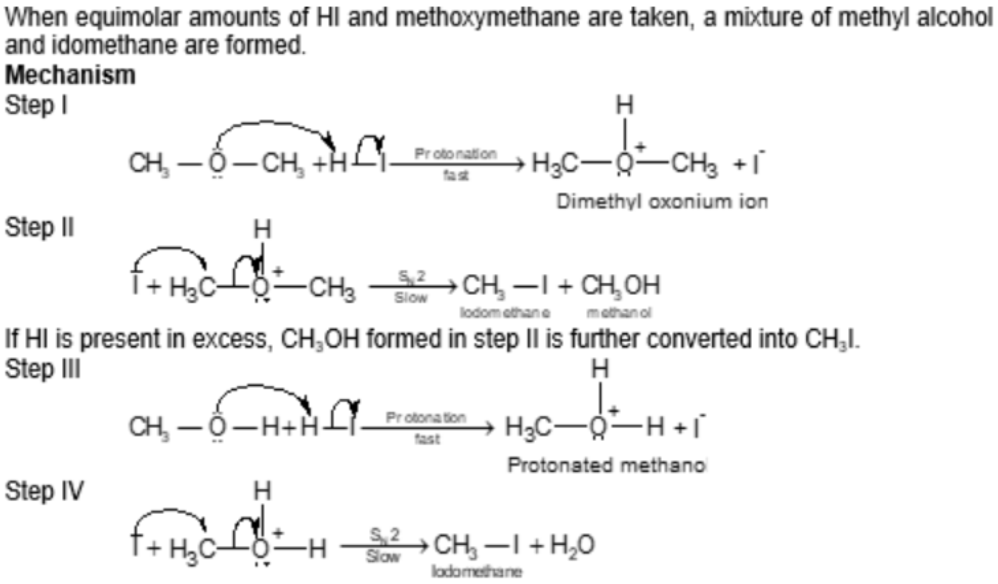

The formation of ether is a nucleophilic bimolecular reaction (S_N2) involving the attack of alcohol molecule on a protonated alcohol, as indicated below:

(i) $CH_3-CH_2-\ddot{O}-H + H^+ \longrightarrow CH_3-CH_2-\overset{H}{\overset{+}{O}}-H$

(ii) $CH_3CH_2-\underset{H}{\ddot{O}}: + CH_3-CH_2-\overset{+}{O}\langle^{H}_{H} \rightarrow CH_3CH_2-\underset{H}{\overset{+}{O}}-CH_2CH_3 + H_2O$

(iii) $CH_3CH_2-\underset{H}{\overset{+}{O}}-CH_2CH_3 \longrightarrow CH_3CH_2-O-CH_2CH_3 + H^+$

- Write the mechanism of reaction of methoxymethane with HI:



When equimolar amounts of HI and methoxymethane are taken, a mixture of methyl alcohol and idomethane are formed.

Mechanism

Step I

$$CH_3-\ddot{O}-CH_3 + H-I \xrightarrow[\text{fast}]{\text{Protonation}} H_3C-\overset{H}{\overset{|}{\ddot{O}^+}}-CH_3 + I^-$$

Dimethyl oxonium ion

Step II

$$I^- + H_3C-\overset{H}{\overset{|}{\ddot{O}^+}}-CH_3 \xrightarrow[\text{Slow}]{S_N2} CH_3-I + CH_3OH$$

Iodomethane methanol

If HI is present in excess, CH_3OH formed in step II is further converted into CH_3I.

Step III

$$CH_3-\ddot{O}-H + H-I \xrightarrow[\text{fast}]{\text{Protonation}} H_3C-\overset{H}{\overset{|}{\ddot{O}^+}}-H + I^-$$

Protonated methanol

Step IV

$$I^- + H_3C-\overset{H}{\overset{|}{\ddot{O}^+}}-H \xrightarrow[\text{Slow}]{S_N2} CH_3-I + H_2O$$

Iodomethane

Multiple Choice Questions:

1. Phenol reacts with bromine in CS_2 at low temperature to give:

a. m-bromophenol
b. o-and p-bromophenol
c. p-bromophenol
d. 2,4,6-tribromophenol
Answer: (b)

2. When phenol is treated with excess bromine water it gives:

a. m-bromophenol
b. o- and p-bromophenol
c. 2,4-dibromophenol
d. 2,4,6-tribromophenol
Answer: (d)

3. The alcohol which does not react with Lucas reagent is at room temperature:

a. isobutyl alcohol
b. n-butanol
c. tert-butyl alcohol
d. sec-butyl alcohol
Answer: (b)

4. Phenol is less acidic than:

a. p-methylphenol
b. p-methoxyphenol
c. p-nitrophenol
d. Ethanol
Answer: (c)

5. Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields.
(a) o-Cresol (b) m-Cresol
(c) 2, 4-Dihydroxytoluene (d) Benzyl alcohol
Ans. (d)

6. CH_3CH_2OH can be converted into CH_3CHO by .
(a) catalytic hydrogenation
(b) treatment with $LiAlH_4$
(c) treatment with pyridinium chlorochromate
(d) treatment with $KMnO_4$
ans. (c)

7. The process of converting alkyl halides into alcohols involves .
(a) addition reaction (b) substitution reaction
(c) dehydrohalogenation reaction (d) rearrangement reaction
Ans. (b) Conversion of alkyl halides into alcohols involves substitution reaction.

8. IUPAC name of m-cresol is .
(a) 3-methylphenol (b) 3-chlorophenol
(c) 3-methoxyphenol (d) benzene- 1,3-diol
Ans. (a)

9. Which of the following compounds will react with sodium hydroxide solution in water?
(a) C_6H_5OH (b) $C_6H_5CH_2OH$ (C) $(CH_3)_3COH$ (d) C_2H_5OH
Ans. (a) Phenol being more acidic reacts with sodium hydroxide solution in water to give sodium phenoxide which is resonance stabilized.
Alcohols are very weak acids.
$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$

10. Arrange the following compounds in increasing order of boiling point. Propan-l-ol, butan-2-ol, pentan-l-ol
(a) Propan-1 -ol, butan-2-ol, butan-1 -ol, pentan-l-ol
(b) Propan-1 -ol, butan-1 -ol, butan-2-ol, pentan-1 -ol
(c) Pentan-1 -ol, butan-2-ol, butan-1 -ol, propan-1 -ol
(d) Pentan-1 -ol, butan-1 -ol, butan-2-ol, propan-1 -ol
Solution: (a) Boiling point increases with increase in molecular mass of the alcohols. Among isomeric alcohols 1° alcohols have higher boiling points than 2° alcohols. Thus, correct order is:
Propan-l-ol < butan-2-ol < butan-l-ol < pentan-l-ol.

Assertion and Reason Type Questions:

In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices:
(a) Assertion and Reason both are correct and Reason is the correct explanation of Assertion.
(b). Both Assertion and Reason are correct but Reason is not the correct explanation of Assertion
(c) Assertion is correct but Reason is wrong.
(d) Assertion is wrong but Reason is correct..

.Question 1. Assertion (A): p-Nitrophenol is more acidic than phenol.
Reason (R): Nitro group helps in the stabilization of the phenoxide ion by dispersal of negative charge due to resonance.
Solution: (a) p-Nitrophenol is more acidic than phenol because nitro group stabilizes phenoxide ion by dispersal of negative charge.

Question 2. Assertion (A): Bond angle in ethers is slightly less than the tetrahedral angle. Reason (R): There is a repulsion between the two bulky (-R) groups.
Solution: (d) Bond angle in ethers is slightly more than the tetrahedral angle due to repulsion between two bulky alkyl group.

.Question 3 Assertion (A): Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid.
Reason (R): Lewis acid polarizes the bromine molecule.
Solution: (d) Bromination of phenol can be carried out in absence of Lewis acid.

Question 4. Assertion (A): Ethanol is a weaker acid than phenol.
Reason (R): Sodium ethoxide may be prepared by the reaction of ethanol with aqueous NaOH.
Solution: (c) Phenol is stronger acid than ethanol as phenoxide ion is stabilized by resonance whereas no such stabilization occurs in ethoxide ion. Sodium ethoxide can be prepared by reaction of ethanol with sodium.

question 5. Assertion (A): Phenols give o-nitrophenol and p-nitrophenol on nitration with cone. HNO_3 and H_2SO_4 mixture.
Reason (R): -OH group in phenol is o-,p-directing.
Solution: (d) Phenols give o, p-nitrophenol on nitration with dil. HNO_3 and with cone.
HNO_3, 2,4, 6-trinitrophenol is formed.

1-Mark Questions:

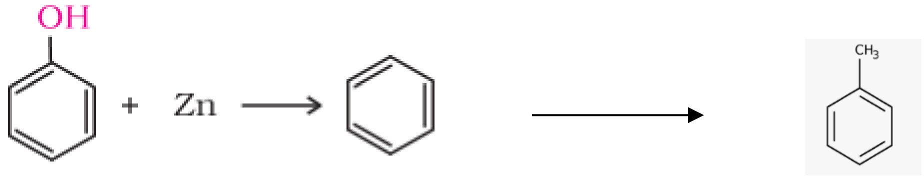
1. How would you convert ethanol to ethene.

   Ans. Ethanol undergoes dehydration by heating it with concentrated H_2SO_4 at 443 K.

   $$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O$$

2. How is toluene obtained from phenol.

   Ans. Phenol is converted to benzene by treating with zinc dust that on Friedel craft alkylation with methyl chloride in presence of anhydrous chloride gives toluene.



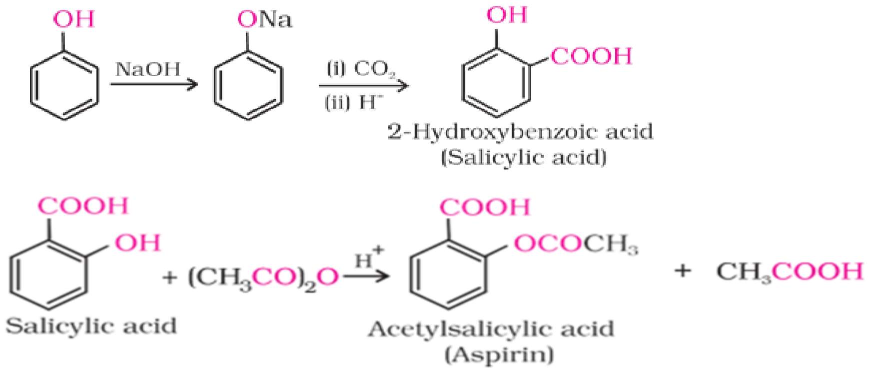
3. Arrange the following compounds in the increasing order of their acid strengths: 4-nitrophenol, phenol, 2,4,6-trinitrophenol.
   Ans. Phenol < 4-nitrophenol < 2,4,6-trinitrophenol
4. Name the reagents used in the following reactions: Friedel-Crafts alkylation of anisole.
   Ans. Alkyl halide in presence of anhydrous $AlCl_3$.
5. What is denatured alcohol?
   Ans. Alcohol is made unfit for drinking by mixing some copper sulphate and pyridine to it. This process is called denaturation of alcohol and alcohol mixed with copper sulphate and pyridine is called denatured alcohol.

6. Out of 2-chloroethanol and ethanol which is more acidic and why?
   Ans. 2-Chloroethanol is more acidic, due to -I effect of chlorine atom.

2- Marks Questions:

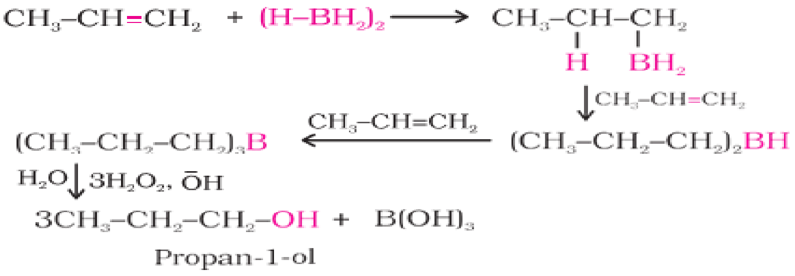
1. Out of o-nitrophenol and p-nitrophenol, which is more volatile? Explain.
   Ans. Ortho nitrophenol is much more volatile in steam due to chelation. Intramolecular hydrogen bonding is present in o-nitrophenol and intermolecular hydrogen bonding in p-nitrophenol.
2. Write steps to carry out the conversion of phenol to aspirin.

Ans. First Phenol is converted to salicylic acid by Kolbe's reaction to produce salicylic acid that on acetylation produces aspirin.

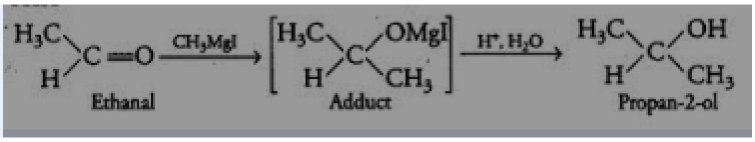


3. How will you convert:
    i. Propene to Propan-1-ol? ii. Ethanal to Propan-2-ol?

Ans.i. Propene to Propan-1-ol:

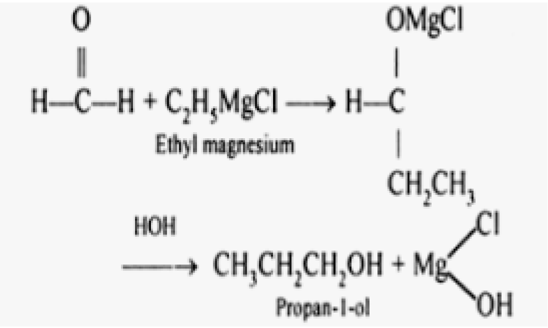


ii. Ethanal to Propan-2-ol

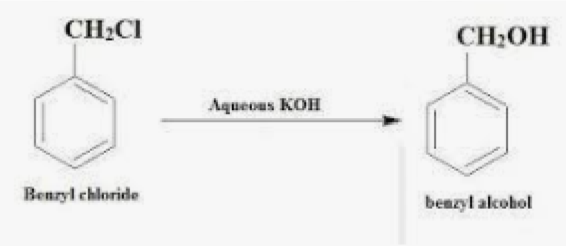


4. How would you carry out the following conversions:
    i. Ethyl magnesium chloride to propan-1-ol
    ii. Benzyl chloride to benzyl alcohol

Ans. i. Ethyl magnesium chloride to propan-1-ol



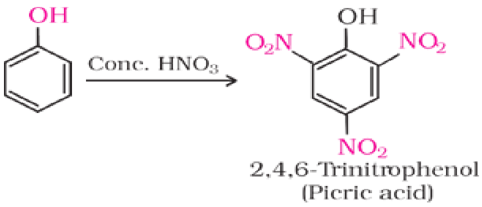
iii. Benzyl chloride to benzyl alcohol



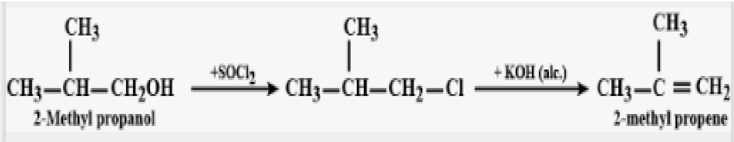
5. How would you obtain:
   - i. Picric acid (2,4,6-trinitrophenol) from phenol?
   - ii. 2-Methylpropene from 2-Methylpropanol?

Ans.

i. Picric acid (2,4,6-trinitrophenol) from phenol:



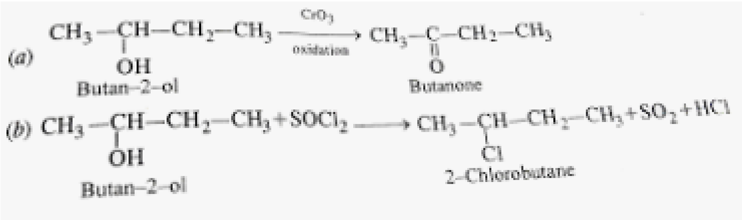
ii. 2-Methylpropene from 2-Methylpropanol:



6. Write the structure of products when Butan-2-ol reacts with the following:

a. CrO_3 b. $SOCl_2$

Ans.



7. i. Arrange the following compounds in the increasing order of their acid strength:

p-cresol, p-nitrophenol, phenol

Ans. i. p-cresol < phenol < p-nitrophenol

8. Answer the following questions:
   - i. Among HI, HBr, HCl, HI is most reactive towards alcohols. Why?
   - ii. Of the two alcohols; (a) $CH_2= CH\text{-}CH_2OH$ and (b) $CH_2 = CH\text{-}CH_2\text{-}CH_2OH$, which one will react most easily with conc. HCl in the presence of $ZnCl_2$?

Ans.i. HI has the lowest bond dissociation energy due to longer bond length that's why it is most reactive.
ii. $CH_2= CH\text{-}CH_2OH$ will react most easily with conc. HCl in the presence of $ZnCl_2$ as carbocation form will be more stable due to resonance.

9. Give reason for the following:
   - i. Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.
   - ii. Ortho-nitrophenol is more acidic than ortho-methoxyphenol.

Ans. i. Alcohols can form hydrogen bonding with water that's why they are more soluble in water, however hydrocarbons cannot form hydrogen bond with water.

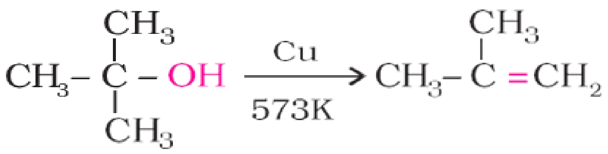
ii. Nitro group is electron withdrawing group and it stabilised the phenoxide ion formed, however methoxy group is electron releasing group that destabilise the phenoxide ion formed. Therefore , ortho-nitrophenol is more acidic than ortho-methoxyphenol.

3-Marks Questions:

1. What happen when:

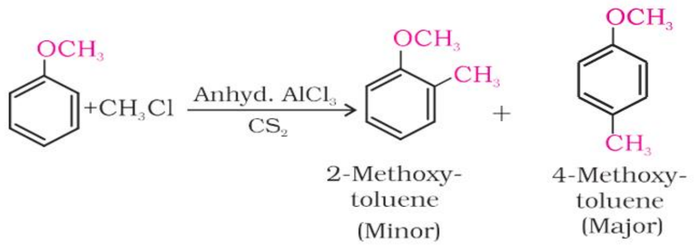
- i. $(CH_3)_3C\text{-}OH$ is treated with Cu at 573 K.
- ii. Anisole is treated with CH_3Cl/anhydrous $AlCl_3$.
- iii. Phenol is treated with Zn dust.

Write chemical reactions in support of your answer.
Ans. i. 3^o alcohol undergo dehydration to form alkene.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow[573K]{Cu} CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$$

ii.



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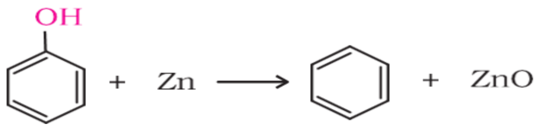


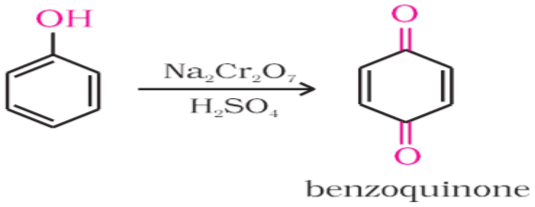
2. How would you obtain the following?

i. Benzoquinone from phenol

ii. 2-Methylpropan-2-ol from methyl magnesium bromide

iii. Propan-2-ol from propene

Ans. i.



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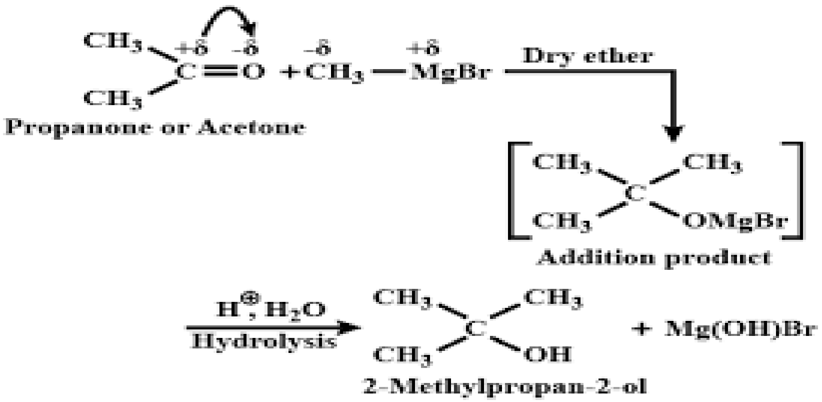

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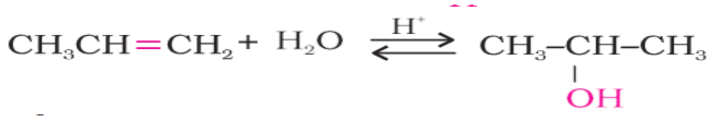
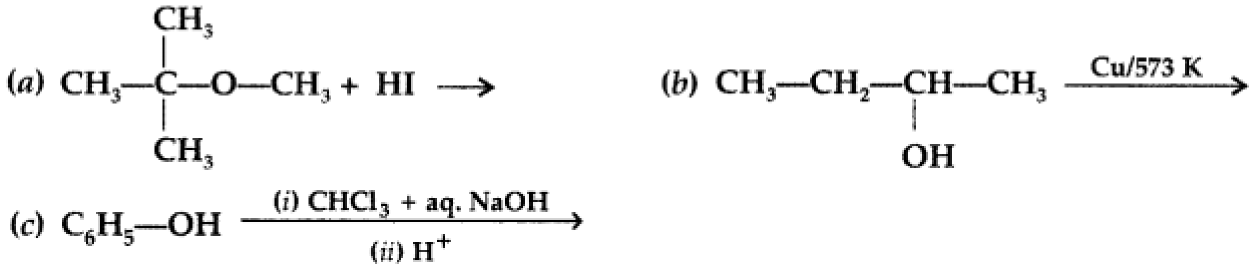


$CH_3CH{=}CH_2 + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3{-}\underset{\underset{OH}{|}}{CH}{-}CH_3$

3. Write the final product(s) in each of the following reactions:

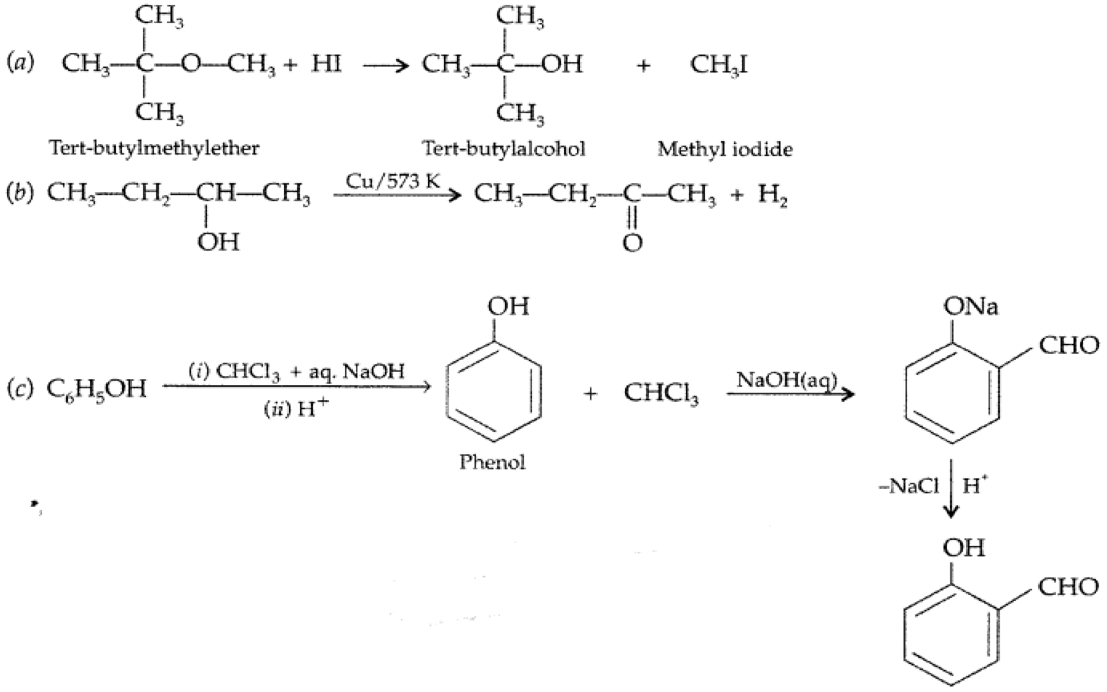


(a) $CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}O{-}CH_3 + HI \longrightarrow$

(b) $CH_3{-}CH_2{-}\underset{\underset{OH}{|}}{CH}{-}CH_3 \xrightarrow{Cu/573\ K}$

(c) $C_6H_5{-}OH \xrightarrow[(ii)\ H^+]{(i)\ CHCl_3\ +\ aq.\ NaOH}$

Answer:



(a) $CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}O{-}CH_3 + HI \longrightarrow CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}OH + CH_3I$

(b) $CH_3{-}CH_2{-}\underset{\underset{OH}{|}}{CH}{-}CH_3 \xrightarrow{Cu/573\ K} CH_3{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + H_2$

Case Study Type Questions:

Read the passage given below and answer the following questions

The facility with which the aromatic ring of phenols and phenol ethers undergoes electrophilic substitution has been noted. Two examples are shown in the following diagram. The first shows the Friedel-Crafts synthesis of the food preservative BHT from para-cresol. The second reaction is interesting in that it further demonstrates the delocalization of charge that occurs in the phenolate anion. Carbon dioxide is a weak electrophile and normally does not react with aromatic compounds; however, the negative charge concentration on the phenolate ring enables the carboxylation reaction shown in the second step. The sodium salt of salicylic acid is the major product, and the preference for ortho substitution may reflect the influence of the sodium cation. This is called the Kolbe-Schmidt reaction, and it has served in the preparation of aspirin, as the last step illustrates.

Q 1. IUPAC name of salicylic acid

(a) o-Hydroxybenzoic acid
(b) p- Hydroxybenzoic acid
(c) 2- Hydroxybenzoic acid
(d) 3- Hydroxybenzoic acid

Ans 1. (c) 2- Hydroxybenzoic acid

Q 2. Salicylic acid heated with acetic anhydride to form a compound which is very useful drug which lower the body temperature as well as use to prevent heart attack. What is the name of compound?

(a) 3-Acetyl Salicylic acid
(b) 2-Acetyl Salicylic acid
(c) 2-Acetoxybenzoic acid
(d) 3-Acetoxybenzoic acid

Ans 2. (c) 2-Acetoxybenzoic acid

Q 3. Salicylic acid is heated with acetic anhydride to form a compound. In this reaction which bond is cleavage in Salicylic acid?

(a) O-H bond of -COOH group
(b) O-O bond of -COOH group
(c) C-O bond of benzene ring and phenolic group
(d) O-H bond of phenolic group

Ans 3. (d) O-H bond of phenolic group

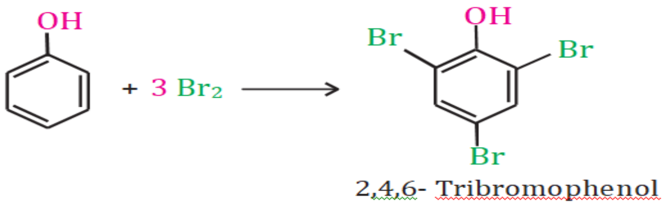
5-Marks Questions:

1. i. What happens when:
   a. Phenol reacts with bromine water?
   b. Ethanol reacts with CH_3COCl/pyridine?
   c. Anisole reacts with HI? Write the chemical reactions involved in the above reactions.

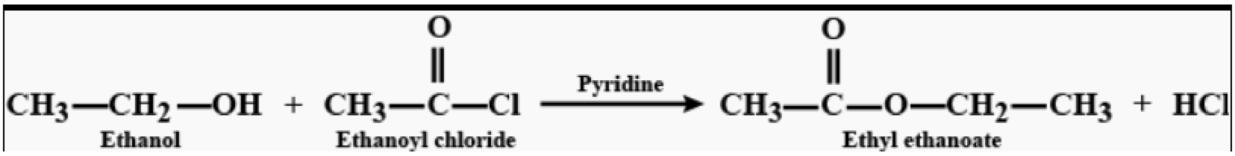
ii. Distinguish between:

   a. Ethanol and Phenol.
   b. Propan-2-ol and 2-methylpropan-2-ol.

Ans. i. a. Phenol reacts with bromine water to form 2,4,6-tribromophenol.

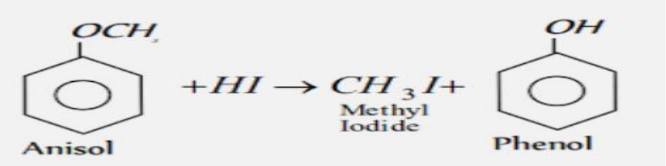


b. Ethanol reacts with CH_3COCl/pyridine to form ethyl ethanoate ester.



$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} + \underset{\text{Ethanoyl chloride}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} \xrightarrow{\text{Pyridine}} \underset{\text{Ethyl ethanoate}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_3} + HCl$$

c. Anisole reacts with HI methyl iodide and phenol.



ii. a.

1	Phenol	Ethanol
Bromine water test	White precipitate formation	No characteristic reaction

Propan-2-ol is 2^{o}- alcohol and give ppt with Lucas reagent (conc. HCl + $ZnCl_2$) after 5 minute at room temperature, however 2-methylpropan-2-ol is 3^{o} alcohol that give ppt with Lucas reagent immediately.

2. i. Write the formula of reagents used in the following reactions:
   a. Bromination of Phenol to 2,4,6-tribromophenol.
   b. Propene to propanol.
   c. Phenol to picric acid

   ii. Arrange the following compounds in the increasing order of their property indicated:
   a. p-nitrophenol, ethanol, phenol (acidic character)
   b. propanol, propane, propanal (boiling point)

   Ans. i. a. Bromine water.

b. Diborane $(BH_3)_2$ reacts with alkenes to give trialkyl boranes as

addition product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.
c. concentrated nitric acid

ii. a. Ethanol < phenol < p-nitrophenol.

b. propane < prop anal < propanol.

3. A compound 'A' with molecular formula $C_4H_{10}O$ is a unreactive towards sodium metal. It does not discourse Bromine water and does not react with NaHSO3 solution. On refluxing 'A' with excess of HI gives 'B' which react with aq. NaOH to form 'C'. 'C'can be converted into 'B' by reacting with P and I_2 . 'C' on heating with conc. H2SO4 forms 'D' decolorizes bromine water. Identify A to D and write the reactions involved.

Ans . A is not alcohol therefore it does not react with Sodium metal. 'A' is not aldehydes and ketones as it does not react with NaHSO3 'A' is not unsaturated hydrocarbon as it does not add Br2 (aq) . It is likely to be ether.

$CH_3CH_2OC2H_5$ + 2HI ---------→ $2C_2H_5I$ + H2O
'A' excess 'B'

$2C_2H_5I$ + NaOH (aq) --------→ C_2H_5OH + NaI
'B' 'C'

C_2H_5OH + (P/I2) ---------→ C_2H_5I
C B

C_2H_5OH + Conc. H_2SO_4 ------→ C_2H_4
C D

CHAPTER 8.

ALDEHYDES KETONES AND CARBOXYLIC ACIDS

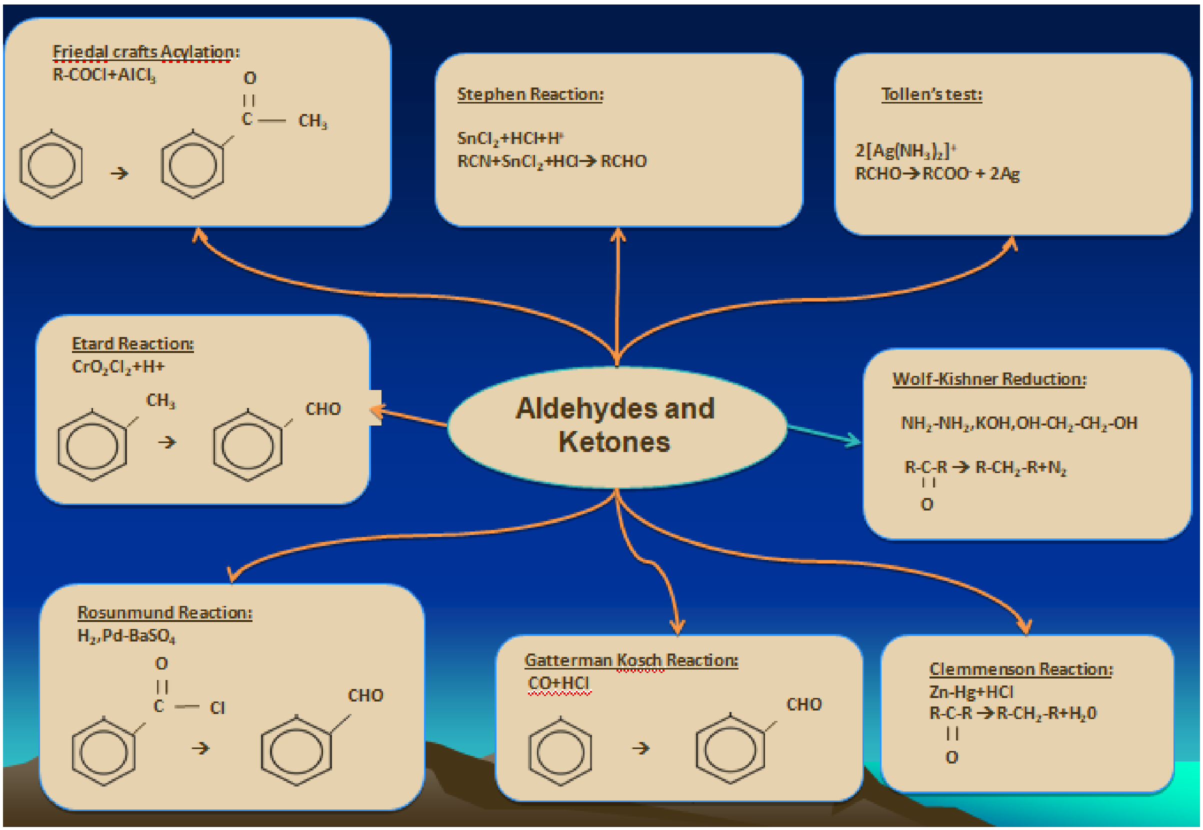
KEY POINTS

1	In aldehydes, the carbonyl group is bonded to a carbon and hydrogen while in the ketones, it is bonded to two carbon atoms. The carbonyl compounds in which carbonyl group is bonded to oxygen are known as carboxylic acids.
2	They boil at higher temperatures than the corresponding hydrocarbons and weakly polar compounds such as ethers.
3	Lower members are soluble in water because they can form H-bond with water. Higher members are insoluble in water due to large size of their hydrophobic group.
4	The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending –e with –al and –one respectively.
5	The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses. It is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions. Also, their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding. The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportions, because they form hydrogen bond with water.
6	Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups

	reduce the electrophilicity of the carbonyl carbon more effectively than in former.
7	Both aldehydes and ketones can be prepared by ozonolysis of alkenes.
8	Aldehydes and ketones are reduced to primary and secondary alcohols respectively by sodium borohydride ($NaBH_4$) or lithium aluminium hydride ($LiAlH_4$) as well as by catalytic hydrogenation.
9	Aldehydes differ from ketones in their oxidation reactions. Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidising agents, mainly Tollens' reagent and Fehlings' reagent also oxidise aldehydes.
10	Ketones are generally oxidised under vigorous conditions, i.e.,strong oxidising agents and at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage to afford a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone.
11	Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom (methyl ketones) are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound.
12	Iodoform reaction with sodium hypoiodite is also used for detection of CH_3CO group or $CH_3CH(OH)$ group which produces CH_3CO group on oxidation.
13	The acidity of α-hydrogen atoms of carbonyl compounds is due to the strong electron withdrawing effect of the carbonyl group and resonance stabilisation of the conjugate base.
14	Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and *meta*-directing group.
15	Physical properties of carboxylic acids: **(i)Solubility:** As the size of alkyl group increases solubility of carboxylic acid decreases because non-polar part of the acid increases **(ii)Boiling points:** Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to extensive association of carboxylic acid molecules through intermolecular hydrogen bonding.
16	Smaller the p*Ka*, the stronger the acid. Carboxylic acids are weaker than mineral acids, but they are stronger acids than alcohols and many simple phenols.
17	Carboxylic acids are reduced to primary alcohols by lithium aluminium hydride or better with diborane. Diborane does not easily reduce functional groups such as ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.
18	Carboxylic acids lose carbon dioxide to form hydrocarbons when their sodium salts are heated with sodalime (NaOH and CaO in the ratio of 3:1). The reaction is known as decarboxylation.
19	Effect of electron donating substituent on the acidity of carboxylic acids: Electron donating substituent decreases stability of carboxylate ion by intensifying

	the negative charge and hence decreases acidity of carboxylic acids.
20	Effect of electron withdrawing substituent on the acidity of carboxylic acids: Electron withdrawing group increases the stability of carboxylate ion by delocalizing negative charge and hence, increases acidity of carboxylic acid.

NAME REACTIONS – FLOW CHART



Aldehydes and Ketones

Friedal crafts Acylation:
$R\text{-}COCl + AlCl_3$
O
| |
C — CH_3

Stephen Reaction:
$SnCl_2 + HCl + H^+$
$RCN + SnCl_2 + HCl \rightarrow RCHO$

Tollen's test:
$2[Ag(NH_3)_2]^+$
$RCHO \rightarrow RCOO^- + 2Ag$

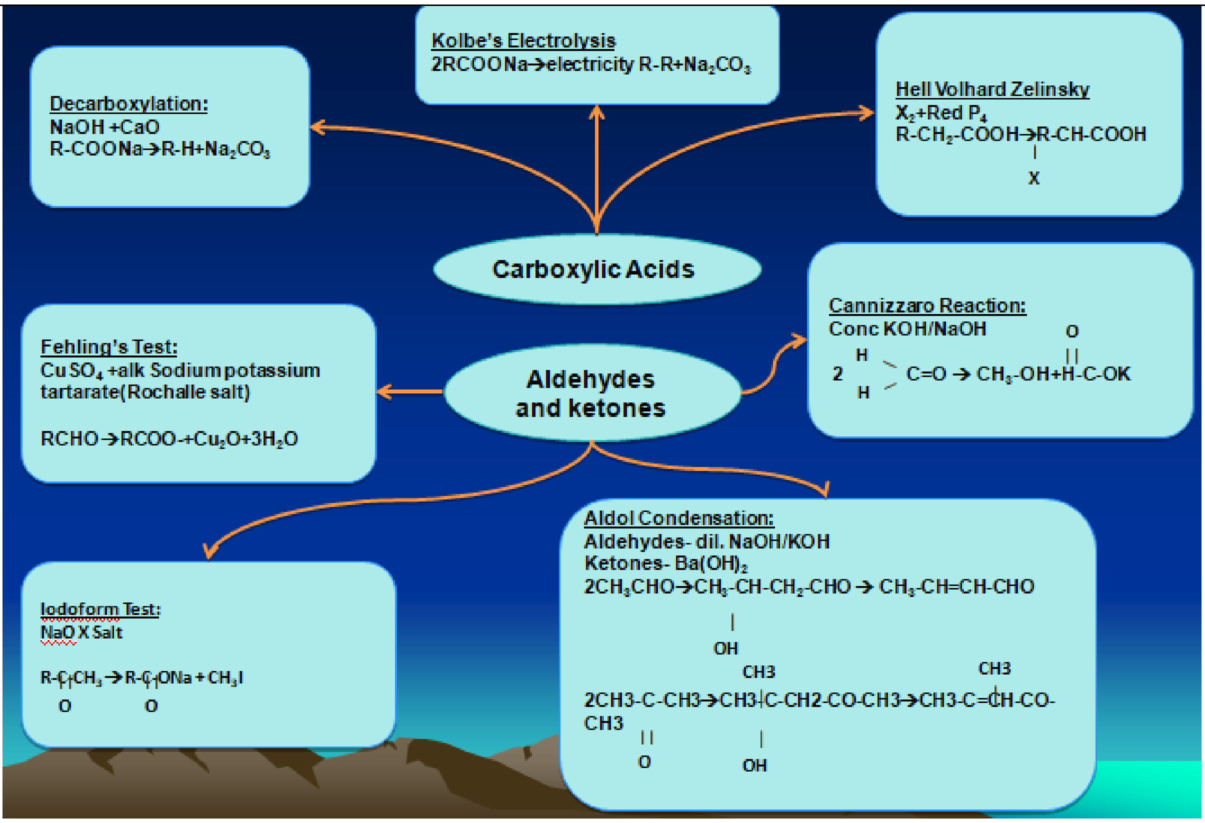
Etard Reaction:
$CrO_2Cl_2 + H+$
CH_3 → CHO

Wolf-Kishner Reduction:
$NH_2\text{-}NH_2, KOH, OH\text{-}CH_2\text{-}CH_2\text{-}OH$
R-C-R → $R\text{-}CH_2\text{-}R + N_2$
| |
O

Rosunmund Reaction:
$H_2, Pd\text{-}BaSO_4$
O
| |
C — Cl
→ CHO

Gatterman Kosch Reaction:
CO+HCl
→ CHO

Clemmenson Reaction:
Zn-Hg+HCl
R-C-R → $R\text{-}CH_2\text{-}R + H_20$
| |
O



Decarboxylation:
NaOH +CaO
$R\text{-}COONa \rightarrow R\text{-}H + Na_2CO_3$

Kolbe's Electrolysis
$2RCOONa \rightarrow$ electricity $R\text{-}R + Na_2CO_3$

Hell Volhard Zelinsky
X_2+Red P_4
$R\text{-}CH_2\text{-}COOH \rightarrow R\text{-}\underset{X}{\underset{|}{CH}}\text{-}COOH$

Carboxylic Acids

Fehling's Test:
$CuSO_4$ +alk Sodium potassium tartarate(Rochalle salt)

$RCHO \rightarrow RCOO^- + Cu_2O + 3H_2O$

Aldehydes and ketones

Cannizzaro Reaction:
Conc KOH/NaOH
$2\ \begin{matrix} H \\ H \end{matrix} > C{=}O \rightarrow CH_3\text{-}OH + H\text{-}\overset{O}{\overset{||}{C}}\text{-}OK$

Aldol Condensation:
Aldehydes- dil. NaOH/KOH
Ketones- $Ba(OH)_2$
$2CH_3CHO \rightarrow CH_3\text{-}\underset{OH}{\underset{|}{CH}}\text{-}CH_2\text{-}CHO \rightarrow CH_3\text{-}CH{=}CH\text{-}CHO$
$2CH3\text{-}\underset{O}{\underset{||}{C}}\text{-}CH3 \rightarrow CH3\text{-}\overset{CH3}{\underset{OH}{\underset{|}{C}}}\text{-}CH2\text{-}CO\text{-}CH3 \rightarrow CH3\text{-}\overset{CH3}{C}{=}CH\text{-}CO\text{-}CH3$

Iodoform Test:
NaO X Salt

$R\text{-}\underset{O}{\underset{||}{C}}\text{-}CH_3 \rightarrow R\text{-}\underset{O}{\underset{||}{C}}\text{-}ONa + CH_3I$

MULTIPLE CHOICE QUESTIONS

1) The most suitable reagent for the conversion of $R\text{-}CH_2OH \rightarrow RCHO$ is
(a) $KMnO_4$ (b) $K_2Cr_2O_7$ (c) CrO_3 (d) PCC (Pyridimium chlorochromate)

Answer: (d) PCC (Pyridimium chlorochromate)

2) The reagent used for separation of acetaldehyde and acetophenone is

(a) $NaHSO_3$ (b) $C_6H_5NH\ NH_2$ (c) NH_2OH (d) $NaOH\text{-}I_s$

Answer: (a) $NaHSO_3$

3) An alkene C_7H_{14} on reductive ozonolysis gives an aldehyde with formula C_3H_6O and a ketone. The ketone is
(a) butan-2-one (b) pentan-2-one (c) pentan-3-one (d) propanone

Answer: (a) butan-2-one

4) HVZ reaction is used to prepare

(a) ß-haloacid (b) α-haloacid (c) α, ß-unsaturated add (d) None of these

Answer: (b) α-haloacid

5) Methyl ketones are usually characterised through

(a) Tollen's reagent (b) Iodoform test (c) Schiff'stest (d) Benedict solution test.

Answer: (b) Iodoform test

6) Ethanal can be prepared from ethyne by
(a) passing a mixture of ethyne and steam over a catalyst, magnesium at 420°C
(b) passing a mixture of ethyne and ethanol over a catalyst zinc chromite
(c) boiling ethyne with water in the presence of $HgSO_4$ and H_2SO_4
(d) treating ethyne with iodine and NaOH

Answer: (c) boiling ethyne with water in the presence of $HgSO_4$ and H_2SO_4
7) The addition of HCN to carbonyl compounds is an example of
(a) nucleophilic addition
(b) electrophilic addition
(c) free radical addition
(d) electromeric addition

Answer: (a) nucleophilic addition

8) Aldehydes other than formaldehyde react with Grignard's reagent to give addition products which on hydrolysis give
(a) tertiary alcohols
(b) secondary alcohols
(c) primary alcohols
(d) carboxylic acids

Answer: (b) secondary alcohols

9) Which of the following will not give aldol condensation?
(a) Phenyl acetaldehyde
(b) 2-Methylpentanal
(c) Benzaldehyde
(d) 1-Phenylpropanone

Answer: (c) Benzaldehyde

10) The product of hydrolysis of ozonide of 1-butene are
(a) ethanol only
(b) ethanal and methanal
(c) propanal and methanal
(d) methanal only

Answer: (c) propanal and methanal

11) α-Hydroxypropanoic acid can be preapred from ethanal by following the steps given in the sequence
(a) Treat with HCN followed by acidic hydrolysis
(b) Treat with $NaHSO_3$ followed by reaction with Na_2CO_3
(c) Treat with H_2SO_4 followed by hydrolysis
(d) Treat with $K_2Cr_2O_7$ in presence of sulphuric acid

Answer: (a) Treat with HCN followed by acidic hydrolysis

12) Which of the following compounds will undergo Cannizzaro reaction?
(a) CH_3CHO
(b) CH_3COCH_3
(c) C_6H_5CHO
(d) $C_6H_5CH_2CHO$

Answer: (c) C_6H_5CHO

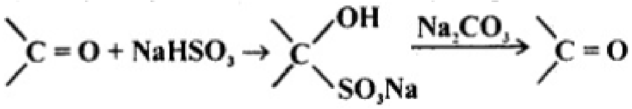
13) Benzoyl Chloride on reduction with H_2/Pd-$BaSO_4$ produces
(a) benzoic acid
(b) benzyl alochol
(c) benzoyl sulphate
(d) benzaldehyde

Answer: (d) benzaldehyde

14) Which of the following does not undergo Cannizzarro's reaction?
(a) Benzaldehyde
(b) 2-Methylpropanal
(c) p-Methoxybenzaldehyde
(d) 2, 2-Dimethylpropanal

Answer: (b) 2-Methylpropanal

15) Study the given reaction and identify the process which is carried out



(a) It is used for purification of aldehydes and ketones
(b) It is used to distinguish aldehydes from ketones
(c) It is used to prepare cyclic aldehydes and ketones
(d) It is used to study polar nature of aldehydes and ketones

Answer: (a) It is used for purification of aldehydes and ketones

16) Hydrocarbons are formed when aldehydes and ketones are reacted with amalgamated zinc and conc. HCl. The reaction is called
(a) Cannizzaro reaction
(b) Clemmensen reduction
(c) Rosenmund reduction
(d) Wolff-Kishner reduction

Answer: (b) Clemmensen reduction

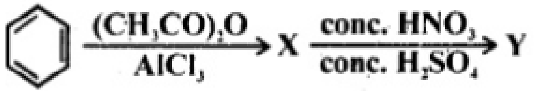
17) When propanal reacts with 2-methylpropanal in presence of NaOH, four different products are formed. The reaction is known as
(a) Aldol condensation
(b) Cross aldol condensation
(c) Cannizzaro reaction
(d) HVZ condensation

Answer: (b) Cross aldol condensation

18) Which of the following does not answer iodoform test?
(a) n-Butyl alcohol
(b) sec-Butyl alcohol
(c) Acetophenone
(d) Acetaldehyde

Answer: (a) n-Butyl alcohol

19) Identify the products (X) and (Y) in the given reaction



(a) X = Acetophenone, Y = m-Nitroacetophone
(b) X = Toluene, Y = m-Nitroacetotoluene
(c) X = Acetophenone, Y = o- and p-Dinitroacetophenone
(d) X = Benzaldehyde, Y = m-Nitrobenzaldehyde

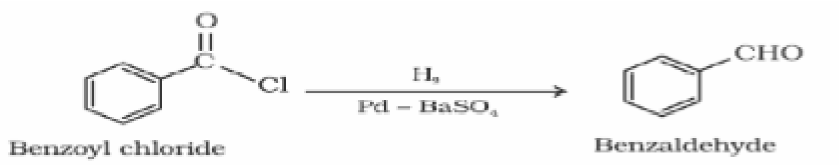
Answer: (a) X = Acetophenone, Y = m-Nitroacetophone

20) Which of the following compound will undergo self aldol condensation in the presence of cold dilute alkali?
(a) $CH \equiv C\text{-}CHO$
(b) $CH_2 = C(CH_3)CHO$
(c) C_6H_5CHO
(d) CH_3CH_2CHO

Answer: (d) CH_3CH_2CHO

NAME RECTIONS

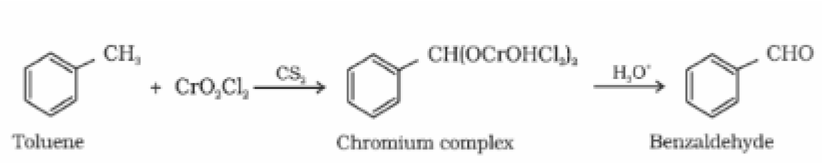
(i) Rosenmund reduction:



(ii) Stephen Reaction:

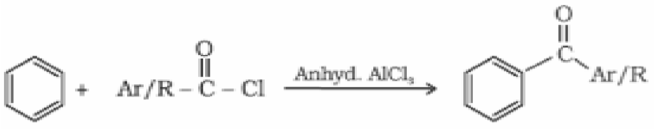
$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3\overset{+}{O}} RCHO$$

(iii) Etard Reaction:



(iv) Gatterman – Koch reaction:

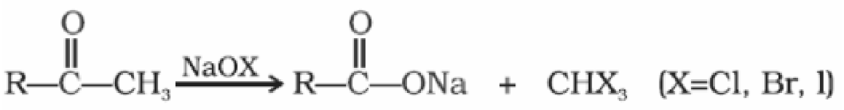
(v) Friedel Crafts acylation reaction:



(vi) Clemmensen reduction:

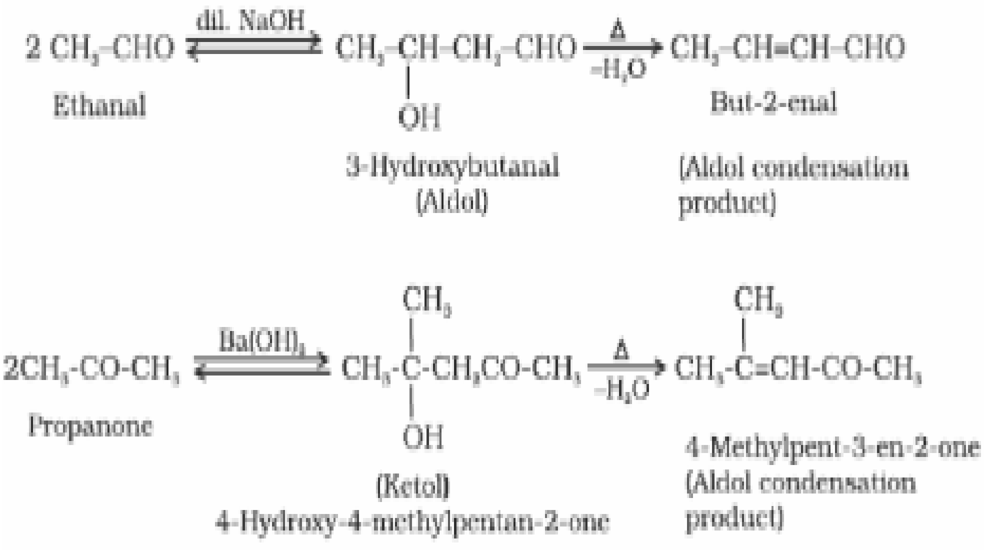
(vii) Wolff-Kishner reduction:

(viii) Haloform reaction:

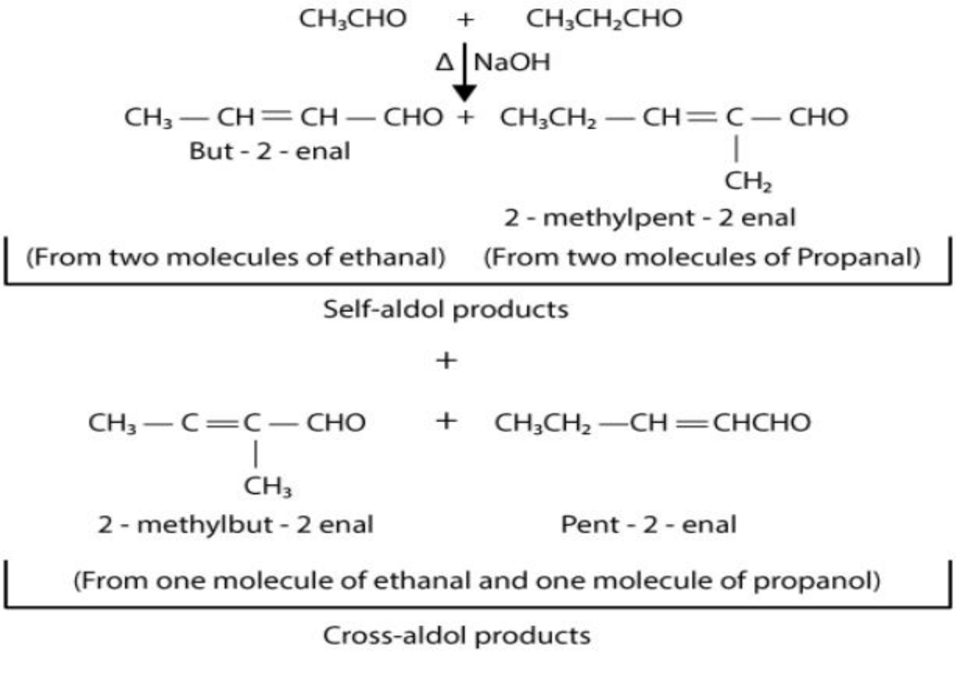


(ix) Aldol condensation:

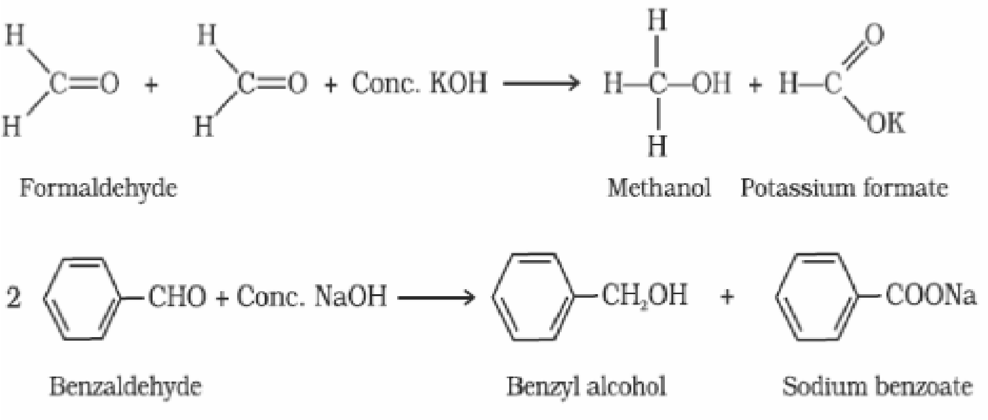
(α -hydrogen containing aldehydes and ketones - e.g. Ethanal, Propanone, Acetophenone)



(x) Cross aldol condensation:

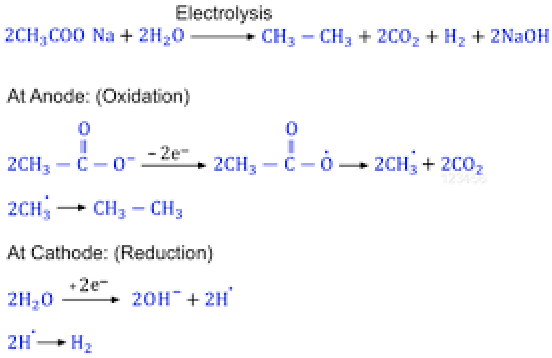


(xi) Canizzaro reaction: (aldehydes which do not contain α-hydrogen - e.g. Methanal, benzaldehyde)



(xii) Kolbe electrolysis

Alkali metal salts of carboxylic acids also undergo decarboxylation on electrolysis of their aqueous solutions and form hydrocarbons having twice the number of carbon atoms present in the alkyl group of the acid.



$$2CH_3COO\,Na + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH$$

At Anode: (Oxidation)

$$2CH_3-\overset{\overset{\large O}{\|}}{C}-O^- \xrightarrow{-2e^-} 2CH_3-\overset{\overset{\large O}{\|}}{C}-\dot{O} \longrightarrow 2CH_3^{\bullet} + 2CO_2$$

$$2CH_3^{\bullet} \longrightarrow CH_3-CH_3$$

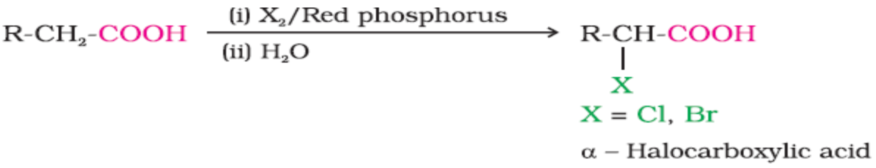
At Cathode: (Reduction)

$$2H_2O \xrightarrow{+2e^-} 2OH^- + 2H^{\bullet}$$

$$2H^{\bullet} \longrightarrow H_2$$

(xiii) Hell-Volhard-Zelinsky reaction

Carboxylic acids having an alpha hydrogen are halogenated at the alpha position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give alpha-halocarboxylic acids.



$$R\text{-}CH_2\text{-}COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{Red phosphorus}} R\text{-}\underset{\underset{X}{|}}{C}H\text{-}COOH$$

X = Cl, Br

α – Halocarboxylic acid

DISTINCTION OF ORGANIC COMPOUNDS

Distinguish between the following:-

a) Phenol and alcohol
b) Benzaldehyde and Propanal
c) Acetic acid and formic acid
d) Benzophenone and acetophenone
e) Ethanal and propanal
f) Propanol and ethanol
g) Pentan-2-one and pentan-3-one
h) Benzoic acid and benzene
i) Phenol and benzoic acid
j) Benzaldehyde and acetophenone
k) Methanol and benzaldehyde

Phenol It gives violet colour with $FeCl_3$	**Alcohol** It doesn't give violet colour with $FeCl_3$
Benzaldehyde It doesn't give brick red ppt with Fehling’s solution A & B	**Propanal** It gives brick red ppt with Fehling’s solution A & B
Acetic acid • It doesn't give silver mirror with Tollen’s reagent(ammonical silver nitrate) • It doesn't give brick red ppt with Fehlings solution A & B	**Formic acid** • It gives silver mirror with Tollen's reagent (ammonical silver nitrate). • It gives brick red ppt with Fehling’s solution A & B
Benzophenone It doesn't give yellow ppt of iodoform with Iodine and NaOH or NaOI	**Acetophenone** It gives yellow ppt of iodoform with Iodine and NaOH or NaOI
Ethanal It gives yellow ppt of iodoform with Iodine and NaOH or NaOI	**Propanal** It does not gives yellow ppt of iodoform with Iodine and NaOH or NaOI
Propanol It does not gives yellow ppt of iodoform with Iodine and NaOH or	**Ethanol** It gives yellow ppt of iodoform with Iodine and NaOH or NaOI

NaOI	
Pentan-2-one It gives yellow ppt of iodoform with Iodine and NaOH or NaOI	**Pentan-3-one** It does not gives yellow ppt of iodoform with Iodine and NaOH or NaOI
Benzoic acid Gives effervescence of CO_2 with $NaHCO_3$	**Benzene** no effervescence of CO_2 with $NaHCO_3$
Phenol • No effervescence of CO_2 with $NaHCO_3$ • It gives violet colour with $FeCl_3$	**Benzoic acid** • Gives Effervescence of CO_2 with $NaHCO_3$ • It doesn't give violet colour with $FeCl_3$
Benzaldehyde • It gives silver mirror with Tollen's reagent • It does not give yellow ppt of iodoform with iodine and NaOH or NaOI	**Acetophenone** • It does not gives silver mirror with Tollen's reagent • It gives yellow ppt of iodoform with Iodine and NaOH or NaOI
Methanal It gives brick red ppt with Fehling's solution A & B	**Benzaldehyde** It does not give brick red ppt with Fehling solution A & B

ASSERTION (A) REASON (R) TYPE QUESTIONS:

Here two statements are given - one labelled Assertion (A) and the other labelled Reason (R).
Select the correct answer to these questions from the codes (i), (ii), (III), and (IV) as given below:

(i) Both assertion (A) and reason (R) are correct statements, and reason (R) is the correct explanation of the assertion (A).
(ii) Both assertion (A) and reason (R) are correct statements, but reason (R) is not the correct
explanation of the assertion (A)
(iii) Assertion (A) is correct statement, but reason (R) is incorrect statement.
(iv) Assertion (A) is incorrect statement, but reason (R) is correct statement.

1) Assertion (A): p-Chloro benzoic acid is stronger acid than benzoic acid
Reason(R): Chlorine has electron donating resonance effect(+R)

Ans: (ii)

2) Assertion (A): Aldehyde and ketone have higher boiling point than alcohols.
Reason(R): Alcohols are associated by intermolecular hydrogen bonding while aldehyde and ketone lack hydrogen bonding.

Ans: (iv)

3) Assertion (A): $LiAlH_4$ is used as a reducing agent in organic synthesis.
Reason(R): $LiAlH_4$ is a hydride donor.
Ans: (i)

4) Assertion (A): Aldehyde and ketone both reacts with Tollen's reagent.
Reason(R): Both aldehyde and ketone contain a carbonyl group.
Ans: (iv)

5) Assertion (A): Formaldehyde is a planar molecule.
Reason (R): It contains sp^2 hybridised carbon atom.
Ans: (i)

6) Assertion (A): Compounds containing -CHO group are easily oxidized to corresponding carboxylic acids.
Reason (R): Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$.
Ans: (ii)

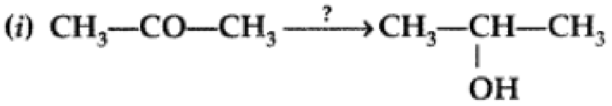
7) Assertion (A): Aldehydes and ketones, both react with Tollen's reagent to form silver mirror.
Reason (R): Both aldehydes and ketones contain a carbonyl group.
Ans: (iv)

8) Assertion (A): $(CH_3)_3C\text{-}COOH$ does not undergo HVZ reaction
Reason (R): It does not have any α- hydrogen
Ans: (i)

9) Assertion (A): Phenol and benzoic acid can be distinguished by NaOH.
Reason (R): Benzoic acid is a stronger acid than phenol.
Ans: (iv)

Short Answer Type-TWO MARKS

1) Name the reagents used in the following reactions :



(*i*) $CH_3{-}CO{-}CH_3 \xrightarrow{?} CH_3{-}\underset{\underset{OH}{|}}{CH}{-}CH_3$

(*ii*) $C_6H_5{-}CH_2{-}CH_3 \xrightarrow{?} C_6H_5{-}COO^-K^+$

Answer:

(i) LiAlH4 (Lithium Aluminium Hydride)
(ii) (ii) KMnO4 (Alkaline Potassium Permanganate)

2) Write the reagents required in the following reactions :

(*i*) $CH_2 = CH{-}CH_2OH \xrightarrow{?} CH_2 = CH{-}CHO$

(*ii*) $CH_3{-}COOH \xrightarrow{?} CH_3{-}CONH_2$

Answer:

(*i*) $CH_2 = CH{-}CH_2OH \xrightarrow{PCC} CH_2 = CH{-}CHO$

(*ii*) $CH_3{-}COOH \xrightarrow[\Delta]{NH_3} CH_3{-}CONH_2$

3) Arrange the following compounds in increasing order of their property as indicated :

(i) CH_3COCH_3, $C_6H_5COCH_3$, CH_3CHO (reactivity towards nucleophilic addition reaction)
(ii) Cl—CH_2—COOH, F—CH_2—COOH, CH_3—COOH (acidic character)

Answer:

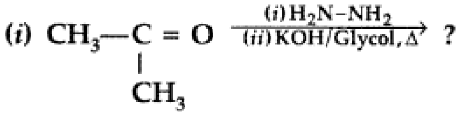
(i) $C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO$ (Reactivity towards nucleophilic addition)
(ii)

$CH_3{-}COOH < \underset{\underset{Cl}{|}}{CH_2}{-}COOH < F{-}CH_2{-}COOH$

(Increasing acidic character)

<u>Short Answer Type –THREE MARKS</u>

1) Predict the products of the following reactions :

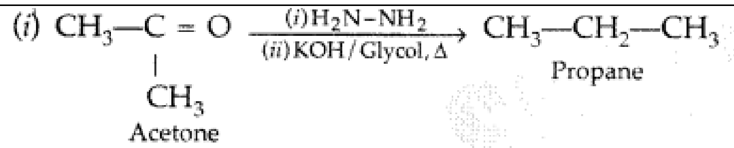


(*i*) $CH_3{-}\underset{\underset{CH_3}{|}}{C} = O \xrightarrow[(ii)\,KOH/Glycol,\,\Delta]{(i)\,H_2N{-}NH_2} ?$

(*ii*) $C_6H_5{-}CO{-}CH_3 \xrightarrow{NaOH/I_2} ? + ?$

(*iii*) $CH_3COONa \xrightarrow[\Delta]{NaOH/CaO} ?$

Answer:



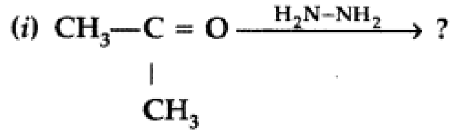
(i) $CH_3-\underset{\underset{CH_3}{|}}{C}=O \xrightarrow[(ii)\,KOH/Glycol,\,\Delta]{(i)\,H_2N-NH_2} \underset{\text{Propane}}{CH_3-CH_2-CH_3}$

Acetone

(ii) $\underset{\text{Acetophenone}}{C_6H_5-CO-CH_3} \xrightarrow{NaOH/I_2} \underset{\text{Sodium benzoate}}{C_6H_5COONa} + \underset{\text{Iodoform}}{CHI_3} + NaI + H_2O$

(iii) $CH_3COONa \xrightarrow[\Delta]{NaOH/CaO} CH_4 + Na_2CO_3$

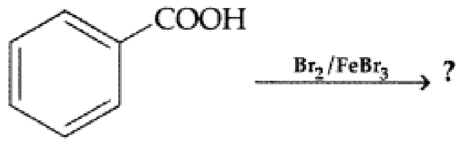
2) Predict the products of the following reactions :

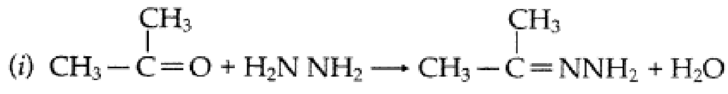


(i) $CH_3-\underset{\underset{CH_3}{|}}{C}=O \xrightarrow{H_2N-NH_2} ?$

(ii) $C_6H_5-CH_3 \xrightarrow[(b)\,H^+]{(a)\,KMnO_4/KOH} ?$

(iii)

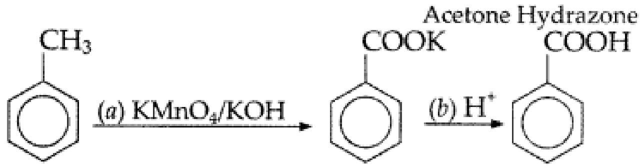




(i) $CH_3-\overset{\overset{CH_3}{|}}{C}=O + H_2N\,NH_2 \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{C}=NNH_2 + H_2O$

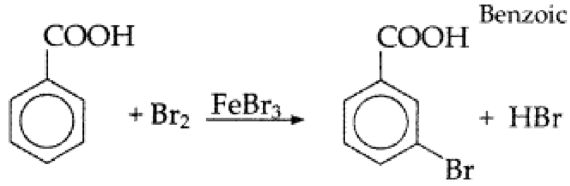
Acetone Hydrazone

(ii)



Benzoic Acid

(iii)

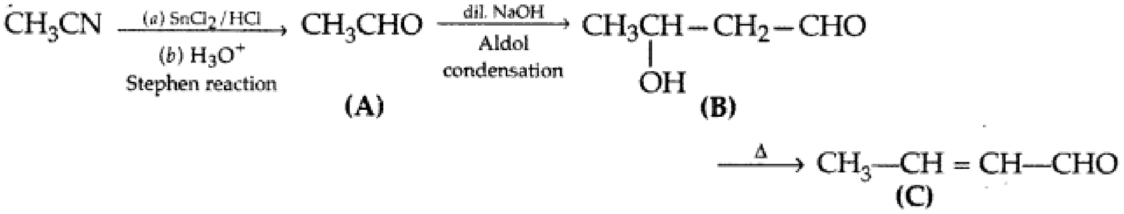


m-bromobenzoic acid

3) Write structures of compounds A, B and C in each of the following reactions:

$$CH_3CN \xrightarrow[(b)\,H_3O^+]{(a)\,SnCl_2/HCl} A \xrightarrow{\text{dil. NaOH}} B \xrightarrow{\Delta} C$$

Answer:

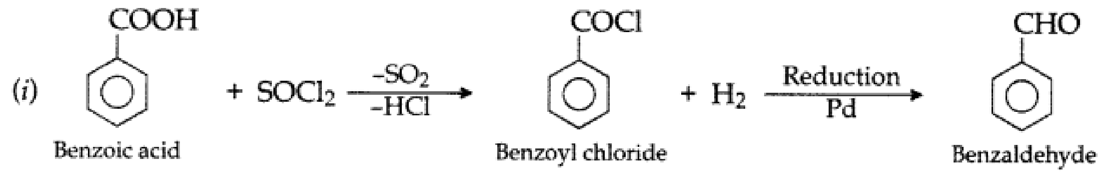


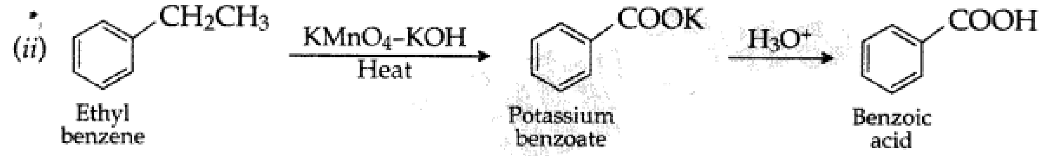
$$CH_3CN \xrightarrow[\substack{(b)\,H_3O^+ \\ \text{Stephen reaction}}]{(a)\,SnCl_2/HCl} \underset{\textbf{(A)}}{CH_3CHO} \xrightarrow[\substack{\text{Aldol} \\ \text{condensation}}]{\text{dil. NaOH}} \underset{\textbf{(B)}}{CH_3\underset{\underset{OH}{|}}{CH}-CH_2-CHO}$$

$$\xrightarrow{\Delta} \underset{\textbf{(C)}}{CH_3-CH=CH-CHO}$$

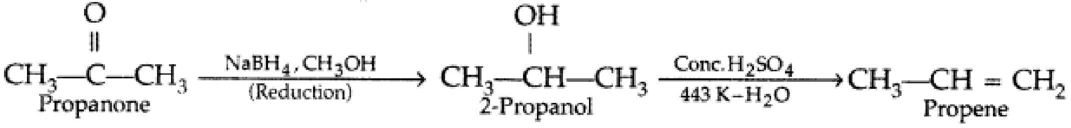
A = Ethanal
B = 3-Hydroxybutanal (Aldol)
C = But-2-enal

4) Do the following conversions in not more than two steps:
(i) Benzoic acid to benzaldehyde
(ii) Ethyl benzene to Benzoic acid
(iii) Propanone to Propene





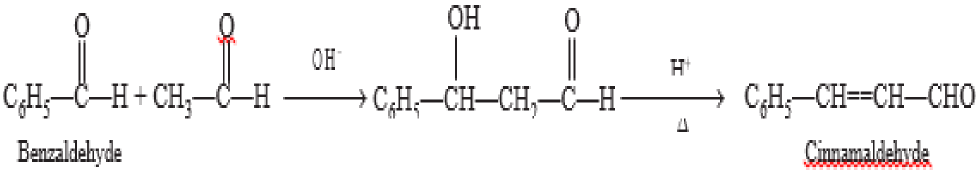
(iii) Propanone to propene



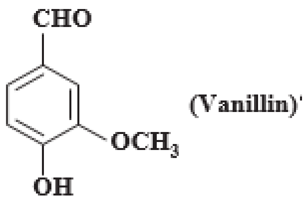
CASE BASED QUESTIONS

1) **Read the given passage and answer the questions that follow**.
Aldehydes, Ketones, Carboxylic acids and their derivatives are collectively called carboxyl compounds which are widely spread both in plants and animal kingdom. They play an important role in biological processes. They are responsible for fragrance and flavour of naturally occurring compounds *e.g.*, Vanilline (from vanilla beans), salicylaldehyde (from meadowsweet), cinnamaldehyde (from cinnamon) and isoamyl acetate (from banana) have pleasant flavour. Acetone and acetic acid are widely used as solvents. Various carboxylic acids are used to prepare drugs (Analgesics, antipyretics etc.).

(a) Convert benzaldehyde to Cinnamaldehyde?

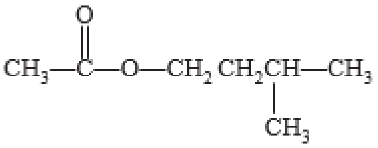


(b) What is IUPAC name of-



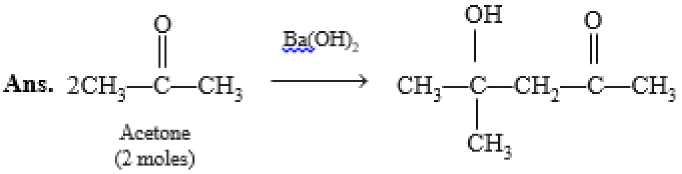
4–hydroxy–3–methoxy-benzaldehyde

(c) Write the structural formula of Isoamyl acetate.



$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_2\underset{CH_3}{\underset{|}{CH}}-CH_3$

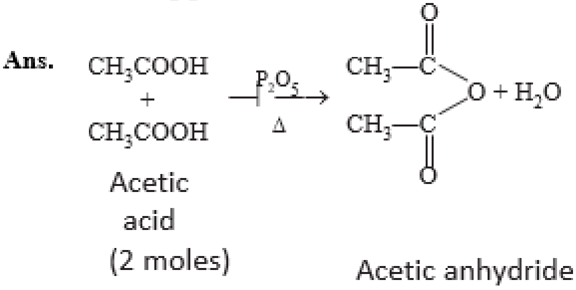
(d) What happens when 2 moles of acetone are condensed in presence of $Ba(OH)_2$? Write chemical equation.



$2CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{Ba(OH)_2} CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

4–hydroxy–4 methyl pentan–2–one

(e) What happens when acetic acid is heated with P_2O_5?



Acetic anhydride is formed.

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

Since aldehydes and ketones both possess the carbonyl functional group, they undergo similar chemical reactions. Contrary to electrophilic addition reactions observed in alkenes, the aldehydes and ketones undergo nucleophilic addition reactions. A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp2 hybridised orbitals of carbonyl carbon. The hybridisation of carbon changes from sp2 to sp3 in this process, and a tetrahedral alkoxide intermediate is produced. This intermediate captures a proton from the reaction medium to give the electrically neutral product. The net result is addition of Nu– and H+ across the carbon oxygen double bond.

(a) Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal?

Ans: Benzaldehyde is less reactive as carbon atom of benzaldehyde is less electrophilic due to resonance.

(b) Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethyl cyclohexanone does not. Why?

Ans: Due to steric effect in the latter compound.

(c) Arrange the following compounds in the increasing order of reactivity towards nucleophilic addition reactions:
CH_3CHO , CH_3CH_2CHO, CH_3COCH_3

Ans: $CH_3CHO > CH_3CH_2CHO > CH_3COCH_3$

(d) Differentiate an electrophile and a nucleophile.

Ans: Electrophile: Electrophiles are generally positively charged or neutral species with empty orbitals attracted to a centre rich in electrons.

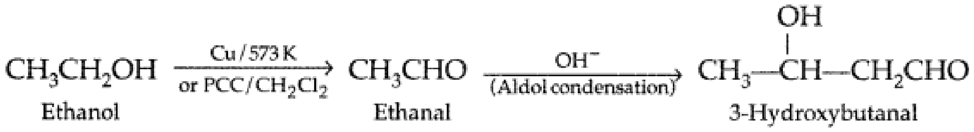
Nucleophile: A nucleophile is usually negatively charged or neutral with a lone pair of electrons.

Long Answer Type-FIVE MARKS

1) (a) How will you bring about the following conversions:
(i) Ethanol to 3-hydroxybutanal
(ii) Benzaldehyde to Benzophenone

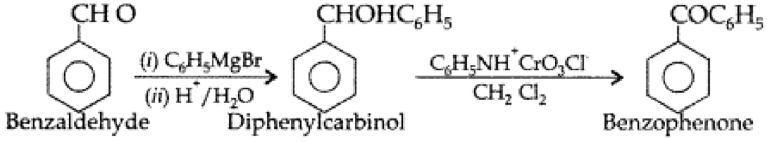
(b) An organic compound A has the molecular formula $C_8H_{16}O_2$. It gets hydrolysed with dilute sulphuric acid and gives a carboxylic acid B and an alcohol C. Oxidation of C with chromic acid also produced B. C on dehydration reaction gives but-1-ene. Write equations for the reactions involved.

Answer:
(a) (i) Ethanol to 3-hydroxybutanal :

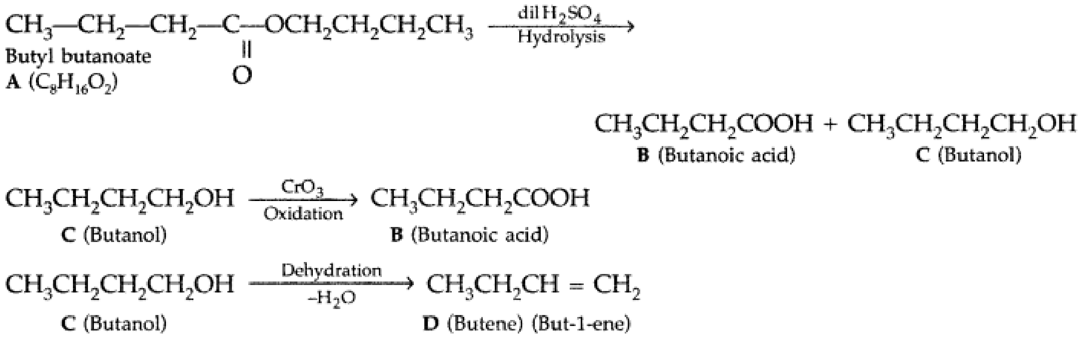


$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{or PCC/CH}_2\text{Cl}_2]{\text{Cu/573 K}} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[\text{(Aldol condensation)}]{OH^-} \underset{\text{3-Hydroxybutanal}}{CH_3-\overset{OH}{\overset{|}{C}H}-CH_2CHO}$$

(*ii*) **Benzaldehyde to Benzophenone :**



(*b*) The compound A with molecular formula is **Butyl butanoate.**



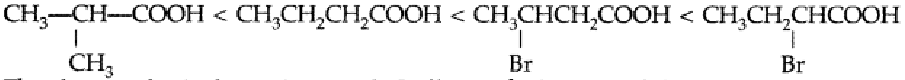
$$\underset{\substack{\text{Butyl butanoate}\\ \text{A }(C_8H_{16}O_2)}}{CH_3-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-OCH_2CH_2CH_2CH_3} \xrightarrow[\text{Hydrolysis}]{\text{dil }H_2SO_4} \underset{\text{B (Butanoic acid)}}{CH_3CH_2CH_2COOH} + \underset{\text{C (Butanol)}}{CH_3CH_2CH_2CH_2OH}$$

$$\underset{\text{C (Butanol)}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[\text{Oxidation}]{CrO_3} \underset{\text{B (Butanoic acid)}}{CH_3CH_2CH_2COOH}$$

$$\underset{\text{C (Butanol)}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[-H_2O]{\text{Dehydration}} \underset{\text{D (Butene) (But-1-ene)}}{CH_3CH_2CH = CH_2}$$

2) (a) Arrange the following compounds in an increasing order of their indicated property : (i) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)
(ii) $CH_3CH_2CH (Br) COOH$, $CH_3CH (Br) CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength)
(b) How would you bring about the following conversions :
(i) Propanone to Propene
(ii) Benzoic acid to Benzaldehyde
(iii) Bromobenzene to 1-phenylethanol

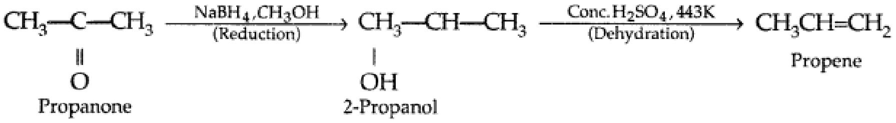
Answer:
(a) (i) 4-Methoxy benzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3, 4-Dinitrobenzoic acid. The order is due to increasing -I effect.

(*ii*) 

$$\underset{\displaystyle CH_3}{CH_3{-}CH{-}COOH} < CH_3CH_2CH_2COOH < CH_3\underset{\displaystyle Br}{CH}CH_2COOH < CH_3CH_2\underset{\displaystyle Br}{CH}COOH$$

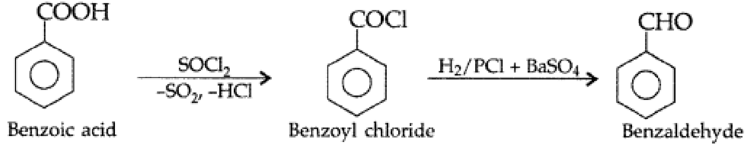
The above order is due to increased –I effect with decrease of distance and decrease of +I effect.

(*b*) (*i*) **Propanone to Propene**

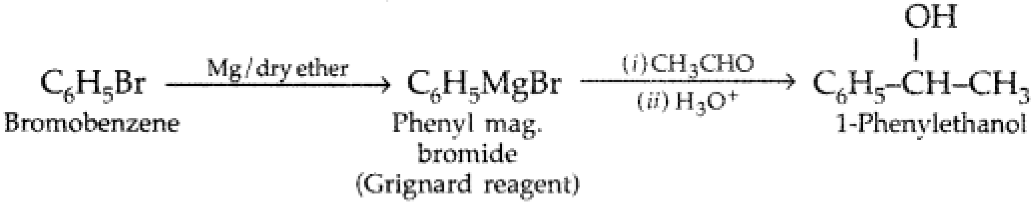


$$\underset{\text{Propanone}}{CH_3{-}\overset{}{\underset{\displaystyle O}{\underset{\|}{C}}}{-}CH_3} \xrightarrow[\text{(Reduction)}]{NaBH_4, CH_3OH} \underset{\text{2-Propanol}}{CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3} \xrightarrow[\text{(Dehydration)}]{\text{Conc.} H_2SO_4, 443K} \underset{\text{Propene}}{CH_3CH{=}CH_2}$$

(*ii*) **Benzoic acid to Benzaldehyde** (*Rosenmund reduction*) :



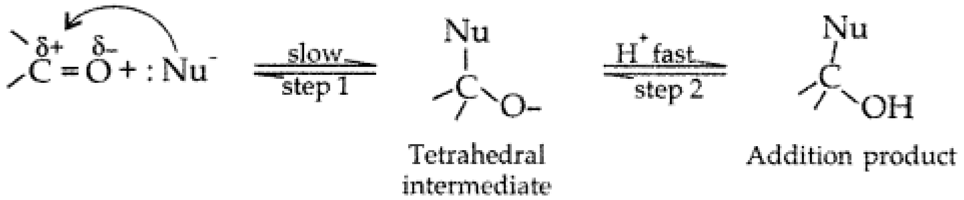
(*iii*) **Bromobenzene to 1-phenylethanol**



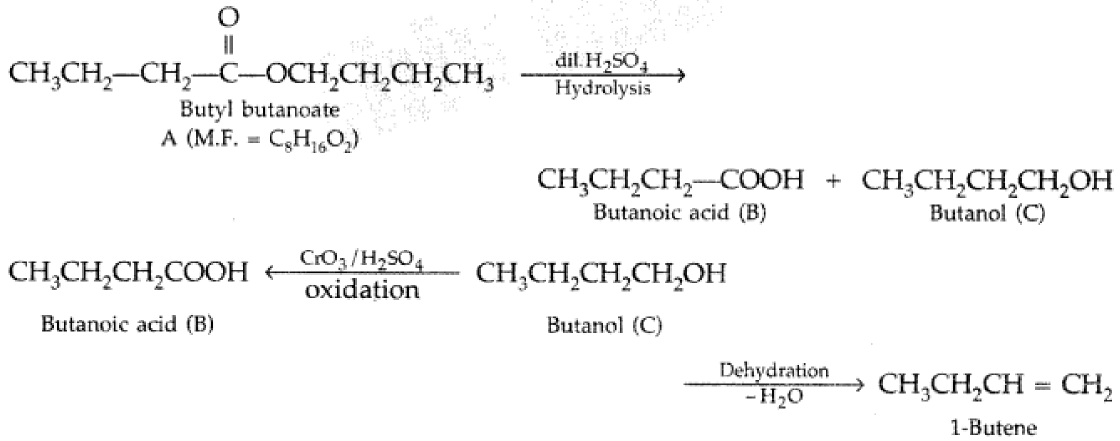
$$\underset{\text{Bromobenzene}}{C_6H_5Br} \xrightarrow{\text{Mg/dry ether}} \underset{\substack{\text{Phenyl mag.}\\\text{bromide}\\\text{(Grignard reagent)}}}{C_6H_5MgBr} \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3CHO} \underset{\text{1-Phenylethanol}}{C_6H_5{-}\overset{\displaystyle OH}{\overset{|}{CH}}{-}CH_3}$$

3) (a) Explain the mechanism of a nucleophilic attack on the carbonyl group of an aldehyde or a ketone.
(b) An organic compound (A) (molecular formula ($C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid also produced (B). On dehydration (C) gives but-1-ene. Write the equations for the reactions involved.

Answer:(a) Mechanism of a nucleophilic attack on the carbonyl group
 is a polar group in which carbon acquires positive charge and O acquires negative charge due to more electronegativity of oxygen. The Nu~ attacks on carbon and forms a tetrahedral intermediate and then electrophile attacks on oxygen and forms a compound.



(b) Since the organic compound (A) with molecular formula (M.F.) $C_8H_{16}O_2$ upon hydrolysis with dil. H2S04 gives carboxylic acid (B) and the alcohol (C) therefore it must be an ester. Further since oxidation of (C) with chromic acid produces the acid (B), therefore both the carboxylic acid (B) and the alcohol (C) must ’.contain the same number of carbon atoms



4) (a) An organic compound ‘A’ which has characteristic odour, on treatment with NaOH forms two compounds ‘B’ and ‘C’. Compound ‘B’ has the molecular formula C_7H_8O which on oxidation with CrO_3 gives back compound ‘A’. Compound ‘C’ is the sodium salt of the acid. ‘C’ when heated with soda lime yields an aromatic hydrocarbon ‘D’. Deduce the structures of ‘A’, ‘B’, ‘C’ and ‘D’.

(b) Give reasons :

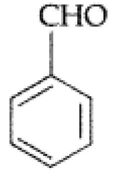
(i) Electrophilic substitution in Benzoic acid takes place at meta position.

(ii) Carboxylic acids do not give characteristic reactions of carbonyl group

Answer:

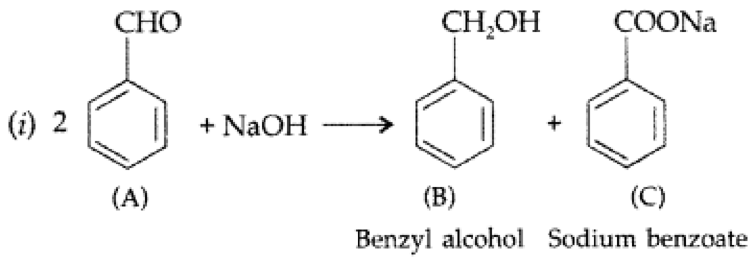
(a) (A) gives characteristic odour which on treatment with NaOH and forms two compounds B and C.

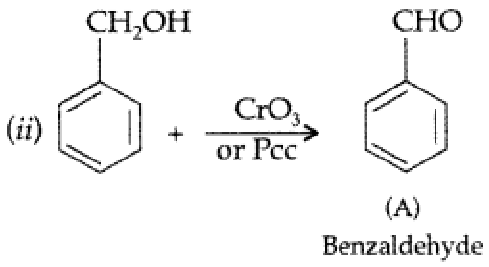
∴ (A) should be benzaldehyde

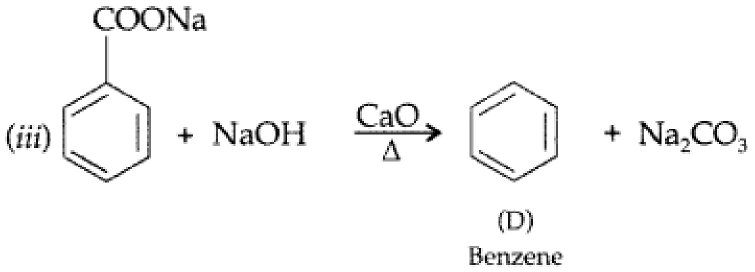


(A)

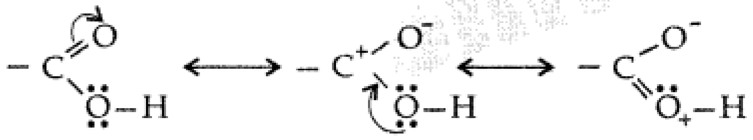
Reactions :



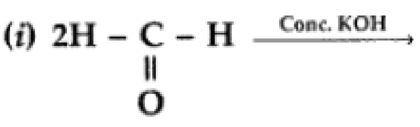




(b) (i) The benzene ring of benzoic acid undergoes electrophilic substitution reaction such as nitration, sulphonation etc. Since the — COOH group in benzene is an electron withdrawing group, therefore it is meta directing group. (ii) The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure.

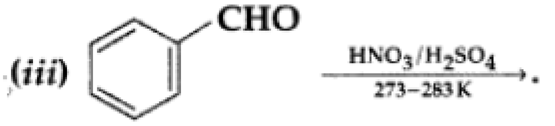


5) (a) Complete the following reactions:



(i) $2H-\underset{\underset{O}{\|}}{C}-H \xrightarrow{\text{Conc. KOH}}$

(ii) $CH_3COOH \xrightarrow{Br_2/P}$



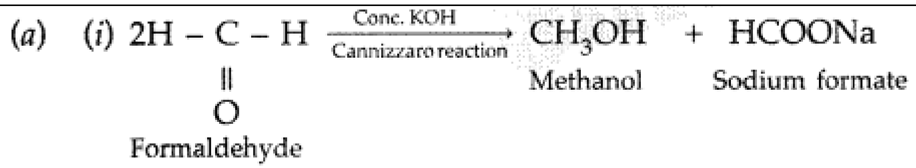
(b) How will you convert the following :

(i) Propanone to Propan-2-ol

(ii) Ethanal to 2-hydroxy propanoic acid

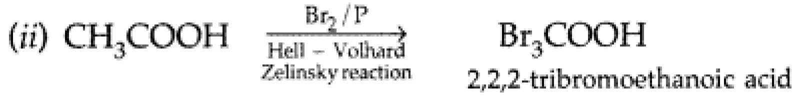
Answer:

(a) (i)



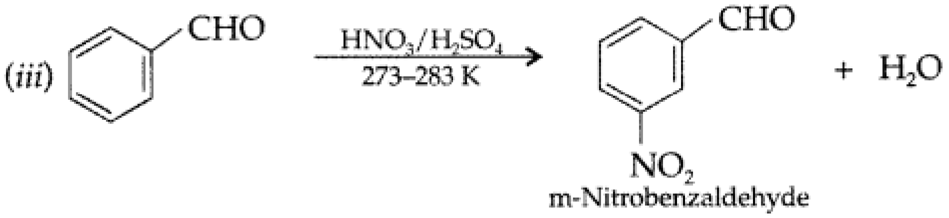
$$2H-\overset{\displaystyle O}{\underset{}{C}}-H \xrightarrow[\text{Cannizzaro reaction}]{\text{Conc. KOH}} CH_3OH + HCOONa$$

(ii)

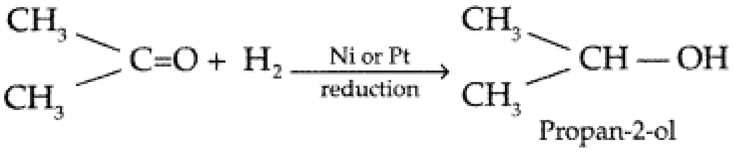


$$CH_3COOH \xrightarrow[\text{Hell – Volhard Zelinsky reaction}]{Br_2/P} Br_3COOH$$

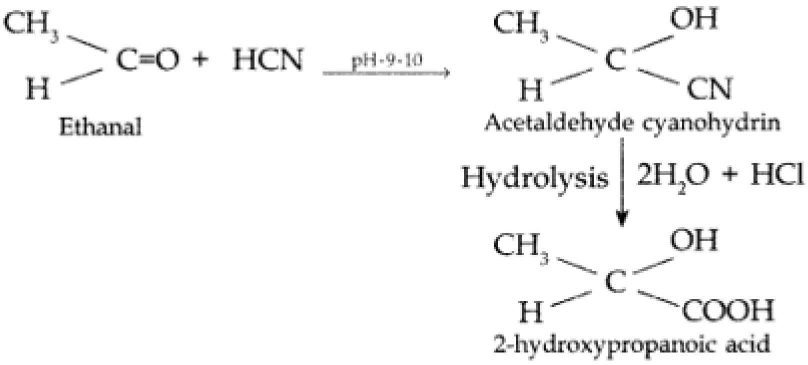
(iii)



(b) (i) Propanone to Propan-2-ol



(ii) **Ethanal to 2-hydroxy propanoic acid**



HOTS

1) The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.

It is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions.

2) The boiling points of aldehydes and ketones are lower than those of alcohols of similar molecular masses.

It is due to absence of intermolecular hydrogen bonding in aldehydes and ketones.

3) The lower members of aldehydes and ketones are miscible with water in all proportions.

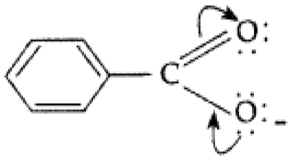
Because they form hydrogen bond with water.

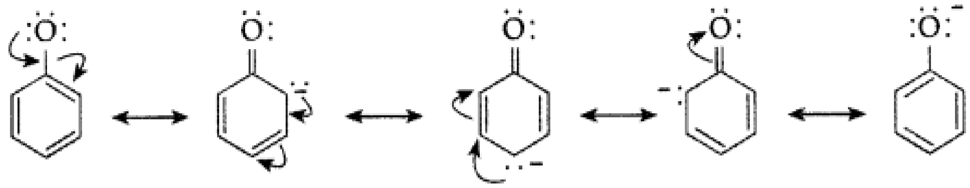
4) Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol.

Carboxylic acid is a stronger acid than phenol because

(i) The release of a proton from carboxylic acids is much easier than from phenols

(ii) In the resonating structure of phenol and carboxylic acid, the negative charge on the carboxylate ion is delocalised over two oxygen atoms while in phenol they are localized on one oxygen atom.



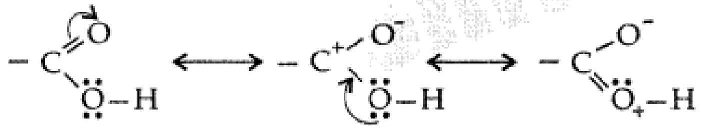


5) Electrophilic substitution in Benzoic acid takes place at meta position.

The benzene ring of benzoic acid undergoes electrophilic substitution reaction such as nitration, sulphonation etc. Since the — COOH group in benzene is an electron withdrawing group, therefore it is meta directing group.

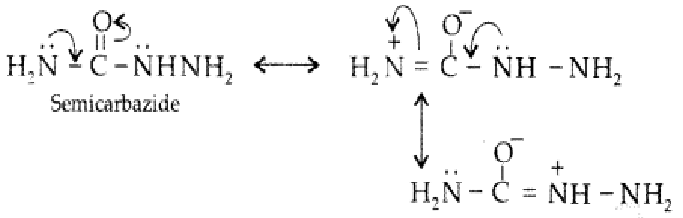
6) Carboxylic acids do not give characteristic reactions of carbonyl group.

The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure.



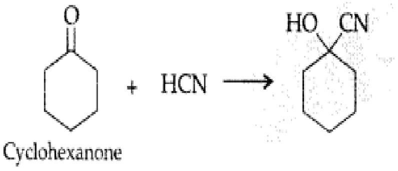
7) There are two – NH_2 groups in semicarbazide. However, only one such group is involved in the formation of semicarbazones.

Because one of the – NH_2 in semicarbazide is involved in the resonance with -CO- group.



8) Cyclohexanone forms cyanohydrin in good yield but 2, 4, 6-trimethylcyclohexanone does not.

Due to steric hinderance in 2, 4, 6-trimethylcyclohexanone, it doesn't react with HCN easily.



9) Ethanal is soluble in water.

Ethanal is soluble in water due to H-bonding between the polar carbonyl group and water molecules.

10) Formaldehyde does not take part in Aldol condensation.

Formaldehyde does not contain alpha hydrogen atom. Therefore it does not take part in aldol condensation.

11) Aldehydes and Ketones have lower boiling points than corresponding alcohols.

It is due to weak molecular association in aldehydes and ketones arising out of the dipole- dipole interactions.

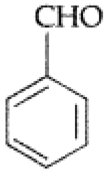
<u>WORD NUMERICALS</u>

1) An organic compound ‘A’ which has characteristic odour, on treatment with NaOH forms two compounds ‘B’ and ‘C’. Compound ‘B’ has the molecular formula C_7H_8O which on oxidation with CrO_3 gives back compound ‘A’. Compound ‘C’ is the sodium salt of the acid. ‘C’ when heated with soda lime yields an aromatic hydrocarbon ‘D’. Deduce the structures of ‘A’, ‘B’, ‘C’ and ‘D’.

Answer:

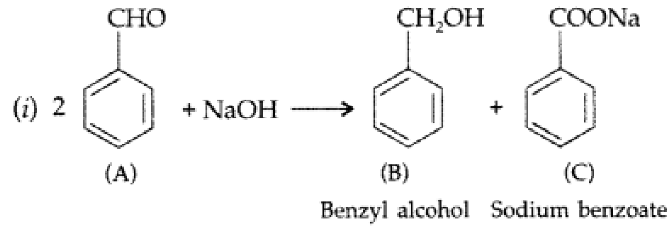
(A) gives characteristic odour which on treatment with NaOH and forms two compounds B and C.

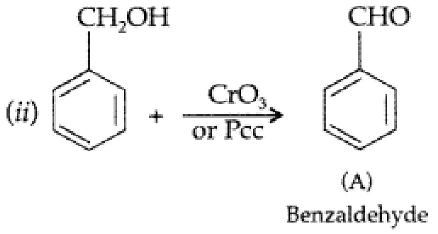
∴ (A) should be benzaldehyde

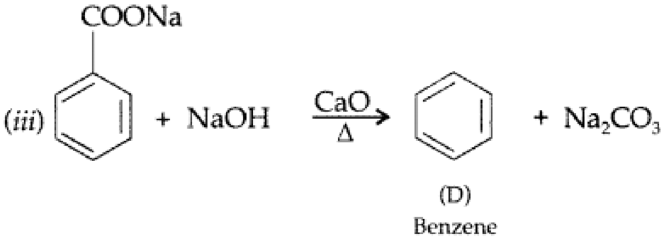


(A)

Reactions :



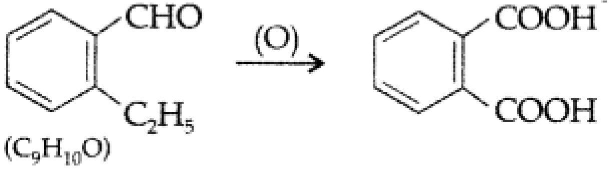




2) An organic compound with molecular formula $C_9H_{10}O$ forms 2, 4, – DNP derivative, reduces Tollens’ reagent and undergoes Cannizzaro’s reaction. On vigorous oxidation it gives 1, 2-benzene-di- carboxylic acid. Identify the compound.

Answer:

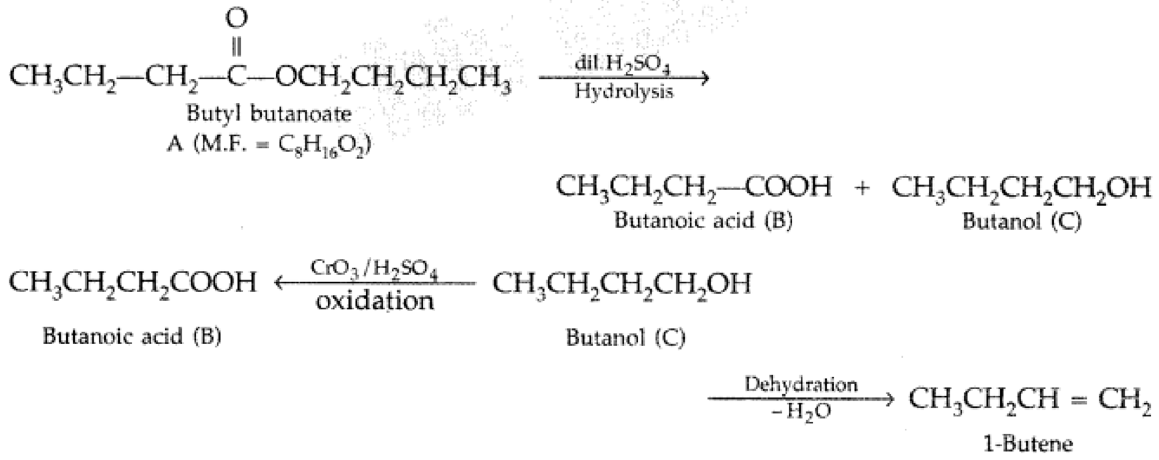
Compound $C_9H_{10}O$ forms 2, 4-DNP derivative, so it contains a carbonyl group. Also it reduces Tollens’ reagent therefore carbonyl group is an aldehyde group. Since it undergoes Cannizzaro’s reaction, aldehyde has no a hydrogen atom, so compound is C_8H_9-CHO. On vigorous oxidation, compound gives l, 2-benzene di-carboxylic acid hence the compound is



3) An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid also produced (B). On dehydration (C) gives but-1-ene. Write the equations for the reactions involved.

Answer:

Since the organic compound (A) with molecular formula (M.F.) $C_8H_{16}O_2$ upon hydrolysis with dil. H_2SO_4 gives carboxylic acid (B) and the alcohol (C) therefore it must be an ester. Further since oxidation of (C) with chromic acid produces the acid (B), therefore both the carboxylic acid (B) and the alcohol (C) must ’.contain the same number of carbon atoms



$$CH_3CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OCH_2CH_2CH_2CH_3 \xrightarrow[\text{Hydrolysis}]{\text{dil.}H_2SO_4} CH_3CH_2CH_2-COOH + CH_3CH_2CH_2CH_2OH$$

Butyl butanoate A (M.F. = $C_8H_{16}O_2$) ; Butanoic acid (B) ; Butanol (C)

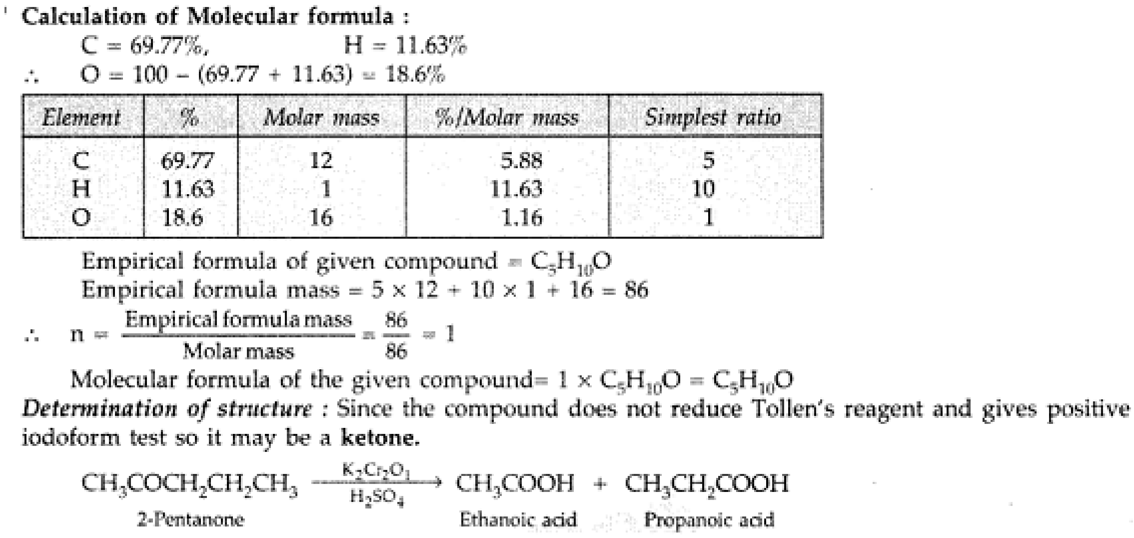
$$CH_3CH_2CH_2COOH \xleftarrow[\text{oxidation}]{CrO_3/H_2SO_4} CH_3CH_2CH_2CH_2OH$$

Butanoic acid (B) ; Butanol (C)

$$\xrightarrow[-H_2O]{\text{Dehydration}} CH_3CH_2CH=CH_2$$

1-Butene

4) An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollen's reagent but forms an addition compound with sodium hydrogen sulphite and gives positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acids. Derive the structure of the compound.



Calculation of Molecular formula :

C = 69.77%, H = 11.63%

∴ O = 100 − (69.77 + 11.63) = 18.6%

Element	*%*	*Molar mass*	*%/Molar mass*	*Simplest ratio*
C	69.77	12	5.88	5
H	11.63	1	11.63	10
O	18.6	16	1.16	1

Empirical formula of given compound = $C_5H_{10}O$

Empirical formula mass = 5 × 12 + 10 × 1 + 16 = 86

$$\therefore \quad n = \frac{\text{Empirical formula mass}}{\text{Molar mass}} = \frac{86}{86} = 1$$

Molecular formula of the given compound= 1 × $C_5H_{10}O$ = $C_5H_{10}O$

Determination of structure : Since the compound does not reduce Tollen's reagent and gives positive iodoform test so it may be a **ketone.**

$$CH_3COCH_2CH_2CH_3 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH + CH_3CH_2COOH$$

2-Pentanone ; Ethanoic acid ; Propanoic acid

(OR)

Since the compound does not reduce Tollen's reagent, it has a ketonic group.
Also, as it forms an addition compound with $NaHSO_3$ and gives positive iodoform test, the presence of methyl ketone is confirmed.
On oxidation, it gives ethanoic acid and propanoic acid.
So, the compound can be

$CH_3CH_2CH_2COCH_3$

This is because in unsymmetrical ketone, the point of cleavage is such that the keto group stays with the smaller alkyl group.

$CH_3CH_2CH_2COCH_3$ -----→ $CH_3CH_2COOH + CH_3COOH$

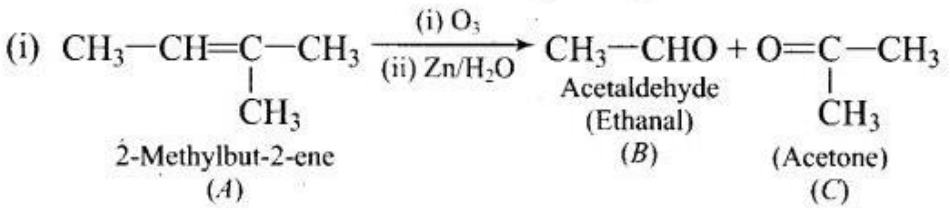
5) An alkene 'A' (Molecular formula C_5H_{10}) on ozonolysis gives a mixture of two compounds 'B' and 'C'. Compound 'B' gives positive Fehling's test and also forms iodoform on treatment with I_2 and NaOH. Compound 'C' does not give Fehling's test but forms iodoform. Identify the compounds A, B and C. Write the reaction for ozonolysis and formation of iodoform from B and C.

Answer:

Compound B gives positive Fehling's test. It shows that it is an aldehyde and gives iodoform test which shows it has $-COCH_3$ group.

Compounds C is a ketone because it does not give Fehling's test but gives iodoform test which shows it also has $-COCH_3$ groups.

Hence the compound is $CH_3-CH=C(CH_3)_2$



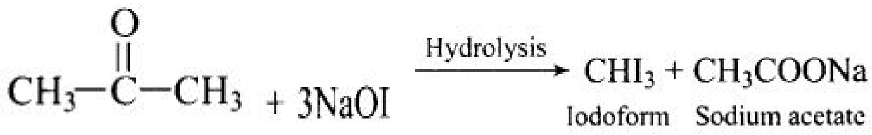
$$\text{(i)}\ \underset{\substack{\text{2-Methylbut-2-ene}\\(A)}}{CH_3-CH=\underset{CH_3}{\underset{|}{C}}-CH_3} \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3} \underset{\substack{\text{Acetaldehyde}\\\text{(Ethanal)}\\(B)}}{CH_3-CHO} + \underset{\substack{\text{(Acetone)}\\(C)}}{O=\underset{CH_3}{\underset{|}{C}}-CH_3}$$

Other isomer of (A) will not give products corresponding to the given test.

$(2NaOH + I_2 \rightarrow NaOI + NaI + H_2O)$

$$\text{(ii)}\ \underset{(B)}{CH_3CHO} + \underset{\substack{\text{Sodium}\\\text{hypoiodite}}}{3NaOI} \longrightarrow \underset{\substack{\text{Tri-iodo}\\\text{acetaldehyde}}}{CI_3CHO} + 3NaOH$$

$$CH_3CHO + NaOH \xrightarrow{\text{Hydrolysis}} \underset{\text{Iodoform}}{CHI_3} + HCOONa$$

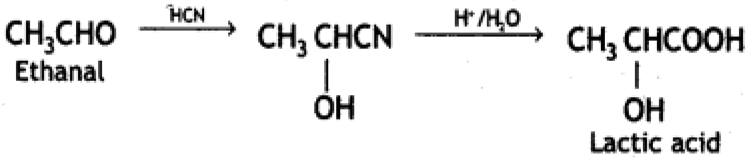


$$CH_3-\overset{\overset{O}{||}}{C}-CH_3 + 3NaOI \xrightarrow{\text{Hydrolysis}} \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sodium acetate}}{CH_3COONa}$$

(C)

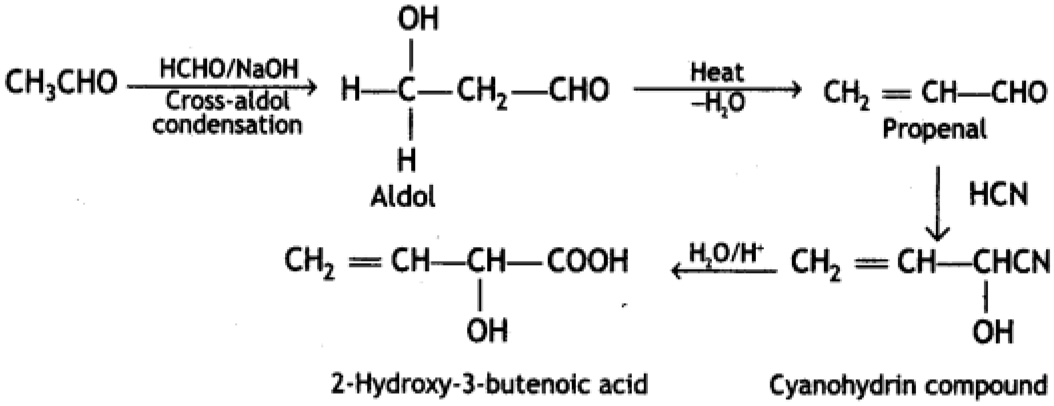
(I) ORGANIC CONVERSIONS

1) ETHANAL TO LACTIC ACID

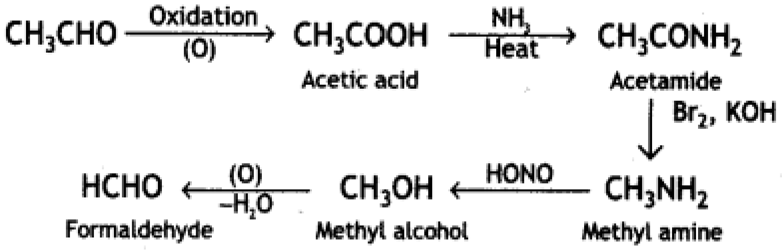


$$\underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{HCN} CH_3\underset{OH}{\underset{|}{C}H}CN \xrightarrow{H^+/H_2O} \underset{\text{Lactic acid}}{CH_3\underset{OH}{\underset{|}{C}H}COOH}$$

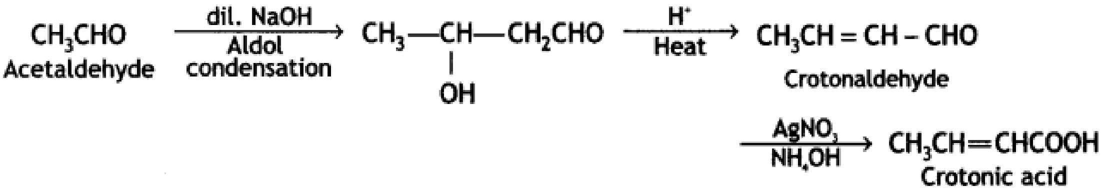
2) ETHANAL TO 2-HYDROXY-3-BUTENOIC ACID



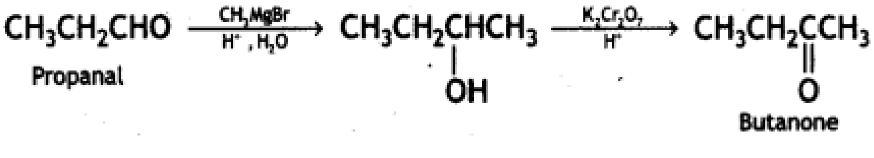
3) ACETALDEHYDE TO FORMALDEHYDE



3) ACETALDEHYDE TO CROTONIC ACID.



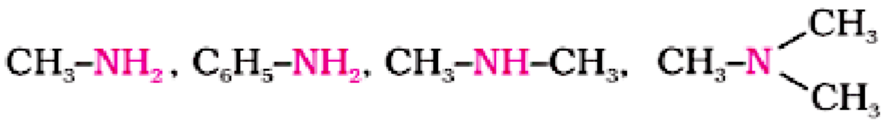
4) PROPANAL TO BUTANONE



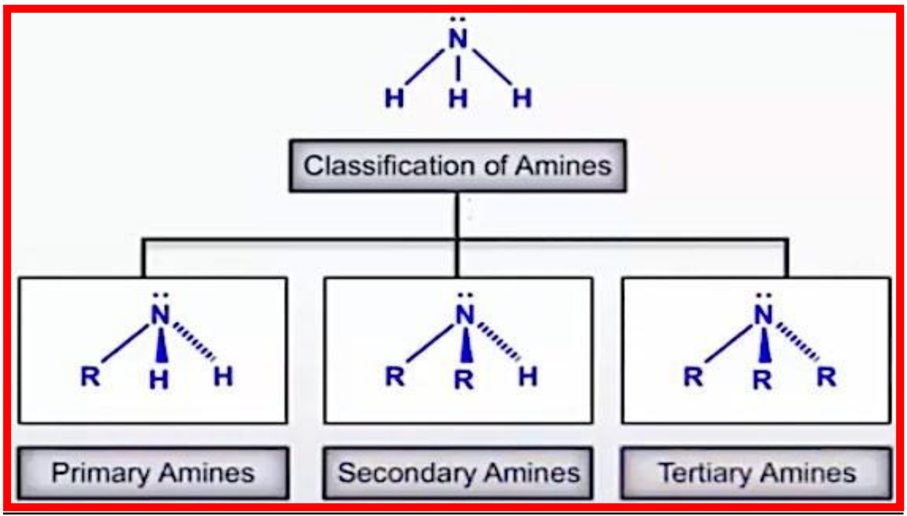
CHAPTER 9

AMINES

*Amines can be considered as derivatives of ammonia, obtained by replacement of one, two orall the three hydrogen atoms by alkyl and/or aryl groups.



CH_3-NH_2, $C_6H_5-NH_2$, $CH_3-NH-CH_3$, $CH_3-N(CH_3)_2$



*METHODS OF PREPARATION OF AMINES

Reduction of Nitro

CompoundsReducing

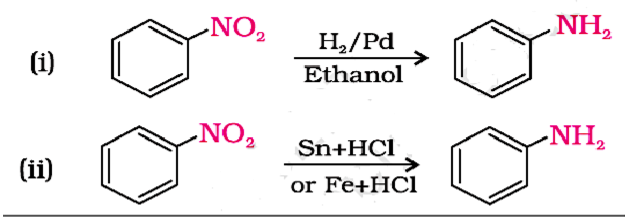
Agents:-

Hydrogen gas in the presence of finely divided Ni,

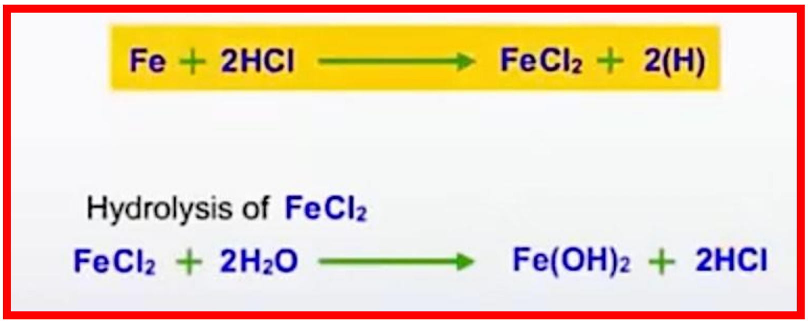
Pd or ptIron scrap and hydrochloric acid(Fe +

HCl)

Tin and hydrochloric acid (Sn + HCl)



Reduction with iron scrap and HCl is preferred because FeCl2 formed gets hydrolysed to release HCl during the reaction. Hence only a small amount of hydrochloric acid is required toinitiate the reaction


$$Fe + 2HCl \longrightarrow FeCl_2 + 2(H)$$

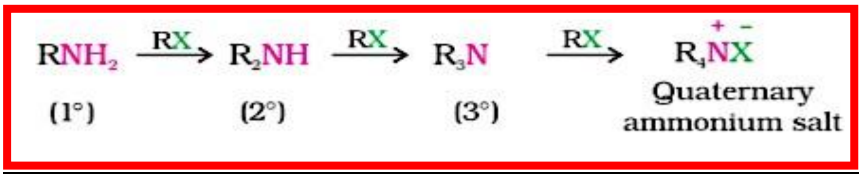
Hydrolysis of $FeCl_2$

$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2 + 2HCl$$

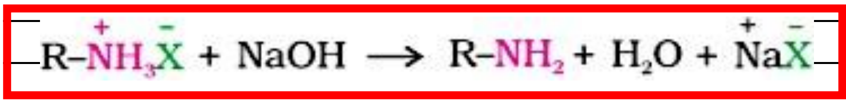
2. Ammonolysis of alkyl halides

- This process of cleavage of the C–X bond by NH3 molecule is known as ammonolysis.

The primary amine thus obtained behaves as a nucleophile and can further react with alkylhalide to form secondary and tertiary amines, and finally quaternary ammonium salt


$$\underset{(1^\circ)}{RNH_2} \xrightarrow{RX} \underset{(2^\circ)}{R_2NH} \xrightarrow{RX} \underset{(3^\circ)}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}\overset{-}{X}}$$

The free amine can be obtained from the ammonium salt by treatment with a strong base


$$R\text{–}\overset{+}{N}H_3\overset{-}{X} + NaOH \longrightarrow R\text{–}NH_2 + H_2O + \overset{+}{Na}\overset{-}{X}$$

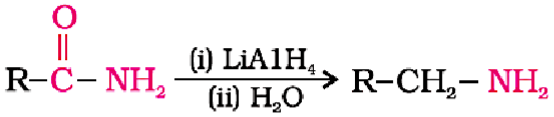
Ammonolysis has the disadvantage of yielding a mixture of 1^o,2^o, 3^o and quaternary ammoniumsalt. However, 1^o is a major product by taking excess of ammonia

3. Reduction of Nitriles:

- Reducing agents:- LiAlH4 or catalytic hydrogenation or Na(Hg)-C2H5OH
- This reaction is used for ascent of amine series

$$R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} R-CH_2-NH_2$$

4. Reduction of Amides

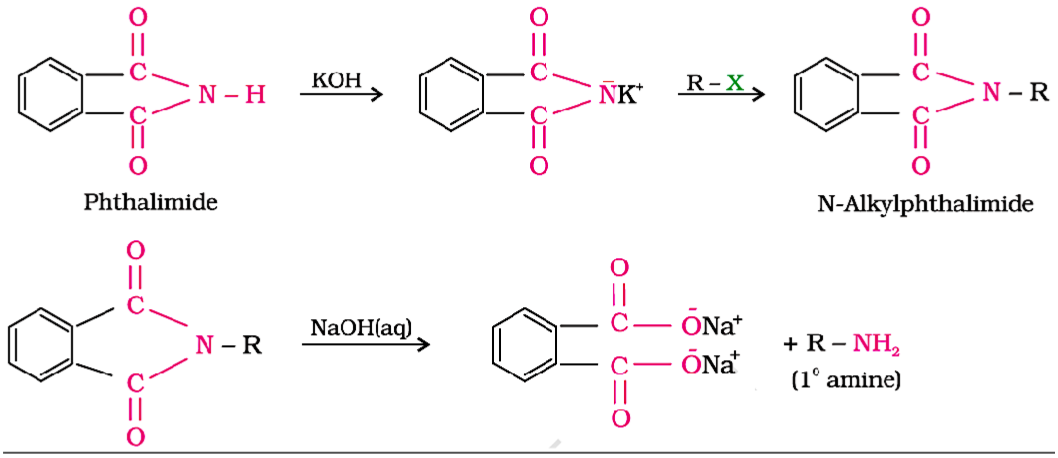


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R-CH_2-NH_2$$

5. Gabriel Phthalimide Synthesis

Gabriel synthesis is used for the preparation of primary amines

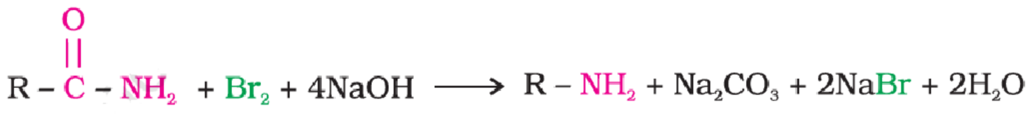
Aromatic primary amines cannot be prepared by this method because aryl halides do notundergo nucleophilic substitution with the anion formed by phthalimide



2. Hoffmann bromamide degradation reaction

- For preparation of primary amines

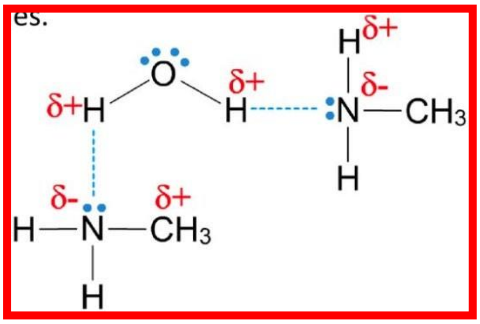
- An amide is treated withBr2 in an aq. or ethanolic solution of NaOH.The amine so formed contains one carbon less than that present in the amide



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

*7.PHYSICAL PROPERTIES

Solubility decreases with increase in molar mass due to increase in size of the hydrophobicalkyl part



Amines are less soluble in water than alcohol having same no. of carbon atoms because O-H bond is more polar than N-H bond (electronegativity of O is 3.5 and N is 3.0) hence H-bondingin alcohols is intense than amines

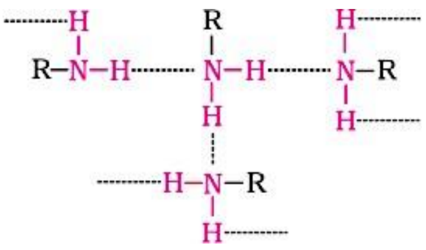
1^{o} amines and 2^{o} amines are engaged in intermolecular association due to H-bonding betweenN of one and H of another molecule.

This intermolecular association is more in 1^{o} amines than in 2^{o} amines as there are two H-atoms available for H-bonding in it.

3^{o}amines don't have intermolecular association due to the absence of H-atom.

The order of boiling points of isomeric amines is as

followsPrimary > Secondary > Tertiary

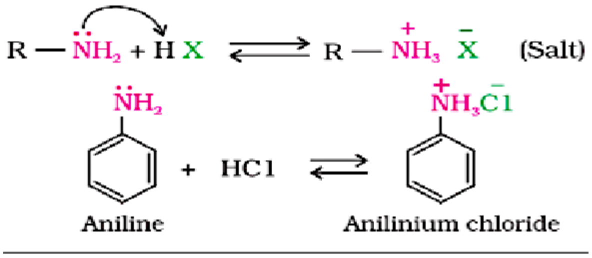


H-bonding in primary amines

*8.CHEMICAL PROPERTIES OF AMINES

Basic Character of Amines

- Amines are Lewis bases due to the presence of a lone pair on N-atom.
- They react with acids to form salts.



$$R-\ddot{N}H_2 + HX \rightleftharpoons R-\overset{+}{N}H_3\ \overset{-}{X} \quad \text{(Salt)}$$

Amine salts on treatment with a base like NaOH, regenerate the parent amine

$$R\overset{+}{N}H_3\overset{-}{X} + \overset{-}{O}H \longrightarrow R\ddot{N}H_2 + H_2O + \overset{-}{X}$$

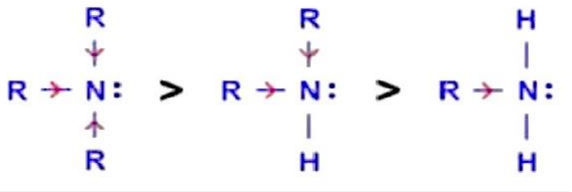
K_b and pK_b values of amines:

The dissociation of primary amines in water can be shown as follows

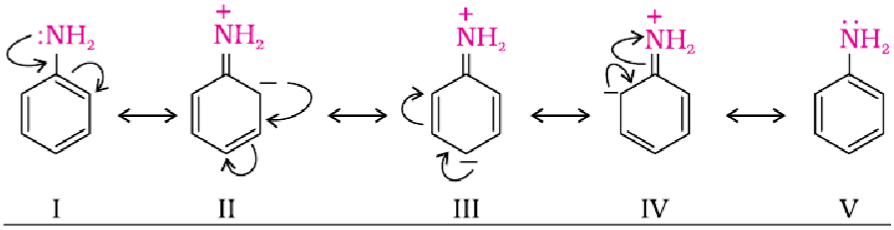
$$R-NH_2 + H_2O \rightleftharpoons R-\overset{+}{N}H_3 + \overset{-}{O}H$$

Where, K_b is the basicity constant

aliphatic amines are stronger bases than ammonia due to
+I effect of alkyl groups leading to high electron density on the nitrogen atom. TheirpK_b values lie in the range of 3 to 4.22



Aromatic amines are weaker bases than ammonia due to the electron withdrawing nature(-I effect) of the aryl group



2. **Solvation effect:**

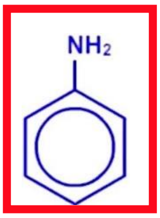
- In aqueous phase, solvation effect also works other than +I or –I effect.

3. **Steric Effect**: Smaller the alkyl groups around the N atom of aliphatic amines, lesserwill be the steric hindrance for H-bonding of protonated amine cation and greater will be the solvation and more will be the basicity

The Inductive effect, Solvation effect and Steric hinderance of the alkyl group whichdecides the basic strength of alkyl amines in the aqueous state.The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows

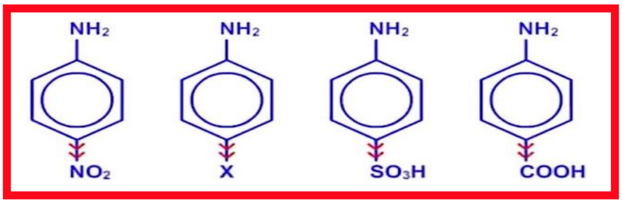
$$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$$
$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

Basicity of substituted aryl amines:

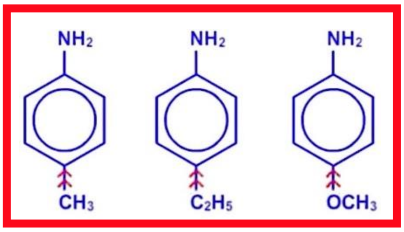


- In case of substituted aniline, it is observed that electron releasing groups like $–OCH_3$, $–CH_3$ increase basic strength whereas electron withdrawing groups like $–NO_2$, $–SO_3$, – COOH, –X decrease it.

Aniline with electron withdrawing groupshave more pK_b than aniline i.e. they are less basic than aniline



Aniline with electron donating groups have less pK_b than anilinei.e. they are more basic than aniline



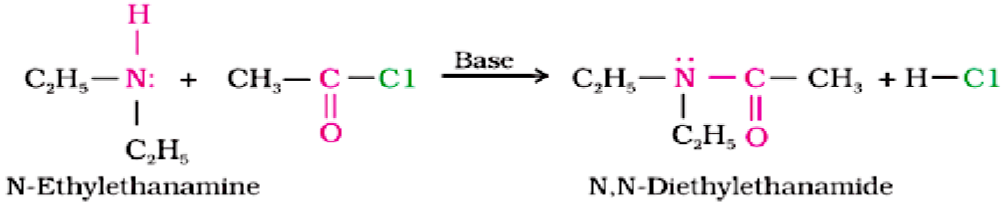
Basicity in gaseous phase: 3° amine > 2° amine > 1° amine > NH_3

Basicity in aqueous phase: NH_3 > 1° amine > 2° amine > 3° amine

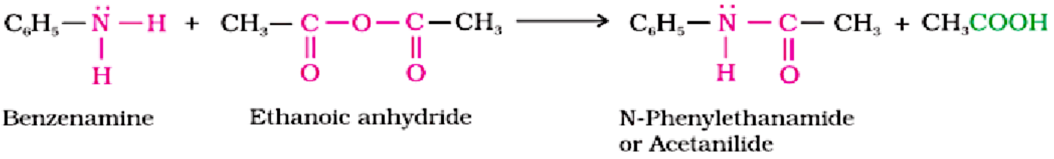
9.**Acylation**

When Aliphatic/aromatic 1° and 2° amines react with acid chloride, esters and anhydrides bynucleophilic substitution to give amides, it is called acylation

Hydrogen atom of –NH2 or >NH group is replaced by the acyl group



$$C_2H_5-NH-C_2H_5 + CH_3-CO-Cl \xrightarrow{Base} C_2H_5-N(C_2H_5)-CO-CH_3 + H-Cl$$



$$C_6H_5-NH_2 + CH_3-CO-O-CO-CH_3 \longrightarrow C_6H_5-NH-CO-CH_3 + CH_3COOH$$

10. Carbylamine reaction

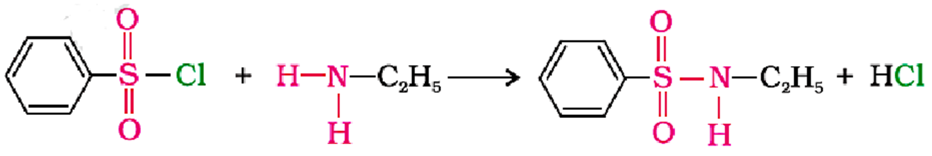
- Aliphatic and Aromatic primary amines on heating with chloroform and ethanolicpotassium hydroxide form isocyanides or carbylamines which are foul smelling substances.
- Secondary and tertiary amines do not show this reaction.
- This reaction is known as carbylamine reaction or isocyanide test and is used as a testfor primary amines.

$$R{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R{-}NC + 3KCl + 3H_2O$$

11. Reaction with Benzenesulphonyl chloride(HINSBERGS TEST)

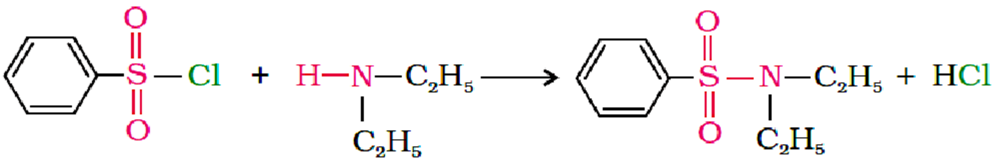
Benzenesulphonyl chloride ($C_6H_5SO_2Cl$), also known as Hinsberg's reagent, is used for thedistinction of 1^o, 2^o and 3^o amines and their separation from each other.

With 1^o amines, benzenesulphonyl chloride yields N-ethylbenzenesulphonyl amide



N-Ethylbenzenesulphonamide

With 2^o amine, Benzenesulphonyl chloride gives N,N diethylbenzenesulphonamide

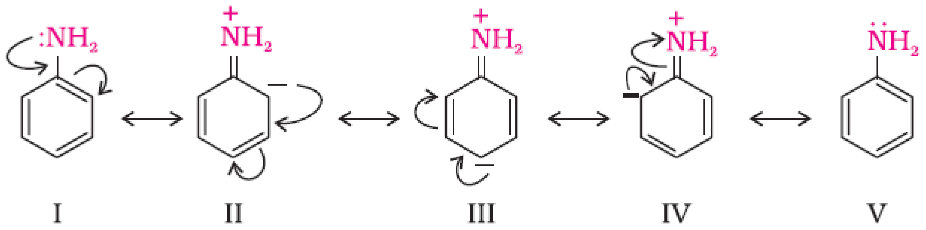


N,N-Diethylbenzenesulphonamide

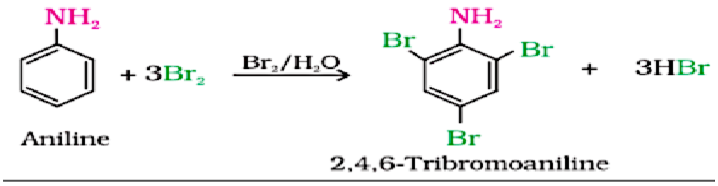
- With 3^o amine, benzenesulphonyl chloride do not react

12. Electrophilic substitution Reactions in Aromatic amines

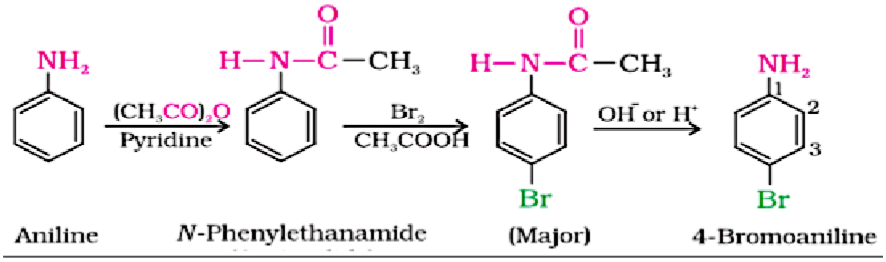
In aniline, due to resonance, ortho- and para-positions become centres of high electron density.Thus –NH2 group is ortho and para directing and a powerful activating group



Bromination: Aniline reacts with bromine water at room temp to give a white precipitate of 2,4,6-tribromoaniline



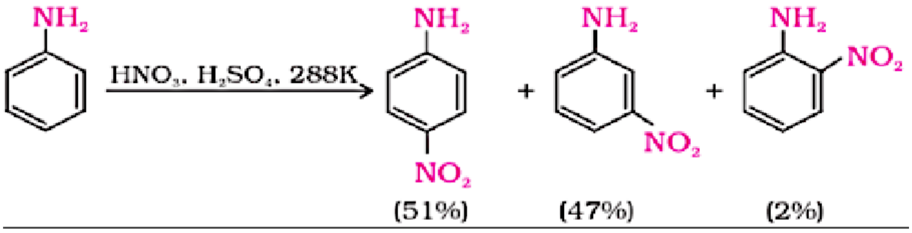
- To prepare monosubstituted aniline derivative, the $-NH_2$ group is deactivated by acetylation with acetic anhydride, which makes the lone pair less available on N-atom.



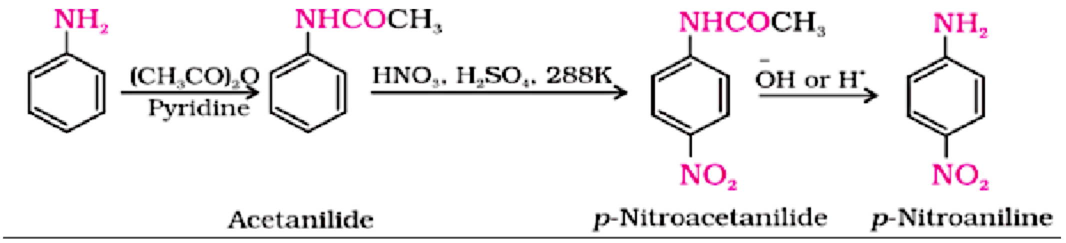
Nitration:

- Direct nitration of aniline yields tarry oxidation products(side products) in addition tothe nitro derivatives.

In the strongly acidic medium, aniline is protonated to form the anilinium ion which is metadirecting

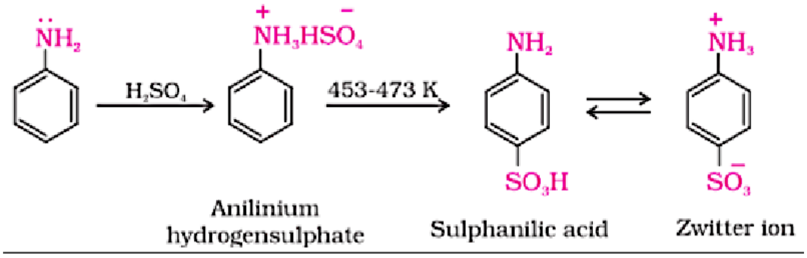


By protecting the $-NH_2$ group by acetylation reaction with acetic anhydride, the nitrationreaction can be controlled and the p-nitro derivative can be obtained as the major product



Sulphonation

Aniline reacts with concentrated sulphuric acid to form anilinium hydrogensulphate which onheating with sulphuric acid at 453-473K produces p-aminobenzene sulphonic acid, sulphanilicacid

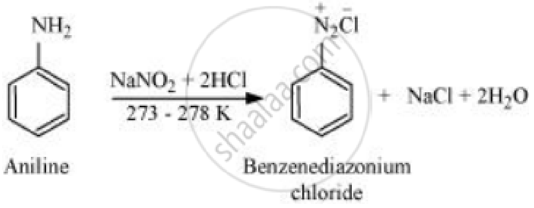


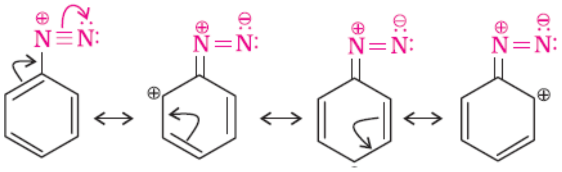
Aniline does not undergo Friedel-Crafts reaction

- Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to saltformation with aluminium chloride, the Lewis acid, which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence acts as a strong deactivatinggroup for further reaction.

DIAZONIUM SALTS

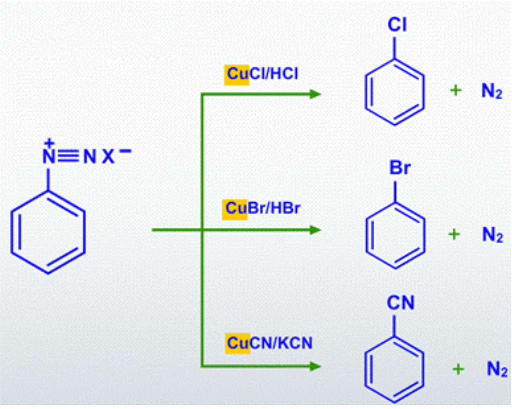
- **DIAZOTISATION :** When a primary aromatic amine, dissolved or suspended in coldaqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed





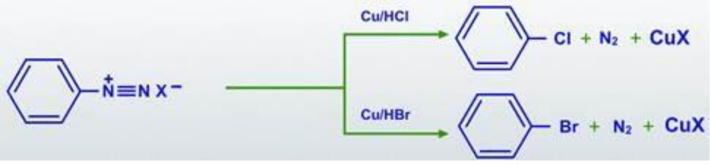
Reactions Involving Displacement of Nitrogen

SANDMEYER REACTION: Diazonium salt with cuprous chloride or cuprous bromideresults in the replacement of the diazonium group by –Cl or –Br or CN-

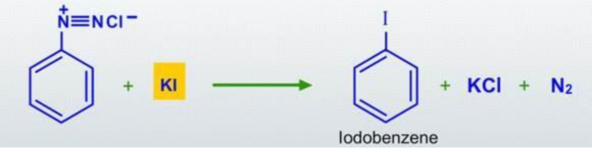


4.GATTERMANN REACTION

Diazonium groups are replaced with Chlorine (or) Bromine by treating the diazonium saltsolution with haloacid in the presence of copper powder.



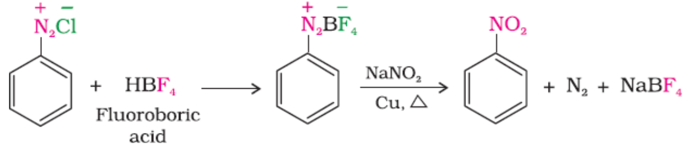
Diazonium group may be replaced by iodine by treatment with potassium iodide.



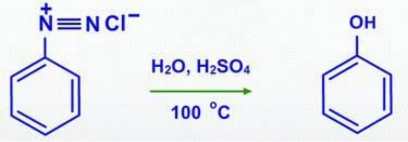
Diazonium group is replaced by hydrogen after treatment with mild reducing agents such ashypophosphorous acid (or) ethanol.

$[C6H5N2]^{+}Cl^{-} + H3PO2 + H2O \rightarrow C6H6 + N2 + H3PO3 +$
$HCl[C6H5N2]^{+}Cl^{-} + CH3CH2OH \rightarrow C6H6 + N2 +$
$CH3CHO + HCl$

In nitration reactions, the diazonium group is replaced by an -NO2 group.

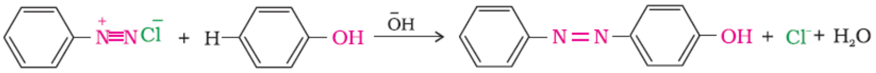


Phenols can be prepared from diazonium salts by hydrolysing with dilute sulphuric acid andheating.

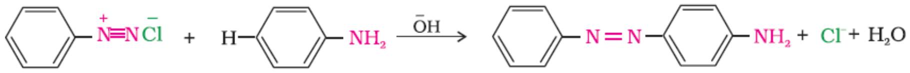


Reactions involving retention of diazo group coupling reactions

Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form coloured azo products in which both thearomatic rings joined through the –N=N– bond.

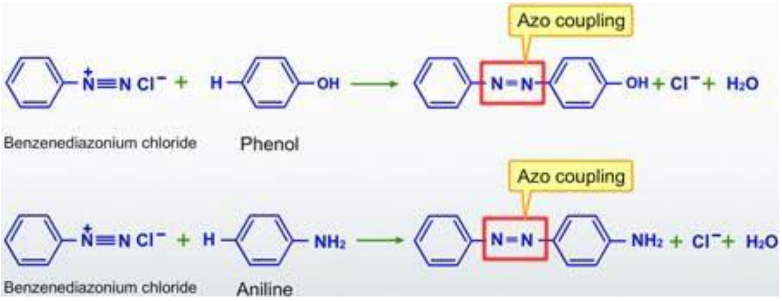


p-Hydroxyazobenzene (orange dye)



p-Aminoazobenzene (yellow dye)

Azo coupling reactions occur when diazonium salts react with phenol (or) aniline.


Azo coupling
Benzenediazonium chloride
Phenol
Azo coupling
Benzenediazonium chloride
Aniline

MULTIPLE CHOICE QUESTIONS AND ANSWERS

1. Benzoic acid is treated with SOCl2 and the product (X) formed is reacted with ammonia togive (Y). (Y) on reaction with Br2 and KOH gives (Z). (Z) in the reaction is

(a) aniline

(b) chlorobenzene
(c) benzamide
(d) benzoyl chloride

Answer: (a) aniline

2. Tertiary amines have lowest boiling points amongst isomeric amines because
(a) they have highest molecular mass
(b) they do not form hydrogen bonds
(c) they are more polar in nature
(d) they are most basic in nature

Answer: (b) they do not form hydrogen bonds

3. Which of the following is used as Hinsberg's reagent?
(a) C6H5SO2Cl
(b) C6H5SO3H
(c) C6H5NHCH3
(d) C6H5COCH3

Answer: (a) $C_6H_5SO_2Cl$

4. Which one of the following is the product that is formed when a primary amine reacts withchloroform in alcoholic KOH?

(a)An isocyanide(b)An alcohol(c)An Aldehyde(d)Cyanide

Answer: (a) An isocyanide

5. Which one of the following reactions helps in preparing amines from

lower amines? (a)Wurtz reaction (b)Grignard reaction(c)Schmidt

reaction(d)Hofmann bromamide reaction**Answer**: **(d)Hofmann bromamide**

reaction

6. What is the correct name for a molecule that has two amino groups in opposing (para)locations around a benzene ring?

(a) Benzenediamine

(b) Benzene-1,4-diamine

(c) p-Aminoaniline

(d) 4-Aminobenzenamine

Answer:(b) Benzene-1,4-diamine

7. Which product is formed when acetonitrile is partially hydrolysed

with cold conc.HCl(a)Methyl cyanide (b)Acetic acid (c)Acetic anhydride

(d)Acetamide

Answer: **(d)Acetamide**

8. Which of the following statements is not correct for

amines?(a). Most alkyl amines are more basic than

ammonia solution. (b). pKb value of ethylamine is

lower than benzylamine.

(c). CH3NH2 on reaction with nitrous acid releases N2 gas.

(d). Hinsberg’s reagent reacts with secondary amines to form sulphonamides

Ans: (c) CH_3NH_2 on reaction with nitrous acid releases N_2 gas

9. Which of the following is incorrect for primary amines?

(a) On reaction with nitrous acid alkylamines produce alcohol

(b) On reaction with nitrous acid arylamines produce phenol

(c) Alkylamines are more basic than ammonia

(d) Alkylamines are more basic than arylamines

Ans: (c) Alkylamines are more basic than ammonia

10. Identify the correct IUPAC name
(a) (CH3CH2)2NCH3 = N-Ethyl-N-methylethanamine
(b) (CH3)3CNH2 = 2-methylpropan-2-amine
(c) CH3NHCH (CH3)2 = N-Methylpropan-2-amine
(d) (CH3)2CHNH2 = 2, 2-Dimethyl-N-propanamine

Ans (a) $(CH_3CH_2)_2NCH_3$ = N-Ethyl-N-methylethanamine

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

(i) Both assertion and reason are correct statements but the reason is not the correctexplanation of assertion.
(ii) Assertion is a correct statement but the reason is a wrong statement.
(iii) Both assertion and reason are correct statements and reason is the correct explanation ofassertion.
(iv) Assertion is the wrong statement but the reason is a correct statement.

1. Assertion: Acylation of amines gives a mono-substituted product whereas alkylation ofamines gives a poly-substituted product.

Reason: Acyl group sterically hinders the approach of further acyl groups.

Ans . (ii)

2. Assertion: Hoffmann's bromamide reaction is given by primary amines.
3. Reason: Primary amines are more basic than secondary amines.

Ans (ii)

4. Assertion: N-Ethylbenzene sulphonamide is soluble in alkali.

Reason: Hydrogen attached to nitrogen in sulphonamide is strongly acidic. Ans (iii)

5. Assertion: N, N-Diethylbenzenesulphonamide is insoluble in alkali.

Reason: Sulphonyl group attached to the nitrogen atom is a strong electron-withdrawing group.

Ans (i)

6. Assertion: Only a small amount of HCl is required in the reduction of nitro compounds withiron scrap and HCl in the presence of steam.

Reason: FeCl2 formed gets hydrolyzed to release HCl during the reaction.

Ans (iii)

.6. Assertion: Acetanilide is less basic than aniline.

Reason: Acetylation of aniline results in a decrease of electron density on nitrogen.

Ans (iii)

7.Assertion (A): Tertiary amines are more basic than corresponding secondary and primaryamines in gaseous state.

Reason (R): Tertiary amines have three alkyl groups which cause +I effect

Ans(iii)

7. **Assertion :** Aromatic 1°amines can not be prepared by Gabriel phthalimide synthesis.

Reason : Aryl halides undergo nucleophilic substitution with anion formed by phthalimide.

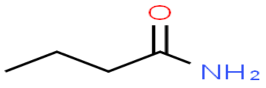
(iii)

TWO MARK QUESTIONS

1. Write structures and IUPAC names of

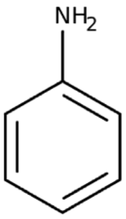
(i) the amide which gives propanamine by Hoffmann bromamide reaction.

Ans :(i) Propanamine contains three carbons. Hence, the amide molecule must contain fourcarbon atoms.



(ii) the amine produced by the Hoffmann degradation of benzamide

Ans:(ii) Benzamide is an aromatic amide containing seven carbon atoms and the amine formedfrom benzamide is aromatic primary amine containing six carbon atoms



2. Complete the following acid-base reactions and name the products:

(i) CH3CH2CH2NH2 + HCl →

Ans:$\mathbf{CH_3CH_2CH_2NH_2 + HCl \rightarrow CH_3CH_2CH_2NH_3{}^{+}Cl^{-}}$

n−Propylammonium chloride

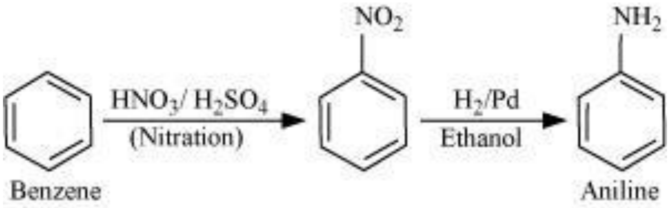
(ii) (C2H5)3N + HCl →

Ans: $\mathbf{(C_2H_5)_3N + HCl \longrightarrow (C_2H_5)_3NH_3{}^{+}Cl^{-}}$

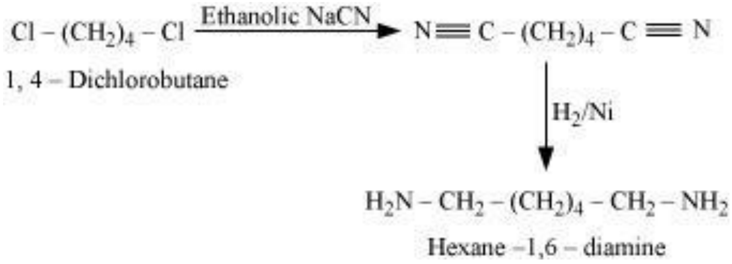
Trimethylammonium chloride

3. How will you convert?

(i) Benzene into aniline

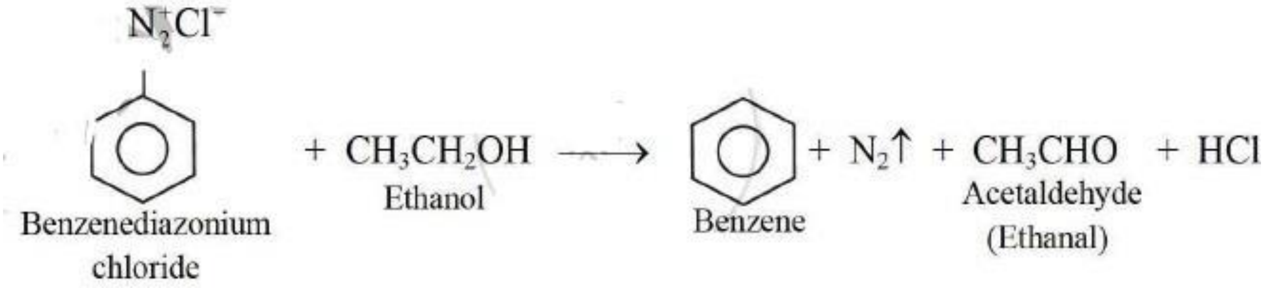


(ii) Cl−(CH2)4−Cl into hexan-1, 6-diamine?

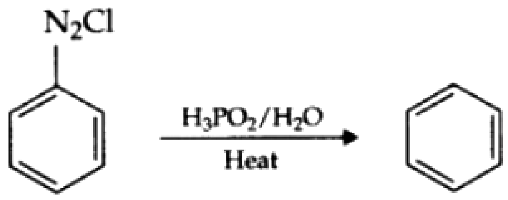


4..How are the following conversions carried out:

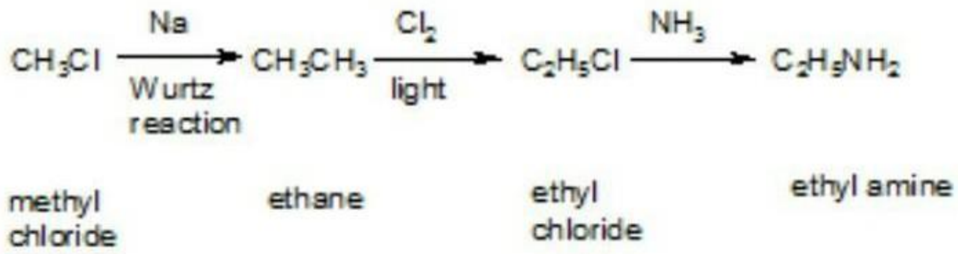
(i) Benzene diazonium chloride to benzene



(OR)



(ii) Methyl chloride to ethylamine



3MARK QUESTIONS

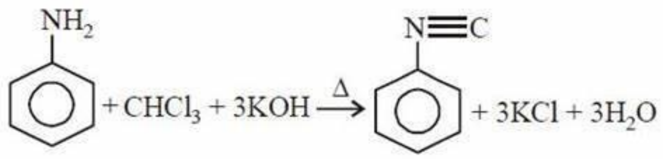
1.Give one chemical test to distinguish between the following pairs of

compounds.(i)Aniline and benzylamine

TEST	ANILINE	BENZYL AMINE
AZO DYE	REDDISH BROWN PPT	NO CHARACTERISTIC REACTION

(ii) Aniline and N-methylaniline.

Carbylamine test : Aniline (Aromatic Primary Amine)when heated with chloroform andethanolic potassium hydroxide, form foul-smelling isocyanides or carbylamines.

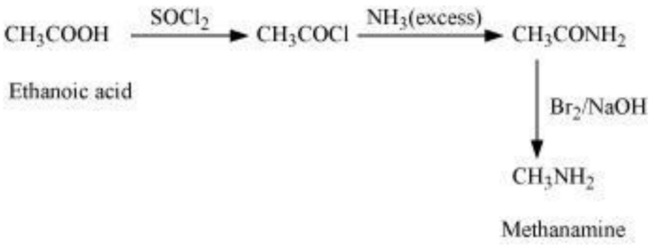


N −methylaniline (secondary amine) does not respond to

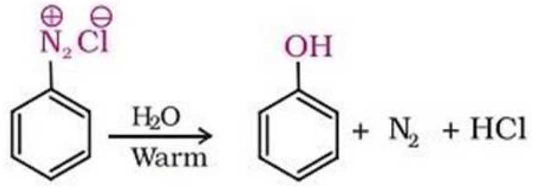
the test.2.How will you convert the following:

(i) Aniline to chlorobenzene

(ii) Ethanoic acid to methanamine

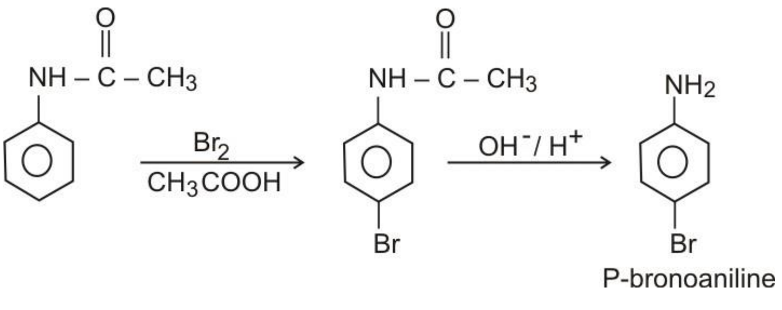


(iii) Benzene diazonium chloride to phenol

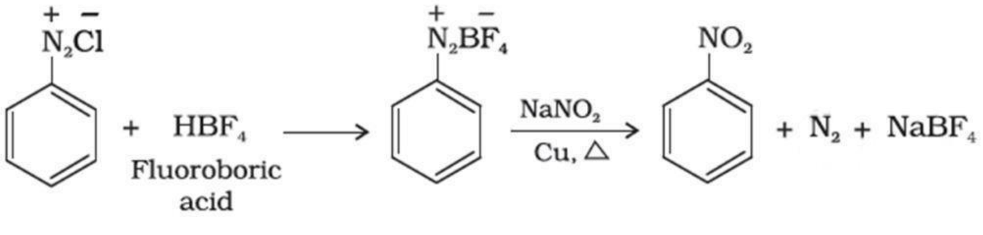


3.How do you convert the following:

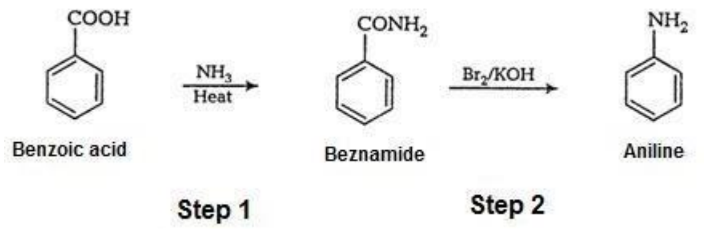
(i) N-phenylethanamide to p-bromoaniline



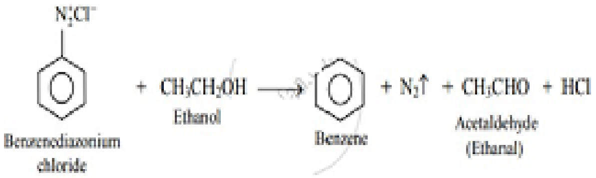
(ii) Benzene diazonium chloride to nitrobenzene



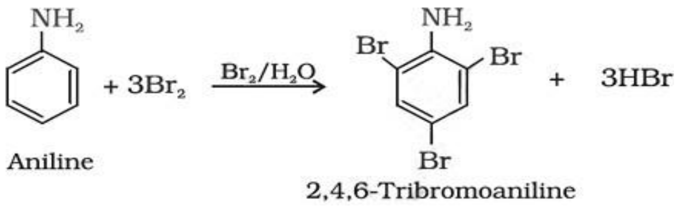
(iii) Benzoic acid to aniline



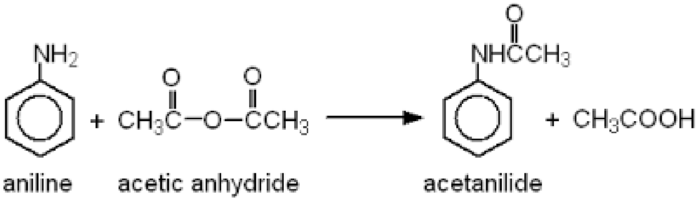
4.Complete the following reactions:



i.



ii)



iii.

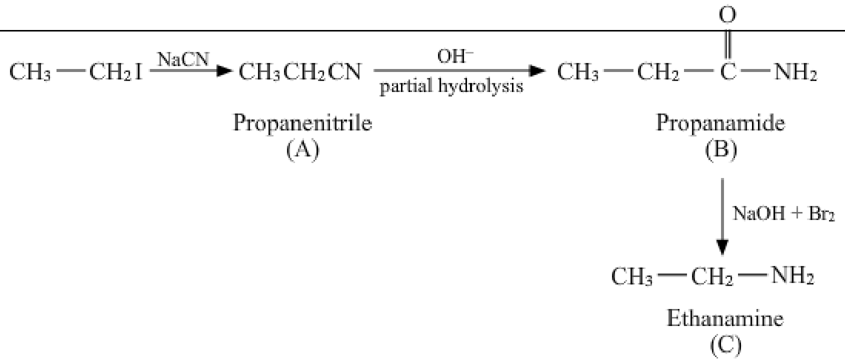
5..Give the structures of A, B and C in the following reactions:

(i) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH,Br_2} C$

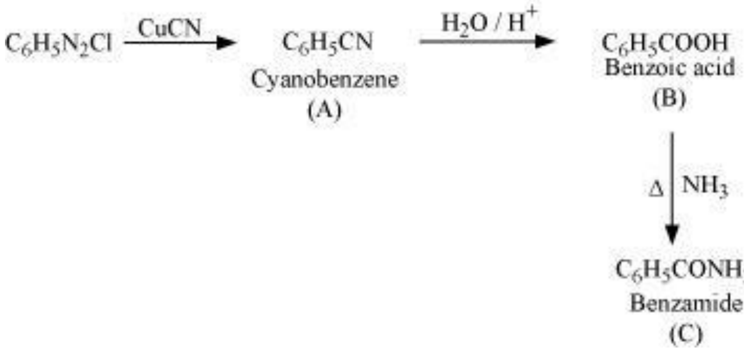
(ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\Delta]{NH_3} C$

(iii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0^0 C]{HNO_2} C$

(i)



(ii)



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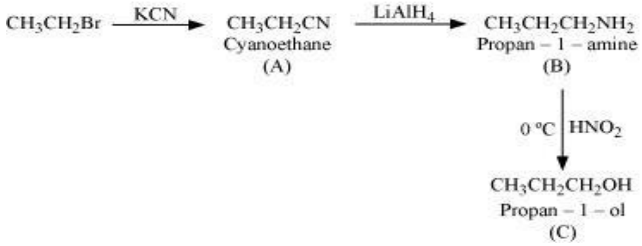


of A, B and C in the following reactions

(i) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{NaNO_2+HCl} B \xrightarrow[\Delta]{H_2O/H^+} C$

(ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

$C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{HNO_2} B \xrightarrow{C_6H_5OH} C$

1.CASE BASED QESTIONS

The conversion of primary amines into diazonium salts is known as diazotization. Arene diazonium salts are generally colourless crystalline solids highly soluble in water. These salts are more stable than aliphatic diazonium salts and undergo a number of substitution reactions due to excellent leaving ability of diazo group as N2. Arene diazonium salts also couple with phenols and amines to form coloured azo dyes. Such type of reactions are known as coupling reactions.

1. What is diazotisation?

Ans. The reaction of converting aromatic primary amines into diazonium salts by treatment with a solution of nitrous acid at 273 K–278 K is called diazotisation

2. Why are arene diazonium salts more stable than aliphatic diazonium salts?

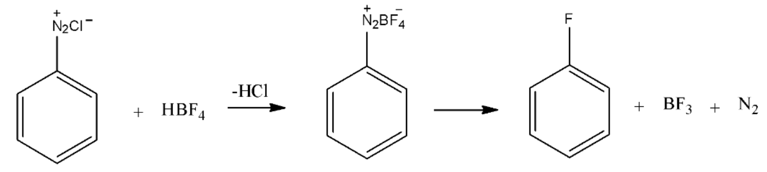
Ans. Arene diazonium salts are more stable than aliphatic diazonium salts due to dispersal of positive charge on the benzene ring as shown below

3. What product is formed when aniline is first diazotised and then reacted with phenol in the alkaline medium?

Ans. p-hydroxyazobenzene

4. How will you convert: Aniline to fluorobenzene?

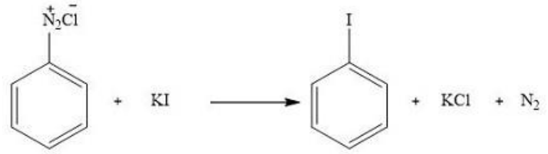
(i) Aniline to fluorobenzene



benzene diazonium salt

fluorobenzene

5. Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt.



2.CASE BASED QUESTIONS

Amines have a lone pair of electrons on nitrogen atom due to which they behave as Lewis base. Larger the value of Kb or smaller the value of pKb stronger is the base. Amines are more basic than alcohols, ethers, esters, etc. The basic character of aliphatic amines should increase with the increase of alkyl substitution. But it does not occur in a regular manner as a secondary aliphatic amine is unexpectedly more basic than a tertiary amine in solutions. Aromatic amines are weaker bases than ammonia and aliphatic amines. Electron-donating groups such as —CH3, —OCH3, —NH2, etc., increase the basicity while electron-withdrawing substituents such as —NO2, —CN, halogens. etc. decrease the basicity of amines. The effect of these substituents is more at p- than at m-positions

1. Arrange the following in increasing order of their basic strength: $C2H5NH2$, $C6H5NH2$, $NH3$, $C6H5CH2NH2$, $(C2H5)2NH$

Ans. $C6H5NH2 < NH3 < C6H5CH2NH2 < C2H5NH2 < (C2H5)2NH$

2. Arrange the following compounds in increasing order of their acidic strength: Methylamine, dimethylamine, aniline, N-methylaniline

Ans. dimethylamine < methylamine < N-methylaniline < aniline.

3. Rearrange the following in increasing order of their basic strength: p-toluidine, N, N-dimethyl-p-toluidine, p-nitroaniline, aniline

Ans. p-nitroaniline < aniline < p-toluidine < N, N-dimethyl-p-toluidine.

4. Which is more acidic, aniline or ammonia?

Ans. Due to delocalization of the lone pair of electrons of the N-atom of aniline over thebenzene ring, aniline is more acidic than ammonia.

5. $(CH3)2NH$ is more basic than $(CH3)3N$ in an aqueous solution. Give reason.

Ans. Combination of three factors, +ve I effect of $CH3$ groups, hydrogen bonding and sterichindrance favour greater stability for ammonium cation of dimethyl amine than ammonium cation of trimethyl amine.

FIVE MARK QUESTIONS

Arrange the following

(i) In decreasing order of the pK_bvalues:
$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

$C6H5NH2 > C6H5NHCH3 > C2H5NH2 > (C2H5)2NH$

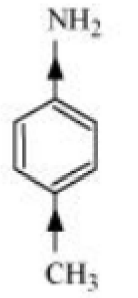
(ii) In increasing order of basic strength:

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

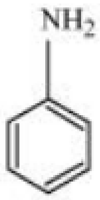
$C6H5NH2 < C6H5N(CH3)2 < CH3NH2 < (C2H5)2NH$

(iii) In increasing order of basic strength:

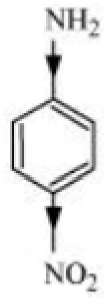
(a) Aniline, p-nitroaniline and p-toluidine



p-Toluidine



Aniline



p-Nitroaniline

p-Nitroaniline < Aniline < p-Toluidine

(iv) In decreasing order of basic strength in gas phase: $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

(C2H5)3N > (C2H5)2NH > C2H5NH2 > NH3

(v) In increasing order of boiling point:

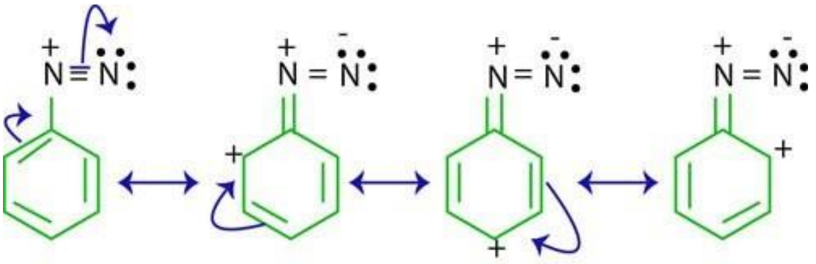
C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

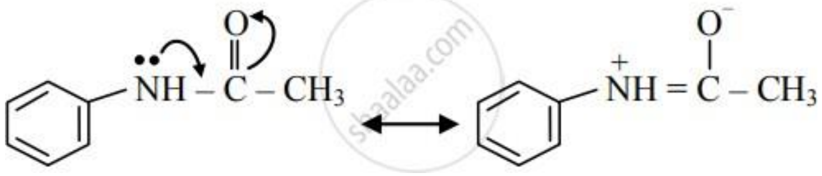
(CH3)2NH < C2H5NH2 < C2H5OH

7.Account for the following:

(a) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

The diazonium salts of aromatic amines are more stable than those of aliphatic amines due toresonance stabilised diazonium ion.





8.Give plausible explanation for each of the following:

(i) Why are amines less acidic than alcohols of comparable molecular masses?

$$R-NH_2 \longrightarrow \underset{\text{Amide ion}}{R-\overset{-}{N}H} + H^+$$

Amide ion (Conjugate base)Alcohol loses a proton to give alkoxide ion.

$$\underset{\text{Alcohol}}{R-OH} \longrightarrow \underset{\text{Alkoxide ion}}{R-\overset{-}{O}} + H^+$$

Alkoxide ion (Conjugate base) + H +Acidic strength a stability of conjugate base or anion

Stability of conjugate base or anion a negative charge density on anion a electronegativity ofatom

Why are aliphatic amines stronger bases than aromatic amines?

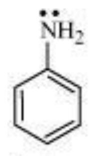
(iii) Due to the −R effect of the benzene ring, the electrons on the N- atom are less available incase of aromatic amines cannot be donated easily. Hence aliphatic amines are stronger bases than aromatic amines

(OR)

Due to the -R effect of the benzene ring, the electrons on the N-atom are less available in aromatic amines. For aliphatic amine R → NH2, R exerts +I effect. Charge density on nitrogenincreases; hence, basic character increases

7.Account for the following:

(i) p*Kb* of aniline is more than that of methylamine.

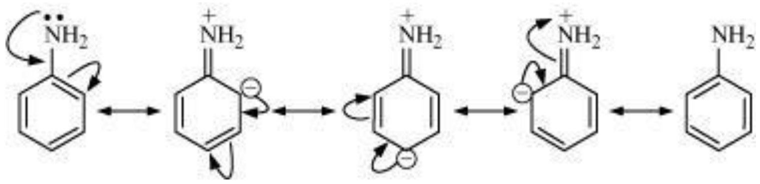


Aniline

$CH_3-\ddot{N}H_2$

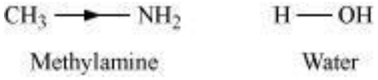
Methylamine

Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring less available to donate.



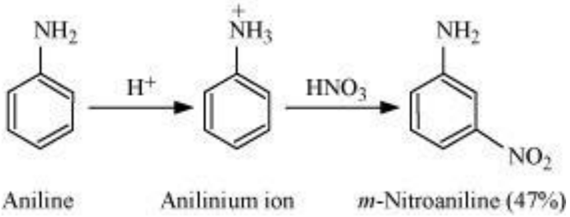
In methylamine (due to the +I effect of methyl group), the electron density on the N-atom is increased, aniline is less basic than methylamine. Thus, *pKb* of aniline is more than that of methylamine

(ii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.



Due to the +I effect of −CH3 group, methylamine is more basic than water. Therefore, in water, methylamine produces OH^- ions by accepting H^+ ions from water.
then, OH^- ion reacts with Fe^{3+} ion to form a precipitate of hydrated ferric oxide.

(iii) Although amino group is *o, p*− directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.
Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).

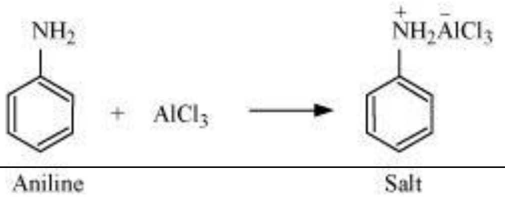


(iv)

For this reason, aniline on nitration gives a substantial amount of m-nitroaniline

(iv) Aniline does not undergo Friedel-Crafts reaction.

Friedel-Crafts reaction is carried out in the presence of AlCl3. But AlCl3 is acidic in nature, while aniline is a strong base. Thus, aniline reacts with AlCl3 to form a salt (as shown in the following equation).



(v)

Due to the positive charge on the N-atom, electrophilic substitution in the benzene ring is deactivated. Hence, aniline does not undergo the Friedel-Crafts reaction

(v) Diazonium salts of aromatic amines are more stable than those of aliphatic amines. The diazonium ion undergoes resonance .

This resonance accounts for the stability of the diazonium ion. Hence, diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vi) Gabriel phthalimide synthesis is preferred for synthesising primary amines.
Gabriel phthalimide synthesis results in the formation of 1° amine only. 2° or 3° amines are not formed in this synthesis. Thus, a pure 1° amine can be obtained. Therefore, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

7.Give reasons for the following observation:

a. Aniline is acetylated before nitration reaction.

Aniline is acetylated, before nitration reaction in order to avoid formation of tarry oxidation products and protecting the amino group, so that p -nitro derivative can be obtained as major product aniline does not react with methyl chloride in the presence of anhydrous $AlCl_3$ catalyst.

Aniline does not react with methylchloride in the presence of $AlCl_3$ catalyst , because aniline is a base and $AlCl_3$ is Lewis acid which lead to formation of salt

10,BIOMOLECULES

Key concepts of the lesson

A **biomolecule** refers to any molecule that is produced by living organisms. The four major groups of biomolecules include Carbohydrates, Proteins, Nucleic acids (DNA and RNA), and Lipids.

Carbohydrates: The carbohydrates are optically active polyhydroxy aldehydes or ketones. They can be classified as

(i) Monosaccharides: A carbohydrate that is not decomposable into simpler sugars by hydrolysis. Examples: Glucose, Fructose, Ribose, etc.

(ii) Oligosaccharides: Carbohydrates that yield two to ten monosaccharide units, on hydrolysis, are called oligosaccharides. Disaccharides give two monosaccharides on hydrolysis.

For example, one molecule of sucrose on hydrolysis gives one molecule of glucose and one molecule of fructose whereas maltose gives two molecules of glucose.

(iii) Polysaccharides: Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called polysaccharides. Some common examples are starch, cellulose, glycogen, gums, etc.

*Polysaccharides are also called **non-sugars** as they are not sweet in taste.

***Reducing sugars**: All those carbohydrates which reduce Fehling's solution and Tollens' reagent as they have free functional group are referred to as reducing sugars. All monosaccharides whether aldose or ketose are reducing sugars.

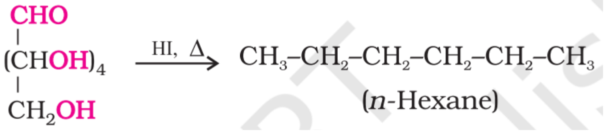
Glucose: $C_6H_{12}O_6$

Glucose can be prepared by hydrolysis of Sucrose

$C_{12}H_{22}O_{11} \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$
Sucrose Glucose + Fructose

Important reactions of Glucose:

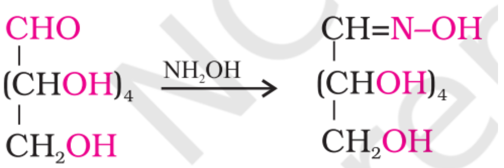
***On prolonged heating with HI, it forms n-hexane (all the six carbon atoms are in a straight chain).



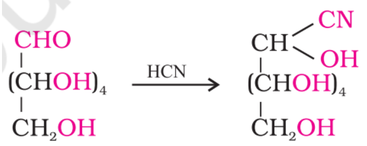
$$CHO-(CHOH)_4-CH_2OH \xrightarrow{HI,\ \Delta} CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$$

(n-Hexane)

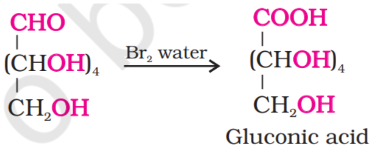
* Glucose reacts with hydroxylamine to form an oxime (Presence of Carbonyl group is confirmed)



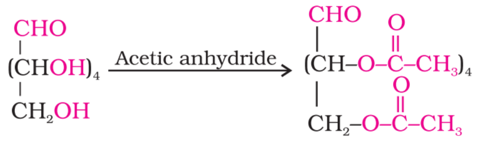
* Glucose adds a molecule of HCN to give cyanohydrin (Presence of Carbonyl group is confirmed)



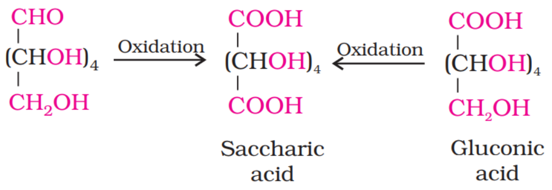
*Glucose on oxidation with Bromine water gives Gluconic acid (Presence of Aldehyde group is confirmed)



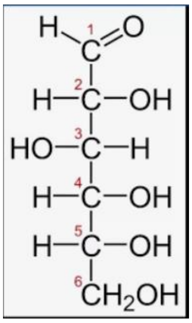
*Glucose forms penta acetate with acetic anhydride confirming the presence of five –OH groups attached to different Carbon atoms



* On oxidation with nitric acid, glucose as well as gluconic acid both yield a dicarboxylic acid, saccharic acid. This indicates the presence of a primary alcoholic (–OH) group in glucose.



*On the basis of the above points glucose can be assigned the following structure



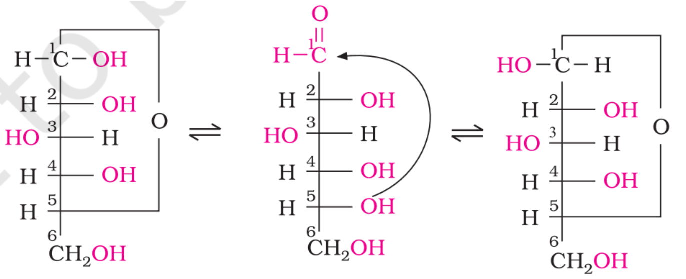
* Cyclic Structure of Glucose

(Some reactions could not explain the open chain structure of glucose)

1. Glucose does not give Schiff's test and it does not form the hydrogen sulphite addition product with $NaHSO_3$.

2. The penta acetate of glucose does not react with hydroxylamine indicating the absence of free —CHO group. Glucose exist in two forms which are named as α form (m.p 419 K and

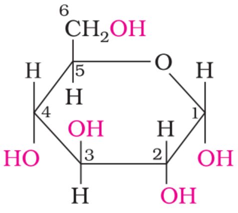
β-form (m.p. 423 K) which exist in equilibrium with open chain structure. Glucose forms a six-membered ring in which —OH at C-5 is involved in ring formation.

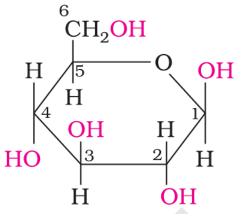

α – D – (+) – Glucose

β – D– (+) – Glucose

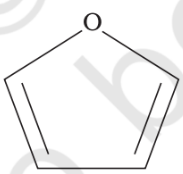
* The two cyclic hemiacetal forms of glucose which differ only in the configuration of the hydroxyl group at C1 are called **anomers.** (α-form and β-form)

* The cyclic structure (Haworth structure) of glucose is represented below.

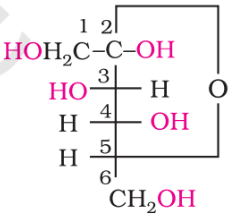

α – D – (+) – Glucopyranose


β – D – (+) – Glucopyranose

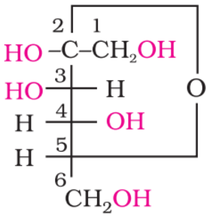
The structure of fructose is as follows



Furan



α – D – (–) – Fructofuranose



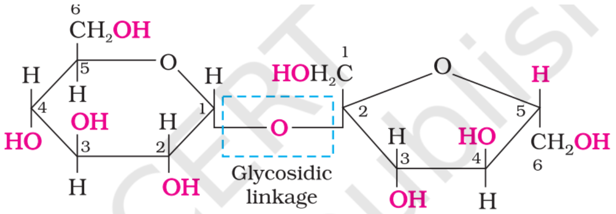
β – D – (–) – Fructofuranose

Disaccharides

Sucrose is hydrolysed to give **D-(+)-glucose and D-(-) fructose.**

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{D-(+)-Glucose}}{C_6H_{12}O_6} + \underset{\text{D-(–)-Fructose}}{C_6H_{12}O_6}$$

*The –O- linkage between two monosaccharides in oligosaccharides/polysaccharides is called **glycosidic linkage**.



α – D – Glucose β – D – Fructose

*Maltose upon hydrolysis gives **two molecules α-D-glucose units**

* Lactose upon hydrolysis gives **β-D-galactose and β-D-glucose**.

Polysaccharides

Starch consists of two component, Amylose and Amylopectin.

Amylose is water soluble component which constitutes about 15-20% of starch. Amylose is a long unbranched chain with 200-1000 α-D-(+)-glucose units.

Amylopectin is insoluble in water and constitutes about 80- 85% of starch.

Amylopectin is a branched chain polymer of α-D-glucose units.

Cellulose is a straight chain polysaccharide composed only of β-D-glucose units

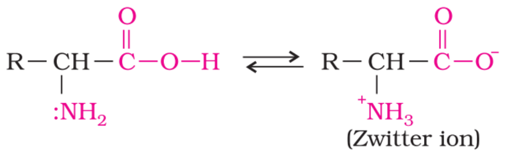
Glycogen: The carbohydrates are stored in animal body as glycogen. It is also known as **animal starch** because its structure is similar to amylopectin. It is present in liver, muscles and brain.

Proteins: Proteins are made up of amino acids. Amino acids contain amino (–NH_2) and carboxyl (–COOH) functional groups. Glycine is the only amino acid which is optically inactive.

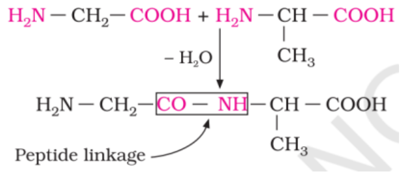
Nonessential amino acids: The amino acids, which can be synthesised in the body, are known as nonessential amino acids. Example: Glycine, Alanine

Essential amino acids: The amino acids which cannot be synthesised in the body and must be obtained through diet, are known as essential amino acids. Example: Valine, Leucine

Zwitter ion: In aqueous solution, the carboxyl group loses a proton and amino group accepts a proton, giving rise to a dipolar ion known as zwitter ion. Amino acids are water soluble, have high melting point and behave like salt due to the presence of both acidic and basic groups. Zwitter ionic form shows amphoteric in nature and react with acid and base.



***Peptide linkage:** A peptide linkage is a CONH bond formed between the carboxyl group of one molecule and the amino group of the other molecule, releasing a molecule of water (H_2O).



*Proteins can be classified into two types on the basis of their molecular shape- Fibrous Proteins and Globular Proteins

Fibrous Proteins	**Globular Proteins**
Usually long and narrow	Typically spherical in shape
Helps to maintain cell shape	Helps to carry out a specific biological function in the body
Insoluble in water	Soluble in water
Amino acid sequence is repetitive	Amino acid sequence is irregular
Example: Keratin, collagen	Example: Haemoglobin, Insulin

***Primary structure of proteins**: The specific sequence of amino acids linked with each other is said to be the primary structure of that protein. Any change the sequence of amino acids creates a different protein.

* The loss of biological activity of a protein when it is subjected to change in heat or change in pH is known as **denaturation of proteins.** The primary structure remains intact whereas the secondary and tertiary structures are disrupted.

***Enzymes** are the globular proteins that catalyse a biochemical reaction.

Example: Maltase catalyses the hydrolysis of Maltose to Glucose

***Vitamins** are vital amines required in the diet in small amounts to perform specific biological functions but their deficiency cause diseases.

*Vitamins are classified into two groups- (i) **Fat soluble vitamins:** Vitamins which are soluble in fat and oils but insoluble in water belong to this group. These are vitamins **A, D, E and K.** (ii) **Water soluble vitamins: B** group vitamins and vitamin **C** are soluble in water.

***Water soluble vitamins must be supplied regularly in diet** because they are readily excreted in urine and cannot be stored (except vitamin B_{12}) in our body.

(Learn the contents of Table 14.3 of your NCERT text book to know about deficiency diseases of various vitamins)

***Nucleic acids**:

DNA	**RNA**
DNA is found in all living organisms and is a genetic material.	RNA is involved in protein synthesis.
DNA contains four bases - adenine (A), guanine (G), cytosine (C) and thymine (T).	RNA contains four bases-adenine (A), guanine (G), cytosine (C), uracil (U).
In DNA molecules, the sugar moiety is β-D-2-deoxyribose	In RNA molecule, the sugar moiety is β-D-ribose.

*There are three types of RNA - rRNA, tRNA and mRNA.

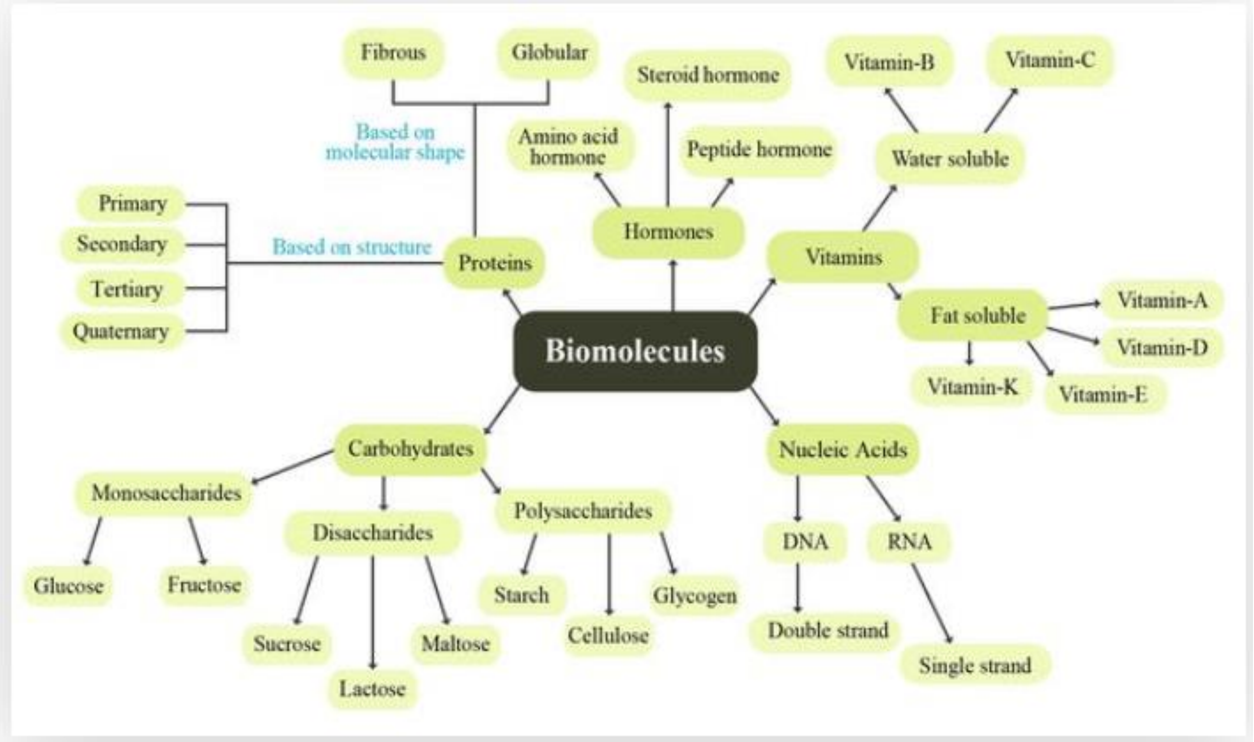
Nucleoside	**Nucleotide**
The chemical composition of Nucleosides = sugar + base	The chemical composition of Nucleotide = sugar + base + a phosphate group

* **Hormones:** Hormones are intercellular messengers. They help to maintain the balance of biological activities in the body.

*Thyroxine is produced in the thyroid gland. Low level of iodine in the diet leads to hypothyroidism and enlargement of the thyroid gland. Hypothyroidism can be controlled by adding sodium iodide to commercial table salt (“Iodised” salt). Higher levels of thyroid lead to hyperthyroidism.

*Testosterone is the hormone produced in males and estradiol is the main hormone produced in females.

Mind map for the lesson BIOMOLECULES



Multiple Choice Questions

1. Consider the following statements.

Statement I Carbohydrates which reduces Fehling’s solution and Tollens’ reagent are referred to as reducing sugars.

Statement II Glucose is a ketohexose

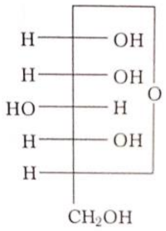
Which of the above statement(s) is/are correct?

(a) Only I	(b) Only II
(c) Both I and II	(d) Neither I nor II

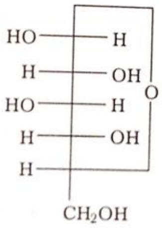
Ans: (a) Only I

2. Which of these cyclic structures of monosaccharides are anomers?

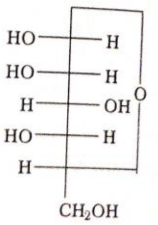
I.



II.



III.



(a) I and III (b) II and III

(c) I and II (d) none

Ans: (c) I and II

3. Which one of the following reactions is not explained by the open chain Structure of glucose?

(a) Formation of pentaacetate of glucose with acetic anhydride.

(b) formation of addition product with 2,4 DNP reagent

(c) Silver mirror formation with Tollen's reagent

(d) existence of alpha and beta forms of glucose.

Ans: (d) existence of alpha and beta forms of glucose.

4. Which hormone is responsible for preparing the uterus for implantation of fertilised egg?

(a) Testosterone (b) Estradiol

(c) Thyroxine (d) Progesterone

Ans: (d) Progesterone

5. Which hormone is an iodinated derivative of amino acid tyrosine?

(a) Thyroxine (b) Epinephrine

(c) Glycogen (d) Insulin

Ans: (a) Thyroxine

6. Nucleic acids are long chain polymers of
(a) nucleosides (b) nucleotides
(c) bases (d) sugars
Ans: (b) nucleotides

7. Which of the following acids is a vitamin?
(a) Aspartic acid (b) Ascorbic acid
(c) Adipic acid (d) Saccharic acid

Ans: (b) Ascorbic acid

8. Which of the following Vitamin helps in blood clotting?
(a) Vitamin-A (b) Vitamin-C
(c) Vitamin-D (d) Vitamin-K
Ans: (d) Vitamin-K
9. Which of the following is incorrect?
(a) Deficiency of riboflavin cause cheilosis
(b) Deficiency of Vitamin-B_6 can cause convulsion
(c) Rickets and osteomalacia are diseases caused by deficiency of Vitamin-K
(d) Deficiency of Vitamin-A can cause night blindness
Ans: (c) Rickets and osteomalacia are diseases caused by deficiency of Vitamin-K
10. The behaviour shown by amino acids in zwitter ionic form is
(a) acidic (b) basic
(c) neutral (d) amphoteric
Ans: (d) amphoteric
11. Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that is said to be the
(a) primary structure of that protein. (b) secondary structure of that protein.
(c) tertiary structure of that protein. (d) quaternary structure of that protein.
Ans: (a) primary structure of that protein.
12. Which of the following statement is correct?
(a) Fibrous proteins are generally soluble in water
(b) Albumin is an example of fibrous proteins
(c) In globular proteins, the structure is stabilised only by hydrogen bonds
(d) pH does not affect the primary structure of protein.
Ans: (d) pH does not affect the primary structure of protein.
13. Which one of the following is correct about glucose?
(a) Glucose is a disaccharide
(b) Glucose is also known as dextrose.
(c) Glucose gets oxidised to saccharic acid on reaction with bromine water.
(d) Glucose gives violet colour with Schiff's reagent
Ans: (b) Glucose is also known as dextrose.
14. On hydrolysis of proteins, we obtain
(a) β Amino Acids (b) α amino acids
(c) γ Amino Acids (d) All of these
Ans: (b) α amino acids
15. Proteins are found to exist in two different types of structures α-helix and β-pleated sheet structure. α-Helix structure is stabilised by
(a) van der Waals' forces (b) dipole-dipole interaction
(c) hydrogen bonds (d) peptide bonds
Ans: (c) hydrogen bonds
16. Vitamin K is essential for
(a) Blood clotting (b) Eye sight
(c) Muscular strength (d) Bone strength
Ans: (a) blood clotting

17. The base that is present in DNA, but not in RNA is

(a) Cytosine (b) guanine

(c) Adenine (d) Thymine

Ans: (d) Thymine

18. Choose the factor which is not responsible for denaturation of protein.

(a) Change in pH (b) Mass of protein

(c) Organic solvents (d) Change in temperature

Ans: (b) Mass of protein

Assertion and Reason type questions

Note: In the following questions a statement of Assertion A followed by a statement of Reason R is given.

Choose the correct answer out of the following choices.

Select the most appropriate answer from the options given below:

a. Both A and R are true and R is the correct explanation of A

b. Both A and R are true but R is not the correct explanation of A.

c. A is true but R is false.

d. A is false but R is true.

1. Assertion A : D (+) – Glucose is dextrorotatory in nature.

Reason R : ‘D’ represents its dextrorotatory nature.

Ans: (c) Assertion A is correct statement and Reason R is wrong statement.

2. Assertion A: Pentaacetate of glucose does not react with hydroxylamine

Reason R: Glucose on reaction with $NaHSO_3$, does not form the hydrogen sulphite addition

product

Ans: (c) Assertion A is correct statement and Reason R is wrong statement.

3. Assertion A: Melting points and solubility in water of amino acids are generally higher than the corresponding halo acids.

Reason R: Dipolar behaviour due to proton acceptor and proton donor moiety results in strong electrostatic interaction

Ans: (a) Assertion A and Reason R both are correct statements and Reason R explains the Assertion

4. Assertion A: Vitamin D can be stored in our body

Reason R: Vitamin D is a fat soluble vitamin

Ans: (a) Assertion A and Reason R both are correct statements and Reason R explains the Assertion

5. Assertion A: RNA has double strand helical structure

Reason R: When RNA is hydrolysed, there is no relationship among the quantities of different bases obtained.

(d) Assertion A is wrong statement and Reason R is correct statement.

6. Assertion A: Glucose is soluble in water but cyclohexane is not.

Reason R: The –OH group in glucose undergo extensive Hydrogen bonding with water. whereas hydrogen bonding is weak in cyclohexane.

Ans: (c) Assertion A is correct statement and Reason R is wrong statement. (There is no hydrogen bonding in cyclohexane)

7. Assertion A: Glycine must be taken through diet.

Reason R: It is a non essential amino acid.

Ans: (c) Both Assertion A and Reason R are wrong statements.

8. Assertion A: All naturally occurring α-amino acids are optically active.

Reason R: Most naturally occurring amino acids have L-configuration

Ans: (d) Assertion A is wrong statement and Reason R is correct statement.

9. Assertion A: Sucrose is optically active

Reason R: Hydrolysis of sucrose brings about a change in rotation, from dextro (+) to laevo (–)

Ans: (b) Assertion A and Reason R both are correct statements but Reason R does not explain Assertion.

2-Marks Questions

1. What is the main differences between α-form of glucose and β-form of glucose?

Ans: (i) α-glucose and β-glucose differ in position of –OH group on C–1, therefore, these are called anomers.

(ii) They differ in specific rotation (optical rotation) and

(iii) They differ in melting points.

2. Write such reactions and facts about glucose which cannot be explained by its open chain structure.

Ans: (i) Glucose does not respond to Schiff’s reagent test.

(ii) It does not react with sodium bisulphite and ammonia.

3. Name the sugar present in milk. How many monosaccharide units are present in it? What are such oligosaccharides called?

Ans: Lactose is present in milk. It is made up of two monosaccharide units- β-D galactose and β-D glucose. Such oligosaccharides are called disaccharides.

4. Which sugar is called invert sugar? Why is it called so?

Ans: Mixture of glucose and fructose is called invert sugar. It is called invert sugar because dextrorotatory sucrose gives mixture of glucose and fructose on hydrolysis which is laevorotatory, therefore, it is called invert sugar.

5. State what do you understand by primary structure and secondary structure of proteins.

Ans: Primary Structure of Protein: The sequence in which the amino acids are arranged in a protein is called the primary structure of protein.

Secondary Structure of Protein: The polypeptide chain gets folded due to intermolecular hydrogen bonding between the carboxyl and amino groups. In an α-helix, the peptide chain coils and the turns of the coil are held together by hydrogen bonds. Another type of secondary structure is possible in which the protein chains are stretched out and hydrogen bond formed between them. This is the β-pleated sheet structure.

6. What are vitamins? Which vitamin deficiency causes (i)Pernicious anaemia?(ii) Convulsions?

Ans: Vitamins are the group of organic compounds which are required in very small amounts for the healthy growth and functioning of animal organism. They cannot be made by organism and so have to be part of our diet. The deficiency of a vitamin can cause a specific disease, e.g. (i) Vitamin B_{12} deficiency causes pernicious anaemia (ii) Vitamin B6 deficiency causes convulsion.

8.What is a (i) glycosidic linkage and (ii) peptide linkage?

Ans: The two monosaccharide units are joined together through an etheral or oxide linkage (-O-) formed by loss of a molecule of water. Such a linkage between two monosaccharide units through oxygen atom is called glycosidic linkage.

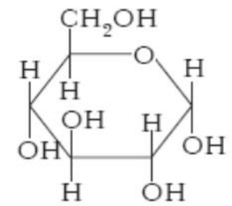
(ii) A peptide linkage (-CO-NH linkage) is a chemical bond formed between the carboxyl group of one molecule and amino group of the other molecule with the elimination of water molecule.

9. What are the products of hydrolysis of (i) sucrose (ii) Lactose?

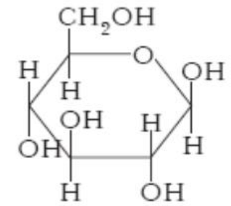
Ans: (i) Glucose and fructose. (ii)Glucose

11. What is meant by pyranose structure of glucose?

The six membered cyclic structure of glucose is called pyranose structure



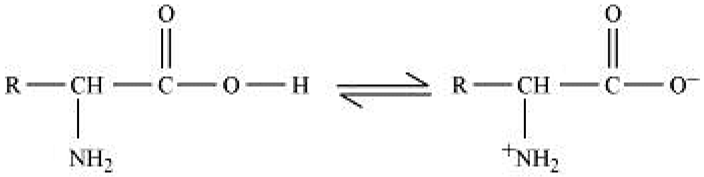
α-D(+)-Glucopyranose



β-D(+)-Glucopyranose

12. The melting points and solubility in water of amino acids are generally higher than that of the corresponding halo acids. Explain.

Ans: Both acidic (carboxyl) as well as basic (amino) groups are present in the same molecule of amino acids. In aqueous solutions, the carboxyl group can lose a proton and the amino group can accept a proton, thus giving rise to a dipolar ion known as a zwitter ion.

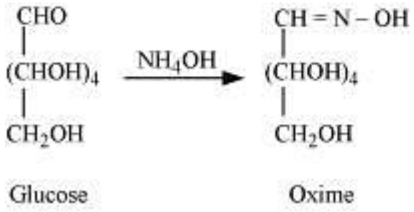


(Zwitter ion)

Due to this dipolar behaviour, they have strong electrostatic interactions within them and with water. But halo-acids do not exhibit such dipolar behaviour.so, the melting points and the solubility of amino acids in water is higher than those of the corresponding halo-acids.

13. How do you explain the absence of aldehyde group in the pentaacetate of D-glucose?

Ans: D-glucose reacts with hydroxylamine (NH_2OH) to form an oxime because of the presence of aldehydic (−CHO) group . This happens as the cyclic structure of glucose forms an open chain structure in an aqueous medium, which then reacts with NH_2OH to give an oxime.



But pentaacetate of D-glucose does not react with NH_2OH as it does not form an open chain structure.

14: What is glycogen? How is it different from starch?

Ans: In animals, carbohydrates are stored as glycogen a carbohydrate (polysaccharide).

Starch is a carbohydrate consisting of two components − amylose (15 − 20%) and amylopectin (80 − 85%).

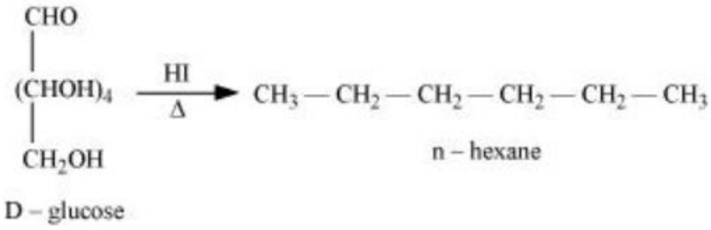
Glycogen consists of only one component whose structure is similar to amylopectin. Also, glycogen is more branched than amylopectin.

3-Marks Questions

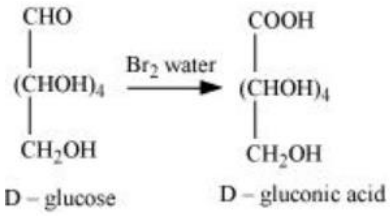
1. What happens when D-glucose is treated with the following reagents?

(i) HI (ii) Bromine water (iii) HNO_3

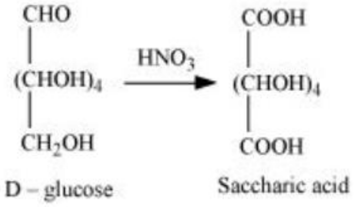
Ans: (i) When D-glucose is heated with HI for a long time it forms n-hexane



(ii) When D- glucose is treated with Br_2 water it gets oxidised to gluconic acid.



(ii) When D- glucose is treated with HNO_3 it gets oxidised to saccharic acid.



2. (i) What is the effect of denaturation on the structure of proteins?

(ii) Give two examples of denaturation.

Ans: (i) As a result of denaturation the globules get unfolded and the helixes get uncoiled. The secondary and tertiary structures get disrupted. The primary structure remains intact and the enzyme loses its activity.

(ii) The coagulation of egg white on boiling and curdling of milk

3. Complete the following statement: In sucrose the two monosaccharide units are held together by _____(A) linkage between C_1 of _______(B) and C of _______(C)

Ans: A= glycosidic B= α -Glucose C= β -Fructose

4. Define the following as related to proteins

(i) Peptide linkage (ii) Primary structure (iii) Denaturation.

Ans (i) Peptide linkage: A peptide linkage (-CO-NH linkage) is a chemical bond formed between the carboxyl group of one molecule and amino group of the other molecule with the elimination of water molecule.

(ii) Primary structure: The primary structure of a protein is defined as the sequence of amino acids linked together to form a polypeptide

(iii) Denaturation. The loss of biological activity of a protein when it is subjected to change in heat or pH is known as denaturation of proteins.

5. Differentiate between the following

(i) Amylose and amylopectin (ii) Peptide linkage and glycosidic linkage (iii) Fibrous proteins and globular proteins

Ans: **(i) Amylose and amylopectin**: Amylose is water soluble component which constitutes about 15-20% of starch. Amylose is a long unbranched chain with 200-1000 α-D-(+)-glucose units. Amylopectin is insoluble in water and constitutes about 80- 85% of starch. Amylopectin is a branched chain polymer of α-D-glucose units.

(ii) **Peptide linkage and glycosidic linkage**: A peptide linkage (-CO-NH linkage) is a chemical bond formed between the carboxyl group of one molecule and amino group of the other molecule. The –O- linkage between two monosaccharides in oligosaccharides/ polysaccharides is called glycosidic linkage.

(iii) Fibrous proteins and globular proteins.

Fibrous Protein: Thread like structures, insoluble in water. Example: Keratin, Myosin Globular Protein: spherical shape, soluble in water. Example: Insulin, Albumin

Case Based Questions – 4 marks

I. Proteins are poly peptide chains made up of amino acids. There are 20 types of amino acids joined together by peptide bond between amino and carboxylic acid group. The amino acids are of two types-essential amino acids and non-essential amino acids. The primary structure of a protein is defined as the sequence of amino acids linked together to form a polypeptide chain. The first amino acid of sequence is called N-terminal amino acid and last amino acid of peptide chain is called C-terminal amino acid. The secondary structure of protein are α-helix, β-pleated sheet structure and collagen helix. The tertiary structure of proteins represents overall folding of the polypeptide chains i.e., further folding of the secondary structure. The spatial arrangement of these subunits with respect to each other is known as quaternary structure.

(i). The tertiary structure of a protein contains

(a) Hydrogen bonds (b) peptide bonds (c) ionic bonds and S linkage (d) all the above

Ans: (d) all the above

(ii). The simplest amino acid is

(a) Phenol (b) formic acid (c) glycine (d) saccharic acid

Ans: (c) glycine

(iii). There is extensive diversity of protein molecule due to

(a) $-NH_2$ group of amino acid (b) R- group of amino acid (c) –COOH group of amino acid

(d) sequence of amino acids

Ans: (d) sequence of amino acids

(iv). Assertion A: Amino acids are monomers of nucleic acid

Reason R: Protein are polymers of amino acids

a. Both A and R are true and R is the correct explanation of A

b. Both A and R are true but R is not the correct explanation of A.
c. A is true but R is false.
d. A is false but R is true.
Ans: (d) A is False and R is false

(v). Glycine and alanine are different with respect to one substituent on the α-carbon. What are the other common substituent groups?
(a) $NH_{2,}$ -COOH, -H (b) -$NH_{2,}$ -H (c) -$NH_{2,}$ -COOH (d) –COOH, -H

Ans: (a) $NH_{2,}$ -COOH, -H

II. Fructose also has the molecular formula $C_6H_{12}O_6$ and on the basis of its reactions it was found to contain a ketonic functional group at carbon number 2 and six carbons in straight chain as in the case of glucose. It belongs to D-series and is a laevorotatory compound. It is appropriately written as D-(–)-fructose. It also exists in two cyclic forms which are obtained by the addition of —OH at C5 to the carbonyl group. The ring, thus formed is a five membered ring and is named as furanose with analogy to the compound furan.

(i) Fructose is ____________ isomer of Glucose

(a) position (b) chain (c) functional (d) optical

Ans: (c) functional

(ii) Fructose is an example of

(a) aldohexose. (b) aldopentose. (c) ketopentose (d) ketohexose.

Ans: (d) ketohexose.

(iii) Fructose is also called

(a) dextrose (b) pyranose (c) furanose (d) hexose

Ans: (c) furanose

(iv) Furan is a five membered cyclic compound with

(a) one oxygen and four carbon atoms (b) one sulphur and four carbon atoms.

(c) one nitrogen and four carbon atoms (d) one oxygen and five carbon atoms.

Ans: (a) one oxygen and four carbon atoms

HOTS

1. Sucrose is a non-reducing sugar, even though it is made up of glucose and fructose which are reducing sugar. Why?
Ans: The reducing group of glucose (C_1) and C_2 of fructose are involved in glycosidic bond formation in sucrose, therefore sucrose is not reducing.

2. Sucrose is dextrorotatory, but after hydrolysis the mixture is laevorotatory. Why?
Ans: Sucrose on hydrolysis gives glucose with dextrorotation (+52.5) and fructose with laevorotation (-92.40), which is higher than the dextrorotation.

3. Both amylose and amylopectin have glycosidic linkage at C_1- C_4 of α D (+) glucose units, amylopectin is insoluble in water whereas amylose is soluble.
Ans: In amylopectin, extra branching occurs by C_1-C_6 glycosidic linkage, therefore it is insoluble.

4. Why can't we digest cellulose, even though both starch and cellulose are made up of glucose units?
Ans: Starch is made up of α D glucose while cellulose is made up of β D glucose. We do not have enzymes which can digest β D glucose.

5. Glucose and sucrose are soluble in water but cyclohexane and benzene are insoluble in water. Why?
Ans: Glucose and sucrose can form hydrogen bonds with water due to the presence of OH group whereas cyclohexane and benzene cannot.

6. Amino acids are polar in nature. Why?
Ans: Due to the formation of zwitter ion.

7. How many peptide bonds will be formed when ten amino acids polymerise?
Nine peptide bonds will be formed.

8. What makes hair, wool, and silk insoluble in water?
Ans: Fibrous structure that is Polypeptide chains run parallel and are held together by hydrogen bonds and disulphide bonds, which makes it insoluble in water.

9. Amino acids have higher melting point and higher solubility than the corresponding haloacids.
Ans: Amino acids have dipoles and exist as zwitter ions which account for the high solubility and strong bonds between the molecules.

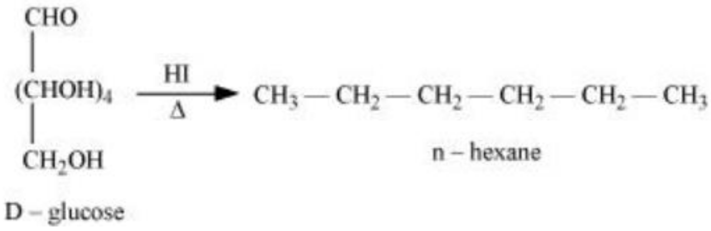
10. Vitamin B and C, should be taken regularly and frequently in our diet, than other vitamins.
Ans: B and C vitamins are water soluble, cannot be stored and are excreted in urine.

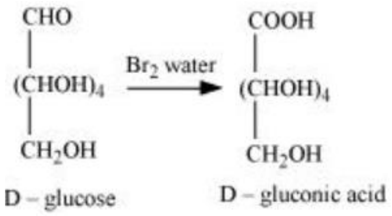
11. What structural difference is there between α glucose and β glucose?
Ans: They differ in the orientation of -OH group on C_1 carbon atom which are known as anomers.

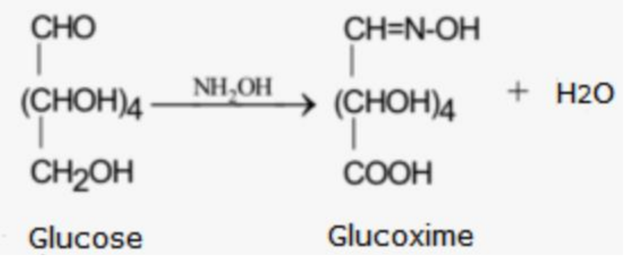
12.If a fragment of one strand in DNA molecule has the base sequence CCATGCATG, what is the base sequence in the complementary strand?
Ans: GGTACGTAC

13.An organic compound A of formula $C_{12}(H_2O)_{11}$ on hydrolysis gives a compound B and C, both of formula $C_6(H_2O)_6$. B on oxidation with bromine water forms a pentahydroxy monocarboxylic acid, while C is not. Identify A, B and C.
Ans:$C_{12}(H_2O)_{11}$= $C_{12}H_{22}O_{11}$ which is sucrose. A is sucrose.
A on hydrolysis gives B and C. B with the mild oxidizing agent gives pentahydroxyacid. i.e. gluconic acid, therefore B is glucose and C is fructose.

14. An organic compound X with formula $C_6H_{12}O_6$ forms hexane on prolonged heating with HI. X also forms an oxime Z with hydroxyl amine, and gets oxidized with a mild oxidizing agent, Br_2/H_2O to Y. Write the equations and identify X, Y and Z.
Ans:X with HI forms hexane, this shows X contains 6 carbons in a straight line.
X gives oxime, this indicates the presence of carbonyl group.
X is oxidized by bromine water, indicates the presence of aldehyde group.
Therefore X should be glucose, Y should be gluconic acid and Z should be an oxime of glucose







15. Complete the following analogy
(i) Ascorbic acid: Vitamin C :: Pyridoxine: _________________(Ans: Vitamin B_6)
(ii) Plants: Starch :: Animals: _________________(Ans: Glycogen)
(iii) Adenine: Thymine :: Cytosine: _________________(Ans: Guanine)
(iv) DNA: Thymine :: RNA:________________(Ans: Uracil)
(v) Insulin: Diabetes :: Corticoids: __________(Ans: Addison’s disease)

KENDRIYA VIDYALAYA, CHENNAI REGION

SAMPLE PAPER 1 (2022 - 23)

(BLUE PRINT)

CHAPTER	MCQ	2MARK	3MARK	CASE STUDY	5MARK	TOTAL
SOLUTIONS			1(3)	1(4)		7
ELECTROCHEMISTRY	1(1)	1(2)			1(5)	8
CHEMICAL KINETICS	3(1)	2(2)				7
d- AND f-BLOCK ELEMENTS	2(1)				1(5)	7
COORDINATION COMPOUNDS	2(1)	1(2)	1(3)			7
HALOALKANES AND HALO ARENES	1(1)	1(2)	1(3)			6
ALCOHOLS, PHENOLS AND ETHERS	3(1)		1(3)			6
ALDEHYDES, KETONES AND CARBOXYLIC ACID	2(1)	1(2)			1(5)	9
AMINES	3(1)		1(3)			6
BIOMOLECULES	1(1)	1(2)		1(4)		7
	18(1)	7(14)	5(15)	2(8)	3(15)	70

NOTE : 1) Number of questions are indicated outside the brackets and marks are indicated inside the brackets.

2) Internal Choice : There is no overall choice in the paper. However, there is an internal choice in two questions of 2 marks weightage, two questions of 3 marks weightage and two questions of 5 marks weightage.

SAMPLE PAPER 1 (2022 - 23)
XII-CHEMISTRY THEORY (043)

MM:70 **Time: 3 hours**

General Instructions:

Read the following instructions carefully.

a) **There are 35 questions in this question paper with internal choice.**
b) **SECTION A consists of 18 multiple-choice questions carrying 1 mark each.**
c) **SECTION B consists of 7 very short answer questions carrying 2 marks each.**
d) **SECTION C consists of 5 short answer questions carrying 3 marks each.**
e) **SECTION D consists of 2 case- based questions carrying 4 marks each.**
f) **SECTION E consists of 3 long answer questions carrying 5 marks each.**
g) **All questions are compulsory.**
h) **Use of log tables and calculators is not allowed**

SECTION A

The following questions are multiple-choice questions with one correct answer.

Each question carries 1 mark. There is no internal choice in this section.

1. If limiting molar conductivity of Ca^{2+} and Cl^{-} are 119.0 and 76.3 S cm^2 mol^{-1}, then the value of limiting molar conductivity of $CaCl_2$ will be

a) 195.3 S cm^2 mol^{-1}

b) 271.6 S cm^2 mol^{-1}

c) 43.3 S cm^2 mol^{-1}

d) 314.3 S cm^2 mol^{-1}

2. $CH_3NH_2 + CHCl_3 + KOH \rightarrow$ Major product is

a) $CH_3\ CH_2CH_2\ NH_2$

b) $CH_3\ CH_2\ NH_2$

c) CH_3CN

d) CH_3NC

3. $KMnO_4$ is the oxo salt of ------------

a) Mn_2O_3

b) MnO_3

c) Mn_2O_7

d) MnO_2

4. The name of reaction in which CO_2 reacts with phenol,NaOH, acid to give salicylic acid is---

a) Reimer Tiemann reaction

b)Kolbe’s reaction

c) Wurtz reaction

d)Swartz reaction

5. Name the chemical used to distinguish between Phenol and Benzyl alcohol

a)$NaHCO_3$

b) Neutral $FeCl_3$

c)Iodine ,KOH

d)Tollen’s Reagent

6. Which among the following is most acidic

a) Phenol

b) 4-nitrophenol

c) cresol

d) anisole

7. which of the following ion is coloured in aqueous solution. [atomic number of Cu-29, Sc-21, Ti- 22, Zn- 30]

a) Cu^{2+}

b) Sc^{3+}

c) Ti^{4+}

d) Zn^{2+}

8. Write the IUPAC name of $Na_3[Co(OX)_3]$

a) sodiumtrioxalatocobaltate (III)
b) sodiumtrisoxalatocobaltate (III)
c) sodiumtrioxalatocobaltate (II)
d) trisodiumtrioxalatocobaltate(III)

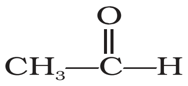
9.Ethanal reacts with HCN followed by complete hydrolysis gives

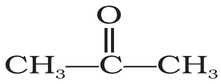
a) 2-butanol
b) 2- butenal
c) 2-hydroxy propanoic acid
d) Ethanal cyano hydrine

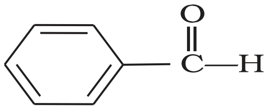
10. If rate constant of a reaction is $2\ mol^{-1}lit^{1}min^{-1}$, the order of the reaction will be---

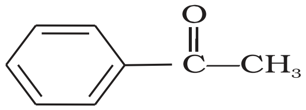
a) zero
b) first
c) second
d) three

11. Which of the following compounds is most reactive towards nucleophilic addition reactions?

(i) 
$CH_3-\overset{\overset{O}{\|}}{C}-H$

(ii) 
$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

(iii) 

(iv) 

12.For every ten degree raise in temperature , the rate constant ---
a) quadruples
b)doubles
c) triples
d) ten times

13. Increasing order of basic strength of : Aniline, p-Nitroaniline , p-Toluidine
a) p-Nitroaniline < Aniline < p-Toluidine
b) Aniline < p-Toluidine < p-Nitroaniline
c) p-Toluidine < p-Nitroaniline < Aniline
d) Aniline< p-Nitroaniline< p-Toluidine

14. A reaction is 50% complete in 2 hours and 75% complete in 4hours.What is the order of the
reaction?
a) zero
b) first

c) third

d) second

15. Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion: Addition of Br_2 to trans-2-butene yields meso-2,3-dibromobutane.

Reason: Bromine addition to an alkene is an electrophilic addition reaction.

Select the most appropriate answer from the options given below:

a) Both A and R are true and R is the correct explanation of A

b) Both A and R are true but R is not the correct explanation of A.

c) A is true but R is false.

d) A is false but R is true.

16. **Assertion:** Tert. butyl methyl ether is not prepared by the reaction of tert. Butyl bromide with sodium methoxide.

Reason: Sodium methoxide is not only a strong nucleophile but also a strong base ,so elimination occurs.

a) Both A and R are true and R is the correct explanation of A

b) Both A and R are true but R is not the correct explanation of A.

c) A is true but R is false.

d) A is false but R is true

17. **Assertion** : Leucine and isoleucine are essential amino acids

Reason : They are synthesized in the body, not required to supply through diet

a) Both A and R are true and R is the correct explanation of A

b) Both A and R are true but R is not the correct explanation of A.

c) A is true but R is false.

d) A is false but R is true

18. **Assertion** : Aniline undergoes Friedel Crafts reaction

Reason: Aniline is basic in nature , anhy AlCl3 used in the reaction is lewis acid , they combine to form anilinium salt.

a) Both A and R are true and R is the correct explanation of A

b) Both A and R are true but R is not the correct explanation of A.

c) A is true but R is false.

d) A is false but R is true

SECTION B

19. A 0.05 M NaOH solution offered a resistance of 31.6 $\wedge$ in a conductivity cell at 298 K. If the cell constant of the cell is 0.367 cm^{-1}, find out the molar conductivity of NaOH.

20. The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to

reduce the initial concentration of the reactant to its 1/10th value ?

21. a)Give the IUPAC name of the following compound $CH_2 = CH - CH_2 - Cl$

b) Write the major product in the following equation $CH_3 - Cl + CH_3CH_2ONa$

?

OR

How are the following conversions carried out ?

(i) Benzyl chloride to Benzyl alcohol

(ii) Ethyl magnesium chloride to Propan-1-ol

22. Indicate the types of isomerism exhibited by any 2 of the following complexes :

(i) $[Co\ (NH_3)_5(NO_2)]^{2+}$

(ii) $[Co\ (en)_3]Cl_3$

(iii) $[Pt(NH_3)_2Cl_2]$

23. How will you convert Ethanal into the following compounds? Give the chemical

Equations involved.

i) $CH_3 - CH_3$

ii) $CH_3CH\ (OH)\ CH_2CHO$

24. (i) What are disaccharides , give an example

(ii) Write the name of vitamin whose deficiency causes bone deformities in children.

OR

Give any 2 differences between fibrous protein and globular protein ?

25. For a reaction $A + B \rightarrow P$, the rate is given by Rate = $k [A] [B]^2$

(i) How is the rate of reaction affected if the concentration of B is doubled?

(ii) What is the overall order of reaction if A is present in large excess?

SECTION C

26. a)Which would undergo SN^2 reaction faster in the following pair :

$C_6H_5CH_2CH_2Br$ and C_6H_5 $CH(Br)$ CH_3

b) How do you convert the following?

(i) Bromobenzene to 2-bromoacetophenone

(ii) 2-bromobutane to But-2-ene

OR

What happens when

(i) Ethyl chloride is treated with NaI in the presence of acetone,

(ii) Chlorobenzene is treated with Na metal in the presence of dry ether,

(iii) methyl chloride is treated with KNO_2 ?

Write chemical equations in support of your answer.

27. Vapour pressure of water at 20^0C is 17.5 mm Hg. Calculate the vapour pressure of water at 20^0C when 15 g of glucose (Molar mass = 180 g mol^{-1}) is dissolved in 150 g of water.

OR

Calculate the mass of NaCl (molar mass = 58·5 g mol^{-1}) to be dissolved in 37·2 g of water to lower the freezing point by 2^0C, assuming that NaCl undergoes complete dissociation. (K_f for water = 1·86 K kg mol^{-1})

28. (i)On the basis of crystal field theory, write electronic configuration for d^4 ion if $\Delta_o < P$.

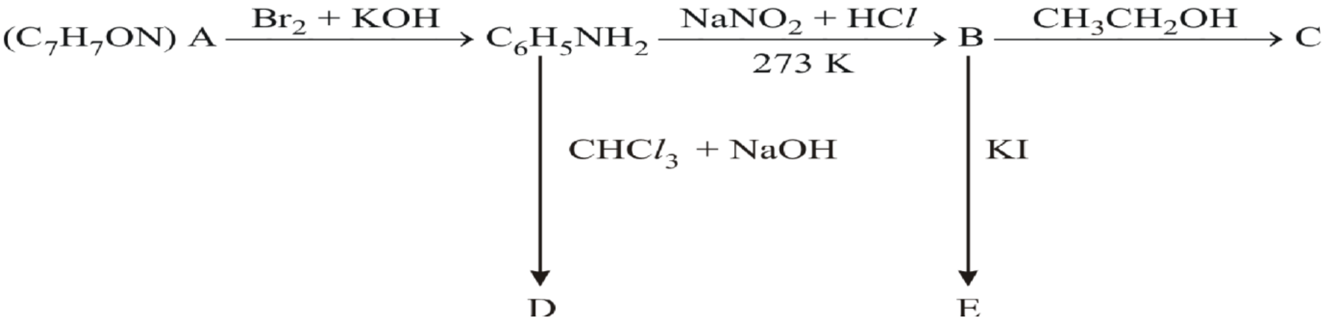
(ii) Write the formula for the following complex : tris(ethane1,2diammine)chromium(III)ion (iii) Write the hybridization and shape of $K_3[Fe(CN)_6]$ (Atomic number of Fe = 26)

29. a)Write the IUPAC name of the given compound $HOCH_2\ CH = C\ (CH_3)_2$

b) write note on Reimer Tiemann reaction

c) distinguish between phenol, ethanol

30. An aromatic compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions



SECTION D

31.Read the passage given below and answer the following questions.

Osmosis and reverse osmosis are two phenomena of paramount significance. Osmosis plays vital role in the transport of water and solutes through biological membranes. It accounts for fluid transport out of the kidney tubules and the gastrointestinal tract, into capillaries, and across cell membranes. Osmosis occurs through biological and artificial membranes of widely different composition. Osmotic pressure method is usually used for determination of molar masses of polymers and biomolecules. When the pressure greater than osmotic pressure is applied on solution side reverse osmosis occurs through the membrane. Reverse osmosis membrane technology has developed over the past 40 years to a 44% share in world desalting production capacity, and an 80% share in the total number of desalination plants installed worldwide. The use of membrane desalination has increased as materials have improved and costs have decreased. Today, reverse osmosis membranes are the leading technology for new desalination installations, and they are applied to a variety of salt water resources using tailored pre-treatment and membrane system design

Answer the following questions

a) Two solutions A,B of equal volume found to have same osmatic pressure at same temperature what will be the relation in their number of moles?

b) Substance is used in synthetic semipermeable membrane for desalination of water?

c) Identify the movement in the phenomenon of reverse osmosis through semi permeable membrane and also in the measurement of osmotic pressure

OR

When blood cell is placed in a solution containing 1.5 % NaCl, it will shrink, whereas in 0.7% it will swell .Justify your answer

32. Read the passage given below and answer the following questions:

EVIDENCE FOR THE FIBROUS NATURE OF DNA

The basic chemical formula of DNA is now well established. It consists of a very long chain, the backbone of which is made up of alternate sugar and phosphate groups, joined together in regular 3' 5' phosphate di-ester linkages. To each sugar is attached a nitrogenous base, only four different kinds of which are commonly found in DNA. Two of these---adenine and guanine--- are purines, and the other two thymine and cytosine-are pyrimidines. A fifth base, 5-methyl cytosine, occurs in smaller amounts in certain organisms, and a sixth, 5-hydroxy-methyl-cytosine, is found instead of cytosine in the T even phases. It should be noted that the chain is unbranched, a consequence of the regular inter-nucleotide linkage. On the other hand, the sequence of the different nucleotides is, as far as can be ascertained, completely irregular. Thus, DNA has some features which are regular, and some which are irregular. A similar conception of the DNA molecule as a long thin fibre is obtained from physicochemical analysis involving sedimentation, diffusion, light scattering, and viscosity measurements. These techniques indicate that DNA is a very asymmetrical structure approximately 20 A wide and many thousands of angstroms long. Estimates of its molecular weight currently centre between $5 \text{ X } 10^6$

and 10^7 (approximately 3 $x10^4$ nucleotides). Surprisingly each of these measurements tend to suggest that the DNA is relatively rigid, a puzzling finding in view of the large number of single bonds (5 per nucleotide) in the phosphate-sugar back bone. Recently these indirect inferences have been confirmed by electron microscopy. DNA Fingerprinting It is known that every individual has unique fingerprints. These occur at the tips of the fingers and have been used for identification for a long time but these can be altered by surgery. A sequence of bases on DNA is also unique for a person and information regarding this is called DNA fingerprinting. (source: Watson, J. D., & Crick, F. H. (1953, January). The structure of DNA. In Cold Spring Harbor symposia on quantitative biology (Vol. 18, pp. 123-131). Cold Spring Harbor Laboratory Press.)

Answer the following questions

a) Name the nitrogenous bases which are commonly found in DNA

b) What products would be formed when a nucleotide from DNA containing thymine is hydrolysed?

c) Write the important structural and functional differences between DNA and RNA

OR

What are the different types of RNA found in the cell? When RNA is hydrolysed, there is no relationship among the quantities of different bases formed?

SECTION E

33a) State Faraday’s first law of electrolysis

b) $\not\subset^0$ for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0Scm^2 mol^1 . Calculate $\not\subset^0$ for HAc

c) Calculate emf of the following cell at 298 K.

Mg(s) /Mg^{2+}(0.001 M) //Cu^{2+} (0.0001 M Cu (s) E^0 Cu^{2+} /Cu = 0.34 V E^0 Mg^{2+} / Mg = -2.37 V.

OR

a)State Kohlrausch law

b)How does the molar conductivity of strong electrolyte vary with dilution? Give reason

c) Write the anode and cathode reactions taking place in Mercury cell
d) Calculate the equilibrium constant E^0 of Zn^{2+} / Zn is – 0.76V and that of Cu^{2-}/ Cu electrode is 0.34 V in Daniel cell.[A log 28 = 1.905]

34.a) Write the structure of 3-oxopentanal

b) How do you convert the following: Ethyne to Ethanal?

c) Aldehydes and Ketones have lower boiling points than corresponding alcohols. Why?

d) An organic compound A, having formula, C_3H_8O, on treatment with copper at 573 K, gives B. B does not reduce Fehling's solution but gives yellow precipitate of compound C with I_2/NaOH. Deduce the structure of A, B and C.

OR

a) Write the structural formula of 1-phenylpentan-1-one

b) How do you convert the following: Toluene to Benzaldehyde

c) Write the equation involved in the following reaction : Stephen reaction

d) Arrange the following compounds in an increasing order of their reactivity in nucleophilic addition reactions: Ethanal, Propanal, Propanone, Butanone.

e) Given reason : pH of reaction should be carefully controlled while preparing ammonia derivatives of carbonyl compounds.

35.a) Explain why Cu^+ ion is not stable in aqueous solutions?

b) Why is Cr^{2+} strongly reducing agent and Mn^{3+} strongly oxidizing agent when both have d^4 configuration

c) Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

d) The higher oxidation states are usually exhibited by the members in the middle of a series of transition elements?

e) Ni^{+2} compounds are thermodynamically more stable than Pt^{+2}compounds

SAMPLE PAPER-1 (2022 - 23)

XII-CHEMISTRY THEORY (043)

ANSWER KEY

1. b) 271.6 S cm^2 mol^{-1}

2. d) CH_3NC

3. c) Mn_2O_7

4. b)Kolbe's reaction

5. b) Neutral $FeCl_3$

6. b) 4-nitrophenol

7. a) Cu^{2+}

8. a) sodiumtrioxalatocobaltate (III)

9. c) 2- hydroxy propanoic acid

10. c) second

11.(i) CH_3CHO

12. b) double

13. p-Nitroaniline < Aniline < p-Toluidine

14. b) first

15. a) Both A and R are true and R is the correct explanation of A

16. a) Both A and R are true and R is the correct explanation of A

17. c) A is true but R is false.

18. d) A is false but R is true.

19. K = 1/R * cell constant = 0.367/31.6

Λ_m = K *1000/C = 0.367*1000/31.6* 0.05 =367 /1.58 = 232.27Scm^2mol^{-1}

20. $K = 60 sec^{-1}$

$$t = \frac{2.303}{K} \log \frac{[A_0]}{[A]}$$

$$t = \frac{2.303}{60} \log \frac{[1]}{[1/10} = \frac{2.303}{60} \log 10 = 0.\ 03838 sec$$

21. . a) 3-chloropropene

b)$CH_3CH_2OCH_3$ Methoxy ethane

(OR)

a)$C_6H_5CH_2Cl + aq\ NaOH \longrightarrow C_6H_5CH_2OH + NaCl$

b) $C_2H_5MgBr + HCHO \longrightarrow C_2H_5\ CH_2OMgBr$ which on $H_3O^+ \longrightarrow C_2H_5\ CH_2OH$

22. a) Linkage isomerism

b) Optical isomerism

c) Geometrical isomerism

23. a) $CH_3CHO + \underset{[4H]}{\underline{\text{Zn-Hg/con HCl}}} \longrightarrow CH_3\ CH_3$

b) $2CH_3CHO + aq\ NaOH \longrightarrow CH_3CH(OH)\ CH_2CHO$

24.a) Carbohydrates which on hydrolysis give two mono saccharides are called disaccharides.

Example any one –sucrose, maltose, lactose

b) Vitamin D

(OR)

Globular proteins:- highly branched or coiled structures ,soluble in water , they have multiple functions as they are used to form enzymes, cellular messengers, amino acids .they are made up of not only primary, secondary but also tertiary and occasionally quaternary structures. Hemoglobin is an example of globular protein (any two).

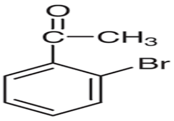
Fibrous proteins:- elongated strand-like structures and are usually present in the form of rods or wires, insoluble in water, they act only as structural proteins, Fibrous proteins have primary and secondary structures. keratin, collagen and elastin are examples .

25. a) $r_1 = k[A]\,[2B]^2 = 4r$

b) second order

26.a) $C_6H_5CH_2Br$

b) (i) C_6H_5Br + CH_3COCl with anhyd $AlCl_3$ ——>



(ii) $CH_3CH(Br)CH_2CH_3$ + alc KOH ——> $CH_3CH{=}CHCH_3$

(OR)

(i)CH_3CH_2Cl + NaI (dry acetone) ——> CH_3CH_2I(SN reaction Ethyl iodide is formed)

(ii) $2C_6H_5Cl$ + Na (dry ether) ——> C_6H_5 - C_6H_5 (Fittig reaction –Diphenyl is formed)

(iii) CH_3Cl + KNO_2 ——> CH_3ONO + KCl (SN reaction methyl nitrite is formed)

27. P^0_A =17.5 mm Hg P_A = ?

Weight of H_2O =150g No of moles of H_2O = 150/18 = 8.333

Weight of glucose =15g No of moles of glucose = 15/180 = 0.0833

$$\frac{P^0_A - P_A}{P^0_A} = \frac{\text{no of moles of Solute}}{\text{moles of solute + moles of solvent}}$$

$$\frac{17.5 - P_A}{17.5} = \frac{0.0833}{0.0833 + 8.333} = 0.00989$$

P_A = 17.32mm

(OR)

27. K_f for water = 1·86 K kg mol^{-1}

$$\Delta T_f = 2 = \underline{K_f \text{ x W solute x } 1000} = \underline{1.86 \text{ xWsolute x}1000}$$

Mwt solute x W solvent 58.5 x 37.2

$$\text{W solute} = \frac{2 \times 58.5 \times 37.2}{1.86 \times 1000} = 2.34g$$

28.i) electronic configuration for d^4 ion if Δ_o <P. high spin weak fild $\mathbf{t_{2g}^3\ e_g^1}$

ii)$[Co(en)_3]^{3+}$

iii) hybridization and shape of $K_3[Fe(CN)_6]$ is d^2sp^3 , octahedral.

29.a)IUPAC name of $HOCH_2\ CH = C\ (CH_3)_2$ is 3-methyl ,2-en butanol.

b) Reimer Tiemann reaction:- When phenol reacts with $CHCl_3$, KOH (alkali) , it forms ` salicylaldehyde (2-Hydroxy Benzaldehyde)

$C_6H_5OH + CHCl_3 + 3\ KOH \longrightarrow 3KCl + C_6H_4(OH)\ CHO$ [2-hydroxy benzaldehyde]

c) Phenol – Neutral $FeCl_3$ gives violet colour

Ethanol – with I_2 +KOH gives yellow precipitate

30.A – $C_6H_5CONH_2$ –Benzamide

B—$C_6H_5N_2Cl$ --Benzene diazonium chloride

C--- C_6H_6 - Benzene

D --- C_6H_5NC – Benzene isonitrile

E ---C_6H_5I – Iodo Benzene

31.a) Their number of moles must be equal

b) Cellulose acetate

c) In reverse osmosis solvent move from its low concentration to high concentration through semi permeable membrane whereas in the measurement of osmotic pressure solvent move from its high concentration to low concentration through semi permeable membrane.

32.a) Nitrogenous bases found in DNA -Adenine ,Guanine, Thymine and Cytosine

b) Deoxy Ribose (5membered sugar) , Thymine, Phophate

c) structural and functional differences between DNA and RNA

	structur	function
DNA	Double helix strand, deoxy ribose , adenine paired with Thymine	Genetic transformation
RNA	Single strand, oxy ribose, adenine paired with Uracil	Protein synthesis

(**OR)**

Two types of RNA are m-RNA, t-RNA,

RNA is single strand.

33.a) The amount of chemical reaction which occurs at any electrode under the influence of electrical energy is proportional to the quantity of electricity passed through the electrolyte.

b) Λ^0 for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0Scm^2 mol^{-1}

Λ^0HAc =Λ^0 HCl + Λ^0 NaAc - Λ^0 NaCl = 425.9 + 91.0 - 126.4 =390.5Scm^2 mol^{-1}

c) $E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$ where n=2

$= [0.34-(-2.36)] - 0.0295 \log (0.001/0.0001)$

Ecell = 2.7 -0.0295 log10 = 2.6705V

OR

a)Kohlrausch Law of independent migration of ion states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte .

b) Molar conductivity of strong electrolyte increases sharply with dilution as interionic distance increase.

c) Cathode :- $HgO + H_2O + 2e^- \longrightarrow Hg + 2OH^-$
Anode :- $Zn(Hg) + 2OH^- \longrightarrow ZnO + H_2O$

d) $E^0cell = \frac{0.059}{n} \log Kc$

$E^0cell = E^0cathode - E^0anode = [0.34-(-0.76)] = 1.1V$

$1.1V = \frac{0.059}{2} \log Kc$, $\log Kc = 37.28$

$Kc = alog (37.28) = 1.905 \times 10^{37}$

34 a) $C_2H_2 + H_2O \xrightarrow{Hg^{2+}/H^+} CH_3CHO$

b) Aldehydes and Ketones do not form inter molecular hydrogen bonding like alcohols.

c) B does not reduce Fehling's solution, B is not an aldehyde.

'A' has formula $C_nH_{2n+2}O$ [C_3H_8O] it's a sec alcohol which on dehydrogenation with Cu/573k gives ketone which is methyl ketone on treatment with I_2/KOH gives yellow precipitate CHI_3. Iodoform

A – 2-Propanol B- propanone C – Iodoform

$CH_3CH(OH)CH_3 + Cu/573k \longrightarrow CH_3COCH_3$

$CH_3COCH_3 + I_2/KOH \longrightarrow CHI_3 + CH_3COOK$

(OR)

a) $C_6H_5COCH_2CH_2CH_2CH_3$

b) $C_6H_5CH_3 + \frac{CrO_2Cl_2/CS_2}{H_3O^+} \longrightarrow C_6H_5CHO$

c) $RCN + \frac{SnCl_2/HCl}{H_3O^+} \longrightarrow RCHO$

d) butanone.< propanone < propanal < ethanal

e) pH of reaction should be carefully controlled while preparing ammonia derivatives of carbonyl compounds, if strongly acidic solution is used then ammonia derivatives get protonated easily , can't act as nucleophile.

35.a) Cu^{+2} is stable , moreover due to high hydration enthalpy Cu^{+} undergoes disproportionation.

b) $Mn^{3+} + e^{-} \longrightarrow Mn^{2+}$

(d^4 system , less stable) (d^5 system , more stable)

$Cr^{2+} \longrightarrow Cr^{3+} + e^{-}$

(d^4 system , less stable (t_{2g}^3 - half filled- more stable)

c) 5f orbitals are comparatively larger and more diffused . Imperfect screening is greater in case of 5f than in case of 4f orbitals.

d) Due to the presence of higher number of unpaired electrons

e) The sum of the first two ionization energies (IE_1+IE_2) of Pt is higher than that of Ni

SAMPLE PAPER 2 (2022 - 23)

BLUEPRINT

	Section A		Section B	Section C	Section D	Section E	Total
	MCQ (14)	R & A (4)	2Marks (7)	3Marks (5)	4Marks (2)	5 Marks (3)	
Solution				3 (1)	4 (1)		7
Electro Chemistry	1 (2)		2 (1)			5 (1)	9
Chemical Kinetics	1 (3)		2 (2)				7
D & F Block	1 (1)	1 (1)				5 (1)	7
Co-ordination Componds	1 (2)		2 (1)	3 (1)			7
Halo alkane	1 (1)		2 (1)	3 (1)			6
Alcohols	1 (2)	1 (1)		3 (1)			6
Aldehyde Ketones & Carboxylic acid	1 (1)		2 (1)			5 (1)	8
Amines	1 (2)	1 (1)		3 (1)			6
Biomolecules		1 (1)	2 (1)		4 (1)		7
No of Qns	**14**	**4**	**2 (7)**	**3 (5)**	**4 (2)**	**5 (3)**	**70 (35)**
Marks	**18**		**14**	**15**	**8**	**15**	**70**

KENDRIYA VIDYALAYA SANGATHAN-CHENNAI REGION
SAMPLE PAPER-2 (2022-23)
XII_CHEMISTRY THEORY (043)

Maximum marks: 70
Time: 3 hours

General Instructions:
Read the following instructions carefully.

a) There are **35** questions in this question paper with internal choice.

b) SECTION A consists of 18 multiple-choice questions carrying 1 mark each.

c) SECTION B consists of 7 very short answer questions carrying 2 marks each.

d) SECTION C consists of 5 short answer questions carrying 3 marks each.

e) SECTION D consists of 2 case- based questions carrying 4 marks each.

f) SECTION E consists of 3 long answer questions carrying 5 marks each.

g) All questions are compulsory.

h) Use of log tables and calculators is not allowed

SECTION A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1 The law that states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte is known as:
(a) Faraday Law (b)Kohlrausch law (c) Avogadro Law (d) Daltons law

2 Fused NaCl on electrolysis gives on cathode.
(a) Chlroine (b) Sodium (c) Sodium amalgam (d) Hydrogen

3 If the rate law is rate = k[Y][X], the overall order of the reaction is
a) zero b) first c) second d) third

4. Why would increasing temperature increase rate?
a) the molecules would collide more often b) the molecules would collide with more force
c) a higher fraction of the molecules overcomes the activation energy d) all of the above

5 What are appropriate units of k for a first-order reaction?

a) M/s b) s^{-1} c) $M^{-1} s^{-1}$ d) none of the above

6 Propanamide on reaction with bromine in aqueous NaOH gives:
a) Propanamine b) Ethanamine c) N-Methyl ethanamine d) Propanenitrile

7 IUPAC name of product formed by reaction of methyl amine with two moles of ethyl chloride
a) N,N-Dimethylethanamine b) N,N-Diethylmethanamine c) N-Methyl ethanamine d) N-Ethyl - N-methylethanamine

8 SN1 reaction of alkyl halides lead to
(a) Retention of configuration (b) Racemisation (c) Inversion of configuration (d) None of these

9 A compound X with the molecular formula C3H8O can be oxidised to another compound Y whose molecular formulae is C3H6O2. The compound X may be
(a) CH3CH2OCH3 (b) CH3CH2CHO (c) CH3CH2CH2OH (d) CH3CHOHCH3

10 Phenol when treated with excess of bromine water gives a white precipitate of
a) 2, 4, 6-tribromophenol (b) o-bromophenol (c) p-bromophenol (d) bromobenzene

11 Ambidentate ligands like NO2 - and SCN- are
a) unidentate b) didentate c) polydentate d) has variable denticity

12 Which of the following is a diamagnetic ion: (Atomic numbers of Sc, V, Mn and Cu are 21, 23, 25 and 29 respectively)
a) V 2+ b) Sc3+ c) Cu2+ d) Mn

13 The Copper based catalyst can be used to convert:
a) propanol to propanonic acid b) propanone to propanoic acid c) propanone to propan-2-ol d) propan-2-ol to propanone

14 The oxidation number of cobalt in K[Co(CO)4]
(a)+1 (b) +3 (c) -1 (d) -3

15 Given below are two statements labelled as Assertion (A) and Reason (R)
Assertion (A): Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam.
Reason (R): FeCl2 formed gets hydrolysed to release HCl during the reaction.

Select the most appropriate answer from the options given below:
a. Both A and R are true and R is the correct explanation of A
b. Both A and R are true but R is not the correct explanation of A.
c. A is true but R is false.
d. A is false but R is true.

16 Given below are two statements labelled as Assertion (A) and Reason (R)
Assertion (A): *p*-nitrophenol is more acidic than phenol.
Reason (R): Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.

Select the most appropriate answer from the options given below:
a. Both A and R are true and R is the correct explanation of A
b. Both A and R are true but R is not the correct explanation of A.
c. A is true but R is false.

d. A is false but R is true.

17 Given below are two statements labelled as Assertion (A) and Reason (R)
Assertion (A): Glucose gets oxidized to gluconic acid on reaction with mild oxidizing agent like bromine water
Reason (R): Glucose contains a keto group

Select the most appropriate answer from the options given below:
a. Both A and R are true and R is the correct explanation of A
b. Both A and R are true but R is not the correct explanation of A.
c. A is true but R is false.
d. A is false but R is true.

18 Given below are two statements labelled as Assertion (A) and Reason (R)

Assertion (A): Cr 2+ is a good reducing agent
Reason (R): Cr 2+ donates one electron to become Cr 3+ which in turn is a stable half filled t 2g

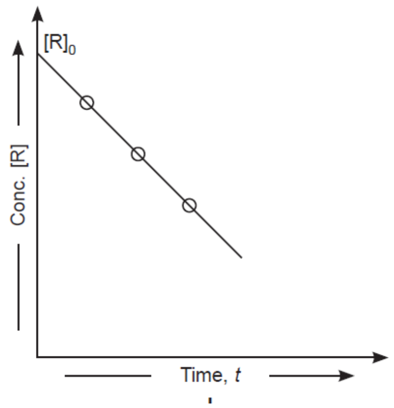
Select the most appropriate answer from the options given below:
a. Both A and R are true and R is the correct explanation of A
b. Both A and R are true but R is not the correct explanation of A.
c. A is true but R is false.
d. A is false but R is true.

SECTION B

This section contains 7 questions with internal choice in two questions. The following questions are very short answer type and carry 2 marks each.

19 Represent the galvanic cell in which the following reactions take place
Zn(s) + 2Ag+(aq) → Zn2+(aq) + 2Ag(s)
i. Which one of the electrodes is negatively charged in the above cell?
ii. Name the carrier of current within the cell.

20



i. What is order of reaction shown in graph?
ii. How does *t*1/2 varies with initial concentration in zero order reaction.

21 i. What is meant by activation energy?

ii. What does e-Ea/RT represent?

22 i. Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.

ii. In the following pairs of halogen compounds, which would undergo SN 2 reaction faster?Why

$C_6H_5CH(CH_3)Br$ or $C_6H_5CH(C_6H_5)Br$

OR

i. Which compound will react faster in SN 2 reaction with –OH? Why? CH_3Br or CH_3I

ii. Write the structure of the major organic product in the following reactions:

$CH_3CH_2CH_2Cl + NaI \rightarrow$

23 Describe the following: (i) Cannizzaro reaction (ii) Aldol condensation reaction

24 i. Using crystal field theory, write the electronic configuration of iron ion in the following complex ion. Also predict its magnetic behaviour of $[Fe(H_2O)_6]^{2+}$

ii. Write the IUPAC name of the coordination complex: $[CoCl_2(en)_2]NO_3]$

25 Define the following as related to proteins:

(i) Peptide linkage (ii) Denaturation

OR

What are vitamins? Which vitamin deficiency causes (i) Pernicious anaemia? (ii) Convulsions?

SECTION C

This section contains 5 questions with internal choice in two questions. The following questions are short answer type and carry 3 marks each.

26 Calculate the temperature at which a solution containing 54 g of glucose, ($C_6H_{12}O_6$), in 250 g of water will freeze. (*Kf* for water =1.86 K mol^{-1} kg)

27 What happens when

i. Bromobenzene is treated with Mg in the presence of dry ether

ii. methyl bromide is treated with sodium in the presence of dry ether

iii. ethyl chloride is treated with aqueous KOH

OR

i. Haloalkanes undergo nucleophilic substitution whereas haloarenes undergo electrophilic substitution. Why?

ii. Explain why?

(a) Alkyl halides, though polar, are immiscible in water.

(b) Grignard reagents should be prepared under anhydrous conditions?

28 i. Predict the geometry of $[Ni(CN)_4]^{2-}$

ii. Calculate the spin only magnetic moment of $[Cu(NH_3)_4]^{2+}$ ion.

iii. Write the ionisation isomer of $[Co(NH_3)_5SO_4]Br$

OR

For the complex $[Fe(en)_2Cl_2]Cl$, identify the following:

(i) Oxidation number of iron.

(ii) Hybrid orbitals and shape of the complex.

(iii) Magnetic behaviour of the complex.

(iv) Number of its geometrical isomers.
(v) Whether there may be optical isomer also.
(vi) Name of the complex.

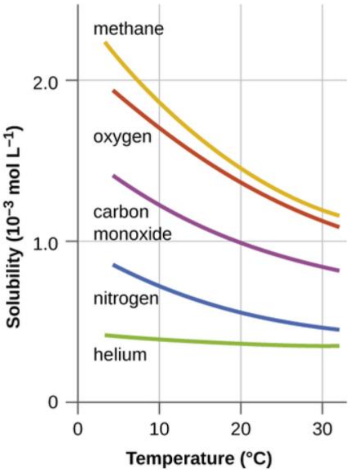
29 Arrange the following in increasing order of property specified:
i. Aniline, ethanamine, 2-ethylethanamine (solubility in water)
ii. Ethanoic acid, ethanamine, ethanol (boiling point)
iii. Methanamine, N, N- dimethylmethanamine and N- methylmethanamine (basic strength in aqueous phase

30 i. Give a chemical test to distinguish between Phenol and benzoic acid
ii. Give the mechanism for the conversion ethanol to ethene

SECTION D

The following questions are case-based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

31 The chemical structures of the solute and solvent dictate the types of forces possible and, consequently, are important factors in determining solubility. For example, under similar conditions, the water solubility of oxygen is approximately three times greater than that of helium, but 100 times less than the solubility of chloromethane, $CHCl_3$. Considering the role of the solvent's chemical structure, note that the solubility of oxygen in the liquid hydrocarbon hexane, C_6H_{14}, is approximately 20 times greater than it is in water.Other factors also affect the solubility of a given substance in a given solvent. Temperature is one such factor, with gas solubility typically decreasing as temperature increases (Figure 13.4.113.4.1). This is one of the major impacts resulting from the thermal pollution of natural bodies of water.



When the temperature of a river, lake, or stream is raised abnormally high, usually due to the discharge of hot water from some industrial process, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills.

i. What is effect of temperature on solubility of gas in liquid?
ii. Name two factors which affect the value of K**H**?

iii. When natural waters subjected to thermal pollution, which result in the death of fish.Give reason

OR

Find the boiling point of a solution containing 0.520 of glucose (C6H12O6) dissolved in 80.2 g of water (Given Kb for water = 0.52 K/m).

32 Proteins are poly peptide chains made up of amino acids. There are 20 types of amino acids joined together by peptide bond between amino and carboxylic acid group. The amino acids are of two types-essential amino acids and non-essential amino acids. The primary structure of a protein is defined as the sequence of amino acids linked together to form a polypeptide chain. The first amino acid of sequence is called N-terminal amino acid and last amino acid of

peptide chain is called C-terminal amino acid. The secondary structure of protein forms helix.There are three types of secondary structure- α-helix, β-pleated sheet structure and collagen helix. The tertiary structure of proteins represents overall folding of the polypeptide chains i.e.,further folding of the secondary structure. The spatial arrangement of these subunits with respect to each other is known as quaternary structure.

(i). The tertiary structure of a protein contains

(a) Hydrogen bonds (b) peptide bonds (c) ionic bonds and S linkage (d) all the above

(ii). The simplest amino acid is

(a) Phenol (b) formic acid (c) glycine (d) saccharic acid

iii. Write the differences between fibrous protein and globular protein

SECTION E

The following questions are long answer type and carry 5 marks each. Two questions have an internal choice.

33 i. Calculate the emf of the cell Mg(s)/Mg^{2+} (0.01M) // ° Cu^{2+} (1 x10-3M)/ Cu(s)

Given E° Cu^{2+} /Cu(s) = + 0.34 V, E° Mg(s)/Mg^{2+} = -2.36 V

ii. Explain how rusting of iron is envisaged as setting up of an electrochemical cell. Also give some ways for prevention from corrosion.

OR

i. State Faraday’s Laws of electrolysis?

ii. A solution of Ni (NO3)2 is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode.

34 i. Compound ‘X’ C5H10O gives 2, 4 DNP test to give orange precipitate and gives yellow precipitate with I2 and NaOH, does not give Tollen’s test. ‘A’ on oxidation with acidified KMnO4 gives ‘Y’, and ‘C’.C is ethanoic acid. Identify X, Y and write equations.

ii. How will you bring about the following conversions

a) Propanone to propene
b) Ethanal to 3-hydroxybutanal

OR

i. State test to distinguish a) Propanal and propanone.
b) methanal and ethanal

ii. Give the IUPAC name of the following compound (CH3)3C CH2 COOH

iii. Give reasons

a) The boiling points of carboxylic acids are higher than the corresponding aldehydes and ketones

b) CH2FCOOH is stronger acid than CH3COOH.

35 Answer the following:

i.Why are all copper halides known except that copper iodide?

ii.Why is the Eo(V3+/V2+) value for vanadium comparatively low?

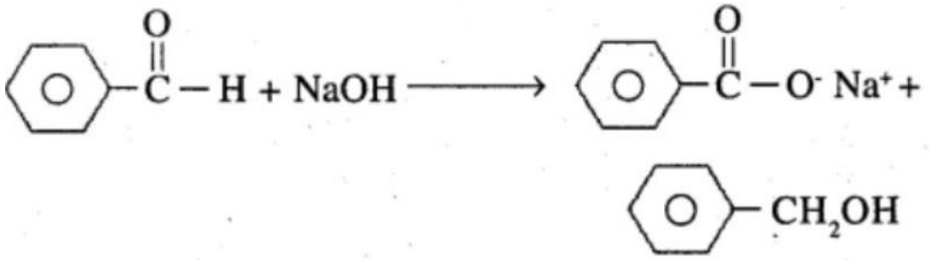
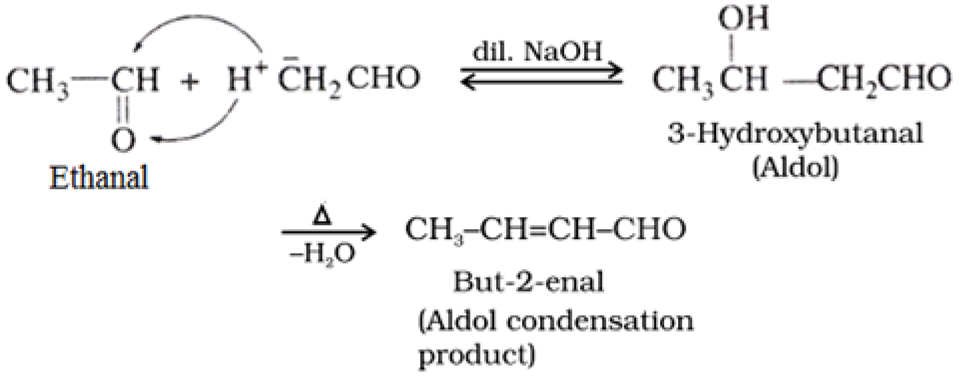
iii.Why HCl should not be used for potassium permanganate titrations?

iv.Explain the observation, at the end of each period, there is a slight increase in the atomic radius of d block elements.

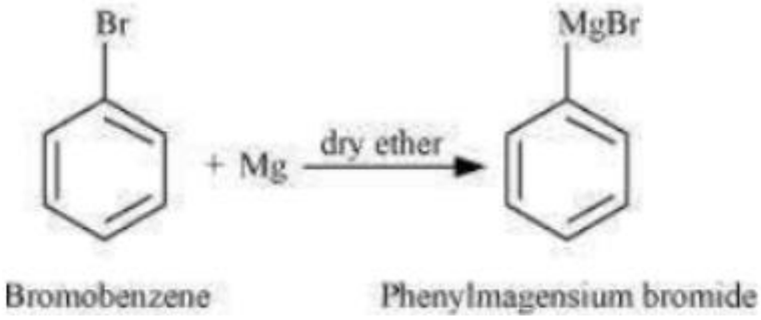
v.What is the effect of pH on dichromate ion solution?

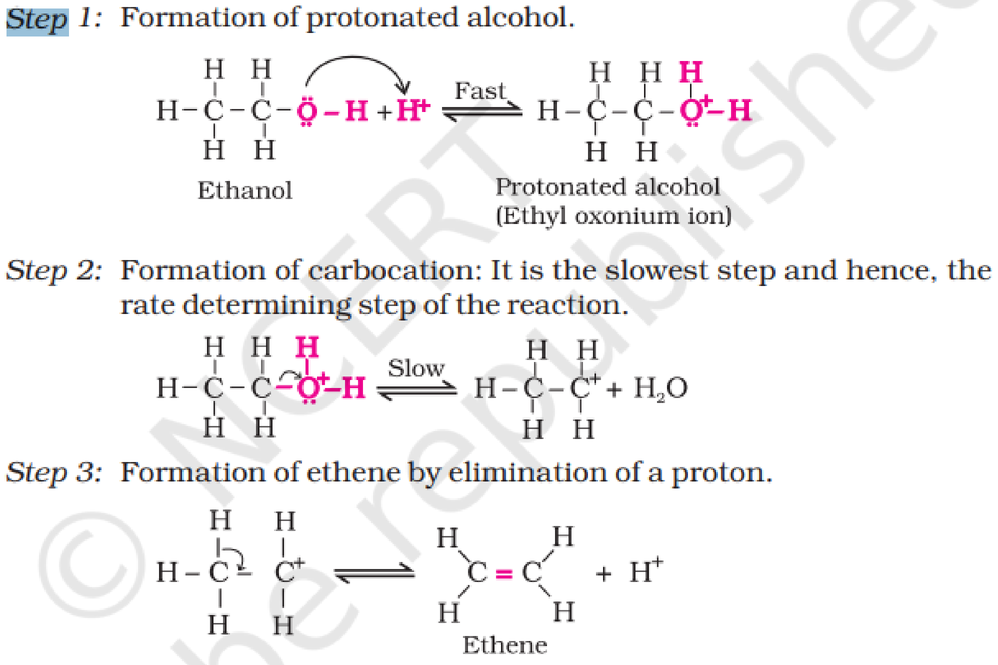
KENDRIYA VIDYALAYA SANGATHAN-CHENNAI REGION
SAMPLE PAPER 2 (2022-23)
CHEMISTRY THEORY (043)
MARKING SCHEME

SECTION A		
1	b) Kohlrausch law	1
2	b) Sodium	1
3	c) second	1
4	d) all of the above	1
5	b) s–1	1
6	b) Ethanamine	1
7	b) N,N-Diethylmethanamine	1
8	b) Racemisation	1
9	c) CH3CH2CH2OH	1
10	a) 2, 4, 6-tribromophenol	1
11	a) unidentate	1
12	b) Sc3+	1
13	d) propan-2-ol to propanone	1
14	c) -1	1
15	a) Both A and R are true and R is the correct explanation of A	1
16	a) Both A and R are true and R is the correct explanation of A	1
17	c) A is true but R is false.	1
18	a) Both A and R are true and R is the correct explanation of A	1
SECTION B		
1	i) Zn electrode is negatively charged	1

9	ii) Ions are the carrier of current within the cell.	1
20	i. Zero order reaction ii. *t*1/2 is directly proportional to initial concentration.	1 1
21	i. The extra energy which must be supplied to reactants in order to undergo effective collision to form products. ii. It represents fraction of molecules possessing activation energy (Ea) or more than Ea.	1 1
22	i. KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C—C bond is more stable than C—N bond. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product ii. Of the two secondary bromides, the carbocation intermediate obtained from C6H5CH(C6H5)Br is more stable than obtained from C6H5CH(CH3)Br because it is stabilised by two phenyl groups due to resonance. Therefore, the former bromide is more reactive than the latter in SN 1 reactions. **OR** i. CH3I. Because I is a better leaving than Br. ii. CH3CH2CH2Cl + NaI → CH3CH2CH2I+ NaCl	1 1 1 1
23	i  ii. 	1 1
24	i) t2g 4 eg 2 Paramagentic ii) Dichloridobis(ethane-1,2-diamine)cobalt(III)nitrate	1 1
25	i) Peptide linkage – in proteins, NH2 group of one α amino acids combine with COOH group of another amino acid and form CONH- bond which is	1

	known as peptidebond or peptide linkage iii) Denaturation - When a protein is subjected to physical change like change in temperature or chemical change like change in pH, protein unfolds 2^0, 3^0 Structure but the 1^0 Structure is retained. OR Vitamins are the group of organic compounds which are required in very small amounts for the healthy growth and functioning of animal organism. They cannot be made by organism and so have to be part of our diet. The deficiency of a vitamin can cause a specific disease, e.g. (i) Vitamin B_{12} deficiency causes pernicious anaemia (ii) Vitamin B6 deficiency causes convulsion.	1 1 1
	SECTION C	
26	Mass of glucose $(W_B) = 54$ g Molecular mass of glucose $(M_B) = 180$ Mass of water $(W_B) = 250$ g K_f for water $= 1.86$ k mol^{-1} kg Applying the formula, $\Delta T_f = \dfrac{K_f \times W_B \times 1000}{M_B \times W_A}$ $\Delta T_f = \dfrac{1.86 \times 54 \times 1000}{180 \times 250} = 2.23$ $T_f = T^\circ{}_f - \Delta T_f = 0 - (2.23)$ $T_f = -2.23^\circ$ C	1 1 ½ ½
27	i.When bromobenzene is treated with Mg in the presence of dry ether, phenylmagnesium bromide is formed	1

	 	1
	ii When methyl bromide is treated with sodium in the presence of dry ether, ethane is formed. This reaction is known as the Wurtz reaction $2\,CH_3-Br + 2\,Na \xrightarrow[\text{(Wurtz reaction)}]{\text{Dry ether}} CH_3-CH_3 + 2NaBr$ Methyl bromide Ethane	
	iii. When ethyl chloride is treated with aqueous KOH, it undergoes hydrolysis to form ethanol $CH_3-CH_2-Cl \xrightarrow[\text{(Hydrolysis)}]{KOH_{(aq)}} CH_3-CH_2-OH + KCl$ Ethyl chloride Ethanol	1
	OR i.Haloalkanes are more polar than haloarenes. As a result the carbon atom carrying the halogen in haloalkanes is more electron-deficient than that in haloarenes. So, haloalkanes undergo nucleophilic substitution more readily than halo arenes. In contrast, haloarenes contain a benzene ring. Since the typical reactions of benzene are electrophilic substitutions, therefore, haloarenes undergo electrophilic substitution while haloalkanes which do not contain a benzene ring do not undergo electrophilic substitution.	1 1
	ii.(a) Alkyl halides are polar in nature but it is insoluble in water because alkyl halide molecules are held together by dipole-dipole attraction and water molecules are held together by H-bonds. More energy is required to overcome these attractive forces between the haloalkanes. But less energy is released when haloalkanes and water molecules come together, so haloalkanes are not soluble in water. (b) Grignard reagents are very reactive, so they react with moisture and form alkane. R-Mg-X + H-OH → R-H + Mg(OH)X Therefore, it must be prepared and stored under anhydrous conditions.	1
28	i) Square planar (ii)$Cu2+ = 3d9$ 1 unpaired electron so $\sqrt{1(3)} = 1.73$BM iii. $[Co(NH_3)_5Br]SO_4$ **OR**	1 1 1

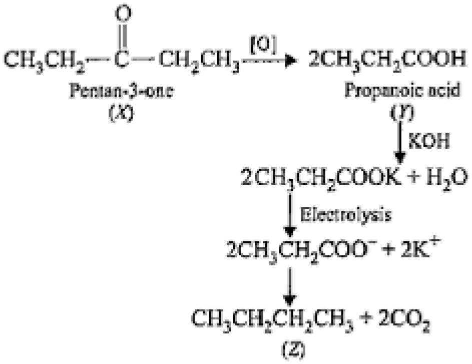
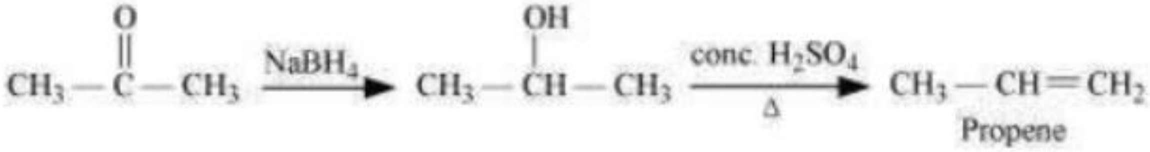
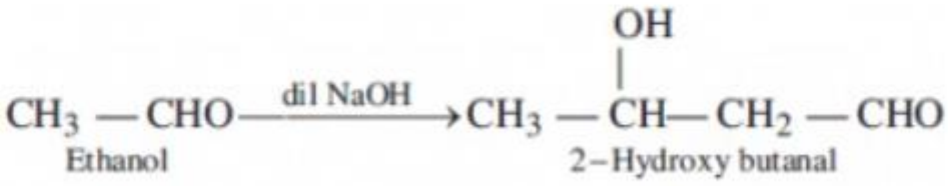
<table>
<tr><td></td><td>(i) +3 (III)
(ii) d2sp3, octahedral
(iii) paramagnetic
(iv) Two geometrical isomers
(v) Yes, there may be optical isomer also due to presence of polydentate ligand.
(vi) Dichlorido bis-(ethane 1, 2-diamine) Iron (III)</td><td>½
½
½
½
½
½</td></tr>
<tr><td>29</td><td>(i) Aniline, N-ethylethanamine, Etanamine
(ii) Ethanamine, ethanol, ethanoic acid
(iii) N, N dimethylmethanamine, methanamine, N-methylmethanamine</td><td>1
1
1</td></tr>
<tr><td>30</td><td>i. a) Benzoic acid reacts with NaHCO3 giving CO2gas with effervescence whereas phenol does not C6H5 COOH + NaHCO3 → C6H5COONa + H2O + CO2

Step 1: Formation of protonated alcohol.
Step 2: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.
Step 3: Formation of ethene by elimination of a proton.

ii.</td><td>1
1
½
½</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td colspan="3">SECTION D</td></tr>
<tr><td>31</td><td>a. Solubility of gas in liquid increase with decrease in temperature.
b. (<i>i</i>) Nature of gas (<i>ii</i>) Temperature
c. The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills.</td><td>1
1
2</td></tr>
<tr><td>32</td><td>i.(d) all the above
ii.(c) glycine
iii.
<table>
<tr><th>Fibrous Proteins</th><th>Globular Proteins</th></tr>
<tr><td>Usually long and narrow</td><td>Typically spherical in shape</td></tr>
<tr><td>Insoluble in water</td><td>Soluble in water</td></tr>
</table></td><td>1
1
2</td></tr>
</table>

helps to maintain cell shape	carry out a specific biological function in the body
Example: Keratin, collagen	Example: Haemoglobin, Insulin

SECTION E

3	i. Ecell = E o cell -0.059 x log [Mg2+]/ [Cu2+]/n	1
3	Ecell= 0.34 - (-2.36) – 0.059 x log (0.01)/(0.001)/2	1
	= 2.6705V	1
	ii. In the process of corrosion, due to the presence of air and moisture, oxidation takes place at a particular spot of an object made of iron. That spot behaves as the anode.	1
	Prevention from corrosion	
	One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmosphere. This can be done by covering the surface with paint or by some chemicals (e.g. bisphenol).	1
	Another simple method is to cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn,etc.) which corrodes itself but saves the object.	
	OR	
	i. Faraday's Laws of electrolysis	1
	First Law: The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte.	1
	Second Law: The amount of different substances liberated by the same quantity of electricity passing through the electrolytic solution is proportional to their chemical equivalent weights.	1
	ii. Current = 5A	
	Time = 20 × 60 = 1200 s	
	∴ Charge = current × time	
	= 5 × 1200	
	= 6000 C	
	According to the reaction,	
	Ni2+ 2e- ----> Ni	1
	Nickel deposited by 2 × 96487 C = 58.71 g	1
	Therefore, nickel deposited by 6000 C $= \frac{58.71 \times 6000}{2 \times 96487}$ g	
	= 1.825 g	
	Hence, 1.825 g of nickel will be deposited at the cathode.	

3 4	i  ii.a.  ii.b.  OR i.a. Propanal has an aldehydic functional group and propanone is a methyl ketone. Propanol on reaction with sodium hypoiodite does not form a yellow coloured precipitate but propanone give yellow precipitate of iodoform. Thus, the reaction with sodium hypoiodite is the distinguishing test between propanal and propanone. This test is known as the iodoform test b. When ethanal is heated with iodine and NaOH solution, it gives yellow crystalline precipitate of iodoform while methanal does not give this test ii. 3,3-dimethylbutanoic acid. iii. a.Carboxylic acids have higher boiling points than aldehydes, ketones of comparable molecular mass. This is because of formation of intermolecular H-bonding b. Because of −I effect of Cl atom in ClCH2COOH and +I effect of CH3 group in CH3COOH the electron density in the O−H bond in ClCH2COOH is much weaker than in CH3COOH therefore loses a proton more easily than CH3COOH	1 1 1 1 1 1 1 1 1 1
3	a. Cu2+ oxidizes iodide ion to iodine. (1)	1

5	b. The low value for V is related to the stability of V2+ (half-filled t2g level) (1) c. Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine. d. The d orbital is full with ten electrons and shield the electrons present in the higher s-orbital to a greater extent resulting in increase in size. e. The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. Increasing the pH (in basic solution)of dichromate ions a colour change from orange to yellow is observed as dichromate ions change to chromate ions.	1 1 1 1

SAMPLE PAPER 3 (2022 - 23)

BLUEPRINT

	Section A		Section B	Section C	Section D	Section E	Total
	MCQ (14)	**R & A (4)**	**2Marks (7)**	**3Marks (5)**	**4Marks (2)**	**5 Marks (3)**	
Solution				3 (1)	4 (1)		7
Electro Chemistry	1 (2)		2 (1)			5 (1)	9
Chemical Kinetics	1 (3)		2 (2)				7
D & F Block	1 (1)	1 (1)				5 (1)	7
Co-ordination Componds	1 (2)		2 (1)	3 (1)			7
Halo alkane	1 (1)		2 (1)	3 (1)			6
Alcohols	1 (2)	1 (1)		3 (1)			6
Aldehyde Ketones & Carboxylic acid	1 (1)		2 (1)			5 (1)	8
Amines	1 (2)	1 (1)		3 (1)			6
Biomolecules		1 (1)	2 (1)		4 (1)		7
No of Qns	**14**	**4**	**2 (7)**	**3 (5)**	**4 (2)**	**5 (3)**	**70 (35)**
Marks	**18**		**14**	**15**	**8**	**15**	**70**

Sample Paper 3   2022-23:

General Instructions **_Maximum Marks_**
_:70_   *Time allotted: 3 hours*

Read the following instructions carefully.

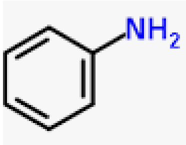
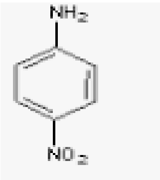
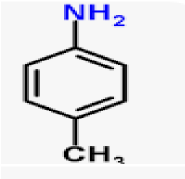
1. a) There are 35 questions in this question paper with internal choice.
2. b) SECTION A consists of 18 multiple-choice questions carrying 1 mark each.
3. c) SECTION B consists of 7 very short answer questions carrying 2 marks each.
4. d) SECTION C consists of 5 short answer questions carrying 3 marks each.
5. e) SECTION D consists of 2 case- based questions carrying 4 marks each.
6. f) SECTION E consists of 3 long answer questions carrying 5 marks each.
7. g) All questions are compulsory.
8. h) Use of log tables and calculators is not allowed

SECTION A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1	Which of the following species can act as the strongest base? (a)$^{----}$ OH (b)$^{—}$OR (c) $^{--}OC_6H_5$ (d) water	1
2	Which reagent will you use for the following reaction? $CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$ (a) Cl_2/ sunlight (b) NaCl +H_2SO_4 (c) Cl_2 gas in dark (d) Cl_2 gas in the presence of Fe in dark	1

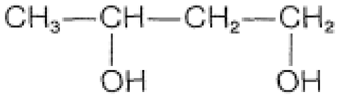
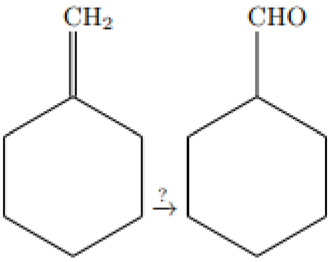
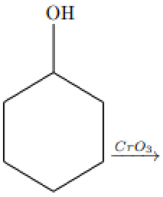
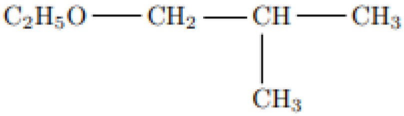
3	Which of the following have maximum and minimum ionic character out of MnO, MnO_2,Mn_2O_7,MnF_2 (a) MnO, Mn_2O_7 (b) , Mn_2O_7 , ,MnF_2 (c) MnO_2, MnO (d) MnO_2,Mn_2O_7	1
4	Half life period of a first order reaction is 1386 seconds. The specific rate constant of the reaction is (a) $0.5x10^{2}$ sec^{-1} (b) 0.5 x $10^{—3}$ sec^{-1} (c) $5x10^{—2}$ sec-1 (d) $5x10^{—3}$ sec^{--1}	1
5	For the reaction $2MnO_4^{--}$ +10 Br^{--} + $16H^{+}$ $\longrightarrow$ $2Mn^{2+}$ +$5Br_2$ +$8H_2O$ Given E^0 MnO_4^{--} / Mn^{2+} = 1.51 v , E^0 Br_2/ Br^{--} = 1.09 v (a) 5x 1.09 v --- 2 x1.51 v= 2.43 v (b)2x1.51 v---- 5x 1.09 v = ---2.43 v (c) 1.51 v—1.09 v = 0.42 v (d) 1.09 v—1.51 v=---0.42 v	1
6	The rate of the reaction A+B $\longrightarrow$ products is given by the equation r= K [A] [B]. If B is taken in large excess the order of reaction would be (a) 2 (b) 1 (c) zero (d) unpredictable	1
7	Which of the following species is not expected to be ligand? (a)NO (b) NH_4^{+} (c) $NH_2CH_2CH_2NH_2$ (d) CO	1
8	The correct increasing order of basic strength for the following compound is	1

	(i)  (ii)  (iii)  (a) ii < iii < I (b)) iii < i < ii (c)) iii < ii < I (d)) ii < i < Iii	
9	The process of converting alkyl halides into alcohols involves (a) addition reaction (b) substitution reaction (c) dehydrohalogenation (d) rearrangement reaction	1
10	Which of the following methods of preparation of amines will not give same number of carbon atoms in the chain of amines as in the reactant? (a) reaction of nitrite with $LiAlH_4$ (b) reaction of amide with $LiAlH_4$ followed by treatment with water (c) heating of alkyl halide with potassium salt of phthalimide followed by hydrolysis (d) treatment of amide with bromine in aqueous solution of NaOH	1
11	The reagent which does not react with both acetone and benzaldehyde is (a) sodium hydrogen sulphite (b) phenyl hydrazine (c) Fehling s solution (d) Grignard reagent	1
12	Higher order >3 reactions are rare due to (a) loss of active species on collision (b) low probability of simultaneous collision of all the reacting species (c) increase in entropy and activation energy as more molecules are involved (d) shifting of equilibrium towards reactants due to elastic collisions	1
13	The colour of the coordination compounds depends on the crystal field splitting. What will be the correct order of adsorption of wavelength of light in the visible region for the complexes [Co ($NH_3)_6$] $^{3+}$, [Co($CN)_6]^{3-}$, [Co ($H_2O)_6$] $^{3+}$ (a) [Co($CN)_6]^{3-}$ > [Co ($NH_3)_6$] $^{3+}$ > , [Co ($H_2O)_6$] $^{3+}$ (b) [Co ($NH_3)_6$] $^{3+\,-}$ > , [Co ($H_2O)_6$] $^{3+\;-}$ >) [Co($CN)_6]^{3-}$ (c) , [Co ($H_2O)_6$] $^{3+\,-}$ > [Co ($NH_3)_6$] $^{3+\;-}$ > [Co($CN)_6]^{3-}$ (d) [Co ($NH_3)_6$] $^{3+}$ > [Co($CN)_6]^{3-}$ > , [Co ($H_2O)_6$] $^{3+}$	1
14	Few simple chemical tests are given below to differentiate between the pairs of organic compounds. Which of the following is not correct for	1

	differentiation?	

a	Prop anal & propanone	Ag mirror test
b	Acetophenone & benzophenone	Iodoform test
c	Ethanal & prop anal	Fehling test
d	Benzoic acid & ethyl benzoate	Sodium bicarbonate test

15	Given below are two statements labelled as Assertion (A) and Reason (R) Select the most appropriate answer from the options given below: a. Both A and R are true and R is the correct explanation of A b. Both A and R are true but R is not the correct explanation of A. c. A is true but R is false. d. A is false but R is true. Assertion: Anisole undergoes electrophilic substitution at ortho & para positions Reason: Anisole is less reactive than phenol towards electrophilic substitution	1
16	Assertion: Maltose & lactose are examples of reducing sugars Reason: Maltose & lactose reduce Fehling's solution & Tollens reagent	1
17	Assertion: Ce^{4+} is a good analytical reagent Reason: Ce^{4+} has the tendency to change to Ce^{3+}	1
18	Assertion: Aniline does not undergo Friedel craft reaction Reason: Friedal craft reaction is an electrophilic substitution reaction	1
	SECTION B This section contains 7 questions with internal choice in two questions. The following questions are very short answer type and carry 2 marks each	
19	(a)What effect does a catalyst have on the activation energy of a reaction? (b) What effect does it have on the change in potential energy for the reaction?	1+1
20	Why are amino acids high melting solids and water soluble? Or (a)Why can vitamin C not stored in the body? (b)Where does the water present in the egg go after the egg is boiled?	2
	(a) Is $(CH_3)_3CO^{--}K^{+}$ an organo metallic compound ? If not why? (b)Draw the structures of all the possible isomers of the monochloro derivative of methyl cyclohexane	1+1
22	(a)Does any of the isomers of $[CoCl_3(NH_3)_3]$ show optical activity? Explain (b)What are the isomers possible for $[Co(NH_3)_4(NO_2)]Br$	1+1
23	Given the half reactions $Fe^{3+} + e^{--} \longrightarrow Fe^{2+}$ ($E^0 = +0.77$ v) and $Sn^{4+} + 2e^{--} \longrightarrow Sn^{2+}$ ($E^0 = +0.15$ V). Construct two redox reactions, & identify their spontaneity	1+1
24	The reaction $A+B \longrightarrow C+D$ is believed to occur in two steps	1

	Step1(fast): $A+B \rightleftharpoons E$ Step 2(slow) $E \longrightarrow C+D$ (a) Which is the rate determining step? (b)What is the molecularity of the rate determining step?	+ 1
25	(a) In a carbonyl compound the Nu^{-} always attack the carbon rather than the oxygen. Explain (b) Show how the following compound can be synthesized from  $CH_3-CH(OH)-CH_2-CH_2OH$ from ethanal	1 + 1
26	**SECTION C** This section contains 5 questions with internal choice in two questions. The following questions are short answer type and carry 3 marks each. Give starting materials, reagents (or) products for the following (a)  (b)  (c)Write the IUPAC name of  $C_2H_5O-CH_2-CH(CH_3)-CH_3$	1 1 1
27	(a) Determine the oxidation state and coordination number of the central metal in the following species (i) $[Cr(ox)_3]^{3-}$ (ii) $[Co(en)_2(NH_3)_2]^{3+}$	1 + 1

	(b) How many unpaired electrons do you expect in the square planar [Pt $(CN)_4]^{2-}$	1
28	(a) What is the estimated freezing point of an aqueous solution of urea that is 10% w/W(molecular mass= 60 amu) K_f= 1.86 KKgmol^{--} (b) Define molarity	2 1
29	(a) Write the chemical reaction of aniline with benzoyl chloride and write the product name (b) Which is more soluble in water? NH_3 or CH_3NH_2	2 1
30	(a)$C_4H_8Cl_2$ (A) on hydrolysis forms C_4H_8O (B) which forms an oxime, but does not reduce Fehling solution. B also answers iodoform test. Identify A & B. Explain the reaction (b) The solubility of alcohols in water decreases with increasing molecular weight	2 1
31	**SECTION D** The following questions are case-based questions. Each question has an internal choice and carries 4 (1+1+2) marks each Read the passage carefully and answer the questions that follow. Nucleic acids are naturally occurring chemical compounds that serve as the primary information-carrying molecules in cells and make up the genetic material. Nucleic acids are found in abundance in all living things, where they create, encode, and then store information of every living cell of every life form on Earth. In turn, they function to transmit and express that information inside and outside the cell nucleus to the interior operations of the cell and ultimately to the next generation of each living organism. The encoded information is contained and conveyed via the nucleic acid sequence, which provides the 'ladder-step' ordering of nucleotides within the molecules of RNA and DNA. They play an especially important role in directing protein synthesis 1. Which bond is used to stabilize the double helix of DNA? a) Hydrophobic bond b) Hydrogen bond c) Covalent bond d) Ionic bond 2. Name the three products formed when a nucleotide from RNA containing adenine is hydrolysed 3. What is the monomer of nucleic acid called? Define a monomer (OR) Write the difference, similarity between RNA & DNA	4

32 The extent of the solubility of a substance in a specific solvent is generally measured as the of the solute concentration in saturated solution, one in which no more solute can be dissolved. At this point, the two substances are said to be at the solubility equilibrium. For some solutes and solvents, there may be no such limit, in which case the two substances are said to be miscible in all proportions" (or just "miscible" 4

The solute can be a solid, a liquid, or a gas, while the solvent is usually solid or liquid. Both may be pure substances, or may themselves be solutions. Gases are always miscible in all proportions, except in very extreme situations, and a solid or liquid can be "dissolved" in a gas only by passing into the gaseous state first.

The solubility mainly depends on the composition of solute and solvent (including their pH and the presence of other dissolved substances) as well as on temperature and pressure. The dependency can often be explained in terms of interactions between the particles (atoms, molecules, or ions) of the two substances, and of thermodynamic concepts such as enthalpy and entropy

Answer the following questions:

1.Bromine and iodine are both soluble inCCl_4, but bromine is much more soluble. Why?
2. One manufacturer's instructions for setting up an aquarium specify that if boiled water is used, the water must be cooled to room temperature and allowed to stand overnight before fish are added. Why is it necessary for the water to stand?
3.. A solution is made by mixing 50.0 mL of liquid A with 75.0 mL of liquid B. Which is the solute, and which is the solvent? Is it valid to assume that the volume of the resulting solution will be 125 mL? Explain your answer.

(OR)

4. Calculate the boiling point of a solution of glucose prepared by dissolving 8.4 g of glucose ($C_6H_{12}O_6$) in 250 g of water.Kb= 0.52 K kg/mole

5

SECTION E

The following questions are long answer type and carry 5 marks each.

Two questions have an internal choice.

1.What is meant by 'limiting molar conductivity'?

2.Express the relation between conductivity and molar conductivity of a solution held in a cell.

3.Determine the values of equilibrium constant (K_c) and ΔG° for the following reaction:
$Ni(s) + 2Ag^+ (aq) \rightarrow Ni^{2+} (aq) + 2Ag(s)$,
E° = 1.05 V
(1F = 96500 C mol^{-1}

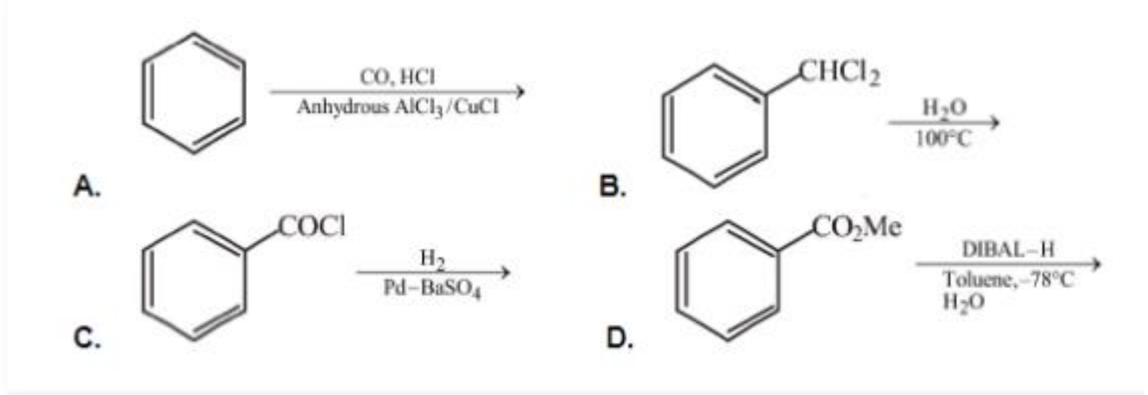
(OR)

1.The conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm2 mol-1. Calculate the molar conductivity of this solution.

2.Define molar conductivity

3.Write the reactions taking place at cathode and anode in lead storage battery when the battery is in use. What happens on charging the battery.

33 1.Among the following the number of reactions that produce benzaldehyde is: 5



2. **The correct statement about the following reaction sequence is(are)**

$$Cumene(C_9H_{12}) \xrightarrow{O_2} [H_3O^+]P \xrightarrow{CHCl_3/NaOH} Q(major) + R(minor)\ Q \xrightarrow{NaOH} S$$

A. R is steam volatile

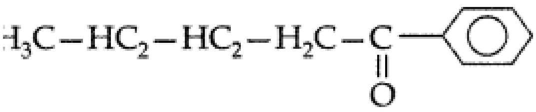
B. Q gives dark violet colouration with 1% aqueous $FeCl_3$ solution

C. S gives a yellow precipitate with 2,4-dinitrophenylhydrazine

D. S gives dark violet colouration with 1% aqueous $FeCl_3$ solution

3. The compound that does not liberate CO_2, on treatment with aqueous $NaHCO_3$ solution, is:

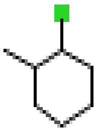
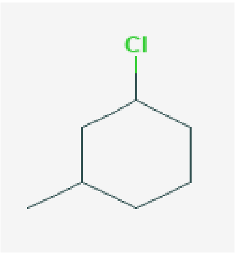
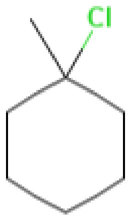
A. Benzoic acid

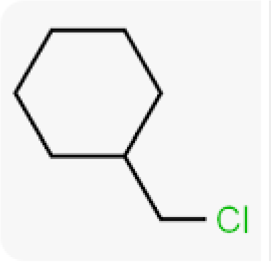
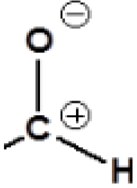
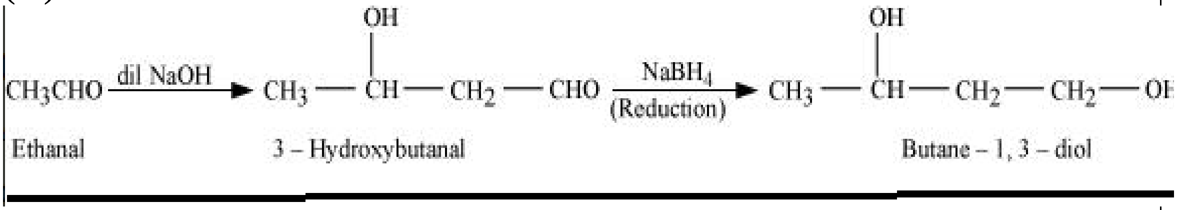
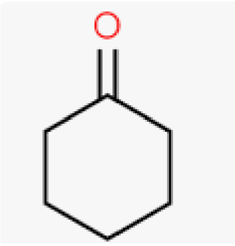
	B. Benzene sulphonic acid C. Salicylic acid D. Carbolic acid **(OR)** 1.Write the IUPAC name of  2. What is Tollens reagent? 3. Arrange the following compounds in an increasing order of their reactivity in nucleophilic addition reactions ethanal, prop anal, propanone, butanone. 4. Explain the difference in structure which makes aldehydes susceptible to oxidation and ketones difficult to oxidize 5. What happens when (a) Ethanal is treated with methyl magnesium bromide and then hydrolysed ?	
35	**1.The correct statement(s) about Cr^{2+} and Mn^{3+} is (are) [Atomic numbers of Cr = 24 and Mn = 25]** **A. Cr^{2+} is a reducing agent** **B. Mn^{3+} is an oxidizing agent** **C. Both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration.** **D. When Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration** **2.** Which one of the following exhibit largest number of oxidation states -Mn or V . Explain why ? 3. Account for the following (i)Why do actinoids show wide range of oxidation states? (ii) Why is actinoid contraction greater than lanthanoid contraction? (iii)E° value for the Mn^{+3}/Mn^{+2} couple is positive (+1.5 V) whereas that of Cr^{+3}/Cr^{+2} is negative (-0.4 V). Why?	5

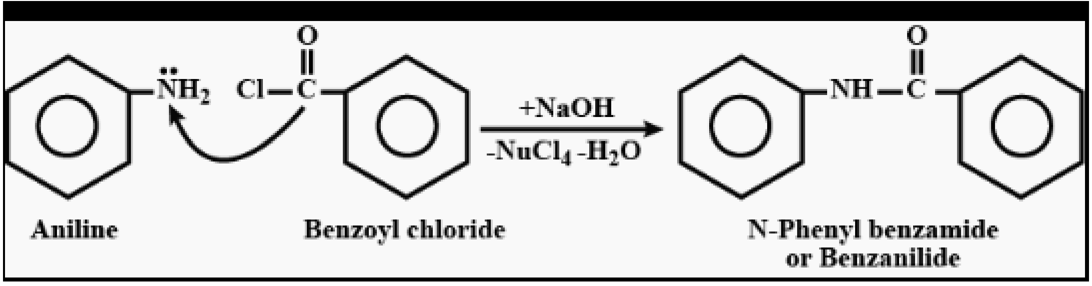
Sample Paper 3 2022-23

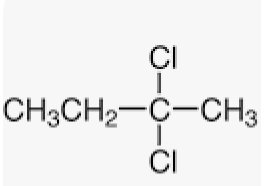
SCORING KEY

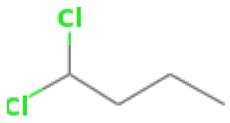
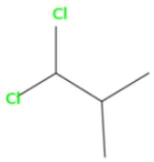
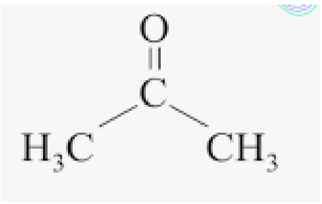
1	(c) $^{--}OC_6H_5$	1
2	(a) Cl_2/ sunlight	1
3	b) , Mn_2O_7 , ,MnF_2	1
4	(b) 0.5 x 10^{-3} sec^{-1}	1
5	(c) 1.51 v—1.09 v = 0.42 v	1
6	(b) 1	1
7	(b) NH_4^+	1
8	(d)) ii < i < Iii	1
9	(b) substitution reaction	1
10	(d) treatment of amide with bromine in aqueous solution of NaOH	1
11	(c) Fehling s solution	1

12	(b) low probability of simultaneous collision of all the reacting species	1
13	(c) , $[Co(H_2O)_6]^{3+}$ -> $[Co(NH_3)_6]^{3+}$ -> $[Co(CN)_6]^{3-}$	1
14	c Ethanal & prop anal Fehling test	1
15	C	1
16	a	1
17	a	1
18	b	1
19	1. Catalyst lowers the activation energy of the reaction. 2. Catalyst has no effect on the potential energy of the reaction.	1 1
20	(a) Due to the dipolar ionic nature , the molecules of amino acids are attracted to each other . They exist as high melting solids. Due to the ionic nature, the amino acids are water soluble. (OR) (a) It is readily soluble in water (b)Protein in egg undergoes denaturation, which causes hardening of white of the yolk.The water present in the egg gets absorbed.	
21	(a) No, the metal is bonded to the oxygen , not to the carbon. . This is an example of an alkoxide salt (b)    	1 1

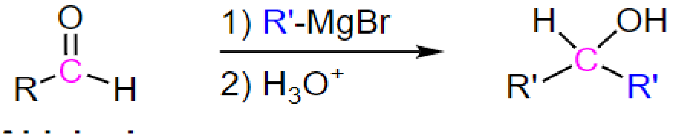
		
22	No, because both the geometrical isomers facial & meridonial of the compound have the same elements of symmetry . They have superimposable mirror images.(b) Ionization isomer , linkage isomer, geometrical isomerism	1 1
23	(i)$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{3+} + Sn^{4+}$ (0.77—0.15)= 0.62 v Spontaneous reaction(ii)$2Fe^{2+} + Sn^{4+} \longrightarrow 2Fe^{3+} + Sn^{2+}$ (0.15 ---0.77)= ----0.62 v Non spontaneous reaction	1 1
24	(a) Slow step (b) unimolecular	1 1
25	(a) Because of polarization, the carbonyl carbon is electrophilic and Nu^{---} attack the carbon. The intermediate  is more stable, because the negative charge is on the more electronegative oxygen. (b)  $CH_3CHO \xrightarrow{\text{dil NaOH}} CH_3-\overset{OH}{CH}-CH_2-CHO \xrightarrow[\text{(Reduction)}]{NaBH_4} CH_3-\overset{OH}{CH}-CH_2-CH_2-OH$	1 1
26	(a) (i) B_2H_6 (ii) PCC (b)  (c) 1-ethoxy -2-methyl propane	½+1/2 1 1

<table>
<tr><td></td><td></td><td></td></tr>
<tr><td>27</td><td>(a)
<table><tr><td>(i)</td><td>Coordination number</td><td>Oxidation state</td></tr><tr><td></td><td>6</td><td>+3</td></tr><tr><td>ii</td><td>6</td><td>+3</td></tr><tr><td>b</td><td>No
Number of unpaired electrons</td><td></td></tr></table></td><td>1
1
1</td></tr>
<tr><td>28</td><td>(a) Formula (b) substitution (c)correct answer
$\Delta Tf = Kf\ m$
$\Delta Tf = 1.86 \times 10/60 \times 1000/90$
$=3.44$ k
Freezing point of the solution= ---3.44 ^{0} c
(b) correct definition</td><td>½+
1/
2+
1
1</td></tr>
<tr><td>29</td><td>(a)


(b) Ammonia is highly soluble in water, due to the formation of H-bonding with water which is strong</td><td>1
1
1</td></tr>
<tr><td>30</td><td>(a)  $CH_3CH_2-\overset{Cl}{\underset{Cl}{C}}-CH_3$ (A) → Diol which is unstable. This</td><td>1</td></tr>
</table>

	compound loses water to give a ketone. The ketone undergoes nucleophilic addition . It undergoes iodoform test    (B)	1
31	(a) H-bonded (b)pentose sugar, phosphoric acid , adenine (c)nucleotide . monomer is small the repeating unit (or) DNA and RNA both have four bases; two purines and two pyrimidines, in the nucleotide chains. The purines adenine and guanine and the pyrimidine cytosine are common to both DNA and RNA Any one difference -	1 1 1+ 1
32	(a)Br_2 is highly soluble , because it is nonpolar liquid having molecular mass less than iodine which is a nonpolar solid . (b) The solubility of oxygen in water decreases at high temperature (c) A is the solute , B is the solvent. (or) On mixing A & B forms ideal solution. (or) $\Delta Tb= Kbm$ $= 0.52 \times 8.4 \times 1000/ 180 \times 250$ $=0.092$ k Boiling point of the solution= 373.24 k	1 1 2

33	Limiting molar conductivity: The molar conductivity of a solution at infinite dilution $\Lambda_m = \frac{\kappa \times 1000}{C}$ *(i) calculation of free energy change (1 ½) (ii) calculation of k(1 ½) $\Delta_r G^\ominus = -nFE^\ominus_{(cell)}$ = --2 x 96500 x 1.05 = --202650 J/ mol Log k = ΔG^0 / 2.303RT = 202650 / 2.303 x 8.314 x 298 = .3552 K = 5.3 (Or) 1. Λm = κ x 1000 / molarity = 138.9 x 1000/ 1.5 = 0.20835 (S cm2 mol–1) 2.. Molar conductivity of a solution at a given concentration is the conductance of the volume V of solution containing one mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length	1 1 3
	3.The cell reactions when the battery is in use are given below: Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$ Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$ i.e. , overall cell reaction consisting of cathode and anode reactions is: $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O$ On charging the battery the reaction is reversed and PbSO4 (s) on anode and cathode is converted into Pb and PbO2 , respectively	1+ 1
34	1. All the four reaction 2. B, C 3. D. Carbolic acid (or) 1. 1-phenyl -1-pentanone 2. Ammoniacal silver nitrate solution	2 2 1

	3. Butanone < propanone < propanal < ethanal 4. Aldehyde has a proton attached to the carbonyl carbon, which can be abstracted. This allows the aldehydes to get easily oxidised 5.  R=CH$_3$, R’=CH3	1 1 1 1 1
35	1.A,B,C 2. Mn (because of the participation of ns & (n-1)d orbitals where the energy difference is very less. 3. (i) It is because 5f, 6d, 7s have comparable energies (ii) 5f orbitals have poor shielding effect than 4forbitals.Therefore effective nuclear charge is more in actinoids than lanthanoids (iii)Mn^{2+} is more stable than Mn^{3+} due to half filled d orbitals d^5 . But Cr^{3+} is more stable due to half filled t$_{2g}$ orbitals	1 1 1 1 1