K M C

PART A : *Physical Chemistry* — P-1-133

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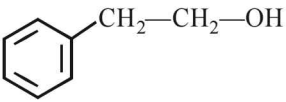
 Approved: 0777 023 444

Board 2016-17 Solved Paper

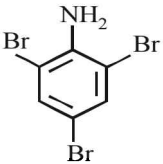
(Organic Chemistry Questions)

1 - WHAT ARE THE IUPAC NAMES/STRUCTURES OF THE FOLLOWING COMPOUNDS

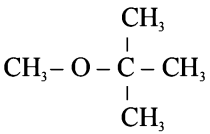
1. Write the IUPAC name of the given compound : **[All India 2016]**



2. Write the IUPAC name of the given compound: **[Delhi 2016]**



3. Write the IUPAC name of the following compound: **[All India 2017]**



2 - HOW WILL YOU DEFINE THE GIVEN REACTIONS ?

4. Write the chemical equations involved in the following reactions :
(i) Hoffmann-bromamide degradation reaction **[All India 2016]**
(ii) Carbylamine reaction

5. Write the chemical reaction involved in Wolff-Kishner reduction. **[All India 2016]**

6. Write the chemical equation for the reaction involved in Cannizzaro reaction. **[Delhi 2016]**

7. Write the reaction involved in the following: **[All India 2017]**
(i) Etard reaction (ii) Stephen reduction

3 - WHAT HAPPENS WHEN ...

8. Write the name of two monosaccharides obtained on hydrolysis of lactose sugar. **[Delhi 2016]**

9. Draw the structure of the semicarbazone of ethanal. **[Delhi 2016]**

10. Write the structures of the products when Butan–2 – ol reacts with the following **[All India 2017]**
(a) CrO_3 (b) $SOCl_2$

4 - WHAT ARE THE MISSING COMPOUNDS/REAGENTS ?

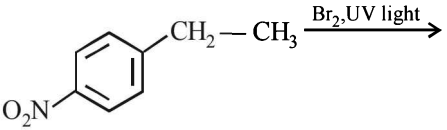
11. Write the final product(s) in each of the following reactions :

(a) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_3 + HI \longrightarrow$ **[All India 2016]**

(b) $CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{Cu/573K}$

(c) $C_6H_5-OH \xrightarrow[(ii)\ H^+]{(i)\ CHCl_3 + aq.NaOH}$

12. Write the major product(s) in the following : **[All India 2016]**

(i) 

(ii) $2CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 \xrightarrow[\text{dry ether}]{Na}$

(iii) $CH_3-CH_2-Br \xrightarrow{AgCN}$

13. Write the structures of A and B in the following reactions: **[All India 2016]**

(i) $CH_3COCl \xrightarrow{H_2, Pd-BaSO_4} A \xrightarrow{H_2N-OH} B$

(ii) $CH_3MgBr \xrightarrow[2.\ H_3O^+]{1.\ CO_2} A \xrightarrow{PCl_5} B$

14. Write the product in the following reaction **[All India 2016]**

$$CH_3CH_2CH=CH-CH_2CN \xrightarrow[2.\ H_2O]{1.\ (i-Bu)_2AlH}$$

15. Write the main product(s) in each of the following reactions:

(i) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_3 + HI \longrightarrow$ **[Delhi 2016]**

(ii) $CH_3-CH=CH_2 \xrightarrow[(ii)\ 3H_2O_2/OH^-]{(i)\ B_2H_6}$

(iii) $C_6H_5-OH \xrightarrow[(ii)\ CO_2, H^+]{(i)\ aq.\ NaOH}$

16. Write the structures of A, B and C in the following : **[Delhi 2016]**

(i) $C_6H_5-CONH_2 \xrightarrow{Br_2/aq.KOH} A \xrightarrow[0-5°C]{NaNO_2+HCl}$

$B \xrightarrow{KI} C$

(ii) $CH_3-Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[\Delta]{CHCl_3+Alc.KOH} C$

17. Write the structures of A, B, C, D and E in the following reactions : **[Delhi 2016]**

$$C_6H_6 \xrightarrow[\text{Anhyd. } AlCl_3]{CH_3COCl} A \xrightarrow{\text{Zn-Hg/conc. HCl}} B \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } KMnO_4-KOH,\ \Delta} C$$

$$A \xrightarrow{NaOI} D + E$$

18. Write the product in the following reaction: **[Delhi 2016]**

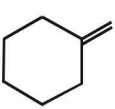
$$CH_3-CH=CH-CH_2CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL-H}}$$

19. Write the structures of compounds A, B and C in the following reactions. **[All India 2017]**

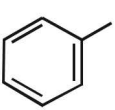
(a) $CH_3-COOH \xrightarrow{NH_3/\Delta} A \xrightarrow{Br_2/KOH(aq)} B \xrightarrow{CHCl_3+alc.KOH} C$

(b) $C_6H_5N_2^+BF_4^- \xrightarrow[\Delta]{NaNO_2/Cu} A \xrightarrow{Fe/HCl} B \xrightarrow{CH_3COCl/pyridine} C$

20. Write the products(s) in the following reactions: **[All India 2017]**

(i) 

$+ HCN \longrightarrow ?$

(ii) 

$+ NaOH \xrightarrow[\Delta]{CaO} ?$

(iii) $CH_3-CH=CH-CN \xrightarrow[\text{(b) } H_2O]{\text{(a) DIBAL-H}} ?$

5 - HOW WILL YOU CARRY OUT THE GIVEN CONVERSIONS ?

21. How do you convert : **[All India 2016]**

(i) Chlorobenzene to biphenyl (ii) Propene to 1-iodopropane

(iii) 2-Bromobutane to but-2-ene

22. How will you convert the following in not more than two steps:

(i) Benzoic acid to benzaldehyde **[All India 2017]**

(ii) Acetophenone to benzoic acid

(iii) Ethanoic acid to 2-Hydroxyethanoic acid

6 - HOW WILL YOU DISTINGUISH THE GIVEN PAIR OF COMPOUNDS ?

23. Write the structural difference between starch and cellulose. **[All India 2016]**

24. Distinguish between : **[All India 2016]**

(i) $C_6H_5-COCH_3$ and C_6H_5-CHO

(ii) CH_3COOH and $HCOOH$

25. What is the difference between a nucleoside and a nucleotide ? **[Delhi 2016]**

26. How can you distinguish between propanal and propanone? **[Delhi 2016]**

27. Give simple chemical tests to distinguish between the following pairs of compounds **[All India 2017]**

(i) Butanal and Butan-2-one (ii) Benzoic acid and phenol

7 - WHAT WILL BE THE MECHANISM OF THE GIVEN REACTIONS?

28. Write the structure of an isomer of compound C_4H_9Br which is most reactive towards S_N1 reaction. **[All India 2016]**

29. Out of $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-Cl$ and **[Delhi 2016]**

$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-Cl$, which is more reactive towards S_N1 reaction and why ?

30. Write the mechanism of the following reaction : **[Delhi 2016]**

$$2CH_3CH_2OH \xrightarrow[413\ K]{Conc.\ H_2SO_4} CH_3-CH_2-O-CH_2-CH_3$$

31. Write the mechanism of free radical polymerization of ethene. **[Delhi 2016]**

32. Write the mechanism (using curved arrow notation) of the following reaction: **[All India 2017]**

$$CH_2=CH_2 \xrightarrow{H_2O^+} CH_3-CH_2^+ + H_2O$$

33. The following compounds are given to you: **[All India 2017]**

2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

(a) Write the compound which is most reactive towards S_N2 reaction.

(b) Write the compound which is optically active.

(c) Write the compound which is most reactive towards β-elimination reaction.

8 - WHY DO THE FOLLOWING HAPPENS ?

34. Give reasons for the following : **[All India 2016]**

(i) Aniline does not undergo Friedel-Craft's reaction.

(ii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.

(iii) Primary amines have higher boiling point than tertiary amines.

35. Why a carboxylic acid does not give reactions of carbonyl group ? **[All India 2016]**

36. Given reasons. **[Delhi 2016]**

(i) C–Cl bond length in chlorobenzene is shorter than C–Cl bond length in CH_3–Cl.

(ii) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(iii) S_N1 reactions are accompanied by racemization in optically active alkyl halides.

37. Why vitamin C cannot be stored in our body ? **[Delhi 2016]**

38. Why pK_a of F-CH_2-COOH is lower than that of Cl–CH_2–COOH? **[Delhi 2016]**

39. Give reasons for the following : **[All India 2017]**

(a) Acetylation of aniline reduces its activation effect.

(b) CH_3NH_2 is more basic than $C_6H_5NH_2$.

(c) Although – NH_2 is *o*/*p* directing group, yet aniline on nitration gives a significant amount of *m*-nitroaniline.

9 - WHAT IS THE CORRECT INCREASING/DECREASING ORDER?

40. Arrange the following polymers in the increasing order of their intermolecular forces : Terylene, Polythene, Neoprene. **[All India 2016]**

41. Arrange the following in the increasing order of their boiling points : **[All India 2016]**

$$CH_3CHO, CH_3COOH, CH_3CH_2OH$$

42. Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction. **[All India 2016]**

$$C_6H_5COCH_3, CH_3-CHO, CH_3COCH_3$$

43. Arrange the following polymers in the increasing order of their intermolecular forces: **[Delhi 2016]**

Polystyrene, Terylene, Buna-S

44. Arrange the following compounds in the increasing order of their acid strength: **[All India 2017]**

p-cresol, *p*-nitrophenol, phenol

10 - HOW TO SOLVE ANALYTICAL PROBLEMS

45. A and B are two functional isomers of the compound C_3H_6O. On heating with NaOH and I_2, isomer B forms yellow precipitate of iodoform, whereas isomer A does not form any precipitate. Write the formulae of A and B. **[All India 2016]**

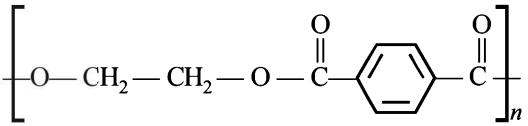
11 - MISCELLANEOUS QUESTIONS

46. (i) What type of linkage is present in nucleic acids ? **[All India 2016]**

(ii) Give one example each for fibrous protein and globular protein. **[All India 2016]**

47. (i) What is the role of sulphur in the vulcanization of rubber ? **[All India 2016]**

(ii) Identify the monomers in the following polymer :



[All India 2016]

48. (i) What is the role of *t*-butyl peroxide in the polymerization of ethene? **[Delhi 2016]**

(ii) Identify the monomers in the following polymer : **[Delhi 2016]**

$$\left[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO \right]_n$$

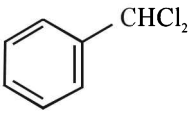
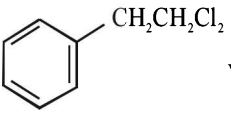
49. Due to hectic and busy schedule, Mr. Angad made his life full of tensions and anxiety. He started taking sleeping pills to overcome the depression without consulting the doctor. Mr. Deepak, a close friend of Mr. Angad, advised him to stop taking sleeping pills and suggested to change his lifestyle by doing Yoga, meditation and some physical exercise. Mr. Angad followed his friend's advice and after few days he started feeling better. **[Delhi 2016]**

After reading the above passage, answer the following:

(i) What are the values (at least two) displayed by Mr. Deepak ?

(ii) Why is it not advisable to take sleeping pills without consulting doctor ?

(iii) What are tranquilizers ? Give two examples.

50. Out of  and  which is an example of benzylic halide? **[All India 2017]**

51. Define the following : **[All India 2017]**

(a) Cationic detergents (b) Broad spectrum antibiotics

(c) Tranquili zers

52. Write the structures of the monomers used for getting the following polymers: **[All India 2017]**

(a) Teflon

(b) Melamine-formaldehyde polymer

(c) Neoprene

53. After watching a programme on TV about the presence of carcinogens (cancer causing agents) Potassium bromate and Potassium iodate in bread and other bakery products, Rupali a class XII student decided to make others aware about the adverse effects of these carcinogens in foods. She consulted the school principal and requested him to instruct the canteen contractor to stop selling sandwiches pizzas, burgers and other bakery products to the students. The principal took an immediate action and instructed the canteen contractor to repalce the bakery products with some protein and vitamin rich food like fruits, salads, sprouts, etc. The decision was welcomed by the parents and the students. **[All India 2017]**

After reading the above passage, answer the following question:

(a) What are the values (atleast two) dispalyed by Rupali?

(b) Which polysaccharide component of carbohydrates is commonly present in bread?

(c) Write the two type of secondary structures of proteins.

(d) Give two examples of water soluble vitamins.

Board 2016-17 Solved Paper

(Physical Chemistry Questions)

1 - WRITE THE DEFINITION/EXAMPLE(S)/TYPE(S)/OF ...

1. Give an example each of a molecular solid and an ionic solid. **[All India 2016]**
2. In non-ideal solution, what type of deviation shows the formation of maximum boiling azeotropes ? **[All India 2016]**
3. Define electrochemical cell. What happens if external potential applied becomes greater than E^0_{cell} of electrochemical cell? **[All India 2016]**
4. What type of colloid is formed when a gas is dispersed in a liquid? Give an example. **[All India 2017]**
5. Write the dispersed phase and dispersion medium of milk. **[All India 2017]**
6. Write the chemical method by which $Fe(OH)_3$ sol is prepared from $FeCl_3$. **[All India 2017]**
7. Define the following terms: **[All India 2017]**
   (i) Molality (m) (ii) Abnormal molar mass

2 - WHY DOES THIS HAPPEN?

8. What is the reason for the stability of colloidal sols? **[All India 2016]**
9. Gas (A) is more soluble in water than gas (B) at the same temperature. Which one of the two gases will have the higher value of K_H (Henry's constant) and why ? **[All India 2016]**
10. Write the main reason for the stability of colloidal sols. **[Delhi 2016]**
11. Out of $MgCl_2$ and $AlCl_3$, which one is more effective in causing coagulation of negatively charged sol and why ? **[Delhi 2016]**
12. Out of 1 M glucose and 2 M glucose, which one has a higher boiling point and why ? **[Delhi 2016]**
13. Why do ferrimagentic substances show better magnetism then antiferromagnetic substances? **[All India 2017]**

3 - WHAT IS THE ROLE/EFFECT OF?

14. What is the effect of adding a catalyst on **[All India 2017]**
    (a) Activation energy (E_a), and
    (b) Gibbs energy (ΔG) of a reaction?
15. What happens when $CdCl_2$ is doped with AgCl? **[All India 2017]**

4 - HOW WILL YOU DIFFERENTIATE BETWEEN?

16. Differentiate between adsorption and absorption. **[Delhi 2016]**

17. Out of sulphur sol and proteins, which one forms multimolecular colloids ? **[Delhi 2016]**

18. Write one difference in each of the following: **[All India 2017]**

(a) Multimolecular colloid and Associated colloid

(b) Coagulation and Peptization

(c) Homogeneous catalysis and Heterogeneous catalysis

19. Write two difference between ideal solutions and non-ideal solutions. **[All India 2017]**

5 - CALCULATION BASED ON FORMULA

20. An element crystallizes in a *bcc* lattice with cell edge of 500 pm. The density of the element is 7.5 g cm^{-3}. How many atoms are present in 300 g of the element ? **[All India 2016]**

21. For the first order thermal decomposition reaction, the following data were obtained : **[All India 2016]**

$$C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)$$

Time/sec	Total pressure/atm
0	0.30
300	0.50

Calculate the rate constant.

(Given : log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021)

22. Calculate E^0_{cell} for the following reaction at 298 K:

$2Al(s) + 3Cu^{2+}(0.01M) \rightarrow 2Al^{3+}(0.01\ M) + 3Cu(s)$

Given : $E_{cell} = 1.98$ V **[All India 2016]**

23. The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is 3.905×10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α). **[All India 2016]**

Given $\lambda^0(H^+) = 349.6$ S cm^2 mol^{-1} and $\lambda^0(CH_3COO^-) = 40.9$ S cm^2 mol^{-1}

24. Calculate e.m.f of the following cell at 298 K. **[Delhi 2016]**

$2Cr(s) + 3Fe^{2+}(0.1\ M) \rightarrow 2Cr^{3+}(0.01M) + 3\ Fe(s)$

Given : $E^0(Cr^{3+}|Cr) = -0.74$ V, $E^0(Fe^{2+}|Fe) = -0.44$ V

25. An element crystallizes in a f.c.c. lattice with cell edge of 250 pm. Calculate the density if 300 g of this element contains 2×10^{24} atoms. **[Delhi 2016]**

26. 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. **[Delhi 2016]**

(K_f for water = 1.86 K kg mol^{-1})

27. When 2.56 g of sulphur was dissolved in 100 g of CS_2, the freezing point lowered by 0.383 K. **[Delhi 2016]**

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}]

28. The cell in which the following reaction occurs: **[All India 2017]**

$$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$$

has $E^\circ_{cell} = 0.236$ V at 298 K. Calculate the standard Gibbs energy of the cell reaction (Given: 1 F = 96,500 C mol^{-1})

29. A first order reaction takes 20 minutes for 25% decomposition. Calculate the time when 75% of the reaction will be completed. (Given : log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021) **[All India 2017]**

6 - NUMERICAL BASED ON LAWS

30. For a reaction : $H_2 + Cl_2 \xrightarrow{h} 2HCl$ **[All India 2016]**

Rate = k

(i) Write the order and molecularity of this reaction.

(ii) Write the unit of k.

31. For a reaction : $2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$ **[Delhi 2016]**

Rate = k

(i) Write the order and molecularity of this reaction.

(ii) Write the unit of k.

32. 30 g of urea (M = 60 g mol^{-1}) is dissolved in 846 g of water. Calculate the vapour pressure of water for this solutions if vapour pressure of pure water at 298 K is 23.8 mm Hg. **[All India 2017]**

7 - NUMERICALS BASED ON APPLICATION/SKILL

33. Using the E^0 values of A and B, predict which is better for coating the surface of iron [$E^0_{(Fe^{2+}/Fe)} = -0.44$V] to prevent corrosion and why ? **[All India 2016]**

Given : $E^\circ_{(A^{2+}/A)} = -2.37$V : $E^0_{(B^{2+}/B)} = -0.14$ V

34. The rate constant for the first-order decomposition of H_2O_2 is given by the following equation. **[Delhi 2016]**

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T} K$$

Calculate E_a for this reaction and rate constant k, if its half-life period be 200 minutes.

(Given : R = 8.314 $JK^{-1}mol^{-1}$)

35. 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 ? **[Delhi 2016]**

(ii) 0.4% sodium chloride solution ?

36. How many electrons flow through a metallic wire if a current of 0.5 A is passed for 2 hours ? **[All India 2017]**

(Given: 1F = 96,500 C mol^{-1})

37. A 10% solution (by mass) of sucrose in water has a freezing point of 269.15K. Calculate the freezing point of 10% glucose in water if the freezing point of pure water is 273.15K **[All India 2017]**

Given:

(Molar mass of sucrose = 342 g mol^{-1})

(Molar mass of glucose = 180 g mol^{-1})

38. Calculate the number of unit cells in 8. 1 g of aluminium if it crystallizes in a face-centred cubic (f.c.c) structure. (Atomic mass of Al = 27 g mol^{-1})

[All India 2017]

8 - MISCELLANEOUS

39. What happens when the external pressure applied becomes more than the osmotic pressure of solution ? **[Delhi 2016]**

40. Write one similarity between physisorption and chemisorption.

[All India 2017]

41. Based on the nature of intermolecular forces, classify the following solids: **[All India 2017]**

Sodium sulphate, Hydrogen

42. 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. **[All India 2017]**

Board 2016-17 Solved Paper

(Inorganic Chemistry Questions)

1 - WHAT ARE THE STRUCTURES/NAMES OF THE FOLLOWING COMPOUNDS ?

1. Write the structures of the following: **[All India 2016, Delhi 2016]**

(i) BrF_3 (ii) XeF_4

2. Draw the structures of the following **[All India 2017]**

(a) XeF_4 (b) BrF_5

3. Using IUPAC norms write the formula for the following:

(a) Potassium Trioxalatoaluminate (III) **[All India 2017]**

(b) Dichloridobis (ethane-1, 2-diamine) cobalt (III)

2 - WHAT IS THE ROLE OF THE FOLLOWING?

4. What is the role of cryolite in the extraction of aluminium ? **[All India 2016]**

5. What is the role of limestone in the extraction of iron from its oxides ? **[All India 2016]**

6. What is the role of coke in the extraction of iron from its oxides ? **[Delhi 2016]**

7. What is the role of depressants in the froth floatation process? **[All India 2017]**

3 - WHAT OR WHICH PRINCIPLE IS INVOLVED IN THE FOLLOWING PROCESSES?

8. Name the method of refining of nickel **[All India 2016]**

9. Name the method of refining of metals such as germanium. **[Delhi 2016]**

10. Write the principle of electrolytic refining. **[All India 2017]**

4 - WHY DO THE FOLLOWING HAPPENS?

11. Give reasons : **[All India 2016]**

(i) SO_2 is reducing while TeO_2 is an oxidizing agent.

(ii) Nitrogen does not form pentahalide.

(iii) ICl is more reactive than I_2.

12. Account for the following : **[All India 2016]**

(i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine, it shows the highest oxidation state of +4.

(ii) Cr^{2+} is a strong reducing agent.

(iii) Cu^{2+} salts are coloured, while Zn^{2+} salts are white.

13. Account for the following : **[Delhi 2016]**

(i) Ozone is thermodynamically unstable.

(ii) Solid PCl_5 is ionic in nature.

(iii) Fluorine forms only one oxoacid HOF.

14. Give reasons: **[Delhi 2016]**

(i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine, it shows the highest oxidation state of +4.

(ii) Transition metals show variable oxidation states.

(iii) Actinoids show irregularities in their electronic configurations.

15. Why is $[NiCl_4]^{2-}$ paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic? (Atomic number of Ni = 28) **[All India 2017]**

16. Why are low spin tetrahedral complexes rarely observed? **[All India 2017]**

17. Why does copper obtained in the extraction from copper pyrites have a blistered appearance? **[All India 2017]**

18. Give reasons for the following: **[All India 2017]**

(a) Red phoshorus is less reactive than white phosphorus.

(b) Electron gain enthalpies of halogens are largely negative

(c) N_2O_5 is more acidic than N_2O_3.

19. Account for the following: **[All India 2017]**

(i) Transition metals show variable oxidation states.

(ii) Zn, Cd and Hg are soft metals.

(iii) E° value for the Mn^{3+}/Mn^{2+} couple is highly positive (+1.57 V) as compared to Cr^{3+}/Cr^{2+}

20. Following are the transition metal ions of 3d series: Ti^{4+}, V^{2+}, Mn^{3+}, Cr^{3+} **[All India 2017]**

(Atomic numbers: Ti = 22, V=23, Mn = 25, Cr = 24)

Answer the following:

(i) Which ion is most stable in an aqueous solutions and why?

(ii) Which ion is a strong oxidising agent and why?

(iii) Which ion is colourless and why?

6 - WHAT HAPPENS WHEN...

21. $Pb(NO_3)_2$ on heating gives a brown gas which undergoes dimerization on cooling ? Identify the gas. **[All India 2016]**

22. When a coordination compound $CoCl_3.6NH_3$ is mixed with $AgNO_3$, 3 moles of AgCl are precipitated per mole of the compound. Write **[All India 2016, Delhi 2016]**

(i) Structural formula of the complex

(ii) IUPAC name of the complex

23. What happens when : **[All India 2016]**

(i) SO_2 gas is passed through an aqueous solution of Fe^{3+} salt ?

(ii) XeF_4 reacts with SbF_5 ?

24. On adding NaOH to ammonium sulphate, a colourless gas with pungent odour is evolved, which forms a blue-coloured complex with Cu^{2+}ion. Identify the gas. **[Delhi 2016]**

25. What type of magnetism is shown by a substance if magnetic moments of domains are arranged in same direction? **[Delhi 2016]**

26. When chromite ore $FeCr_2O_4$ is fused with NaOH in presence of air, a yellow-coloured compound (A) is obtained, which on acidification with dilute sulphuric acid gives a compound (B). Compound (B) on reaction with KCl forms an orange coloured crystalline compound (C). **[Delhi 2016]**

(i) Write the formulae of the compounds (A), (B) and (C).

(ii) Write one use of compound (C).

27. Write the formula of the compound of iodine which is obtained when conc. HNO_3 oxidises I_2. **[All India 2017]**

7 - COMPLETE THE FOLLOWING

28. Complete the following equations : **[All India 2016]**

(i) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta}$

(ii) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow$

29. Complete the following chemical equations. **[Delhi 2016]**

(i) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow$

(ii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow$

30. Complete the following equations: **[All India 2017]**

(i) $2MnO_4^- + 16\ H^+ + 5S^{2-} \longrightarrow$

(ii) $KMnO_4 \xrightarrow{heat}$

8 - WHAT IS THE CORRECT INCREASING/DECREASING ORDER?

31. Arrange the following in the increasing order of property mentioned : **[Delhi 2016]**

(a) H_3PO_3, H_3PO_4, H_3PO_2 (Reducing character)

(b) NH_3, PH_3, AsH_3, SbH_3, BiH_3 (Base strength)

32. (a) For the complex $[Fe(H_2O)_6]^{3+}$, write the hybridization, magnetic character and spin of the complex. **[All India 2016]**
(At. number : Fe = 26)

(b) Draw one of the geometrical isomers of the complex $[Pt(en)_2Cl_2]^{2+}$ which is optically inactive.

33. The elements of 3*d* transition series are given as :

Sc Ti V Cr Mn Fe Co Ni Cu Zn

Answer the following : **[All India 2016]**

(i) Write the element which shows maximum number of oxidation states. Give reason.

(ii) Which element has the highest m.p ?

(iii) Which element shows only + 3 oxidation state ?

(iv) Which element is a strong oxidizing agent in + 3 oxidation state and why ?

34. From the given cells : **[Delhi 2016]**

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 ?

(iv) Which cell does not have a long life ?

35. In the extraction of Al, impure Al_2O_3 is dissolved in conc. NaOH to form sodium aluminate and leaving impurities behind. What is the name of this process ? **[Delhi 2016]**

36. (a) For the complex $[Fe(CN)_6]^{3-}$, write the hybridization type, magnetic character and spin nature of the complex.
(At. number : Fe = 26). **[Delhi 2016]**

(b) Draw one of the geometrical isomers of the complex $[Pt(en)_2Cl_2]^{2+}$ which is optically active. **[Delhi 2016]**

37. (i) Compare the oxidizing action of F_2 and Cl_2 by considering parameters such as bond dissociation enthalpy, electron gain enthalpy and hydration enthalpy. **[Delhi 2016]**

(ii) Write the conditions to maximize the yield of H_2SO_4 by contact process. **[Delhi 2016]**

38. What type of isomerism is shown by the complex $[Co(NH_3)_5(SCN)]^{2+}$? **[All India 2017]**

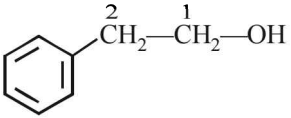
39. Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements. **[All India 2017]**

Hints and Solutions

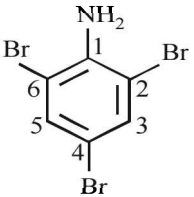
Organic Chemistry

1 - WHAT ARE THE IUPAC NAMES/STRUCTURES OF THE FOLLOWING COMPOUNDS

1. The IUPAC name of the given compound is 2-phenylethanol.



2. The IUPAC name of the given compound is 2, 4, 6-tribromoaniline.



3. IUPAC name of the given compound is 2-methoxy-2-methylpropane.

2 - HOW WILL YOU DEFINE THE GIVEN REACTIONS ?

4. (i) The Hofmann bromamide degradation reaction

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

(ii) Carbylamine reaction

$$R-NH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta} R-NC + 3KCl + 3H_2O$$

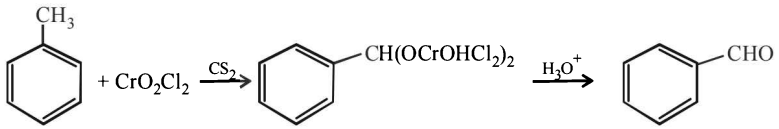
5.

$$\underset{\text{Acetaldehyde}}{CH_3-\underset{\underset{\displaystyle H}{|}}{C}=O} + NH_2NH_2 \xrightarrow[-H_2O]{} \underset{\text{Hydrazone}}{CH_3-\underset{\underset{\displaystyle H}{|}}{C}=NNH_2} \xrightarrow[\text{Glycol}]{\text{KOH, 453–473 K}} CH_3-CH_3 + N_2$$

6. (a) Cannizzaro reaction

$$2\,H-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{NaOH} H-CH_2OH + H-\overset{\overset{\displaystyle O}{\|}}{C}-ONa$$

7. (*i*) **Etard Reaction:** Chromyl chloride (CrO_2Cl_2) oxidises methyl group of toluene to a chromium complex, which on hydrolysis gives corresponding benzaldehyde. This reaction is called **Etard reaction**.



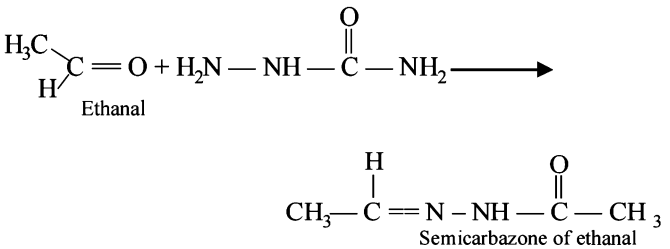
(*ii*) **Stephen Reaction:** Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde. This reaction is called **Stephen reaction**.

$$RCN + SnCl_2 + HCl \longrightarrow RCH{=}NH \xrightarrow{H_3O^+} RCHO$$

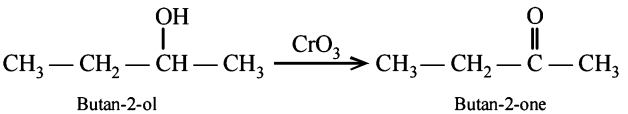
3 - WHAT HAPPENS WHEN ...

8. Upon hydrolysis, lactose produces one molecule of D-glucose and one molecule of D-galactose.

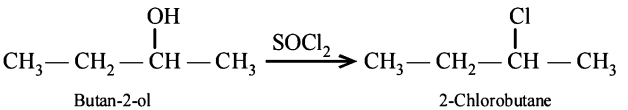
9. Semicarbazone of ethanal



10. (a) Secondary alcohol (Butan-2-ol) on reaction with chromic anhydride (CrO_3) oxidises to ketone (Butan-2-one).



(b) Butan-2-ol on treating with $SOCl_2$ forms 2-chlorobutane



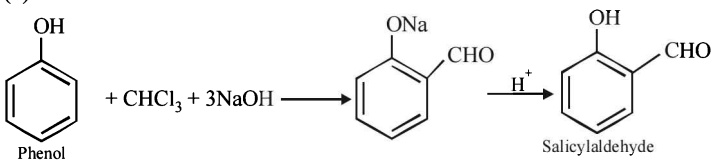
4 - WHAT ARE THE MISSING COMPOUNDS/REAGENTS ?

11. The final products of the given reactions are :

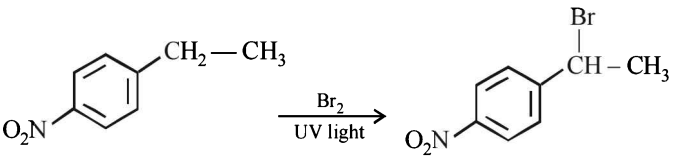
(a) $CH_3-C(CH_3)_2-O-CH_3 + HI \longrightarrow CH_3-C(CH_3)_2-I + CH_3-OH$

(b) $CH_3-CH_2-CH(OH)-CH_3 \xrightarrow{Cu/573K} CH_3-CH_2-C(=O)-CH_3 + H_2$

(c)



12. (i)



(ii) $2CH_3-CH(Cl)-CH_3 \xrightarrow[\text{dry ether (Wurtz reaction)}]{Na} CH_3-CH-CH_3$ / $CH_3-CH(CH_3)-CH_3$

(iii) $CH_3-CH_2-Br \xrightarrow{AgCN} CH_3-CH_2-NC$

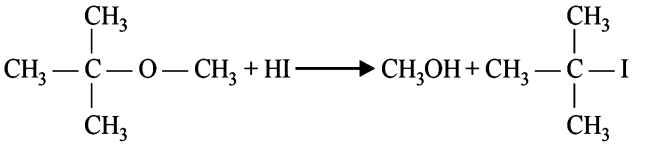
13. (i) $CH_3COCl \xrightarrow{H_2, Pd-BaSO_4} \underset{A}{CH_3CHO} \xrightarrow{H_2N-OH} \underset{B}{CH_3CH=N-OH}$

(ii) $CH_3MgBr \xrightarrow[2.\ H_3O^+]{1.\ CO_2} \underset{A}{CH_3COOH} \xrightarrow{PCl_5} \underset{B}{CH_3COCl}$

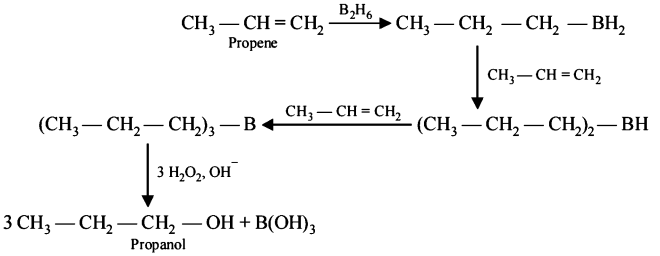
14. $CH_3CH_2CH=CHCH_2CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) } (i\text{–}Bu)_2AlH}$ (K M C)

$CH_3CH_2CH=CH-CH_2-CHO$

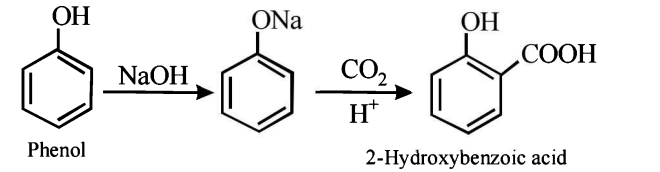
15. (i)



(ii)



(iii)



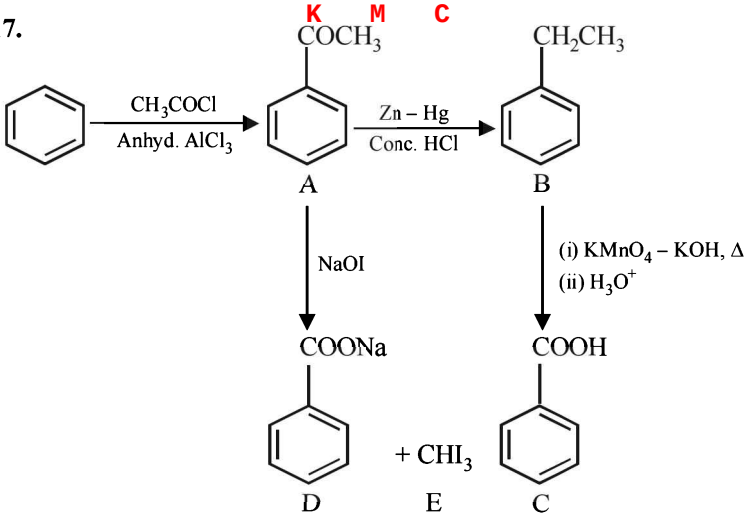
16. (i) $C_6H_5-CONH_2 \xrightarrow{Br_2/aq.\ KOH} \underset{A}{C_6H_5NH_2} \xrightarrow[0-5°C]{NaNO_2 + HCl}$

$\underset{B}{C_6H_5N_2Cl} \xrightarrow{KI} \underset{C}{C_6H_5I}$

(ii) $CH_3-Cl \xrightarrow{KCN} \underset{A}{CH_3CN} \xrightarrow{LiAlH_4} \underset{B}{CH_3CH_2-NH_2}$

$\xrightarrow[\Delta]{CHCl_3 + \text{Alc. KOH}} \underset{C}{CH_3CH_2NC}$

17.



18. $CH_3-CH=CH-CH_2CN \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL–H}} CH_3-CH=CH-CH_2CHO$

19. (a) A. CH_3CONH_2 (Ethanamide)

B. CH_3NH_2 (Methanamine)

C. CH_3NC (Methyl isocyanide)

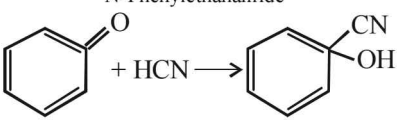
(b) A. $C_6H_5NO_2$ (Nitrobenzene)

B. $C_6H_5NH_2$ (Aniline)

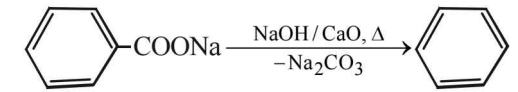
C. $C_2H_3-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{||}}{C}-CH_3$

N-Phenylethanamide

20. (i)



(ii)

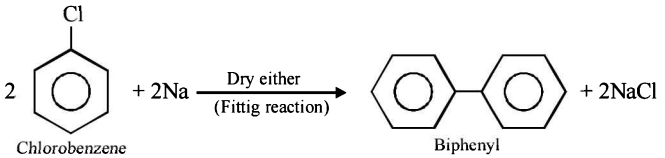


Sodium Benzoate (C) Benzene (D)

(iii) $CH_3-CH=CH-CN \xrightarrow[\text{(a) ICQ}]{\text{(a) DIBAL-H}} CH_3-CH=CH-CHO$

5 - HOW WILL YOU CARRY OUT THE GIVEN CONVERSIONS ?

21. (i)

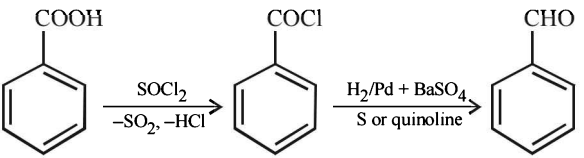


(ii) $H_2C = CH - CH_3 + HBr \xrightarrow[\text{(anti-Markownikoff's)}]{\text{Peroxide}} CH_3CH_2CH_2Br$

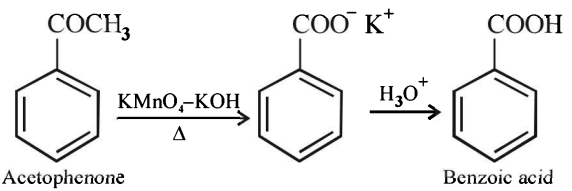
$\xrightarrow[\text{KI/acetone}]{\text{(Finkelstein reaction)}} \underset{\text{1-Iodopropane}}{CH_3CH_2CH_2I}$

(iii) $CH_3 - \underset{\underset{Br}{|}}{CH} - CH_2 - CH_3 \xrightarrow{\text{alc KOH}} \underset{\text{(But-2-ene)}}{CH_3 - CH = CH - CH_3}$

22. (*i*) Benzoic acid to benzaldehyde:



(ii) Acetophenone to Benzoic acid



(iii) Ethanoic acid to 2-Hydroxyethanoic acid

$$\underset{\text{Ethanoic acid}}{CH_3 - COOH} \xrightarrow[-HCl]{Cl} CH_2(Cl) - COOH \xrightarrow[-KCl]{KOH} \underset{\text{2-Hydroxyethanoic acid}}{CH_2(OH) - COOH}$$

6 - HOW WILL YOU DISTINGUISH THE GIVEN PAIR OF COMPOUNDS ?

23. Cellulose is a linear polymer made up of β-glucose having the C1-C4 glycosidic linkage, whereas starch is a polymer of α-glucose having two components: amylose and amylopectin. Amylose is a long, unbranched chain with 200-1,000 α-D-(+) glucose units held by the C1-C4 glycosidic linkage. Amylopectin is a branched-chain polymer of α-D-glucose unit in which the chain is formed by the C1-C4 glycosidic linkage and branching occurs at the C1-C6 glycosidic linkage.

24. (i) $C_6H_5-COCH_3$ is a methyl ketone and therefore, gives a yellow precipitate of iodoform when reacted with NaOH and I_2 (haloform test).

$$C_6H_5-COCH_3 \xrightarrow[I_2]{NaOH} C_6H_5COONa + CHI_3$$

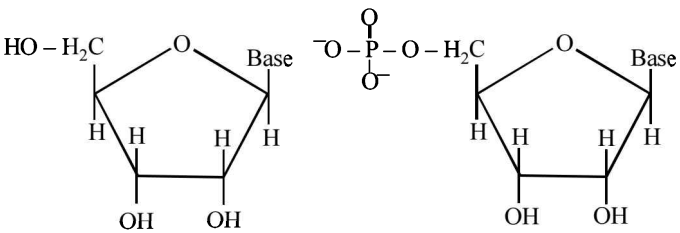
C_6H_5-CHO does not give this reaction

(ii) As shown below, methanoic acid gives silver mirror test, while ethanoic acid will not give this test.

$$HCOOH + 2[Ag(NH_3)_2]NO_3 \rightarrow 2Ag + CO_2 + 2NH_4NO_3 + 2NH_3$$

25. A nucleoside is formed by the attachment of purine or pyrimidine base to the 1-position of a pentose sugar.

On the other hand, a nucleotide is a unit formed by the attachment of nucleoside to phosphoric acid at the 5'-position of the sugar moiety.



Nucleoside Nucleotide

26.

Propanal	Propanone
It forms silver mirror on reaction with Tollen's reagent.	It is not oxidised by Tollen's reagent.
It does not respond iodoform test.	It gives positive iodoform test
On reacting with Schiff's reagent, reagent.	It does not react with Schiff's it gives pink colour.

27. (i) Tests to distinguish between the butanal and butan -2-one :

1. Butanal gives positive test with Tollen's reagent whereas Butan-2-one gives negative test
2. Butanal gives negative iodoform test whereas Butan -2-one gives positve iodoform test.

		Butanal	Butan-2 one
1.	Tollen's test	Positive test	Negative test

Reaction :

$$CH_3 - CH_2 - CH_2 - CHO + 2\,[Ag(NH_3)_2]^+ + 3OH^-$$

$$\downarrow$$

$$RCOO + 2^+AG + 2H_2O + 4\,NH_3)_2$$

(Bright Silver Mirror)

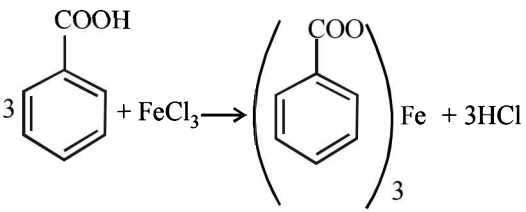
2.	Iodoform test	Negative test	Positive test

Reaction :

$$CH_3 - CH_2 - \overset{\overset{O}{||}}{C} - CH_3 \xrightarrow{NaOI} CH_3 - CH_2 - \overset{\overset{O}{||}}{C} - ONa + CHI_3$$

(Yellow ppt)

(ii) **Benzoic Acid:** It gives a coloured ppt with neutral $FeCl_3$ solution

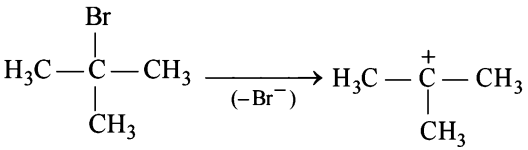


Phenol: It gives a violet colour with neutral $FeCl_3$ solution

$$3\,C_6H_5OH + FeCl_3 \longrightarrow \underset{\text{Violet}}{(C_6H_5O)_3Fe} + 3HCl$$

7 - WHAT WILL BE THE MECHANISM OF THE GIVEN REACTIONS?

28. The isomer of C_4H_9Br, which is most reactive towards S_N1 reaction, is the one that forms a tertiary carbocation upon the elimination of the leaving group. Its structure is shown below:



29. Since formation of carbocation is the rate-determining step in the S_N1 reaction, the stability of carbocation would determine its reactivity.

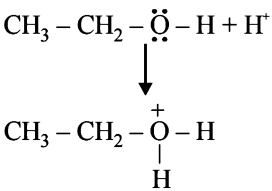
The order of stability of carbocation is as follows :

Tertiary > Secondary > Primary > Methyl

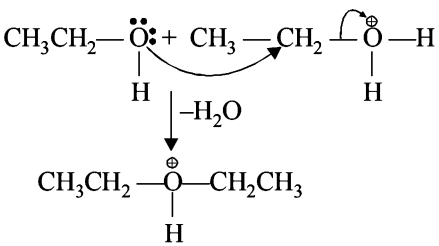
Here, 1-chloro-1-methylpropane would form secondary carbocation, while 1-chloro-2-methylpropane will form primary carbocation, which is less stable than secondary carbocation. Hence, reactivity towards the S_N1 reaction would be higher for 1-chloro-1-methylpropane.

30. The mechanism of the given reaction is as follows:

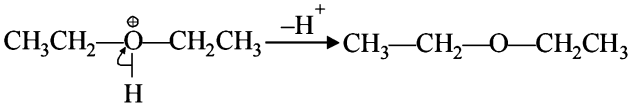
(i) Protonation of an alcohol molecule



(ii) Attack of other alcohol molecule on the protonated molecule

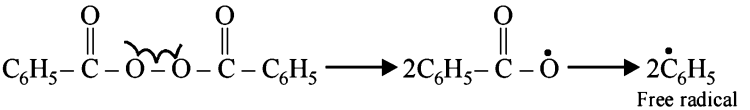


(iii) Deprotonation



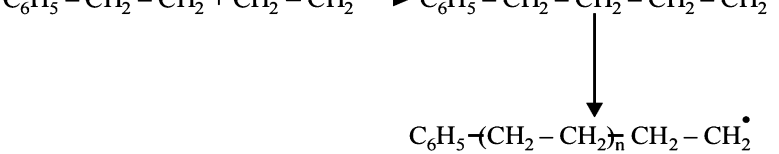
31. Free radical mechanism for polymerisation of ethene.

Chain-initiating step

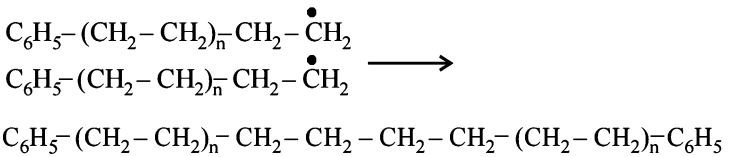


$$\dot{C}_6H_5 + CH_2 = CH_2 \longrightarrow C_6H_5 - CH_2 - \dot{C}H_2$$

Chain-propagating step



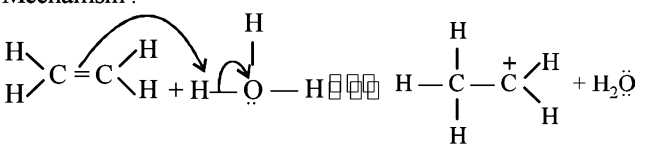
Chain-terminating step



32. Reaction :

$$CH_2 = CH_2 \xrightarrow{H_3O^+} CH_3 - CH_2^+ + H_2O$$

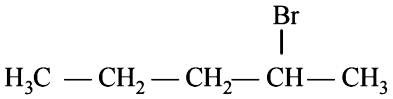
Mechanism :



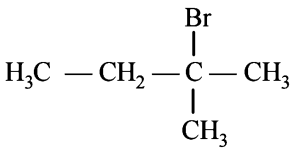
33. Structure of the given compounds are :

$$H_3C - CH_2 - CH_2 - CH_2 - CH_2 - Br$$

1-Bromopentane
(A)



2-Bromopentane
(B)



2-Bromo-2-methylbutane
(C)

(a) As we can see in the above figures, (A), contains the least steric hindrance so towards the S_N2 reaction 1-bromopentane will be most reactive.

(b) 2-bromopentane (Figure B) contain chiral carbon in it. So, this compound is optically active.

(c) 2-bromo-2-methylbutane will be most reactive towards the β-elimination since it will form most stable alkene (on account of highest no of α-hydrogens)

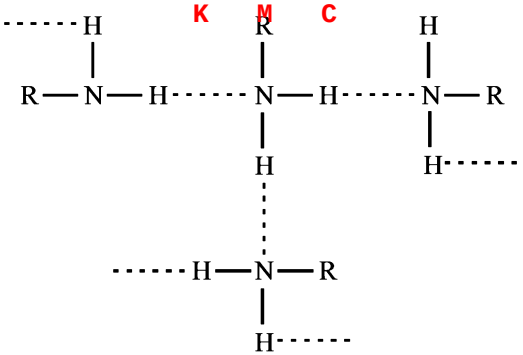
8 - WHY DO THE FOLLOWING HAPPENS ?

34. (i) Aniline forms salt with aluminium chloride, the catalyst of the Friedel-Crafts reaction. As a result, the nitrogen atom in aniline acquires a positive charge, which deactivates the group towards the reaction. Thus, aniline does not undergo the Friedel-Crafts reaction

(ii) There are two factors that affect the basicity of the amines in an aqueous solution : solvation of ammonium ions and inductive effect. Inductive effect of the alkyl group is greater in $(CH_3)_3N$ than in $(CH_3)_2NH$. However, due to greater stabilisation by increased hydrogen bonding in $(CH_3)_2NH$ on solvation with water molecules, $(CH_3)_2NH$ is more basic than $(CH_3)_3N$.

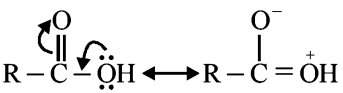
(iii) Primary amines are engaged in intermolecular association because of hydrogen bonding between nitrogen of one molecule and hydrogen of another molecule, as shown below.

K M C



On the other hand, no such interaction is possible in tertiary amines because of absence of the hydrogen atom directly attached to nitrogen. Therefore, due to stronger intermolecular forces, the boiling point of primary amines is higher than that of secondary amines.

35. The carbon of carboxylic acid is much less electrophilic as compared to aldehydes acd ketones because the lone pair of oxygen attached to hydrogen is involved in resonance, as shown below:



36. (i) In chlorobenzene, the C–Cl bond gets partial double bond character because of the +M effect (resonance) shown by the Cl group. Due to double bond character, the bond length decreases in chlorobenzene as compared to the normal CH_3–Cl (no resonance or + M effect) bond length. Therefore, the C–Cl bond length in chlorobenzene is shorter than the C–Cl bond length in CH_3–Cl.

(ii) Reasons behind the dipole moment of chlorobenzene being lower than that of cyclohexyl chloride are follows:

(a) In chlorobenzene, the C–Cl bond is shorter due to partial double bond character.

(b) Hybridisations of C in C–Cl in chlorobenzene and cyclohexyl chloride are sp^2 and sp^3, respectively (sp^2 C being more electronegative than sp^3C).

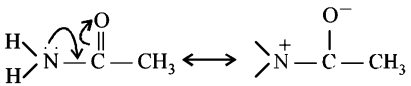
As dipole moment is the product of charge and bond distance, both the factors in chlorobenzene are lower as compared to cyclohexyl chloride. Therefore, the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(iii) In S_N1 reactions, formation of carbocation as an intermediate takes place. This carbocation is sp^2–hybridised and has planar structure. This planar carbocation is attacked by nucleophile from both the sides equally to form *d* and *l* isomers in equal proportion. Such products are called racemic mixture. Hence, S_N1 reactions are accompanied by racemisation in optically active alkyl halides.

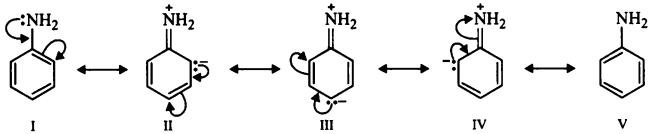
37. Vitamin C is water-soluble in nature. It cannot be stored in the human body as it is eliminated through urine.

38. Fluorine is more electronegative than chlorine. The presence of fluorine in a molecule will make it more acidic. Thus, the pK_a of F-CH_2-COOH is lower than that of Cl-CH_2-COOH.

39. (a) The lone pair present on nitrogen will get involved in resonance with the carbonyl group. It will reduce the activation effect in aniline. The resonance is shown below.



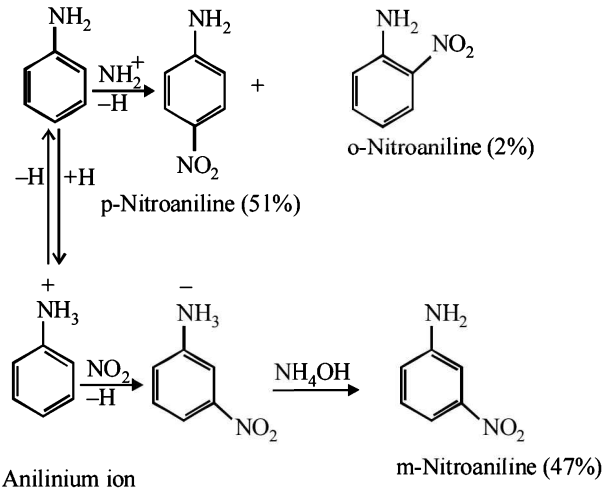
(b) Due to resonance in aniline. Aniline may be regarded as a resonance hybrid of the following structures:



As a result of resonance, the lone pair of electrons on the nitrogen atom gets delocalized over the benzene ring and thus is less easily available for protonation. Therefore, aromatic amines are weaker bases than ammonia.

(c) Nitration is carried out with a mixture of concentrated HNO_3 and concentrated H_2SO_4. Aniline gets protonated to form anilinium ion. Therefore, in presence of acids, the reaction mixture consists of aniline and anilinium ion. Nitration of aniline due to steric

hindrance at ortho position mainly gives para nitroaniline and the nitration of anilinium ion gives m-nitroaniline. In actual practice approximately 1 : 1 mixture of p-nitroaniline and m-nitroaniline is obtained.



Thus due to protonation of the amino group nitration of aniline gives a substantial amount of m-nitroaniline.

9 - WHAT IS THE CORRECT INCREASING/DECREASING ORDER?

40. Fibres have the strongest intermolecular forces, while elastomers have the least. Thermoplastics have the intermolecular forces intermediate between elastomers and fibres.

Thus, the increasing order of the intermolecular forces of the given polymers is as follows :

Neoprene < Polythene < Terylene

41. The boiling point of the given compounds can be compared on the basis of the extent of intermolecular hydrogen bond formation. Hydrogen bonding will be most extensive in acetic acid, followed by ethanol. It is the least in acetaldehyde.

Hence, the increasing order of boiling points of the given compounds is as follows :

$CH_3CHO < CH_3CH_2OH < CH_3COOH$

42. Aldehydes are more reactive than ketones towards the nucleophillic addition reaction. Among the ketones, aromatic ketones are more susceptible to nucleophilic attack than an aliphatic one.

Hence, the increasing order of reactivity towards nucleophilic addition reaction for the given compounds is as follows:

$$CH_3COCH_3 < C_6H_5COCH_3 < CH_3-CHO$$

43. Elastomers or rubbers have the weakest intermolecular forces of attraction, while fibres have the strongest intermolecular forces of attraction. Plastics have intermediate forces of attraction.

The increasing order of intermolecular forces of attraction of the given polymers is as follows :

Terylene > Polystyrene > Buna-S

44. Increasing order of acid strength is

p-cresol < phenol < p-nitrophenol

10 - HOW TO SOLVE ANALYTICAL PROBLEMS

45. The possible functional isomers of C_3H_6O are

CH_3-CH_2-CHO and $H_3C-\overset{\overset{O}{\|}}{C}-CH_3$. Out of these, methyl ketone can give iodoform test as shown :

$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\Delta]{NaOH+I_2} H_3C-COONa + CHI_3$$

Hence, isomer A is CH_3-CH_2-CHO and B is

$$H_3C-\overset{\overset{O}{\|}}{C}-CH_3$$

11 - MISCELLANEOUS QUESTIONS

46. (i) Hydrogen bonds

(ii) Fibrous protein: Keratin

Globular protein: Egg albumin

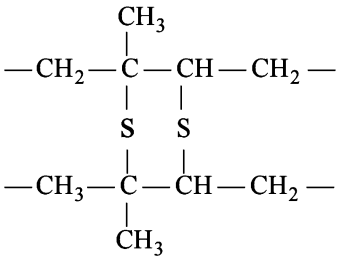
47. (i) Role of sulphur in the vulcanisation of rubber

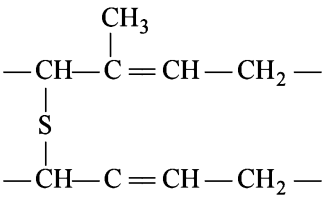
Natural rubber becomes soft at high temperatures (> 335K) and brittle at low temperatures (< 283K).

Moreover, it is soluble in non-polar solvents and is non-resistant to the attacks by oxidising agents.

Sulphur is therefore added during its manufacturing to overcome these limitations. Sulphur forms cross linkages at reactive sites of double bonds and thus, the rubber gets stiffened.

The following are the probable structures of a vulcanised rubber:





(ii) Name of the polymer : Glyptal

Monomers:

(a) Ethylene glycol (b) Phthalic acid

48. (i) In polymerisation of ethene, source of free radical is needed to initiate the chain reaction. Such free radicals are usually produced by decomposition of peroxides like *t*-butyl peroxide or benzoyl peroxide.

(ii) The given polymer is nylon 6, 6. Monomers of nylon 6, 6 are adipic acid ($HOOC(CH_2)_4COOH$) and hexamethylenediamine ($H_2N(CH_2)_6NH_2$).

49. (i) The following values are displayed by Mr. Deepak :

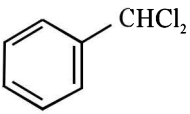
(a) Care and concern : He cared for the well-being of his friend, Mr. Angad.

(b) Knowledge : He suggested his friend effective measures to counter stress and anxiety.

(ii) Sleeping pills are prescribed by doctors to patients in stress, pain or depression. It should not be taken without a prescription or a doctor's consultancy because these pills have several side effects. Sleeping pills slow down the functioning of the brain and the nervous system.

(iii) Tranquillisers are those class of organic compounds which are neurologically active. They perform their function by inhibiting the message transfer mechanism from nerve to receptor. They induce a sense of well-being and are used in the treatment of stress, anxiety, irritability and mental diseases. Their examples are chlordiazepoxide, iproniazid, phenelzine, meprobamate and equanil.

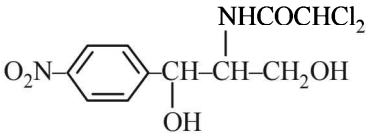
50. The example of benzylic halide is



In benzylic halides the halogen atom is bonded to an sp^3-hybridised carbon atom which is directly attached with an aromatic ring.

51. (a) **Cationic detergents :** Cationic detergent are quartenary ammounium salts of acetates with amines chlorides or bromides as anions. Cationic part consist of a long hydrocarbon chain and a positive charge on nitrogen atom. Therefore, these are called cationic detergents. Example Cetyltrimethyl ammonium bromide

(b) **Broad spectrum antibiotics :** These are the antibiotics which are effective against a variety of diseases. The common examples are *Tetracycline*, *Chloromycetin* and *Chlroramphenicol* which are effective against a variety of diseases. Therefore, these can be used for curing typhoid, acute fever, dysentery, whooping cough, pneumonia, eye infection, certain urine infection. The structure of chloramphenicol is :



Chloramphenicol

(c) The chemical substances used to cure mental diseases are called **tranquilizers**. These are used to release mental tension and reduce anxiety. These are the constituents of sleeping pills. They act on higher centres of nervous system. Examples of tranquilizers are iproniazid, phenolzine, equanil, valium etc.

52. (a) Teflon

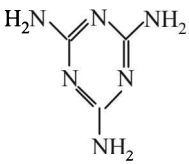
Polymer-Teflon

Monomer-Tetrafluroethene

Structure :

$CF_2 = CF_2$

(b) melamine and formaldehyde are monomers used in the melamine-formaldehyde polymer.



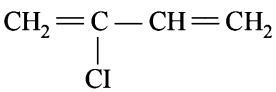
Melamine

and

HCHO

Formaldehyde

(c) Neoprene : Monomeric unit chloroprene.



Chloroprene

53. (a) The values displayed by Rupali are self awareness, confidence, decision making and concern towards adverse effect of harmful ingredients used in school canteen.

(b) Polysaccharide component commonly present in bread is starch.

(c) α-helix and β-pleated sheet are the two types of secondary structure of proteins.

(d) Water soluble vitamins are B and C.

Physical Chemistry

1 - WRITE THE DEFINITION/EXAMPLE(S)/TYPE(S) OF ...

1. The examples of molecular solids are ice (H_2O) and solid ammonia. The examples of ionic solids are sodium chloride (NaCl), magnesium oxide (MgO) and zinc sulphide (ZnS).
2. A maximum boiling azeotrope shows negative deviation from the Raoult's law.
3. An electrochemical cell is a device capable of generating electrical energy from chemical reaction.

   If external potential is higher than $E°_{cell}$ potential value of the cell, the flow of current and cell reactions are reversed. The cell now functions as electrolytic cell, a device for using electrical energy to carry non-spontaneous chemical reactions.
4. When a gas is disperesed in a liquid then foam type of colloid is formed.

   Example : Froth and Shaving cream.
5. Liquid fat is dispersed phase and water is dispersion medium in milk.
6. Fe $(OH)_3$ sol is prepared from $FeCl_3$. by hydrolysis method.

$$FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} Fe(OH)_3(sol) + 3HCl$$

7. (i) **Molality :** It is defined as the number of moles of a solute present in 1000g (1kg) of a solvent.

$$\text{Molality}\,(m) = \frac{\text{Number of moles of solute}}{\text{Weight of solvent in kg}} = \frac{n}{W}$$

   (ii) **Abnormal molar mass :** Due to association or dissociation of molecules, the expected molar mass is either lower or higher than calculated molar mass. Such molar mass is called abnormal molar mass.

2 - WHY DOES THIS HAPPEN?

8. There are two main reasons for the stability of colloidal sols :
   (i) **Electrostatic stabilisation :** The presence of equal and similar charges on the colloidal particles prevents coagulation of the colloidal sol.
   (ii) **Solvation :** Colloidal particles are covered by a sheath of liquid in which they are extensively solvated and thereby acquiring stability

9. According to Henry's law, the solubility of a gas is inversely related to the Henry's constant (K_H) for that gas. Hence, gas (B), being less soluble, would have a higher K_H value

10. There are two main reasons for the stability of colloidal sols :
    1. Electrostatic stabilisation : Presence of equal and similar charges on the colloidal particles prevents coagulation of the colloidal sol.
    2. Solvation : Colloidal particles are covered by a sheath of liquid in which they are extensively solvated, thereby providing stability.

11. According to the Schulze-Hardy rule, the effectiveness of the salt causing flocculation depends on the charge on the ion of opposite sign to the charge on the sol particles. The greater the magnitude of the opposite charge, the higher the ability of a salt to coagulate the sol.

    Thus, salt containing trivalent cation i.e. $AlCl_3$ is more effective in causing the coagulation of a negatively charged sol than the salt containing divalent cation, i.e. $MgCl_2$.

12. The elevation in the boiling point of a solution is a colligative property; therefore, it is affected by the number of particles of the solute. Since the amount of solute is higher in 2 M glucose solution as compared to in 1 M glucose solution, the elevation in the boiling point is higher in 2 M glucose solution. Hence, 2 M glucose solution has a higher boiling point than 1 M glucose solution.

13. In Antiferromagnetic substances equal number of magnetic moments are aligned in opposite directions so as to give zero net magnetic moment whereas in Ferrimagnetic substances unequal number of magnetic moments are aligned in opposite directions so the net magnetic moment is not zero. Hence, ferromagnetic substance show better magnetism than antiferromagnetic substance.

3 - WHAT IS THE ROLE/EFFECT OF?

14. (a) The catalyst provides an alternate pathway for the reaction by lowering the activtion energy (E_a) between reactants and products.

    (b) The catalyst does not affect the energy of reactants or products and thus there will be no effect of catalyst on Gibbs energy.

15. When $CdCl_2$ is doped with AgCl impurity defect arises. Cd^{2+} is divalent and Ag^+ is univalent so there will be cationic vacancies when $CdCl_2$ will be added.

4 - HOW WILL YOU DIFFERENTIATE BETWEEN?

16. Adsorption is a surface phenomenon that causes the accumulation of molecules of a substance at the surface of a solid or liquid rather than in the bulk. In adsorption, the substance gets concentrated at the surface only. It does not penetrate through the surface to the bulk of the solid or liquid. For example, when a chalk stick is dipped into an ink solution, only its surface becomes coloured.

On the other hand, the process of absorption is a bulk phenomenon. In absorption, the absorbed substance gets uniformly distributed throughout the bulk of the solid or liquid.

17. Out of sulphur sol and proteins, sulphur sol forms multimolecular colloids. Sulphur sol consists of particles containing a thousand or more S_8 molecules. On the other hand, proteins form macromolecular colloids.

18. (a)

	Multimolecular colloids		Associated Colloids
(i)	They are formed by the aggregation of a large number of atoms or molecules which generally have diameters less than 1 nm.	(i)	They are formed by the aggregation of a large number of ions in concentrated solution.
(ii)	Examples – sols of gold and sulphur.	(ii)	Examples – soap sol.

(b) Coagulation and Peptization

Coagulation	Peptization
Settling of colloidal particles is called coagulation or precipitation of the sol	Conversion of precipitate into colloidal sol by shaking it with dispersion medium in presence of small amount of electrolyte (peptising agent) is also known as associated peptization.

(c) Homogeneous catalysis and Heterogeneous catalysis

Homogeneous Catalysis	Heterogeneous Catalysis
The catalysts and the reactants are in same phase	The catalysts and the reactants are in different phases.
The catalyst dissolves in the reaction medium.	The catalyst does not dissolve in the reaction medium.

19. Ideal solutions and non-ideal solutions

Ideal Solutions	Non- ideal solutions
Solutions which obey Raoult's law over the entire range of concentration are know as non-ideal solutions. Intermolecular foces of attraction between molecules of solute (A – A) and those between the molecular of solvent (B – B) are nearly equal to those between solute and solvent molecules (A – B).	Solutions which do not obey Raoult's law over the entire range of concentration are know as non-ideal solutions. Intermolecular forces of atrraction between the molecules of solute (A – A) and those between the molecules of solvent (B – B) are not equal to those between solute and solvent molecules (A – B).

5 - CALCULATION BASED ON FORMULA

20. Given :

$a = 500 \text{ pm} = 500 \times 10^{-10} \text{ cm}$

$z = 2$

$m = 300 \text{ g}$

$m = \frac{M}{N_A}$ (M is molar mass)

$$\text{Density, d} = \frac{2 \times M}{a^3 \times N_A}$$

$$7.5 = \frac{2 \times M}{(500)^3 \times 10^{-30} \times 6.02 \times 10^{23}}$$

$$M = \frac{7.5 \times (500)^3 \times 10^{-30} \times 6.02 \times 10^{23}}{2} = 282.1 \text{g/mol}$$

$$\text{Molar mass, M} = \frac{\text{Mass of compound} \times N_A}{\text{Number of atoms}}$$

$$282.1 = \frac{300 \times 6.02 \times 10^{23}}{\text{Number of atoms}}$$

Number of atoms $= 6.4 \times 10^{23}$

Therefore, the number of atoms present in 300g of compound is 6.4×10^{23}.

21. Given :

$P_i = 0.30$ atm

$P_t = 0.50$ atm

$C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)$

P_i	0	0	(At $t = 0$ s)
$P_i - x$	x	x	(At $t = 300$ s)

$\therefore \quad P_i - x + x + x = P_t$

$0.30 + x = 0.50$

$x = 0.20$

$P_i - x = 0.30 - 0.20$

$= 0.10$ atm

For a first-order decomposition reaction, we know that

$$k = \frac{2.303}{t}\log\left(\frac{P_i}{P_i - x}\right)$$

$$= \frac{2.303}{300}\log\left(\frac{0.30}{0.10}\right)$$

$$= \frac{2.303 \times \log 3}{300}$$

$$= \frac{2.303 \times 0.4771}{300}$$

$$k = 0.0037\ s^{-1}$$

22. $E_{cell} = E^o_{cell} - \frac{RT}{nF}\ ln\,Q$

$$E_{cell} = E^o_{cell} - \frac{2.303RT}{nF}\log Q$$

$$E^\circ_{cell} = E_{cell} + \frac{2.303RT}{nF}\log Q$$

$$E^\circ_{cell} = 1.98 + \frac{0.0591}{6} = 1.99\ V$$

23. $\Lambda_m = \frac{\kappa}{C} \times 1000 = 39.05\ S\,cm^2 mol^{-1}$

Here,

κ = Measured conductivity

C = Electrolyte concentration

Degree of dissociation = Molar conductance/Molar conductance at infinite dilution

$= 39.05/390.5 = 0.1$

24. The balanced chemical reaction can be written as follows:

$2\,Cr(s) + 3Fe^{2+}(0.1\,M) \rightarrow 2Cr^{3+}(0.01M) + 3\,Fe(s)$

Given :

$E^0_{Cr^{3+}/Cr} = -0.74\,V$

$E^0_{Fe^{2+}/Fe} = -0.44\,V$

The cell can be represented as follows :

$Cr(s)\,|\,Cr^{3+}(0.01\,M)\,||\,Fe^{2+}(0.1\,M)\,|\,Fe(s)$

E^0_{Cell} can be calculated as follows :

$E^0_{Cell} = E^0_{Fe^{2+}/Fe} - E^0_{Cr^{3+}/Cr}$

$E^0_{Cell} = -0.44 - (-0.74) = 0.30V$

$$E_{Cell} = E^0_{Cell} - \frac{2.303RT}{nF}\log\frac{\left|Cr^{3+}\right|^2}{[Fe^{2+}]^3}$$

$$E_{Cell} = 0.30 - \frac{0.0591}{6}\log\frac{(0.01)^2}{(0.1)^3}$$

$E_{Cell} = 0.30 + 0.01$

$E_{Cell} = 0.31\,V$

25. Given :

$a = 250\,pm = 250 \times 10^{-12}\,m$

$z = 4$

$m = 300\,g$

$$m = \frac{M}{N_A}\ (M \text{ is molar mass.})$$

$$\text{Molar mass, } M = \frac{300 \times 6.02 \times 10^{23}}{2 \times 10^{24}} = 90.3\ g/mol$$

$$\text{Density, } d = \frac{zM}{a^3 N_A}$$

$$d = \frac{4 \times 90.3}{(250)^3 \times 10^{-36} \times 6.02 \times 10^{23}} = 38.4\,g/cm^3$$

Therefore, the density of the given element is $38.4\ g/cm^3$

26. Given :

$K_f = 1.86\ K\ kg\ mol^{-1}$

Mass of solute = 1.9 g

Mass of solvent = 50 g

Therefore,

Molality of the solution, $m = \frac{1.9}{95} \times \frac{1000}{50} = 0.4\ m$

Also, $MgCl_2$ undergoes complete ionisation and thereby yielding 3 moles of consituent ions for every mole of $MgCl_2$.

$\therefore \quad i = 3$

Now, depression in freezing point is given as

$\Delta T_f = iK_f m$

$= 3 \times 1.86 \times 0.4 = 2.232\ K$

$T_f = 273.15 - 2.232 = 270.918\ K$

Hence, the new freezing point of the solution is 270.92 K.

27. Given :

$K_f = 3.83\ K\ kg\ mol^{-1}$

Mass of solute = 2.56 g

Mass of solvent = 100 g

$\Delta T_f = 0.383\ K$

Therefore,

Molality of the solution, $m = \frac{2.56}{32} \times \frac{1000}{100} = 0.8\ m$

The depression in freezing point of a solution is given as

$\Delta T_f = iK_f m$

$0.383 = i \times 3.83 \times 0.8$

$i = \frac{1}{8}$

Hence, 8 sulphur atoms are undergoing association, as shown below: $8S \square S_8$

28. Here $n = 2$ $E^{\theta}_{cell} = 0.236\ V$, $T = 298\ K$

We know that

$\Delta, G^{\theta} = -nFE^{\theta}_{cell} = -2 \times 96500 \times 0.236$

$= -45548\ J\ mol^{-1} = -45.548\ kJ\ mol^{-1}$

29. For a first order reaction

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

$$k = \frac{2.303}{20\,\text{min}}\log\frac{100}{100-25}$$

$$= \frac{2.303}{20\,\text{min}}\log\frac{4}{3} = \frac{2.303}{20\,\text{min}}(\log 4 - \log 3)$$

$$= \frac{2.303}{20\,\text{min}}(0.6021 - 0.4771) = 1.44\times10^{-2}\ \text{min}^{-1}$$

The time when 75% of the reaction completed can be calculated as

$$t = \frac{2.303}{k}\log\frac{100}{100-75}$$

$$= \frac{2.303}{1.44\times10^{-2}}\log 4 = \frac{2.303}{1.44\times10^{-2}}(0.6021)$$

$= 96.3$ min (approximately)

6 - NUMERICAL BASED ON LAWS

30. (i) Based on given information : rate = *k*, it can be inferred that the given reaction is a zero-order reaction.

(ii) Since it is a zero-order reaction, the unit of rate constant is mole L^{-1} sec^{-1}.

31. (i) This reaction is catalysed by Pt at high pressure. So, it is a zero-order reaction with molecularity 2.

(ii) The rate law expression for this reaction is
Rate = k
Hence, the unit of k is mol $L^{-1}s^{-1}$.

32. It is given that vapour pressure of water, $P_1^\circ = 23.8\,\text{mm}$ of Hg

Weight of water taken, $w_1 = 846$ g
Weight of urea taken, $w_2 = 30$g

Molecular weight of water $M_1 = 18\ g\ mol^{-1}$

Molecular weight of urea, $M_2 = 60\ g\ mol^{-1}$

Now, we have to calculate vapour pressure of water in the solution we take vapour pressure as P_1.

Now from Raoult's law, we have :

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{n_2}{n_1 - n_2}$$

$$\Rightarrow \frac{P_1^0 - P_1}{P_1^0} = \frac{\frac{m_2}{M_2}}{\frac{m_1}{M_1} - \frac{m_2}{M_2}} \Rightarrow \frac{23.8 - P_1}{23.8} = \frac{\frac{30}{60}}{\frac{846}{18} + \frac{30}{60}}$$

$$\Rightarrow \frac{23.8 - P_1}{23.8} = 0.0105 \quad \Rightarrow P_1 = 23.5501\ \text{mm of Hg}$$

Hence, the vapour pressure of water in the given solution is 23.5501 mm of Hg and its relative lowering is 0.0105.

7 - NUMERICALS BASED ON APPLICATION/SKILL

33. For electroplating of iron, we require cathode couple that gives positive E^o_{cell} value.

When we compare the values of given options, we get

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

Case 1

$$E^o_{cell} = E^o(A^{2+}/A) - E^o(Fe^{2+}/Fe) = (-2.37 + 0.44) = -1.93\,V$$

Case 2

$$E^o_{cell} = E^o(B^{2+}/B) - E^o(Fe^{2+}/Fe) = (-0.14 + 0.44) = 0.3\,V$$

Due to B's positive E° value, it is the obvious choice for coating the surface of iron.

34. Given :

$t_{1/2} = 200$ minutes $= 200 \times 60 = 12{,}000$ seconds

The relation between $t_{1/2}$ and k for first order reaction is given by

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

$k = 0.693/12000 = 5.7 \times 10^{-5}$

The rate constant for the first-order decomposition of H_2O_2 is given by

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T} K \quad ...(i)$$

By Arrhenius equation

$$\log k = \log A - \frac{E_a}{2.303\ RT} \quad ...(ii)$$

Comparing (i) and (ii), we get

$E_a = 1.91 \times 10^5$

35. (i) 1.2% sodium chloride solution is hypertonic wrt 0.9% sodium chloride solution. Therefore, when the blood cells are paced in 1.2% sodium chloride solution, water flows out of the cells and the cells shrink.

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

36. $i = 0.5\ A$

$t = 2$ hours $= 2 \times 60 \times 60\ s = 7200\ s$

Thus $Q = it$

$= 0.5\ A \times 7200\ s = 3600\ C$

We know that $96500\ C = 6.023 \times 10^{23}$ number of electrons.

Then, $3600\ C = \frac{6.023 \times 10^{23} \times 3600}{96500}$ number of electrons

$= 2.25 \times 10^{22}$ number of electrons

Hence. 2.25×10^{22} number of electrons will flow through the wire.

37. Here $\Delta T_f = (273.15 - 269.15)\ K = 4\ K$

Molar mass of sugar $(C_{12}H_{22}O_{11}) = 12 \times 12 + 22 \times 1 + 11 \times 16$

$= 342\ g\ mol^{-1}$

10% solution (by mass) of sucrose (cane sugar) in water means 10 g of cane sugar is present in $(100 - 10)g = 90$ g of water.

Now, number of moles of cane sugar $= \frac{10}{342} = 0.0292$ mol

Therefore, molality (m) of the solution,

$$= \frac{0.0292 \times 1000}{90} = 0.3244\ mol\ kg^{-1}$$

Applying the relation,

$\Delta T_f = K_f \times m$

$$\Rightarrow K_f = \frac{\Delta T_f}{m} = \frac{4}{0.3244} = 12.33\,K\,Kg\,mol^{-1}$$

Molar mass of glucose $(C_6H_{12}O_6) = 6 \times 12 + 12 \times 1 + 6 \times 16$

$= 180\ g\,mol^{-1}$

10% glucose in water means 10g of glucose is present in (100 – 10) g

= 90 g of water.

$$\therefore \text{ Number of mole of glucose } = \frac{10}{180} mol = 0.0555\ mol$$

Therefore, molality (m) of the solution

$$= \frac{0.0555 \times 1000}{(K)} = 0.6166\ mol\ kg^{-1}$$

Applying the relation,

$\Delta T_f = K_f \times m$

$= 12.33\ K\,kg\,mol^{-1} \times 0.6166\ mol\,kg^{-1}$

= 7.60 K (approximately)

Hence, the freezing point of 10% glucose solution is (273.15– 7.60) K = 265.55 K

38. Number of Al atoms present in 27 g (1 mol) of Al = 6.023×10^{23}

Number of Al atoms present in 8.1 g (1 mol) of Al

$$= \frac{6.023 \times 10^{23}}{27} \times 8.1$$

Since, aluminium crystallizes in a face-centred cubic (f.c.c.) structure the number of atoms per unit cell is 4

Number of unit cells in 8.1 g of aluminimum

$$= \frac{1}{4} \times \frac{6.023 \times 10^{23}}{27} \times 8.1 = 4.5 \times 10^{22}$$

Hence, the number of unit cells in 8.1 g of aluminium if it crystallizes in a face-centred cubic (f.c.c.) structure is 4.5×10^{22}.

39. When the external pressure exerted on the solution is higher than the osmotic pressure, the pure solvent starts flowing out of the solution through the semi-permeable membrane. This process is known as reverse-osmosis.

40. Both physical adsorption and chemisorption increases with increase of surface area of the adsorbent

41. Sodium sulphate is lonic solid

Hydrogen is Molecular solid (Non-polar molecular solid)

42. The dry cell also known as Leclanche cell is used in transistors.

The reactions taking place at the anode and cathode are given below.

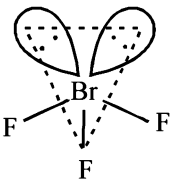
Cathode Reaction : $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

Anode Reaction : $Zn - 2e^- \longrightarrow Zn^{++}$

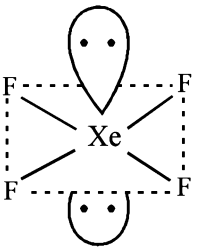
$$Zn^{2+} + 2NH_3 \longrightarrow [Zn(NH_3)_2]^{2+}$$

1 - WHAT ARE THE STRUCTURES/NAMES OF THE FOLLOWING COMPOUNDS

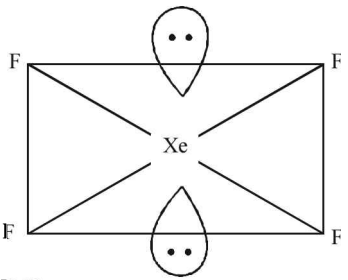
1. (i) **Structure of BrF_3 :** Bent T-shaped



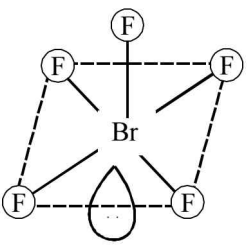
(ii) **Structure of XeF_4 :** Square planar



2. (a) XeF_4



(b) BrF_5



3. (a) $K_3[Al(C_2O_4)_3]$ (b) $[CoCl_2(en)_2]^+$

2 - WHAT IS THE ROLE OF THE FOLLOWING?

4. Cryolite is used in the electrolytic reduction of alumina for lowering its melting point and making it a good conductor of electricity.
5. In the blast furnace, limestone decomposes to form CaO, which reacts with the silicate impurity to form slag.

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow \underset{\text{Slag}}{CaSiO_3}$$

6. Coke reduces the iron oxide to molten iron metal. Also, coke, when burnt in the blast furnace, supplies the heat required for carrying out the extraction of iron from its oxide.

$$FeO + C \longrightarrow Fe + CO$$

7. In the froth floatation process the role of the depressants is to separate two sulphide ores by selectively preventing one ore from forming froth. For example to separate two sulphide ores (ZnS and Pbs). NaCN is used as a depressant which selectively allows PbS to come with froth but prevents ZnS from coming to froth. This happens because NaCN reacts with ZnS to form Na|[Zn(CN)$_2$]

$$4NaCN + ZnS \longrightarrow Na_2[Zn(CN)_4] + Na_2S$$

3 - WHAT OR WHICH PRINCIPLE IS INVOLVED IN THE FOLLOWING PROCESSES?

8. The Mond's process is used for refining nickel
9. Zone refining method is the most suitable method for refining metals like germanium (used as semiconductor).
10. **Electrolytic refining:**

Many metals, such as Cu, Ag, Au, Al, Pb, etc., are purified by this method. The impure metal is made the anode while a thin sheet of pure metal acts as a cathode. The electrolytic solution consists of a salt or a complex of the metal. On passing the current, the pure metal is deposited on the cathode while the impurities fall down as anode mud.

$$\text{Anode}: \ M \rightarrow M^{n+} + ne^-$$

$$\text{Cathode}: \ M^{n+} + ne^{-1} \rightarrow M$$

4 - WHY DO THE FOLLOWING HAPPENS?

11. (i) SO_2 is a reducing agent because sulphur has empty *d*-orbitals and it can easily expand its +4 oxidation state to +6 oxidation state. However, as Te is a heavy element; therefore, due to inert pair effect, its lower oxidation state is more stable, and TeO_2 acts as oxidising agent.

(ii) Due to unavailability of empty *d*-orbitals in nitrogen, it cannot expand its valency. Hence, nitrogen does not form pentahalide.

(iii) In general, interhalogen compounds are more reactive because of lower bond dissociation energy than halogen molecules (except F_2)

12. (i) Mn shows the highest oxidation states of +7 with oxygen because it can form $p\pi - d\pi$ multiple bonds involving 2*p*-orbitals of oxygen and 3*d* orbitals of Mn. On the other hand, Mn shows the highest oxidation state of +4 with F because it forms single bond with F owing of unavailability of *d*-orbitals in F for multiple bonding.

(ii) E° value of Cr^{3+}/Cr^{2+} is negative (– 0.41 V). This means Cr^{2+} ions can lose electrons to form Cr^{3+} ions and act as a reducing agent.

(iii) Cu^{2+} has availability of vacant d-orbitals, thereby allowing for the d-d transition and forming coloured salts, whereas Zn^{2+} has no vacant d-orbitals and does not form coloured salts.

13. (i) Ozone decomposes into O_2 with the evolution of heat, i.e. ΔH is negative (exothermic).

$$O_3 \rightarrow O_2 + O, \Delta H = \text{negative}$$

Since the decomposition of O_3 increases the number and freedom of particles, entropy also increases.

$$\therefore \quad \Delta S = \text{positive}$$

$$\text{Now, } \Delta G = \Delta H - T\Delta S$$

Both $-\Delta H$ and $-T\Delta S$ (since ΔS is positive) result into large negative ΔG. Hence, O_3 becomes thermodynamically unstable and decomposes into oxygen easily.

(ii) PCl_5 is ionic in solid state because it exists as $[PCl_4]^+ [PCl_6]^-$ in which the cation has tetrahedral geometry and the anion has octahedral geometry.

(iii) Fluorine forms only one oxoacid, HOF. Because for the formation of other oxoacids *d* orbitals are required for the multiple $p\pi$-$d\pi$ bonding between extra oxygen atom and fluorine.

High electronegativity and small size of fluorine also favours only the formation of one oxoacid.

14. (i) Mn shows the highest oxidation states of +7 with oxygen because it can form $p\pi - d\pi$ multiple bonds involving $2p$-orbitals of oxygen and $3d$ orbitals of Mn. On the other hand, Mn shows the highest oxidation state of +4 with F because it forms single bond with F owing of unavailability of d-orbitals in F for multiple bonding.

(ii) The variable oxidation states of transition elements are due to the participation of ns and $(n-1)\,d$–electrons in bonding. Lower oxidation state is exhibited when the ns-electrons take part in bonding. Higher oxidation states are exhibited when the $(n-1)\,d$- as well as ns electrons take part in bonding.

(iii) The actinoids involve the gradual filling of $5f$-subshell in their atoms. Actinium has the outer electronic configuration of $6d^1 7s^2$. From thorium (Z = 90) onward $5f$-subshell gets progressively filled. Because of almost equal energies of $5f$ and $6d$-subshells, there are some doubts regarding the filling of $5f$ and $6d$-subshells.

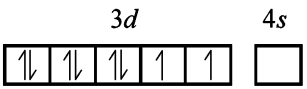
15. $[Ni(CN)_4]^{2-}$: Ni(28) : $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^8$

or, last shell EC is

$3d^8\,4s^2$

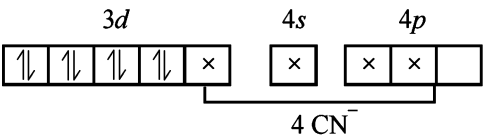
in $[Ni(CN)_4]^{2-}$, Ni is in +2 state

$\therefore$ Ni^{2+} : $3d^8\,4s^0$



CN^- being a strong field ligand pairs up the e^{-1}s, thus

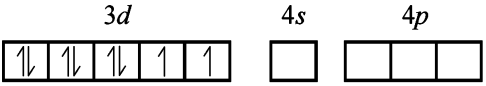
$[Ni(CN)_4]^{2-}$:



No unpaired e^-, hence $[Ni(CN)_4]^{2-}$ is diamagnetic

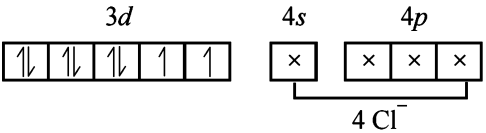
$[NiCl_4]^{2-}$: Ni is in +2 state, thus

Ni^{2+} : $3d^8\,4s^2$



Cl^- being a weak field ligand cannot pair up the e^{-1}s

\ $[NiCl_4]^{2-}$:



Due to unpaired e^{-1}s, $[NiCl_4]^{2-}$ is paramagnetic

16. The orbital splitting energies are not sufficiently large thus always pairing doen't takes place therefore low spin complexes rarely observed.

17. Due to the evolution of SO_2 the solidified copper obtained has blistered appearance so it is called blister copper.

18. (a) Presence of angular strain in any molecule make it reactive. Such angular strain is found in the white phosphorus P_4 molecule where the angles are only 60° making it more reactive. White phosphorous is made of discrete tetrahedral P_4 molecules while red phosphorus is consist of chains of P_4 tetrahedra linked together. Due to these facts it can be concluded that red phosphorus is less reactive than white phosphorus.

(b) Halogens have largely negative electron gain enthalpies because they have only one electron less than stable noble gas configurations.

(c) Oxidation state of N in $N_2O_5 = +5$

Oxidation state of N in $N_2O_3 = +3$

In N_2O_5 nitrogen is present in highest oxidation state of +5. The oxide of an element in its highest oxidation state is least stable and most strongly acidic. Thus N_2O_5 is more acidic than N_2O_3.

19. (i) Transition metals exhibit a variety of oxidation states. The variable oxidation states of transition metals are due to involvement of *ns* and $(n-1)$ *d*-electrons in bonding. The lower oxidation state is generally exhibited when only *ns*-electrons are involved in bonding and higher oxidation states when *ns* as well as $(n-1)$ *d* electrons are involved.

K M C

(ii) Zn Cd and Hg are soft metals due to completely filled orbitals or absence of any unpaired electrons resulting weak metal-metal bonding.

(iii) Mn^{2+} exists in half-filled d^5 state which is very stable while Mn^{3+} is d^4 which is not so stable. Conversion from d^4 to d^5 will be quick and have negative ΔG value. Hence because of the stability factor the E° value is high for this process. While, Cr^{3+}, d^3 is half filled ($t_{2g}{}^2$) is stable in nature and Cr^{2+} is d^4 has one extra electron which it would like to donate to attain the stable half filled ($t_{2g}{}^3$) configuration. Hence for the process Cr^{3+} to Cr^{2+} the value of E° is less.

20. (a)

Transition Metal ion	Number of unpaired electrons
(i) $Tr^{4+}[Ar]3d^0$	0
(ii) $V^{2+}[Ar]3d^3$	3
(iii) $Mn^{3+}[Ar]3d^4$	4
(iv) $Cr^{2+}[Ar]3d^3$	3

(i) V^{2+} and Cr^{3+} are the most stable ions in aqueous solutions owing to a t_{2g}^3 configuration.

(ii) An examination of the E° values for the redox couple M^{3+}/M^{2+} (from electrode potential table) shows that Mn^{3+} ion are the strongest oxidising agents in aqueous solutions.

(iii) Those ions which have unpaired electrons in d-orbital and in which d-d transition is possible will be coloured while the ions in which d-orbitals are empty or completely filled will be colourless as no d-d transition is possible in those configuratioon.

Only Ti^{4+} has an empty d-orbital so it is colourless ion among these metal lons.

6 - WHAT HAPPENS WHEN...

21. On heating $Pb(NO_3)_2$ undergoes decomposition reaction and gives nitrogen dioxide NO_2 which dimerises to give N_2O_4 gas.

$$2\,Pb(NO_3)_2 \rightarrow 2PbO + 4\,\underset{\text{(brown)}}{NO_2\uparrow} + O_2$$

$$2\,NO_2 \rightarrow N_2O_4$$

22. (i) Since 3 moles of AgCl get precipitated, all 3 Cl^- ions in the coordination compound are present outside the coordination sphere. Thus structural formula of the complex is $[Co(NH_3)_6]Cl_3$.

(ii) The IUPAC name of the complex is hexaamminecobalt (III) chloride.

23. (i) When SO_2 gas is passed through an aqueous solution of Fe^{3+} salt, SO_2 acts as a reducing agent, forming Fe^{2+} thereby turning the brown coloured solution green.

(ii) When XeF_4 reacts with SbF_5, the following reaction takes place:

$$XeF_4 + SbF_5 \rightarrow [XeF_3]^+ [SbF_6]^-$$

24. On adding NaOH to ammonium sulphate, ammonia gas is evolved. It has a pungent odour and forms a blue-coloured complex with the Cu^{2+} ion.

The concerned chemical reactions are as follows:

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + Na_2SO_4 + 2H_2O$$

$$4NH_3 + Cu^{2+} \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$$

25. Ferromagnetism is shown by the substances for which magnetic moments of domains are arranged in the same direction.

26. Chromite ore, on fusion with NaOH, forms sodium chromate (yellow-coloured compound):

$$4\,FeCr_2O_4 + 16\,NaOH + 7\,O_2 \rightarrow \underset{(A)}{8\,Na_2CrO_4} + 2\,Fe_2O_3 + 8\,H_2O$$

Sodium chromate (A), on acidification, gives sodium dichromate (B)

$$\underset{(A)}{2\,Na_2CrO_4} + H_2SO_4 \rightarrow \underset{(B)}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

Sodium dichromate (B), on reaction with KCl, forms potassium dichromate (orange-coloured crystalline compound):

$$\underset{(B)}{Na_2Cr_2O_7} + 2\,KCl \rightarrow \underset{(C)}{K_2Cr_2O_7} + 2\,NaCl$$

(i) $\underset{(A)}{Na_2CrO_4}$, $\underset{(B)}{Na_2Cr_2O_7}$, $\underset{(C)}{K_2Cr_2O_7}$

(ii) One use of potassium dichromate is that it is a powerful oxidising agent. It is used in preparation of azo compounds. It is also used in leather industry.

27. Iodine is oxidised to iodic acid when it reacts with conc. HNO_3.

$$I_2 + 10\,HNO_3 \rightarrow 2\,HIO_3 + 10\,NO_2 + 4\,H_2O$$

7- COMPLETE THE FOLLOWING

28. (i) $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

(ii) $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

29. (i) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

(ii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$

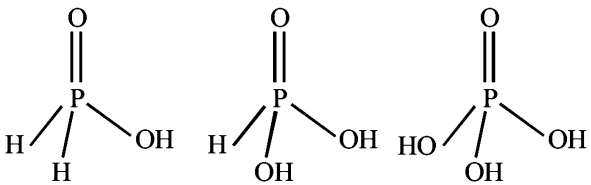
30. (b) (i) $2MnO_4^- + 16H^+ + 5S^{2-} \rightarrow 2Mn^{2+} + 8H_2O + 5S$

(ii) $2KMnO_4 \xrightarrow{heat} K_2MnO_4 + MnO_2 + O_2$

8 - WHAT IS THE CORRECT INCREASING/DECREASING ORDER?

31. (a) Reducing character : $H_3PO_4 < H_3PO_3 < H_3PO_2$

This trend can be explained on the basis of structures of oxyacids of phosphorus.



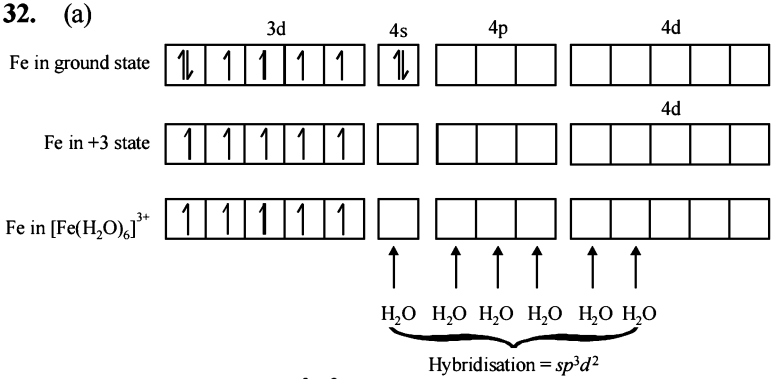
H_3PO_2 H_3PO_3 H_3PO_4

The higher the number of P-H bond, the higher the reducing power of the oxyacid of phosphorus. There are two P-H bonds in H_3PO_2, one P-H bond in H_3PO_3 and no P-H bond in H_3PO_4. So, this explains the reducing trend of the given oxyacids of phosphorus.

(b) Base strength : $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$

On moving down the group, the size of the central atom increases. This decreases the electron density on the central atom and thereby affecting the electron-donating ability of the atom. Hence, the basic strength decreases on moving down the group.

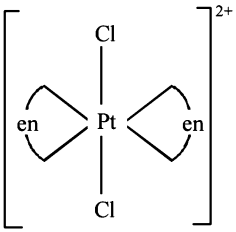
32. (a)



Hybridisation: sp^3d^2

Magnetic character: Paramagnetic

(b) *trans*-isomer of $[Pt(en)_2Cl_2]^{2+}$ is optically inactive.



33. (i) Mn shows maximum oxidation state of +7. This is because the valence shell electronic configuration of Mn is $3d^5 4s^2$. In Mn, d-orbitals are half-filled so that it can lose all seven valence electrons.

(ii) Cr has the highest melting point due to availability of maximum number of unpaired electrons, which results an increase in strength of metallic bond.

(iii) Sc shows only the +3 oxidation state because it has one 3d and two 4s electrons. So, it can lose maximum of three electrons.

(iv) Mn shows strong oxidising character in the +3 oxidation state because it acquires highly stable $3d^5$ configuration in the +2 oxidation state.

34. (i) Mercury cell is used in hearing aids.

(ii) Fuel cell was used in the Apollo space programme.

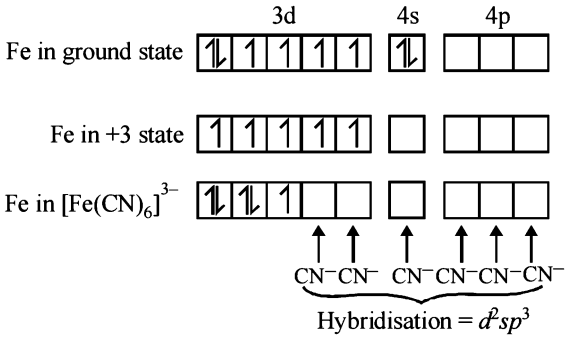
(iii) Lead storage cell is used in automobiles and inverters.

(iv) Dry cell does not have a long life.

35. In the extraction of aluminium, impure Al_2O_3 is dissolved in concentrated NaOH to form $NaAlO_2$. This method is known as leaching of alumina.

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(\ell) \longrightarrow 2Na[Al(OH)_4](aq)$$

36. (a)

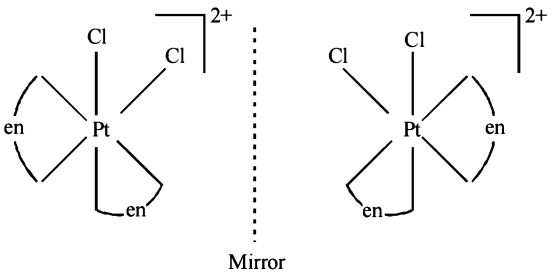


Hybridisation : d^2sp^3

Magnetic character : Paramagnetic

Spin nature of complex : Low-spin complex

(b) *cis*-isomer of $[Pt(en)_2Cl_2]^{2+}$ is optically active.



37. (i) Although electron gain enthalpy of fluorine is less than that of chlorine because of the small size of fluorine, but the oxidising power depends on other factors like bond dissociation energy and hydration energy. The smaller the size of the atom, the greater the hydration enthalpy. Fluorine being small in size has higher hydration enthalpy as compared to chlorine.

Also, fluorine faces greater inter-electronic repulsion among its lone pairs of electrons because of its small size, while there is very less repulsion in chlorine. Hence, the bond dissociation enthalpy of fluorine is lower than that of chlorine.

Thus, the high hydration enthalpy and low bond dissociation enthalpy of fluorine result in its higher oxidising power as compared to that of chlorine.

(ii) Manufacturing of sulphuric acid via the contact process involves three steps :

(1) Burning of ores to form SO_2

(2) Conversion of SO_2 to SO_3 using V_2O_5 as a catalyst

(3) Absorption of SO_3 in H_2SO_4 to give oleum

The second step, i.e. conversion of SO_2 to SO_3 is the key step. Since this reaction is exothermic in nature and two moles of gaseous reactant give one mole of gaseous product. Thus, in accordance with Le Chatelier's principle, to obtain the maximum amount of SO_3, low temperature and high pressure are required.

38. Linkage isomerism

39. **Similarity :** They both show contraction of radii, the progressive decrease in the radii of atoms of the lanthanoid and actionoid elements as the atomic number increases.

Difference : Actionids show a large number of oxidation states where as or actionoid primarily show only three oxidation states.

Board 2014-15 Solved Paper

(Organic Chemistry Questions)

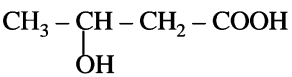
1 - WHAT ARE THE IUPAC NAMES/STRUCTURES OF THE FOLLOWING COMPOUNDS

1. Write the structure of *p*-methylbenzaldehyde. **[All India 2014]**

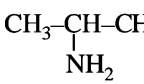
2. Write the structure of 4-chloropentan-2-one. **[All India 2014]**

3. Write the structure of 2-hydroxybenzoic acid. **[All India 2014]**

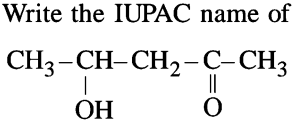
4. Write the IUPAC name of the compound. **[Delhi 2014]**



5. Write the IUPAC name of the compound **[Delhi 2014]**

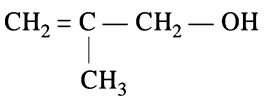


6. Write the IUPAC name of the compound. **[Delhi 2014]**

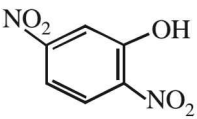


7. Write the structure of 2-methylbutanal **[All India 2015]**

8. Write the IUPAC name of the given compound. **[All India 2015]**



9. Write the IUPAC name of the given compound **[Delhi 2015]**



2 - HOW WILL YOU DEFINE THE GIVEN REACTIONS ?

10. The conversion of primary aromatic amines into diazonium salts is known as _____. **[All India 2014]**

11. Write the equations involved in the following reactions:

(i) Reimer – Tiemann reaction **[All India 2014]**

(ii) Williamson synthesis

12. Write the chemical equations to illustrate the following name reactions:

(i) Rosenmund reduction

(ii) Cannizzaro's reaction **[All India 2014]**

13. Write the equation involved in Reimer-Tiemann reaction.
[Delhi 2014, Also appeared in 2012C, AI 2009C, 2010C, 2011C, 2013]

14. Write the chemical equations to illustrate the following name reactions :

(i) Wolff-Kishner reduction

(ii) Aldol condensation

(iii) Cannizzaro reaction **[Delhi 2014]**

3 - WHAT HAPPENS WHEN ...

15. Write the products formed when CH_3CHO reacts with the following reagents: **[All India 2014]**

(i) HCN

(ii) $H_2N–OH$

(iii) CH_3CHO in the presence of dilute NaOH

16. Write the product formed on reaction of D-glucose with Br_2 water.
[Delhi 2014, Also appeared in AI 2008, 2010C, 2012C]

17. Write the product formed when glucose is treated with HI.
[Delhi 2014]

18. Write the chemical equations involved when aniline is treated with the following reagents. **[All India 2015]**

(i) Br_2 water

(ii) $CHCl_3 + KOH$

(iii) HCl

19. Write the structures of the main products when acetone ($CH_3 – CO – CH_3$) reacts with the following reagents.
[All India 2015]

(i) Zn – Hg/conc. HCl

(ii) $H_2NNHCONH_2/H^+$

(iii) CH_3MgBr and then H_3O^+

20. Write the product obtained when D-glucose reacts with $H_2N–OH$. **[All India 2015]**

21. Write the equation involved in the acetylation of salicylic acid.
[Delhi 2015]

22. Write the structures of main products when aniline reacts with the following reagents.

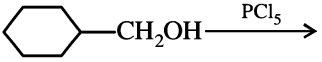
(i) Br_2 water

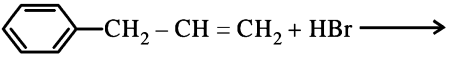
(ii) HCl

(iii) $(CH_3CO)_2O$/pyridine **[Delhi 2015]**

4 - WHAT ARE THE MISSING COMPOUNDS/REAGENTS ?

23. Draw the structures of major monohalo products in each of the following reactions : **[All India 2014]**

(i) 

(ii) 

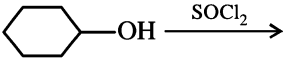
24. Give the structures of A, B and C in the following reactions:

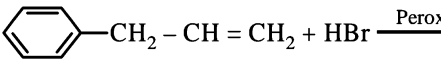
(i) $C_6H_5NO_2 \xrightarrow{Sn+HCl} A \xrightarrow[273K]{NaNO_2+HCl} B \xrightarrow{H_2O} C$

(ii) $CH_3CN \xrightarrow{H_2O/H^+} A \xrightarrow[NH_3]{\Delta} B \xrightarrow{Br_2+KOH} C$

[All India 2014]

25. Draw the structure of major monohalo product in each of the following reactions :

(i)  **[Delhi 2014, Also appeared in Delhi 2009]**

(ii)  **[Delhi 2014]**

26. Give the structures of A, B and C in the following reactions :

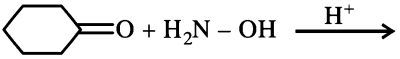
(i) $CH_3Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273K]{HNO_2} C$

[Delhi 2014, Also appeared in AI 2013]

(ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{Br_2+KOH} B \xrightarrow{CHCl_3+NaOH} C$

[Delhi 2014, Also appeared in AI 2013]

27. Write the products of the following reactions :

(i) 

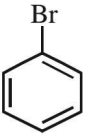
(ii) $2C_6H_5CHO + \text{conc. NaOH} \longrightarrow$

(iii) $CH_3COOH \xrightarrow{Cl_2/P}$ **[Delhi 2014]**

28. Write the structure of the major product in each of the following reactions. **[All India 2015]**

(i) $CH_3 - CH = \underset{\displaystyle CH_3}{\underset{|}{C}} - CH_3 + HBr \longrightarrow$

(ii) $CH_3-CH_2-CH_2-\underset{\underset{Br}{|}}{\overset{K}{C}}H-\overset{M}{C}H-\overset{C}{C}H_3 + KOH \xrightarrow{\text{ethanol/heat}}$

(iii) 

$+ CH_3Cl \xrightarrow{\text{anhyd.}AlCl_3}$

29. A compound 'A' of molecular formula C_2H_3OCl undergoes a series of reactions as shown below. Write the structures of A, B, C and D in the following reactions. **[All India 2015]**

$$(C_2H_3OCl)A \xrightarrow{H_2/Pd-BaSO_4} B \xrightarrow{\text{dil. NaOH}} C \xrightarrow{\text{Heat}} D$$

30. Name the reagents used in the following reactions:

(i) $CH_3-CO-CH_3 \longrightarrow CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

(ii) $C_6H_5-CH_2-CH_3 \longrightarrow C_6H_5-COO^-K^+$ **[Delhi 2015]**

31. Predict the products of the following

(i) $CH_3COCH_3 \xrightarrow[\text{(ii) KOH/Glycol, }\Delta]{\text{(i) }H_2N-NH_2} ?$

(ii) $C_6H_5-CO-CH_3 \xrightarrow{NaOH/I_2} ? + ?$

(iii) $CH_3COONa \xrightarrow[\Delta]{NaOH/CaO} ?$ **[Delhi 2015]**

32. 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. **[Delhi 2015]**

$$(C_7H_7ON)\,A \xrightarrow{Br_2 + KOH} C_6H_5NH_2 \xrightarrow{NaNO_2 + HCl} B \xrightarrow{CH_3CH_2OH} C$$

$$C_6H_5NH_2 \xrightarrow{CHCl_3 + NaOH} D \qquad B \xrightarrow{KI} E$$

5 - HOW WILL YOU CARRY OUT THE GIVEN CONVERSIONS ?

33. How will you convert the following : **[Delhi 2014]**

(i) Nitrobenzene into aniline

(ii) Ethanoic acid into methanamine

(iii) Aniline into N-phenylethanamide

(Write the chemical equations involved.)

34. How do you convert the following. **[All India 2015]**

(i) $C_6H_5CONH_2$ to $C_6H_5NH_2$

(ii) Aniline to phenol

(iii) Ethanenitrile to ethanamine

35. How do you convert the following?

(i) Phenol to anisole

(ii) Propan-2-ol to 2-methylpropan-2-ol

(iii) Aniline to phenol **[Delhi 2015]**

6 - HOW WILL YOU DISTINGUISH THE GIVEN PAIR OF COMPOUNDS ?

36. Give simple chemical tests to distinguish between the following pairs of compounds:

(i) Benzoic acid and Phenol

(ii) Propanal and Propanone **[All India 2014, Also appeared in Delhi 2009C, 2012C, 2010, 2012, 2013, AI 2008, 2009, 2012 C]**

37. Out of $CH_3CH_2–CO–CH_2–CH_3$ and $CH_3CH_2–CH_2–CO–CH_3$, which gives iodoform test?

[All India 2014, Also appeared in Delhi 2012, 2013]

38. Give simple chemical tests to distinguish between the following pairs of compounds :

(i) Benzaldehyde and Benzoic acid **[Delhi 2014]**

(ii) Propanal and Propanone

[Delhi 2014, Also appeared in Delhi 2007, 2011, 2012, 2012C, AI 2008, 2009, 2011]

39. Give a simple chemical test to distinguish between the following pair of compounds: **[All India 2015]**

CH_3CH_2CHO and $CH_3CH_2COCH_3$

40. Distinguish between the following. **[All India 2015]**

(i) $C_6H_5 – COCH_3$ and $C_6H_5 – CHO$

(ii) Benzoic acid and methyl benzoate

41. Give a simple chemical test to distinguish between the following pair of compounds.

$(CH_3)_2NH$ and $(CH_3)_3N$ **[Delhi 2015]**

7 - WHAT WILL BE THE MECHANISM OF THE GIVEN REACTIONS?

42. Write the mechanism of the following reaction: **[All India 2014]**

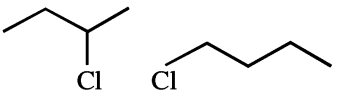
$$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$$

43. Write the mechanism of the following reaction:

$$2CH_3CH_2OH \xrightarrow{H^+} CH_3CH_2 — O — CH_2CH_3$$ **[Delhi 2015]**

8 - WHY DO THE FOLLOWING HAPPENS ?

44. Identify the chiral molecule in the following pair: **[All India 2014]**



45. Account for the following:

(i) Primary amines ($R\text{-}NH_2$) have higher boiling point than tertiary amines (R_3N). **[All India 2014, Also appeared in Delhi 2008C, AI 2011]**

(ii) Aniline does not undergo Friedel - Craft reaction **[All India 2014, Also appeared in Delhi 2008, AI 2008C, 2010C, 2011C]**

(iii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution. **[All India 2014, Also appeared in Delhi 2008, AI 2008C, 2010C, 2011C]**

46. Account for the following:

(i) $Cl–CH_2COOH$ is a stronger acid than CH_3COOH. **[All India 2014, Also appeared in Delhi 2013C]**

(ii) Carboxylic acids do not give reactions of carbonyl group. **[All India 2014, Also appeared in Delhi 2012C, AI 2013C]**

47. Which of the following isomers is more volatile :
o-nitrophenol or *p*-nitrophenol **[Delhi 2014, Also appeared in Delhi 2002C, 2013C]**

48. Why is use of aspartame limited to cold food and soft drinks ? **[Delhi 2014]**

49. Account for the following :

(i) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN. **[Delhi 2014, Also appeared in Delhi 2008, AI 2013C]**

(ii) Carboxylic acid is a stronger acid then phenol. **[Delhi 2014, Also appeared in AI 2013]**

50. Give reasons for the following. **[All India 2015]**

(i) Phenol is more acidic than ethanol.

(ii) Boiling point of ethanol is higher in comparison to methoxymethane

(iii) $(CH_3)_3C - O - CH_3$ on reaction with HI gives CH_3OH and $(CH_3)_3C - I$ as the main products and not $(CH_3)_3C - OH$ and CH_3I.

51. Amino acids show amphoteric behaviour. Why? **[All India 2015]**

52. Why cannot vitamin C be stored in our body? **[All India 2015]**

53. 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. **[Delhi 2015]**

9 - WHAT IS THE CORRECT INCREASING/DECREASING ORDER?

54. Which halogen compound in each of the following pairs will react faster in S_N2 reaction:

(i) CH_3Br or CH_3I

(ii) $(CH_3)_3C–Cl$ or $CH_3–Cl$ **[All India 2014, Also appeared in Delhi 2008, AI 2010C]**

55. Arrange the following compounds in increasing order of solubility in water : **[Delhi 2014, Also appeared in Delhi 2011, AI 2011C]**

$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$

56. (i) Which alkyl halide from the following pair is chiral and undergoes faster S_N2 reaction ?

(a)

(b)

(ii) Out of S_N1 and S_N2, which reaction occurs with

(a) Inversion of configuration

(b) Racemisation ? **[Delhi 2014]**

57. Arrange the following in increasing order of basic strength:
$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$ **[Delhi 2014]**

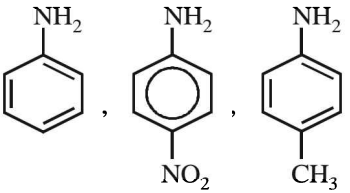
58. Arrange the following in increasing order of basic strength :
$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5N(CH_3)_2$ **[Delhi 2014]**

59. Which would undergo S_N1 reaction faster in the following pair?

$$CH_3-CH_2-Br \text{ and } CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$ **[All India 2015]**

60. Arrange the following in increasing order of their basic strength. **[All India 2015]**

(i) $C_6H_5-NH_2$, $C_6H_5-CH_2-NH_2$, $C_6H_5-NH-CH_3$

(ii) 

61. Arrange the following in the increasing order of their boiling points. **[All India 2015]**

C_2H_5OH, CH_3-CHO, CH_3-COOH

62. Which would undergo S_N2 reaction faster in the following pair and why?

$$CH_3-CH_2-Br \text{ and } CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$ **[Delhi 2015]**

63. Arrange the following in the increasing order of their boiling point.
$C_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$ **[Delhi 2015]**

11 - MISCELLANEOUS QUESTIONS

64. Which of the following is a natural polymer?
Buna-S, protein, PVC **[All India 2014, Also appeared in Delhi 2008C]**

65. What are the products of hydrolysis of sucrose? **[All India 2014, Also appeared in Delhi 2010, AI 2013 Foreign 2011]**

66. Write the names of monomers used for getting the following polymers:

(i) Bakelite **[All India 2014, Also appeared in Delhi 2013, AI 2009C, 2010, AI 2010C, 2013C]**

(ii) Neoprene **[All India 2014, Also appeared in Delhi 2008, 2010, 2010C, 2011C, 2012, 2013, AI 2011, Foreign 2012]**

67. Define the following terms as related to proteins:

(i) Peptide linkage **[All India 2014, Also appeared in Delhi 2008, 2009, 2011, 2012, AI 2008, Forign 2011]**

(ii) Primary structure **[All India 2014, Also appeared in Delhi 2011, AI 2008, 2012 Foreign 2011]**

(iii) Denaturation **[All India 2014, Also appeared in Delhi 2008, AI 2008C, 2009, 2012C]**

68. On the occasion of World Health Day, Dr. Satpal organized a 'health camp' for the poor farmers living in a nearby village. After check-up, he was shocked to see that most of the farmers suffered from cancer due to regular exposure to pesticides and many were diabetic. They distributed free medicines to them. Dr. Satpal immediately reported the matter to the National Human Rights Commission (NHRC). On the suggestions of NHRC, the government decided to provide medical care, financial assistance, setting up of super-speciality hospitals for treatment and prevention of the deadly disease in the affected villages all over India.

(i) Write the values shown by

(a) Dr. Satpal

(b) NHRC

(ii) What type of analgesics are chiefly used for the relief of pains of terminal cancer?

(iii) Give an example of artificial sweetener that could have been recommended to diabetic patients. **[All India 2014]**

69. What are the products of hydrolysis of maltose? **[All India 2014]**

70. Write the names of monomers used for getting the following polymers:

(i) Terylene **[All India 2014, Also appeared in Delhi 2010C, 2011C, 2013 AI 2009C, AI 2011, 2011C, 2013]**

(ii) Nylon-6,6 **[All India 2014, Also appeared in Delhi 2010C, 2013]**

71. Define the following terms:
(i) Glycosidic linkage
(ii) Invert sugar
(iii) Oligosaccharides **[All India 2014]**

72. Which of the following is a fibre?
Nylon, Neoprene, PVC **[All India 2014]**

73. Write the products of the hydrolysis of lactose.

74. Write the names of monomers used for getting the following polymers:
(i) Teflon
(ii) Buna-N **[All India 2014]**

75. Define the following terms:
(i) Nucleotide **[All India 2014, Also appeared in Delhi 2009C, AI 2013C]**
(ii) Anomers
(iii) Essential amino acids **[All India 2014, Also appeared in Delhi 2012C, AI 2008C, 2010, 2013C]**

76. Which of the two components of starch is water soluble ? **[Delhi 2014, Also appeared in Foreign 2012]**

77. (i) Give two examples of macromolecules that are chosen as drug targets.
(ii) What are antiseptics ? Give an example. **[Delhi 2014, Also appeared in Delhi 2009, AI 2010, 2010C, Foreign 2011]**

78. (i) Deficiency of which vitamin causes night blindness?
(ii) Name the base that is found in nucleotide of RNA only. **[Delhi 2014, Also appeared in Delhi 2011, Foreign 2012]**
(iii) Glucose on reaction with HI gives n-hexane. What does it suggest about the structure of glucose ? **[Delhi 2014, Also appeared in AI 2008, 2010C, 2012C]**

79. After the ban of plastic bags, students of one school decided to make the people aware of the harmful effects of plastic bags on environment and Yamuna River. To make the awareness more impactful, they organized rally by joining hands with other schools and distributed paper bags to vegetable vendors, shopkeepers and departmental stores.

All students pledged not to use polythene bags in future to save Yamuna River.

After reading the above passage, answer the following questions.

(i) What values are shown by the students ?

(ii) What are biodegradable polymers ? Give an example.

(iii) Is polythene a condensation or an addition polymer ? **[Delhi 2014]**

80. Write the mechanism of the following reaction:

$$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$$ **[Delhi 2014]**

81. Which component of starch is a branched polymer of α-glucose and insoluble in water? **[Delhi 2014, Also appeared in Foreign 2012]**

82. (i) Name sweetening agent used in the preparation of sweets for a diabetic patient. **[Delhi 2014, Also appeared in Delhi 2009C, AI 2009, 2011, Foreign 2011]**

(ii) What are antibiotics? Give an example. **[Delhi 2014, Also appeared in AI 2009C, 2010, 2010C, 2012C]**

(iii) Give two examples of macromolecules that are chosen as drug targets. **[Delhi 2014]**

83. (i) Deficiency of which vitamin causes rickets?

(ii) Give an example each for fibrous protein and globular protein. **[Delhi 2014, Also appeared in Delhi 2010C, AI 2010C]**

84. What type of intermolecular attractive interaction exists in the pair of methanol and acetone? **[Delhi 2014]**

85. Name the products of hydrolysis of sucrose. **[Delhi 2014, Also appeared in Delhi 2010, AI 2013, Foreign 2011]**

86. (i) What are disinfectants? Give an example. **[Delhi 2014, Also appeared in Delhi 2012, AI 2009]**

(ii) Give two examples of macromolecules that are chosen as drug targets.

(iii) What are anionic detergents? Give an example. **[Delhi 2014, Also appeared in Delhi 2009C, 2013C, AI 2010C]**

87. (i) Deficiency of which vitamin causes scurvy?

(ii) What type of linkage is responsible for the formation of proteins? **[Delhi 2014, Also appeared in Delhi 2008, 2009, 2011, 2012, AI 2008, 2011, 2012, 2013, Foreign 2011]**

88. Write the names and structures of the monomers of the following polymers. **[All India 2015]**

(i) Buna-S

(ii) Glyptal

(iii) Polyvinyl chloride

89. Seeing the growing cases of diabetes and depression among young children, Mr. Lugani, the principal of a reputed school organized a seminar in which he invited parents and principals. They all resolved this issue by strictly banning junk food in schools and introducing healthy snacks and drinks like soup, lassi, milk, etc. in school canteens. They also decided to make compulsory half and hour of daily physical activities for the students in the morning assembly. After six months, Mr. Lugani conducted the health survey in most of the schools and discovered a tremendous improvement in the health of the students. **[All India 2015]**

After reading the above passage, answer the following questions.

(i) What are the values (at least two) displayed by Mr. Lugani?

(ii) As a student, how can you spread awareness about this issue?

(iii) What are antidepressant drugs? Give an example.

(iv) Name the sweetening agent used in the preparation of sweets for a diabetic patient.

90. Write the names and structures of the monomers of the following polymers.

(i) Nylon-6, 6

(ii) PHBV

(iii) Neoprene **[Delhi 2015]**

91. (i) Which one of the following is a disaccharide: Starch, Maltose, Fructose, Glucose?

(ii) What is the difference between fibrous protein and globular protein?

(iii) Write the name of vitamin whose deficiency causes bone deformities in children. **[Delhi 2015]**

92. Mr. Roy. the principal of one reputed school organized a seminar in which he invited parents and principals to discuss the serious issue of diabetes and depression in students. They all resolved this issue by strictly banning the junk food in schools and to introduce healthy snacks and drinks like soup, lassi, milk etc. in school canteens. They also decided to make compulsory half an hour physical activities for the students in the morning assembly daily. After six months, Mr. Roy conducted the health survey in most of the schools and discovered a tremendous improvement in the health of students.

After reading the above passage, answer the following.

(i) What are the values (at least two) displayed by Mr. Roy?

(ii) As a student, how can you spread awareness about this issue?

(iii) What are tranquillizers? Give an example.

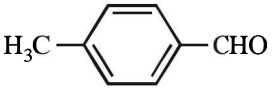
(iv) Why is use of aspartame limited to cold foods and drinks?

[Delhi 2015]

Hints and Solutions

1 - WHAT ARE THE IUPAC NAMES/STRUCTURES OF THE FOLLOWING COMPOUNDS ?

1.



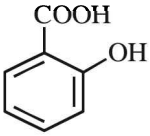
p-Methylbenzaldehyde

2.

$$\overset{1}{C}H_3-\overset{2}{C}(=O)-\overset{3}{C}H_2-\overset{4}{C}H(Cl)-\overset{5}{C}H_3$$

4-Chloropentan-2-one

3.



2-Hydroxybenzoic acid

4.

$$\overset{4}{C}H_3-\overset{3}{C}H(OH)-\overset{2}{C}H_2-\overset{1}{C}OOH$$

3-Hydroxybutanoic acid

5.

$$\overset{4}{C}H_3-\overset{3}{C}H(NH_2)-\overset{2}{C}H_2-\overset{1}{C}HO$$

3-Aminobutanal

6.

$$\overset{5}{C}H_3-\overset{4}{C}H(OH)-\overset{3}{C}H_2-\overset{2}{C}(=O)-\overset{1}{C}H_3$$

4-Hydroxypentan-2-one

7.

$$CH_3-CH_2-CH(CH_3)-CHO$$

2–Methylbutanal

8. 2—Methylprop–2–ene–1– ol.

9. 2, 5 -Dinitrophenol

2 - HOW WILL YOU DEFINE THE GIVEN REACTIONS ?

10. Refer solution no. 27 on Page-23

11. (i) Refer solution no. 14 on Page-19

(ii) Refer solution no. 5 on Page-16

12. (i) Refer solution 10 on Page-18

(ii) Refer solution 17 on Page-20

13. Refer solution 14 on Page-19

14. (i) Refer solution 16 on Page-19

(ii) Refer solution 8 on Page-17

(iii) Refer solution 10 on Page-18

3 - WHAT HAPPENS WHEN ...

15. (i) $\underset{\text{Acetaldehyde}}{CH_3CHO} + HCN \longrightarrow \underset{\text{Acetaldehyde cyanohydrin}}{CH_3\overset{\overset{OH}{|}}{C}HCN}$

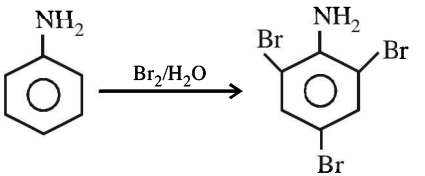
(ii) $CH_3CHO + H_2NOH \longrightarrow \underset{\text{Acetaldoxime}}{CH_3CH = NOH}$

(iii) $CH_3CHO + CH_3CHO \xrightarrow[\text{(aldol conden.)}]{\text{dil. NaOH}} \underset{\text{3-Hydroxylbutanal (Aldol)}}{CH_3\overset{\overset{OH}{|}}{C}HCH_2CHO}$

16. Refer solution E (i) (b) on Page-30

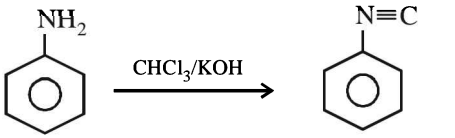
17. $\underset{\text{Glucose}}{\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}} \xrightarrow[\text{(reduction of – CHO, and – OH)}]{\text{HI/red P}} \underset{\textit{n}\text{-Hexane}}{\begin{array}{c} CH_3 \\ | \\ (CH_2)_4 \\ | \\ CH_3 \end{array}} \xrightarrow{\text{HI}} \underset{\text{2-Iodohexane}}{\begin{array}{c} CH_3 \\ | \\ CHI \\ | \\ (CH_2)_3 \\ | \\ CH_3 \end{array}}$

18. (i)



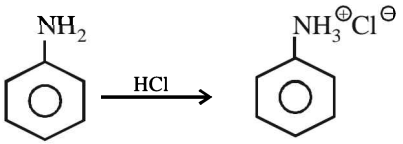
Aniline 2,4,6-Tribromoaniline

(ii)



Aniline Benzene isocyanide

(iii)



Aniline Anilinium chloride

19. (i) $CH_3COCH_3 \xrightarrow{Zn-Hg/conc.HCl} CH_3CH_2CH_3$

Propanone Propane

(ii) $CH_3COCH_3 \xrightarrow[H^+]{H_2N-NHCONH_2}$

Propanone

$$CH_3-\underset{\underset{CH_3}{|}}{C}=NNHCONH_2+H_2O$$

Propanone semicarbazone

(iii) $CH_3COCH_3 \xrightarrow[(ii)\,H_3O^+]{(i)\,CH_3MgBr} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

Propanone tert-Butyl alcohol

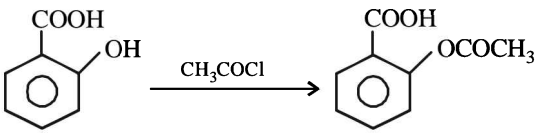
20. $HOH_2C-(CHOH)_4-CHO+NH_2OH \longrightarrow$

D-Glucose

$$HOH_2C-(CHOH)_4-CH=N-OH+H_2O$$

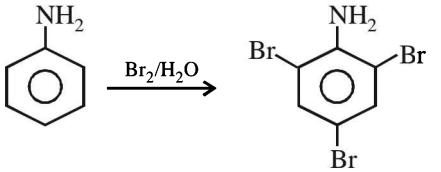
Glucose oxime

21.



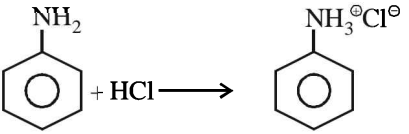
Salicylic acid Aspirin

22. (i)



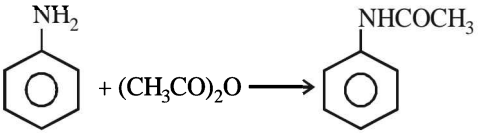
Aniline 2,4,6-Tribromoaniline

(ii)



Aniline Anilinium chloride

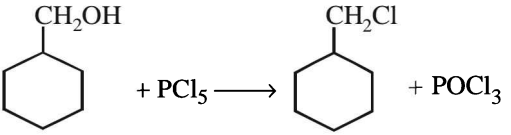
(iii)



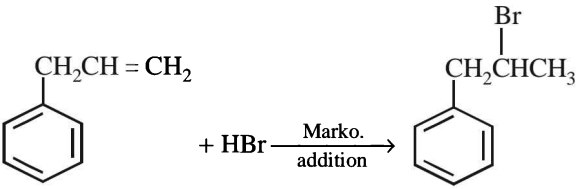
Aniline Acetanilide

4 - WHAT ARE THE MISSING COMPOUNDS/REAGENTS ?

23. (i)



(ii)



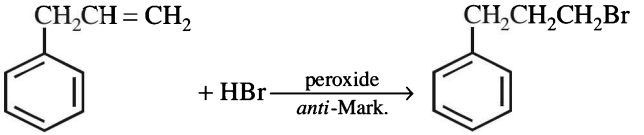
24. (i) Refer solution 2 (v) on Page-44

(ii) $CH_3CN \xrightarrow{H_2O/H^+} \underset{(A)}{CH_3COOH} \xrightarrow[NH_3]{\Delta} [CH_3COONH_4]$

$\xrightarrow[(-H_2O)]{} \underset{(B)}{CH_3CONH_2} \xrightarrow[\text{Hofmann bromamide}]{Br_2-KOH} \underset{(C)}{CH_3NH_2}$

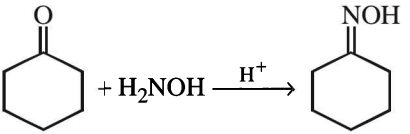
K M C

25. (i) Refer solution B (i) on Page-38

(ii) 

26. (i) Refer solution 2 (ii) on Page-43

(ii) Refer solution 2 (vi) on Page-44

27. (i) 

(ii) $2C_6H_5CHO \xrightarrow[\text{Cannizzaro reaction}]{\text{conc. NaOH}} C_6H_5COONa + C_6H_5CH_2OH$

(iii) $CH_3COOH \xrightarrow[\text{HVZ reaction}]{Cl_2/P} ClCH_2COOH$

28. (i) $CH_3-CH=C(CH_3)-CH_3 + HBr \longrightarrow$

2-Methylbut-2-ene

$CH_3-CH_2-C(CH_3)_2-Br$

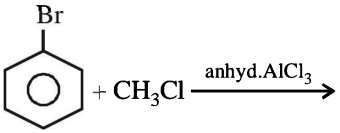
2-Bromo-2-methylbutane

(ii) $CH_3-CH_2-CH_2-CH(Br)-CH_3 + KOH \xrightarrow{\text{ethanol/heat}}$

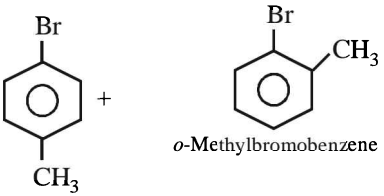
2-Bromopentane

$CH_3-CH_2-CH=CH-CH_3$ (Major)

Pent-2-ene

(iii) 

Bromobenzene



p-Methylbromobenzene *o*-Methylbromobenzene

29. A = CH_3COCl

B = CH_3CHO

C = $CH_3\underset{\underset{OH}{|}}{C}H-CH_2CHO$

D = $CH_3CH=CH-CHO$

$$\underset{\text{Acetyl chloride}}{\underset{(A)}{CH_3COCl}} \xrightarrow{H_2/Pd \text{ on } BaSO_4} \underset{\text{Acetaldehyde}}{\underset{(B)}{CH_3CHO}} \xrightarrow{\text{dil.NaOH}}$$

$$\underset{\beta\text{–hydroxy butyraldehyde}}{\underset{(C)}{CH_3-\underset{\underset{OH}{|}}{C}H-CH_2-CHO}}$$

$$\Big\downarrow \text{Heat}$$

$$\underset{\text{Crotonaldehyde}}{\underset{(D)}{CH_3CH=CHCHO}}$$

30. (i) $NaBH_4$ (Sodium borohydride)

(ii) $KMnO_4 - KOH$ (Alkaline potassium permanganate)

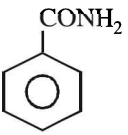
31. (i) $\underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow[\text{(ii)KOH, Glycol, }\Delta]{\text{(i)}H_2N-NH_2} \underset{\text{Propane}}{CH_3CH_2CH_3}$

(ii) $\underset{\text{Acetophenone}}{C_6H_5-CO-CH_3} \xrightarrow{NaOH/I_2}$

$\underset{\text{Iodoform}}{CHI_3} + \underset{\text{sodium benzoate}}{C_6H_5COONa} + NaI + H_2O$

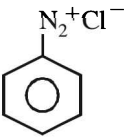
(iii) $\underset{\text{Sodium acetate}}{CH_3COONa} \xrightarrow[\Delta]{NaOH/CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$

32.

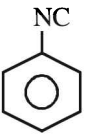
A = 

Benzamide

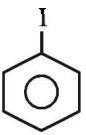
C =
Benzene

B = 

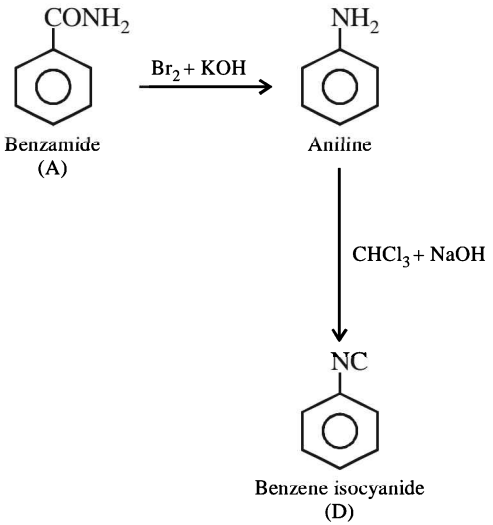
Benzene diazonium chloride

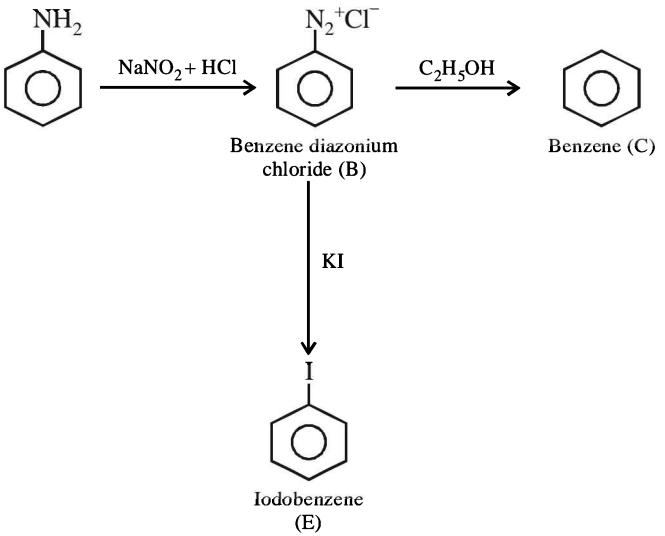
D = 

Benzene isocyanide

E = 

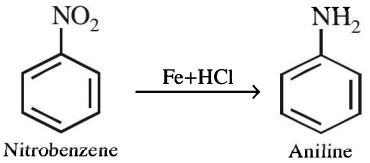
Iodobenzene


CONH2
Br2 + KOH
NH2
Benzamide
(A)
Aniline
CHCl3 + NaOH
NC
Benzene isocyanide
(D)


NH2
NaNO2 + HCl
N2+Cl−
C2H5OH
Benzene diazonium
chloride (B)
Benzene (C)
KI
I
Iodobenzene
(E)

5 - HOW WILL YOU CARRY OUT THE GIVEN CONVERSIONS ?

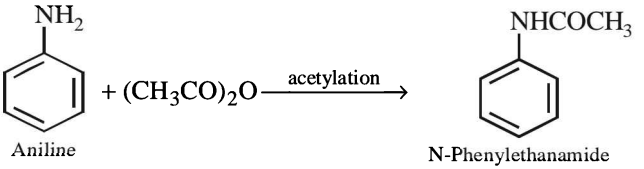
33. (i)



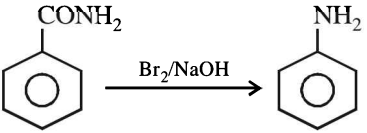
(ii) $CH_3COOH \xrightarrow[\text{(ii) } \Delta]{\text{(i) } NH_3} CH_3CONH_2 \xrightarrow[\text{Hofmann bromamide}]{Br_2+KOH} CH_3NH_2$

Ethanoic acid → Acetamide → Methanamine

(iii)



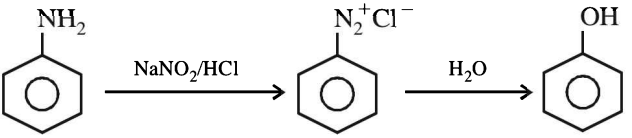
34. (i)



(Hofmann's bromamide reaction)

Benzamide → Aniline

(ii)



Aniline → Benzenediazonium chloride → Phenol

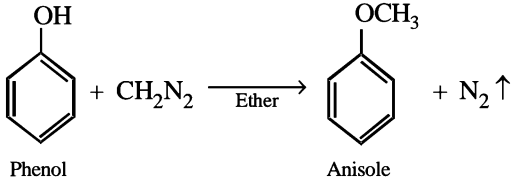
(iii) $CH_3CH_2CN \xrightarrow{H_2O/H^+} CH_3CH_2COOH \xrightarrow[NH_3]{\Delta}$

Ethanenitrile → Propanoic acid

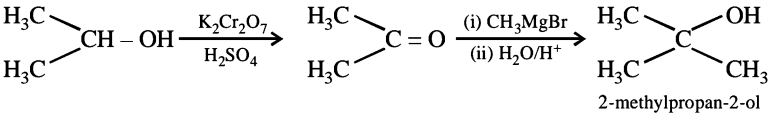
$CH_3CH_2CONH_2 \xrightarrow{Br_2/KOH} CH_3CH_2NH_2$

Propanamide → Ethylamine

35. (i)

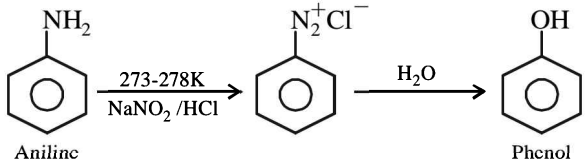


(ii)



Propan-2-ol

(iii)



6 - HOW WILL YOU DISTINGUISH THE GIVEN PAIR OF COMPOUNDS ?

36. (i) Refer solution C (xii) on Page-73

(ii) Refer solution C (vi) on Page-73

37. Refer solution C (viii) on Page-73

38. (i) Refer solution C (xv) on Page-74

(ii) Refer solution C (vi) on Page-73

39. $CH_3CH_2COCH_3$ gives iodoform test while CH_3CH_2CHO does not give this test.

$$CH_3CH_2COCH_3 + 3NaOI \longrightarrow \underset{\text{Iodoform}}{CHI_3\downarrow} + CH_3CH_2COONa + 2NaOH$$

40. (i) Benzaldehyde and acetophenone can be distinguished by iodoform test.

$$C_6H_5COCH_3 + 3NaOI \longrightarrow C_6H_5COONa + \underset{\text{(Yellow ppt.)}}{CHI_3\downarrow} + 2NaOH$$

$$C_6H_5CHO + NaOI \longrightarrow \text{No yellow ppt.}$$

(ii) Benzoic acid and methyl benzoate can be distinguished by $NaHCO_3$ test

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaHCO_3 \longrightarrow \underset{\text{Sodiumbenzoate}}{C_6H_5COONa} + H_2O + CO_2\uparrow$$

$$C_6H_5COOCH_3 + NaHCO_3 \longrightarrow \text{No } CO_2 \text{ is formed}$$

41. Given pair of compounds can be distinguised on the basis of Hinsberg test.

$$(CH_3)_2NH + \underset{\text{Benzenesulphonyl chloride}}{C_6H_5SO_2Cl} \xrightarrow{KOH}$$

$$\underset{\substack{\text{N,N–Dimethylbenzene sulphonamide} \\ \text{(insoluble in aq. NaOH)}}}{(CH_3)_2N-SO_2C_6H_5} + HCl$$

$$\underset{\text{3°amine}}{(CH_3)_3N} \xrightarrow[KOH]{C_6H_5SO_2Cl} \text{No reaction.}$$

7 - WHAT WILL BE THE MECHANISM OF THE GIVEN REACTIONS?

42. Mechanism of the reaction,

$$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$$

pri-Alkyl halides undergo S_N2 reaction.

$$CH_3CH_2-OH \xrightarrow{H^+} CH_3CH_2-\overset{+}{O}H_2$$

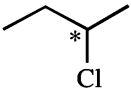
$$Br + CH_3-CH_2-\overset{+}{O}H_2 \longrightarrow \overset{-}{Br} \cdots\cdots CH_2(CH_3) \cdots\cdots \overset{+}{O}H_2$$

$$\longrightarrow CH_3CH_2-Br + H_2O$$

43. $$CH_3CH_2OH \xrightarrow{H^+} CH_3CH_2\overset{+}{O}H_2 \xrightarrow[(-H_2O)]{} CH_3\overset{+}{C}H_2 \xrightarrow[\text{(2nd molecule)}]{CH_3CH_2OH}$$

$$CH_3CH_2-\overset{+}{O}(H)-CH_2CH_3 \xrightarrow[(-H^+)]{} \underset{\text{Diethyl ether}}{CH_3CH_2-O-CH_2CH_3}$$

8 - WHY DO THE FOLLOWING HAPPENS ?

44. 

* represents chiral carbon.

45. (i) Refer solution D (2) on Page-103

(ii) Refer solution 15 on Page-106

(iii) In aqueous solution basicity is controlled by three factors : +I effect of alkyl group, H-bonding of the protonated base (conjugate acid) with water and steric factors. The latter two factors are in favour of $(CH_3)_2NH$ and their combined effect outweighs the +I effect of the $-CH_3$ groups which is more in favour of $(CH_3)_3N$. Hence $(CH_3)_2NH$ is a stronger base than $(CH_3)_3N$ in aq. medium.

46. (i) Refer solution 14 on Page-102

(ii) Refer solution 9 on Page-101

47. Refer solution 22 on Page-96

48. Refer solution E 4 on Page-107

49. (i) Refer solution C (5) on Page-99

(ii) Refer solution B 3 (ii) on Page-23

50. (i) Since the phenoxide ion left after the removal of a proton is stabilized by resonance whereas alkoxide ion left after the removal of a proton from alcohol is not resonance stabilized. Thus phenol is more acidic than alcohol.

(ii) The boiling points of ethers are lower than their isomeric alcohols, due to the absence of hydrogen bonds between ether molecules. Low polarity in ethers does not cause any hydrogen bonding and hence, their boiling points are low.

On the other hand, alcohol molecules are polar and get associated through intermolecular hydrogen bonds and hence their boiling points are high.

(iii) Given reaction occurs by S_N1 mechanism and the formation of products is controlled by the stability of the carbocation resulting from the cleavage of C–O bond in protonated ether. Since tert-butyl carbocation is more stable than methyl carbocation, therefore $(CH_3)_3C-O-CH_3$ on reaction with HI gives methyl alcohol and the more stable tert-butyl iodide.

$$(CH_3)_3C-O-CH_3 \xrightarrow{H^+} \underset{\text{(more stable)}}{(CH_3)_3\overset{+}{C}} + HOCH_3$$

or

$$(CH_3)_3C-O-CH_3 \xrightarrow{H^+} (CH_3)_3COH + {}^{+}CH_3$$

(less stable)

51. Amino acids are amphoteric because they exist as dipolar ions and react with both acids as well as bases.

- **Reaction with acids**

$$R-\underset{\underset{\overset{+}{N}H_3}{|}}{CH}-COO^- \xrightarrow{H^+} R-\underset{\underset{\overset{+}{N}H_3}{|}}{CH}-COOH$$

- **Reaction with bases**

$$R-\underset{\underset{\overset{+}{N}H_3}{|}}{CH}-COO^- \xrightarrow{OH^-} R-\underset{\underset{NH_2}{|}}{CH}-COO^-$$

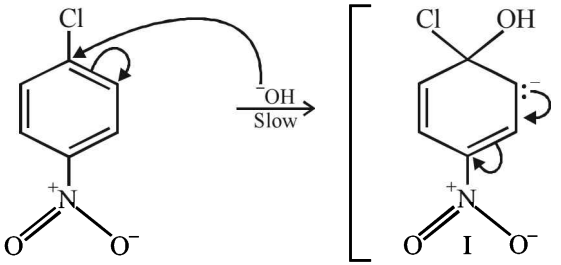
52. Vitamin C cannot be stored in the body because it is water soluble and is, therefore, easily excreted in urine.

53. (a) *n*-Butyl bromide has higher boiling point than *t*-butyl bromide as the boiling point decreases with branching. This is due to the reason that with branching the surface area of alkyl halide decreases and hence the magnitude of the van der Waal's forces of attraction also decreases.

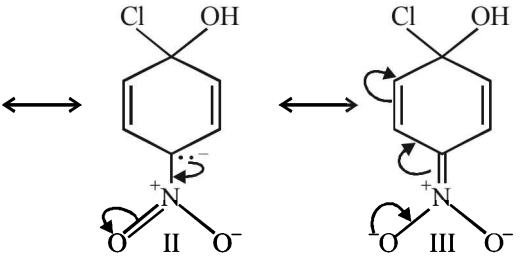
(b) Racemic mixture is an inactive form which does not rotate the plane of polarized light at all. This mixture contains equal amounts of both enantiomers (+) and (–) — forms and hence it is optically inactive.It is named (±) - mixture or racemic mixture.

(c) The presence of electron-withdrawing groups such as $-NO_2$, – CN, etc. at *o*-and *p*-positions (but not at *m*-position) w.r.t. the halogen greatly activates the halogen towards nucleophilic displacemnt. Further, greater the number of such groups at *o*-and *p*-positions w.r.t. the halogen, more reactive is the haloarene.

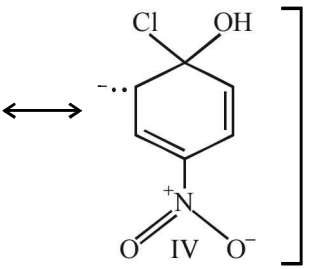
The presence of NO_2 groups at *o*- and *p*- positions withdraws electrons from the benzene ring and thus facilitates the attack of the nucleophile on haloarenes. The carbanion thus formed is stabilized by resonance as shown below:

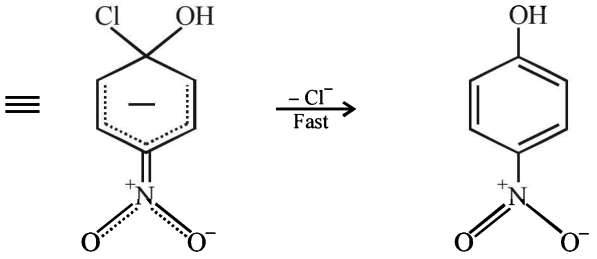


p-Chloronitrobenzene



Resonating structures





Resonance hybrid *p*-Nitrophenol

9 - WHAT IS THE CORRECT INCREASING/DECREASING ORDER?

54. (i) Refer solution 2 (i) on Page-115

(ii) Refer solution 2 (iii) on Page-115

55. Refer solution C (1) on Page-123

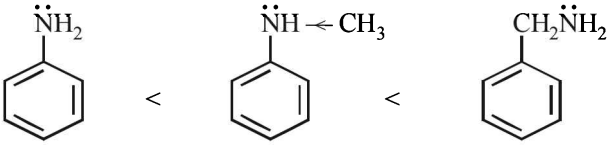
56. (i) (a) undergoes faster S_N2 because it is 1° alkyl bromide.

(b) is chiral due to chiral (*) carbon.

(ii) (a) Inversion in configuration occurs in S_N2 reactions.

(b) Racemisation occurs in S_N1 reactions, since here carbocations are formed as intermediate.

57.

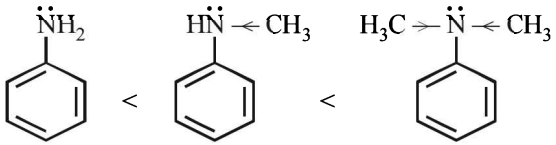


Least basic (due to delocalisation of *e* pair on N)

(Delocalisation of *e* pair possible, +I effect of $-CH_3$ gp. supplies *e* to N)

Most basic (delocalisation of *e* pair, not possible)

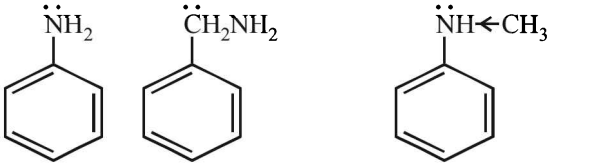
58.



No + I gp. < One + I gp. < Two + I gps.

59. S_N1 reactions involve the formation of carbocations, order of stability of carbocations is 3° > 2° > 1° hence higher the stability of carbocation, more will be the reactivity of the parent alkyl halide. Thus $(CH_3)C - Br$ undergoes S_N1 reaction faster in comparison to C_2H_5Br.

60. (i)



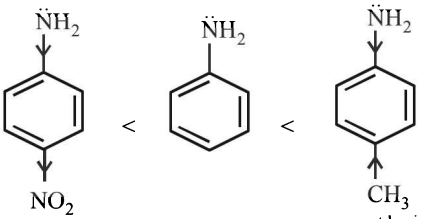
e pair of N delocalised | *e* pair on N, not delocalised | *e* pair on N delocalised ; – CH_3 group increases, *e* density on N due to +I effect (two opposite factors)

Thus the order of increasing basic strength is

$C_6H_5NH_2$ < $C_6H_5NHCH_3$ < $C_6H_5CH_2NH_2$

least basic — most basic

(ii) Nitro group is electron withdrawing and decreases basic character, while methyl group is electron repelling and increases basic character of aniline. Thus the correct order of the strength will be



least basic (*p*-nitroaniline) < (aniline) < most basic (*p*-toluidine)

61. $CH_3CHO < CH_3CH_2OH \overset{K}{<} CH_3\overset{M}{C}OO\overset{C}{H}$

The increasing order of boiling points is :

$CH_3CHO < C_2H_5OH < CH_3COOH$

The lowest boiling point of acetaldehyde is due to absence of H – bonding whereas both ethanol and acetic acid have H–bonding present in them. Now, the boiling point of acetic acid is higher due to stronger intermolecular H – bonding in it, which is due to the fact that the O – H bond in carboxylic acid is more polarized due to the presence of electron withdrawing carbonyl $(-\overset{O}{\overset{\|}{C}}-)$ group. Moreover, the negatively polarized oxygen atom of one molecule of acetic acid can form H – bond with H-atom of the other molecule. Due to this acetic acid has higher boiling point than ethanol.

62. CH_3CH_2Br would undergo S_N2 reaction faster in comparison to $(CH_3)_3C - Br$. The order of reactivity of alkyl halides towards $S_N{}^2$ reactions is affected by steric hindrance around the halogen; greater the steric hindrance around halogen, smaller will be reactivity towards $S_N{}^2$ reaction.

63. $C_2H_5OH > C_2H_5NH_2 > (CH_3)_3N$

Since the electronegativity of O is higher than that of N, therefore, alcohols form stronger H-bonds than amines. Therefore, the b.p. of C_2H_5OH (molecular mass = 46) is higher than those of $(CH_3)_3N$ and $C_2H_5NH_2$. Further, since, the extent of H-bonding depends upon the number of H-atoms on the N-atom. Therefore, 1° amines with two H-atoms on the N-atom have higher b.ps than 3° amines (of comparable molecular mass) having no H-atom. In other words, the b.p. of $C_2H_5NH_2$ is higher than that of $(CH_3)_3N$.

11 - MISCELLANEOUS QUESTIONS

64. Protein is a natural polymer.

65. Refer solution (E) (ii) on Page-30

66. (i) Refer solution 24. (viii) on Page-174

(ii) Refer solution 24. (iii) on Page-174

67. (i) Refer solution 4 (i) on Page-160

(ii) Refer solution 1(vi) on Page-159

(iii) Refer solution 1 (ix) on Page-159

68. (i) (a) Dr. Satpal performed his duty very well and showed awareness about World Health Day and tried to benefit poor people.

(b) NHRC responded quickly and so showed concern for the villagers.

(ii) Non-narcotic analgesics are used for relieving pains of terminal cancer.

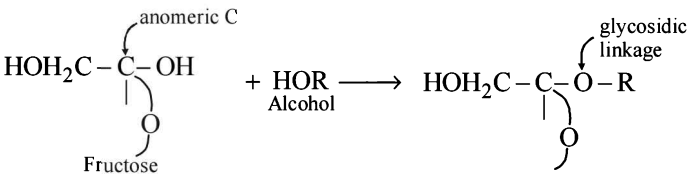
(iii) The artificial sweetening agent that can be given to diabetic patients is aspartame, saccharin, etc.

69. Refer solution 17 (b) on Page-157

70. (i) Refer solution 24 (xi) on Page-174

(ii) Refer solution 24 (x) on Page-174

71. (i) **Glycosidic linkage :** An ether type of linkage formed between the hydroxyl group of the anomeric carbon of a monosaccharide and the other –OH group (either ROH molecule or –OH group of other monosaccharide unit).



(ii) Refer solution 15 on Page-156

(iii) Refer solution 4 (2) on Page-153

72. Nylon is a synthetic fibre, neoprene is a synthetic rubber, PVC is a synthetic plastic.

73. Refer solution 17 (c) on Page-157

74. (i) Teflon : $CF_2 = CF_2$ (Tetrafluoroethylene), an addition polymer.

(ii) Buna-N : $CH_2 = CH - CH = CH_2$ and $CH_2 = CHCN$

1, 3-Butadiene Acrylonitrile (Vinyl cyanide)

75. (i) Refer solution 3 on Page-162

(ii) **Anomers :** A pair of stereoisomers which differ in configuration of C_1 in aldoses and C_2 in ketoses are called anomers.

(iii) Refer solution 1 (ii) on Page-158

76. Refer solution 18 on Page-157

77. (i) Macromolecules chosen as drug targets are proteins, nucleic acids etc.

(ii) Refer solution 3 (iv) on Page-177

78. (i) Refer solution 9 on Page-162

(ii) Refer solution 7 on Page-163

(iii) Refer solution E (i) (a) on Page-30

79. (i) The students showed awareness about the environmental hazards and were eco-friendly and trying to save Yamuna river and de-pollute the environment.

(ii) Biodegradable polymers are those which degrade in the environment and thus do not cause environmental pollution. For example : nylon-2, nylon-6

(iii) Polythene is an addition polymer as it is formed by the repeated addition of various ethene molecules as shown below :

$$\underset{\text{Ethene}}{nCH_2=CH_2} \longrightarrow \underset{\text{Polythene}}{(-CH_2-CH_2-)_n}$$

80. Refer solution 17 of All India 2014

81. Refer solution 18 on Page-157

82. (i) Refer solution 4 on Page-175

(ii) Refer solution 3 (ix) on Page-177

(iii) Macromolecules chosen as drug targets are proteins, nucleic acids, etc.

83. (i) Deficiency of vitamin D causes rickets.

(ii) Refer solution 2 on Page-160

84. Both methanol and acetone are polar molecules. Hence intermolecular interactions in them are dipole-dipole interactions.

85. Refer solution E (ii) on Page-30

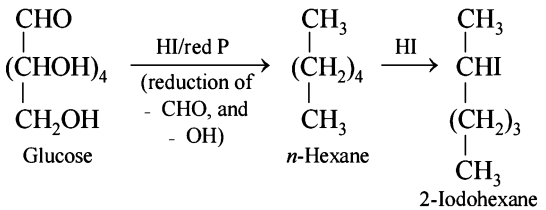
86. (i) Refer solution 3 (v) on Page-177

(ii) Macromolecules chosen as drug targets are proteins, nucleic acids, etc.

(iii) Refer solution 4 on Page-176

87. (i) Deficiency of vitamin C causes scurvy.

(ii) Refer solution 4 (i) on Page-160

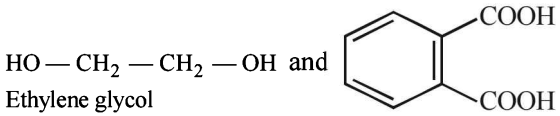
(iii)


88. (i) Monomers of buna-S are K M C

Styrene

Buta-1, 3-diene

(ii) Monomers of glyptal are phthalic acid and ethylene glycol.



Ethylene glycol

Phthalic acid

(iii) Monomer of polyvinyl chloride is vinyl chloride

$CH_2 = CHCl$

Vinyl chloride

89. (i) Some of the values displayed by Mr. Lugani are awareness, intelligence, decision making and concern for health of students.

(ii) A student can spread awareness about the concerned issue in following manners

(a) One should take part and encourage others to be a part of nutritional awareness compaigns.

(b) One should educate friends and neighbourhood about the issue.

(c) One can convince and motivate other students to form a health commitee with catchy names i.e., "eat healthy stay healthy."

(iii) **Antidepressants :** These drugs are given to patients with shattered confidence. These produce a feeling of well being and confidence in the person of depressed mood. Therefore, these are also called mood booster drugs. The common examples are vitalin, cocaine, methedrine etc.

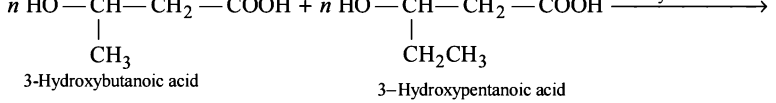
(iv) Saccharine, aspartame or alitame may be used in the preparation of sweets for a diabetic patient.

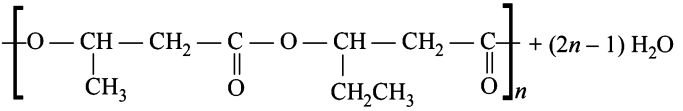
90. (i) Hexamethylenediamine and adipic acid are the monomers of nylon-6,6

$H_2NCH_2(CH_2)_4CH_2NH_2$ — Hexamethylene diamine

$HOOC\cdot(CH_2)_4\cdot COOH$ — Adipic acid

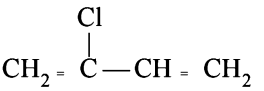
(ii)





PHBV

(iii) The monomer of neoprene is



Chloroprene or 2-chloro-1,3-butadiene.

91. (i) Maltose

(ii) **Fibrous proteins:** These have thread like molecules which lie side by side to form fibres. The various molecules are held together by hydrogen bonds. These are insoluble in water but soluble in concentrated acids and alkalies. Examples are keratin of hair, nails, wood, feathers and horn, myosin of muscles, and fibroin of silk.

Globular proteins: This type of protein has molecules folded into compact units which often acquire spheroidal shape. Such proteins are soluble in water, dilute acids and alkalies. Examples are insulin, haemoglobin, albumin, etc.

(iii) Vitamin D

92. (i) Some of the values displayed by Mr. Roy are awareness, intelligence, decision making and concern for health of students.

(ii) A student can spread awareness about the given issue in following manners

(a) One should take part and encourage others to be a part of nutritional awareness campaigns.

(b) One should educate friends and neighbourhood about the issue.

K M C

(c) One can convince and motivate other students to form a health commitee with catchy names i.e., eat healthy stay healthy

(iii) Drugs which are used for the treatment of stress, fatigue, mild and severe mental diseases are called *tranquillizers*. Examples are equanil, veronal, meprobamate, iproniazid, etc.

(iv) Use of aspartame is limited to cold foods and soft drinks because it is unstable at cooking temperature.

Board-2015 Solved Paper

(Physical Chemistry Questions)

1 - WRITE THE DEFINITION/EXAMPLE(S)/TYPE(S) OF ...

1. Write the dispersed phase and dispersion medium of butter. **[All India 2015]**

2. Define rate of reaction ? Write two factors that affect the rate of reaction. **[All India 2015]**

3. Define the following terms. **[All India 2015]**

(i) Primitive unit cells

(ii) Schottky defect

(iii) Ferromagnetism

4. Define the following terms. **[All India 2015]**

(i) Brownian movement

(ii) Peptization

(iii) Multimolecular colloids

5. What is meant by positive deviations from Raoult's law? Give an example. What is the sign of $\Delta_{mix}H$ for positive deviation? **[Delhi 2015]**

OR

Define azeotropes. What type of azeotrope is formed by positive deviation from Raoult's law? Give an example. **[Delhi 2015]**

6. Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with the decrease in concentration? **[Delhi 2015]**

2 - WHY DOES THIS HAPPEN?

7. Why does a solution containing non-volatile solute have higher boiling point than the pure solvent? **[All India 2015]**

Why is elevation of boiling point a colligative property?

8. Out of $BaCl_2$ and KCl, which one is more effective in causing coagulation of a negatively charged colloidal sol? Give reason. **[Delhi 2015]**

9. Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution:

$$Ag^+(aq) + e^- \longrightarrow Ag(s), E° = +0.80\ V$$

$$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g), E° = 0.00\ V$$

On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why?

[Delhi 2015]

10. Give reasons for the following observations:

(i) Leather gets hardened after tanning.

(ii) Lyophilic sol is more stable than lyophobic sol.

(iii) It is necessary to remove CO when ammonia is prepared by Haber's process. **[Delhi 2015]**

5 - CALCULATION BASED ON FORMULA

11. Calculate the freezing point of the solution when 31 g of ethylene glycol ($C_2H_6O_2$) is dissolved in 500 g of water (K_f for water = 1.86 K kg mol^{-1}) **[All India 2015]**

12. The rate constant of a first order reaction increases from 2×10^{-2} to 4×10^{-2} when the temperature changes from 300 K to 310 K. Calculate the energy of activation (E_a). **[All India 2015]**

(log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021)

13. Calculate e.m.f and ΔG for the following cell : **[All India 2015]**

$Mg(s) | Mg^{2+}(0.001\ M) || Cu^{2+}(0.0001\ M) | Cu(s)$

Given : $E°_{(Mg^{2+}/Mg)} = -2.37V$, $E°_{(Cu^{2+}/Cu)} = +0.34V$.

OR

The conductivity of 0.20 mol L^{-1} solution of KCl is 2.48×10^{-2} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α). Given $\lambda°(K^+) = 73.5$ S cm^2 mol^{-1} and

$\lambda°(Cl^-) = 76.5$ S cm^2 mol^{-1}. **[All India 2015]**

14. 3.9g 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}) **[Delhi 2015]**

15. An element with molar mass 27 g mol^{-1} forms a cubic unit cell with edge length 4.05×10^{-8} cm. If its density is 2.7 g cm^{-3}, what is the nature of the cubic unit cell? **[Delhi 2015]**

16. Calculate *emf* of the following cell at 25°C:

$Fe \mid Fe^{2+} (0.001\ M) \mid\mid H^+ (0.01\ M) \mid H_2 (g) (1\ bar) \mid Pt (s)$

$E^\circ_{(Fe^{2+} \mid Fe)} = -0.44\ V,\ E^\circ_{(H^+ \mid H_2)} = 0.00\ V$ **[Delhi 2015]**

17. (a) 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?

(b) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction. ($\log 2 = 0.3010$) **[Delhi 2015]**

6 - NUMERICAL BASED ON LAWS

18. How much charge is required for the reduction of 1 mol of Zn^{2+} to Zn ? **[All India 2015]**

7 - NUMERICALS BASED ON APPLICATION/SKILL

19. What is the formula of a compound in which the element Y forms *ccp* lattice and atoms of X occupy $1/3^{rd}$ of tetrahedral voids? **[Delhi 2015]**

20. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained.

t/s	0	30	60
$[CH_3COOCH_3]$mol L^{-1}	0.60	0.30	0.15

(i) Show that it follows pseudo first order reaction, as the concentration of water remains constant.

(ii) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

(Given $\log 2 = 0.3010$, $\log 4 = 0.6021$) **[Delhi 2015]**

8 - MISCELLANEOUS

21. What type of battery is mercury cell? Why is it more advantageous than dry cell? **[All India 2015]**

Hints and Solutions

1 - WRITE THE DEFINITION/EXAMPLE(S)/TYPE(S) OF ...

1. Butter is a gel colloid. Thus,
Dispersed phase is liquid
Dispersion medium is solid

2. Rate of reaction is defined as the change in concentration of reactant or product per unit time. It is always a positive quantity.
Rate of reaction

$$= \frac{\text{Total change in concentration of reactant or product}}{\text{change in time (in sec)}}$$

Factors affecting rate of reaction.
(a) Concentration of reactants
(b) Temperature
(c) Catalyst

3. (i) Primitive unit cells are defined as the unit cells in which the constituent particles are present only at the corner positions.
(ii) **Schottky defect:** It occurs when equal number of cations and anions are missing from the lattice sites. It decreases the density of the solid.
For example: NaCl, KCl.
(iii) Ferromagnetism is the phenomenon shown by substances which are strongly attracted by magnetic field. These substances show magnetism even in the absence of a magnetic field. Examples are Fe, Co, Ni and CrO_2.

4. (i) **Brownian movement :** The continuous zig-zag movement of the colloidal particles in a colloidal solution is called Brownian movement. The molecules of dispersion medium due to their kinetic motion strike against the colloidal particles from the sides with different forces.
(ii) **Peptization :** The dispersion of freshly precipitated substance into colloidal solution by the addition of some electrolytes having one common ion is known as peptization. The electrolyte used is called peptizing agent e.g., a freshly precipitated $Fe(OH)_3$ is converted into colloidal solution by adding small quantity of $FeCl_3$ to the solution of $Fe(OH)_3$.

(iii) **Multimolecular colloids :** They are formed by the aggregation of a large number of atoms or molecules which generally have diameters less than 1 nm. Their molecular masses are not very high. Their atoms or molecules are held together by weak van der Waal's forces. eg : sols of gold, sulphur, etc.

5. When the *A-B* interactions are weaker than the *A-A*/*B-B* interactions such that the total vapour pressure of the solution becomes greater than the expected vapour pressure the solution is said to show positive deviation from Raoult's law.

Solution of acetone and ethyl alcohol show positive deviation from Raoult's law.

For positive deviations, $\Delta H_{mix} = +$ ve

- $\Delta H_{mix} > 0$, Endothermic dissolution ; heat is absorbed

OR

Azeotropes are binary mixtures of two liquids having same composition in liquid and vapour phase and boil at a constant temperature and can be distilled without any change in their composition. They are formed by non–ideal solutions.

Minimum boiling azeotropes are formed by solutions showing positive deviation from Raoult's law.

These are the mixture of two liquids, whose boiling point is less than either of the two pure components.

E.g., ethanol (95.5%) + water (4.5%) mixture boiling at 351.15K.

6. Limiting molar conductivity is the molar conductivity at infinite dilution. Limiting molar conductivity of electrolytic solution is equal to sum of conductivities of individual ions which are present in electrolyte i.e.,

$$\lambda^{\infty}_{eq} = \lambda^{\infty}_{c} + \lambda^{\infty}_{a}$$

Here λ^{∞}_{eq} = Equivalent conductivity at infinite dilution

λ^{∞}_{c} = Conductivity of cation

λ^{∞}_{a} = Conductivity of anion

The specific conductivity of an electrolyte falls with dilution because the number of current-carrying particles, *i.e.*, ions present per centimeter cube of the solution becomes less and less on dilution.

2 - WHY DOES THIS HAPPEN?

7. Boiling point is a temperature at which vapour pressure of the substance becomes equal to atmospheric pressure. As the vapour pressure of the solution containing non-volatile solute is lower than that of the pure solvent and vapour pressure increases with increase in temperature. Hence, the solution has to be heated more to make its vapour pressure equal to the atmospheric pressure so that it starts boiling.

Elevation of boiling point is a colligative property because, it depends upon the number of particles of solute dissolved in solution.

8. The higher the valency of the flocculating ion, the greater is its precipitating power. Thus for the precipitation of negatively charged colloidal sol, the precipitating power of Ba^{2+} and K^{+} ions is in the order: $Ba^{2+} > K^{+}$

9. The reaction $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)., E^{\circ} = +80\ V$

is feasible at cathode, because its reduction potential has greater value.

10. (i) Tannin, which is obtained from plants, is a mixture of derivatives of polyhydroxy benzoic acids. It contains negatively charged colloidal particles. Animal hides are also colloidal in nature and contain positively charged particles. When they are soaked in tannin, their mutual coagulation takes place and leather becomes hard.

(ii) The strong forces of attraction between dispersed phase (colloidal particles) and the dispersion medium (solvent) make lyophilic colloid more stable. Lyophobic sols are electrically charged and repulsion between dispersed phase particles causes them to coagulate slowly and thus make them unstable.

(iii) CO acts as a poison for the catalyst used in the manufacture of ammonia by Haber's process. Hence, it is necessary to remove it.

5 - CALCULATION BASED ON FORMULA

11. $W_2 = 31g, W_1 = 500\ g, K_f = 1.86\ K\ kg\ mol^{-1}$

$M_2\ (C_2H_6O_2) = 24 + 6 + 32 = 62g\ mol^{-1}$

$$\Delta T_f = \frac{1000 K_f \times W_2}{W_1 \times M_2}$$

$$= \frac{1000 \times 1.86 \times 31}{500 \times 62} = 1.86\ K$$

Freezing point of pure water = 273.15 K

$\therefore$ Freezing point of solution = $T_f^\circ - \Delta T_f$

$= 273.15 - 1.86\,K$

$= 271.29\,K$

12. Given, $k_1 = 2 \times 10^{-2}$, $k_2 = 4 \times 10^{-2}$

$T_1 = 300K, T_2 = 310\,K$

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314}\left(\frac{310 - 300}{300 \times 310}\right)$$

$$\Rightarrow E_a = \frac{0.301 \times 2.303 \times 8.314 \times 300 \times 310}{10}$$

$$= 53.598\,kJ\,mol^{-1}$$

13. $Mg + Cu^{2+} \longrightarrow Mg^{2+} + Cu$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$= 0.34 - (-2.37) - \frac{0.0591}{2}\log\frac{10^{-3}}{10^{-4}}$$

$$= 2.71 - 0.02955(\log 10)$$

$$= 2.68V$$

$\Delta G = -nFE_{cell}$

$= -2 \times 96500 \times 2.68\,J$

$= -517240\,J\,mol^{-1} = -517.24\,kJ\,mol^{-1}$

OR

$$\lambda_m = \frac{\kappa \times 1000}{\text{Molarity}}$$

Molarity = $0.20\,mol\,L^{-1}$, $\kappa = 2.48 \times 10^{-2}\,S\,cm^{-1}$

$$\lambda_m = \frac{2.48 \times 10^{-2} \times 1000}{0.20} S\,cm^2 mol^{-1}$$

$$= 124\,S\,cm^2\,mol^{-1}$$

Degree of dissociation, α

$$\alpha = \frac{\lambda_m^{\,c}}{\lambda_m^{\,\infty}}$$

$$\lambda_m^{\,\infty} = \lambda^\circ(K^+) + \lambda^\circ(Cl^-)$$
$$= (73.5 + 76.5)\ S\ cm^2\ mol^{-1}$$
$$= 150.0\ S\ cm^2\ mol^{-1}$$

$$\alpha = \frac{124}{150} = 0.826$$

or 82.6 %

14. Using the relation,

$$M_2(\text{observed}) = \frac{1000\ K_f W_2}{W_1\ \Delta T_f}$$

$$= \frac{1000 \times (4.9K\ kg\ mol^{-1}) \times 3.9g}{49g \times 1.62K}$$

$$= 240.7\ g\ mol^{-1}$$

M_2 (calculated) = 122g mol^{-1}

$$i = \frac{M_2(\text{calculated})}{M_2(\text{observed})}$$

$$= \frac{122}{240.7} = 0.51$$

$$i < 1$$

Nature of solute is associated.

15. Given: Density, $d = 2.7 \times 10^3\ kg\ m^{-3}$

$a = 405\ pm$

$= 405 \times 10^{-12}\ m$

$M = 2.7 \times 10^{-2}\ kg\ mol^{-1}$

Density of a unit cell is given as

$$d = \frac{Z \times M}{a^3 N_A}$$

$$\Rightarrow Z = \frac{d\ a^3 N_A}{M}$$

$$= \frac{(2.7 \times 10^3)(405 \times 10^{-12})^3\ (6.022 \times 10^{23})}{2.7 \times 10^{-2}}$$

$$= 3.99 \simeq 4$$

Therefore, it is a *fcc* unit cell.

16. Cell reaction for given cell :

$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2 \ (n = 2)$

Nernst equation:

$$E_{cell} = E^\circ_{cell} - \frac{0{\cdot}0591}{2} \log \frac{[Fe^{2+}]}{[H^+]^2}$$

$$\therefore E_{cell} = 0 - (-0{\cdot}44) - \frac{0{\cdot}0591}{2} \log \frac{10^{-3}}{(10^{-2})^2}$$

$$= 0{\cdot}44 - \frac{0{\cdot}0591}{2} \times \log(1)$$

$$= 0{\cdot}44 - 0.02955$$

$$= 0.41045\text{V} \approx 0.41\text{V}$$

17. (a) Rate $= k[A]\,[B]^2$

(i) If concentration of B is doubled, then rate will be increased by 4 times.

Rate $= [B]^2 = (2)^2 = 4$

(ii) If A is present in large excess, then the reaction will be independent of the concentration of A and will be dependent only on concentration of B. As $[B]^2$ will be the only determining factor in the order of reaction, the overall order of reaction will be two.

(b) $t_{1/2} = \dfrac{0.693}{k}$

$$\Rightarrow k = \frac{0.693}{30} = 0.0231 \text{ min}^{-1}$$

On substituting

$$t = \frac{2.303}{k} \log \frac{a}{a - x}$$

$$= \frac{2.303}{0.0231} \times \log \frac{100}{100 - 90}$$

$$= \frac{2.303}{0.0231} \times \log 10$$

$= 99.69$ minutes.

6 - NUMERICAL BASED ON LAWS

18. The electrode reaction is $Zn^2 + 2e^- \rightarrow Zn$

Number of electrons involved = 2

$\therefore$ Quantity of charge required for reduction of 1 mol of $Zn^{2+} = 2 \times F$

$= 2 \times 96500$ C

$= 193000$ C

7 - NUMERICALS BASED ON APPLICATION/SKILL

19. Let the number of atoms of element Y present in $ccp = x$

Therefore, the number of tetrahedral voids $= 2x$

As 1/3rd of tetrahedral voids are occupied by atoms of element X,

therefore, number of atoms of X present $= \frac{1}{3} \times 2x = \frac{2x}{3}$.

$\therefore$ Ratio of Y : X $= x : \frac{2x}{3} = 3x : 2x = 3 : 2$

$\therefore$ The formula of the compound will be $= Y_3X_2$ or X_2Y_3.

20. (i) $CH_3COOCH_3 + H_2O \rightleftharpoons CH_3COOH + CH_3OH$

Rate $= k' [CH_3COOCH_3] [H_2O]$

But, $[H_2O]$ concentration remains constant therefore,

we put $k' [H_2O] = k$, so rate $= k [CH_3COOCH_3]$

Hence, it a pseudo first order reaction.

(ii) Rate of reaction between 30-60 seconds

$$= \frac{c_2 - c_1}{t_2 - t_1} = \frac{0.30 - 0.15}{60 - 30} = \frac{0.15}{30}$$

$= 5 \times 10^{-3}$ mol L^{-1} s^{-1}

8 - MISCELLANEOUS

21. Mercury cell is a type of primary battery. In primary batteries, the charging reaction occurs only once and after it has been used over a period of time, the battery becomes dead and cannot be reused. Mercury cell is more advantageous than dry cell because dry cell has a very short life span due to the conversion of zinc to zinc chloride that makes the zinc casing porous. Due to this porous casing, the substance inside the cell leaks out and corrodes the metal, reducing the lifetime of the cell. While, in the case of mercury cell, the overall reaction does not involve formation of any ion in the solution whose concentration can change during its life time.

Board-2015 Solved Paper

(Inorganic Chemistry Questions)

1 - WHAT ARE THE STRUCTURES OF THE FOLLOWING COMPOUNDS/IONS?

1. Write the structure of the following molecules. **[All India 2015]**

(i) H_2SO_3 (ii) $XeOF_4$

2. Write down the IUPAC name of the complex $[Pt(en)_2Cl_2]^{2+}$. What type of isomerism is shown by this complex? **[All India 2015]**

OR

Using IUPAC norms write the formulae for the following coordination compounds. **[All India 2015]**

(i) Hexaamminecobalt (III) chloride

(ii) Potassium tetrachloridonickelate (II)

3. Write the hybridization and shape of the following complexes. **[All India 2015]**

(i) $[CoF_6]^{3-}$

(ii) $[Ni(CN)_4]^{2-}$

(Atomic number : Co = 27, Ni = 28)

4. (i) Write down the IUPAC name of the following complex:
$[Cr(NH_3)_2Cl_2(en)]Cl$ (en = ethylenediamine)

(ii) Write the formula for the following complex:
Pentaamminenitrito-o-cobalt (III) **[Delhi 2015]**

5. Draw the geometrical isomers of the complex $[Pt(NH_3)_2Cl_2]$ **[Delhi 2015]**

6. Draw the structures of the following.

(i) ClF_3

(ii) XeF_4 **[Delhi 2015]**

2 - WHAT IS THE ROLE OF THE FOLLOWING?

7. What is the role of silica in the extraction of copper? **[All India 2015, Delhi 2015]**

3 - WHAT OR WHICH PRINCIPLE IS INVOLVED IN THE FOLLOWING PROCESSES?

8. What is the principle behind the zone refining of metals? **[All India 2015]**

9. Indicate the principle behind the method used for the refining of zinc. **[Delhi 2015]**

4 - WHY DO THE FOLLOWING HAPPENS?

10. Zn^{2+} salts are, white while Cu^{2+} salts are coloured. Why? **[All India 2015]**

11. Give reasons for the following. **[All India 2015]**

(i) N_2 is less reactive at room temperature.

(ii) H_2Te is the strongest reducing agent amongst all the hydrides of Group 16 elements.

(iii) Helium is used in diving apparatus as a diluent for oxygen.

12. Out of NH_3 and CO, which ligand forms a more stable complex with a transition metal and why? **[All India 2015]**

13. Account for the following. **[All India 2015]**

(i) Zr and Hf have almost similar atomic radii.

(ii) Transition metals show variable oxidation states.

(iii) Cu^+ ion is unstable in aqueous solution.

14. (a)

$E^\circ_{M^{2+}/M}$	Cr	Mn	Fe	Co	Ni	Cu
	–0.91	–1.81	–0.44	–0.28	–0.25	–0.34

From the given data of E° values, answer the following questions.

(i) Why is $E^\circ_{(Cu^{2+}/Cu)}$ value exceptionally positive?

(ii) Why is $E^\circ_{(Mn^{2+}/Mn)}$ value highly negative as compared to other elements?

(iii) Which is a stronger reducing agent Cr^{2+} or Fe^{2+} ? Give reason.

(b) Why do actinoids show a wide range of oxidation states? Write on similarity between the chemistry of lanthanoids and actinoids. **[All India 2015]**

15. How would you account for the following :

(i) Actinoid contraction is greater than lanthanoid contraction.

(ii) Transition metals form coloured compounds **[Delhi 2015]**

16. Account for the following.

(i) Acidic character increases from HF to HI.

(ii) There is large difference between the melting and boiling points of oxygen and sulphur.

(iii) Nitrogen does not form pentahalide. **[Delhi 2015]**

17. (i) Which allotrope of phosphorus is more reactive and why?

(ii) How the supersonic jet aeroplanes are responsible for the depletion of ozone layer?

(iii) F_2 has lower bond dissociation enthalpy than Cl_2. Why? **[Delhi 2015]**

7 - COMPLETE THE FOLLOWING

18. Complete the following equations. **[All India 2015]**

(i) $2\,MnO_2 + 4\,KOH + O_2 \rightarrow$

(ii) $2\,Na_2CrO_4 + 2H^+ \rightarrow$

(iii) $2MnO_4^- + 6H^+ + 5NO_2^- \rightarrow$ **[Delhi 2015]**

19. Complete the equation:

$XeF_2 + PF_5 \rightarrow$ **[Delhi 2015]**

9 - MISCELLANEOUS

20. How is 'cast iron' different from 'pig iron'? **[All India 2015]**

21. What is the basicity of H_3PO_4? **[Delhi 2015]**

22. What are the transition elements? Write two characteristics of the transition elements. **[Delhi 2015]**

23. Which form of the iron is the purest form of commercial iron? **[Delhi 2015]**

24. On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_0 < P$. **[Delhi 2015]**

25. Write the hybridization and magnetic behaviour of the complex $[Ni(CO)_4]$.

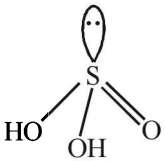
(At.no. of Ni = 28) **[Delhi 2015]**

26. Which noble gas is used in filling balloons for meteorological observations? **[Delhi 2015]**

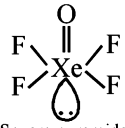
Hints and Solutions

1 - WHAT ARE THE STRUCTURES OF THE FOLLOWING COMPOUNDS/IONS?

1. (i) Sulphurous acid (H_2SO_3)



(ii)



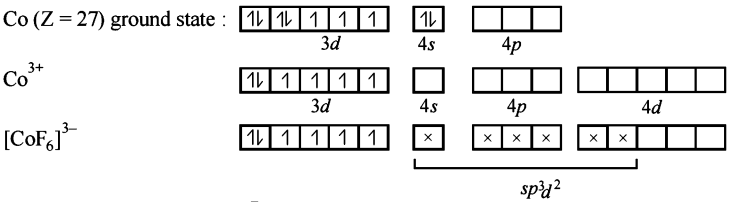
Square pyramidal

2. IUPAC name :
Dichlorido bis(ethylenediamine) platinum (IV)
Geometrical isomerism is shown by this complex.

OR

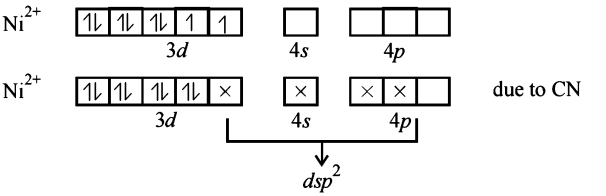
(i) $[Co(NH_3)_6]Cl_3$
(ii) $K_2[NiCl_4]$

3. (i) $[CoF_6]^{3-}$ is sp^3d^2 hybridised, octahedral in shape and paramagnetic in nature.



As F^- ions are weak ligands, pairing of electrons does not take place.

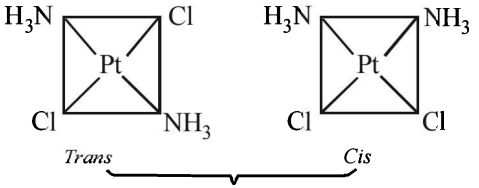
(ii) $[Ni(CN)_4]^{2-}$ is dsp^2 hybridised, square planar in shape and diamagnetic in nature.



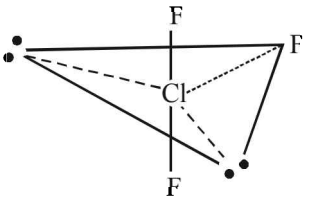
As CN^- ions are strong ligands, pairing of electrons will take place

4. (i) Diamminedichloroethylenediaminechromium (I) chloride
   (ii) $[Co(NH_3)_5(ONO)]^{2+}$

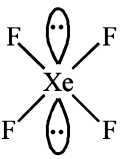
5. Geometrical isomers of $Pt(NH_3)_2Cl_2$ are following



6. (i)



   (ii) **XeF_4**



Square planar

2 - WHAT IS THE ROLE OF THE FOLLOWING?

7. SiO_2 acts as an acidic flux. Copper ore is heated with silica in a reverberatory furnance when FeO is removed as $FeSiO_3$ (slag) and copper is produced in the form of copper matte.

3 - WHAT OR WHICH PRINCIPLE IS INVOLVED IN THE FOLLOWING PROCESSES?

8. Zone refining is based on the fact that the impurities are more soluble in the melt than in the solid state of the metal. In the process, one end of the impure metal rod is heated by means of a movable heater. The molten zone carrying impurities moves forward. In this way impurities are concentrated at the other end of the rod which is cut off. The process is repeated several times to obtain ultrapure metals (Ge, Si, Ga and In) used as semiconductors.

9. **Electrolytic refining :** Impure zinc is made the anode while pure zinc strip is made the cathode. $ZnSO_4$ solution acidified with dil. H_2SO_4 is the electrolyte used. On passing electric current, pure zinc gets deposited on the cathode.

4 - WHY DO THE FOLLOWING HAPPENS?

10. Zn^{2+} has completely filled *d*-orbitals, while Cu^{2+} has incompletely filled *d*-orbitals. That is why, Zn^{2+} salts are white whereas Cu^{2+} salts are coloured.

11. (i) Due to presence of triple bond between two N-atoms (N ≡ N), the bond dissociation energy of N_2 is very high. As a result, N_2 becomes less reactive at room temperature.
    (ii) The reducing character increases from H_2S to H_2Te. This is because as the size of the atom E in H_2E increases, the bond H—E becomes weaker and thus breaks more easily on heating.
    (iii) Because of low solubility of the (as compared to N_2) in blood, a mixture of oxygen and helium is used in diving apparatus used by deep sea divers.

12. Since CO can form σ as well as π bond, whereas NH_3 has lone pair of electrons and can form σ bond only.
    Therefore, CO is better complexing reagent and forms a more stable complex than NH_3.

13. (i) Zr and Hf have similar atomic radii due to lanthanide contraction. In lanthanoid series, with increasing atomic number, there is a progressive decrease in atomic as well as ionic radii of trivalent ions from La^{3+} to Lu^{3+}. This regular decrease in the atomic and the ionic radii of lanthanoids with increasing atomic number is known as lanthanoid contraction.
    (ii) The transition elements show variable oxidation states because the energies of $(n-1)d$ orbitals and *ns* orbitals are very close. Hence, electrons from both of these orbitals can participate in bonding.
    (iii) Copper (I) compound are unstable in aqueous solution and undergo disproportionation to give more stable Cu^{2+} and Cu.

$$2Cu^{+} \longrightarrow Cu^{2+} + Cu$$

The high stability of Cu^{2+} (aq) rather than Cu^{+} (aq) is due to the much more negative $\Delta_{hyd}H$ of Cu^{2+} (aq) than Cu^{+} (aq), which is more than that compensates for the second ionisation enthalpy of Cu.

14. (a) (i) $E^\circ_{M^{2+}/M}$ for any metal is related to the sum of enthalpy changes taking place in following steps :

$$M(s) + \Delta_a H \rightarrow M(g)$$
$$M(g) + \Delta_i H \rightarrow M^{2+}(g)$$
$$M^{2+}(g) + aq \rightarrow M^{2+}(aq) + \Delta_{hyd} H$$

Cu has a high enthalpy of atomisation ($\Delta_a H$) and a low enthalpy of hydration ($\Delta_{hyd} H$). The high energy required to transform Cu(s) to $Cu^{2+}(aq)$ is not balanced by its hydration enthalpy. Hence, $E^\circ(Cu^{2+}/Cu)$ is positive.

(ii) $E^\circ_{Mn^{2+}/Mn}$ is highly negative because it is difficult to reduce Mn^{2+} to Mn as it has already half-filled d-orbital which leads to extra stability. However, Mn can be easily oxidized to Mn^{2+}.

(iii) Cr^{2+} is a stronger reducing agent than Fe^{2+}. This is because $E^\circ(Cr^{3+}/Cr^{2+})$ is negative (– 0.41V) whereas $E^\circ(Fe^{3+}/Fe^{2+})$ is positive (+ 0.77V). Thus, Cr^{2+} is easily oxidised to Fe^{3+} but Fe^{2+} cannot be easily oxidised to Fe^{3+}.

(b) Actinoid elements show wide range of oxidation states due to comparable energies of 5f, 6d and 7s levels.

(i) **Electronic configuration :** In both lathanoids and actionoids, f-orbitals are progressively filled. In lanthanoids 4f- orbitals are progressively filled, whereas in actinoids 5f-orbitals are progressively filled.

(ii) **Oxidation states :** Common oxidation state of lanthanoids and actinoids is +3. Some lanthanoids show +2 and +4 oxidation state also. Actinoids shows +3, +4, +5 +6, +7 oxidation states. Although +3 and +4 are most common.

(iii) Lanthanoids and actinoids both shows atomic/ionic size contraction.

(iv) **Chemical reactivity :** Both are highly reactive and exhibit similar chemical properties.

15. (i) Actinoid contraction is greater than lanthanoid contraction due to poor shielding effect of 5f electrons. Further, 5f orbitals extend in space beyond 6s and 6p orbitals whereas 4f orbitals are buried deep.

(ii) Transition metals have incompletely filled d-orbitals and thus unpaired electrons which can undergo $d - d$ transitions by absorbing radiations from visible region. As a result of absorption of light in visible region, they radiate complimentary colour.

K M C

16. (i) The strength of an acid depends upon its degree of ionization which, in turn, depends upon bond strength.

$$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$$

Thus, higher the bond dissociation energy, lower is the degree of ionization and hence weaker is the acid. The bond dissociation energies of the halogen acids increase in the order :

K_a	HF	<	HCl	<	HBr	<	HI
	7×10^{-4}		7×10^{8}		7×10^{10}		7×10^{11}

Thus HF is the weakest acid and HI is the strongest acid.

(ii) As we move down the group, the atomic size increases. As a result, van der Waal's, forces of attraction also increases from O to S. Due to small size and high electronegativity, oxygen atom forms $p\pi - p\pi$ double bond with other oxygen atom to form $O = O$ bonds. Oxygen has weak van der Waal's forces, so exists as gas, i.e. boils at low temperature as compared to sulphur.

(iii) Electronic configuration of N is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. It has no vacant *d*-orbitals. Nitrogen can only form $p\pi$ - $p\pi$ multiple bonds, hence NX_5 is not possible.

17. (i) White phosphorus is less stable and more reactive due to angular strain in the P_4 molecule where the angles are only 60°.

(ii) Nitrogen oxides (emitted from jet aeroplanes) combine rapidly with ozone resulting in its depletion in upper atmosphere.

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

(iii) Actually, the bond energy should have decreased from F – F to I – I but in practice it starts decreasing from Cl – Cl to I – I.

F – F	Cl – Cl	Br – Br	1 – I
38 kcal/mole	57 kcal/mole	45.5 kcal/more	35.6 kcal/mole

The lower value of bond dissociation energy of F – F bond than Cl – Cl bond is due to larger inter-electronic (electron-electron) repulsion between the non-bonding electrons in the 2*p*-orbitals of fluorine atom than those in the 3*p*-orbitals of chlorine atoms. Moreover, the X – X bond in Cl_2, Br_2 and I_2 is much stronger due to hybridisation of *p*- and *d*-orbitals.

7 - COMPLETE THE FOLLOWING

18. (i) $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$

(ii) $2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

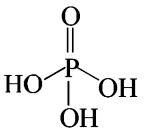
(iii) $2MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow 2Mn^{2+} + 3H_2O + 5NO_3^-$

19. $XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^-$

20. The iron obtained from blast furnace is called **pig iron**. It contains about 4% carbon and many other impurities in smaller amount (*eg.*, S, P, Si and Mn).

Cast iron is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

21. Orthophosphoric acid, H_3PO_4 contains three P – OH bonds and is therefore, tribasic.



Orthophosphoric acid

22. The elements which lie between '*s*' and '*p*' block are called '*d*' block elements or transition elements because of their position between *s*- and *p*-block elements.

General electronic configuration of '*d*' block elements is $(n-1)d^{1-10}ns^{1-2}$.

Alternatively, elements which have incomplete *d*-subshell or partly filled '*d*'- orbital in ground or common oxidation state are called as transition elements.

Two Important Characteristic Properties of Transition Elements

(i) Coloured ions : Most of the transition metal compounds are coloured. This is due to the presence of unpaired electrons in their '*d*' orbitals. They require less amount of energy to undergo excitation of electrons. Hence they absorb energy in visible region of light and thus exhibit colour.

(ii) Complex formation : Transition metal ions have small size and high positive charge i.e., high charge density. Due to this, they have a tendency to accept electrons. As they have vacant *d*-orbitals, they can accept lone pairs of electrons thus forming coordinate covalent bond.

23. **Wrought or malleable iron** is the purest form of iron containing about 0.1 to 0.25% carbon. It is malleable.

24. When $\Delta_0 < P$, the d^4 has configuration $t_{2g}3_{e_g}1$

e_g

i.e.,

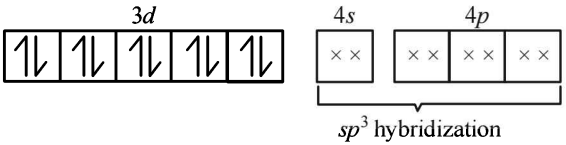
t_{2g}

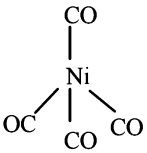
25. Oxidation state of Ni in $\overset{K}{Ni}(\overset{M}{CO})_4$ is $\overset{C}{zero}$

$Ni = 3d^8\,4s^2$

CO being a strong field ligand transfers the 4*s* electrons into 3*d* orbitals and makes the 4*s* orbital available for bonding as shown below

Ni =

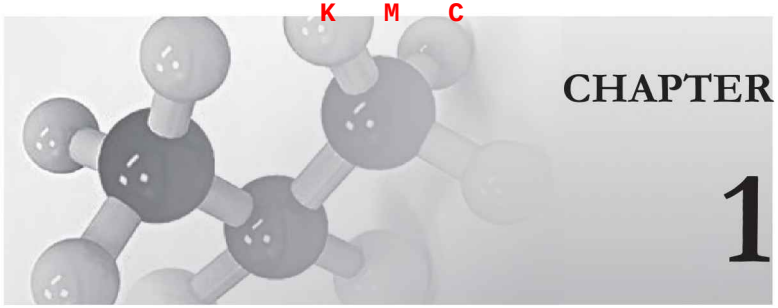




Structure : Tetrahedral

Magnetic behaviour : Diamagnetic

26. Helium is used for a number of reasons. It is light, cheap, and does not dissolve in blood the same way that nitrogen does. Being inert it cannot be toxic to the diver or corrosive to equipment. Moreover at extreme depths the pressure is high enough that if you had nitrogen in the tank it would become saturated enough in your blood that you would develop nitrogen narcosis. Helium won't be absorbed across the alveoli and will not react with your body so it is used for extreme depth's.



CHAPTER

1

What are the IUPAC names/structures of the following compounds ?

(A) Hydrocarbons and halogen derivatives.

Q1. What will be the IUPAC name of the following?

(i) $(CH_3)_3CCH_2Br$ **(Delhi 2011, AI 2010C)**

(ii) $CH_2{=}CHCH_2Br$ **(AI 2011)**

(iii) $CH_2{=}\underset{\underset{CH_3}{|}}{C}{-}CH_2Br$ **(Delhi 2012)**

(iv) $CH_3{-}\underset{\underset{Cl}{|}}{CH}{-}CH_2{-}CH{=}CH_2$ **(Delhi 2013)**

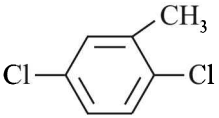
(v) $CH_3CH{=}CH{-}\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}{-}CH_3$ **(Delhi 2013)**

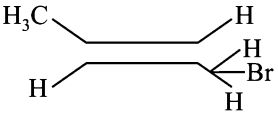
(vi) $(CH_3)_2CHCH(Cl)CH_3$ **(Delhi 2013)**

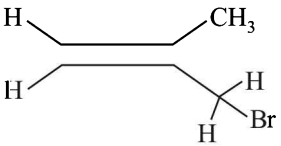
(vii) $CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}\underset{\underset{Cl}{|}}{CH}{-}CH_3$ **(AI 2013)**

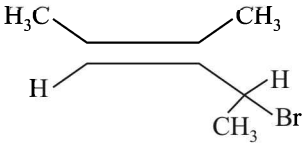
(viii) $CH_3{-}\underset{\underset{Br}{|}}{CH}{-}CH_2{-}\underset{\underset{Cl}{|}}{CH}{-}CH_3$ **(AI 2013)**

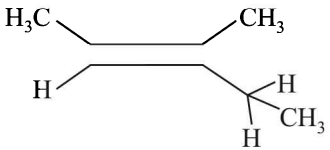
113 Approved: 0777 023 444

(ix)  **(AI 2013)**

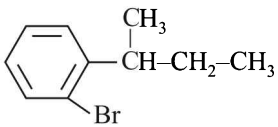
(x)  **(Delhi 2008)**

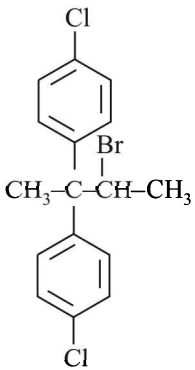
(xi)  **(AI 2011, 2012)**

(xii) 

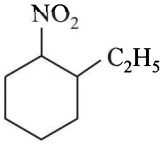
(xiii)  **(AI 2012 C)**

(xiv) $ClCH_2C{\equiv}CCH_2Br$ **(AI 2008C)**

(xv)  **(AI 2008C)**

(xvi)  **(AI 2008C)**

(xvii) $CH_3-\underset{CH_3}{\underset{|}{C}}=\underset{Br}{\underset{|}{C}}-CH_2OH$ **(AI 2013C)**

(xviii) 

(Delhi 2013C)

Q2. What will be the structure of the compound (s) given below?

(i) 2-Chloro-3-methylpentane. **(AI 2009C, 2011C)**

(ii) 4-*tert*-Butyl-3-iodoheptane. **(AI 2010C)**

(iii) 1-Chloro-4-ethylcyclohexane. **(AI 2010C)**

(iv) 1, 4-Dibromobut-2-ene. **(Delhi 2011C, AI 2010C)**

(v) 2-(2-Bromophenyl) butane. **(Delhi 2011C)**

(vi) 1-(4-Chlorophenyl)-2-methylpropane. **(Delhi 2011C)**

(vii) 2-(2-Chlorophenyl)-1-iodooctane. **(AI 2011C)**

(viii) 1-Bromo-4-*sec*-butyl-2-methylbenzene. **(AI 2011C)**

(ix) 4-Methylpent-3-en-2-one **(Delhi 2013C)**

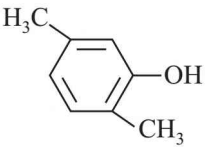
(B) Alcohols and Ethers.

Q1. What will be the IUPAC name of the following?

(i) $CH_3CH{=}CH{-}\underset{\underset{OH}{|}}{CH}{-}CH_2CH_3$ **(Foreign 2012)**

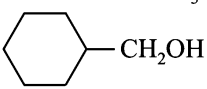
(ii) $CH_2{=}CH{-}\underset{\underset{OH}{|}}{CH}{-}CH_2CH_2CH_3$ **(Delhi 2012, AI 2009)**

(iii) $CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_2{-}\underset{\underset{OH}{|}}{CH}{-}\underset{\underset{CH_3}{|}}{CH}CH_2OH$ **(Delhi 2008)**

(iv) 

(AI 2008 C)

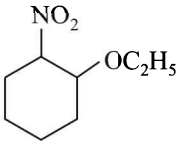
(v) $CH_3{-}O{-}CH_2{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_2CH_3$ **(Delhi, 2008, AI 2008)**

(vi) 

(vii) $CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}CH_2{-}CH_2OH$

(viii) $CH_3{-}\underset{\underset{Br}{|}}{CH}{-}\underset{\underset{Br}{|}}{CH}{-}CH_2{-}\underset{\underset{OH}{|}}{CH}{-}CH_3$

(ix) $CH_3-\underset{OH}{CH}-\underset{OH}{CH}-\underset{Br}{CH}-CH_2OH$ **(AI 2002)**

(x)  **(Delhi 2009, AI 2012C)**

(xi) $CH_3-O-CH_2-\underset{CH_3}{CH}-CH_3$ **(Foreign 2012)**

(xii) $CH_3-\overset{CH_3}{\overset{|}{C}}=\underset{Br}{\underset{|}{C}}-CH_2OH$ **(AI 2012C, Foreign 2011)**

Q2. What will be the structure of the compound (s) given below?

(i) Hex-1-en-3-ol. **(Delhi 2012)**

(ii) 2-Methylpropan-2-ol. **(Delhi 2012)**

(iii) 2, 6-Dimethylphenol. **(AI 2011)**

(iv) 1-Phenylpropan-2-ol. **(AI 2010)**

(v) 2-Methyl-2-ethoxypentane. **(Delhi 2009 C)**

(C) Aldehydes and ketones.

Q1. What will be the IUPAC name of the following?

(i) $CH_3-CH_2-CH=CH-CHO$ **(AI 2012)**

(ii) $CH_3-\underset{O}{\underset{\|}{C}}-CH=\underset{CH_3}{\underset{|}{C}}-CH_3$ **(Delhi 2010C, AI 2011C, Foreign 2010)**

(iii) $CH_3-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_2COCH_3$ **(Delhi 2009C)**

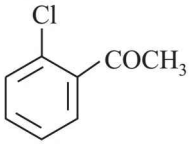
(iv) $(CH_3)_2CH-CH_2-\underset{O}{\underset{\|}{C}}-CH(CH_3)_2$ **(AI 2009C)**

(v) $CH_3-\underset{O}{\underset{\|}{C}}-CH_2-\underset{Cl}{\underset{|}{CH}}-CH_3$ **(Delhi 2009)**

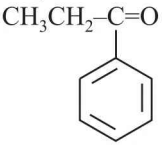
(vi) $CH_3-\underset{CH_3}{\underset{|}{CH}}-CO-\underset{CH_3}{\underset{|}{CH}}-CH_3$ **(Delhi 2007)**

(vii) $CH_3COCH_2COCH_3$ **(AI 2006, 2007, Foreign 2007)**

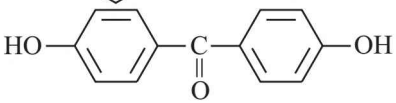
(viii) $CH_3CH(CH_3)CH_2C(CH_3)_2COCH_3$ **(Foreign 2006)**

(ix) 

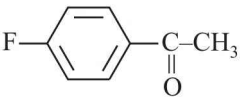
(AI 2010C)

(x) 

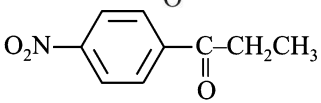
(Delhi 2009 C, 2011C)

(xi) 

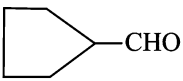
(Delhi 2008C)

(xii) 

(Delhi 2010C)

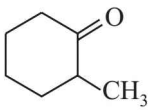
(xiii) 

(Delhi 2010C, 2011C)

(xiv) 

(AI 2010 C)

(xv) Ph–CH=CHCHO **(AI 2012)**

(xvi) 

(AI 2012C)

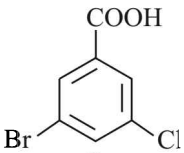
Q2. What will be the structure of the compound (s) given below?

(i) 3-Methylbutanal. **(Delhi 2011, 2013)**
(ii) 4-Chloropent-2-one. **(Delhi 2013, AI 2008, 2011)**
(iii) 4-Methylpent-3-en-2-one. **(Foreign 2012)**
(iv) 3-Oxopentanal. **(Delhi 2009, Foreign 2009, 2011)**
(v) 2-Chloro-3-methylpentanal. **(AI 2011 C)**
(vi) 1-Phenylpropan-1-one. **(Delhi 2010)**
(vii) Pent-2-en-1-al. **(Foreign 2009)**
(viii) 1-Phenylpentan-1-one. **(AI 2009)**
(ix) *p*-Methylbenzaldehyde. **(Delhi 2013)**
(x) *p*-Nitropropiophenone. **(Foreign 2012)**
(xi) 3-Methylbutanal. **(Delhi 2011, Foreign 2012)**
(xii) 4-Hydroxy-4-methylpentan-2-one. **(Foreign 2012)**
(xiii) Hexan-1, 6-dioic acid. **(Foreign 2012)**

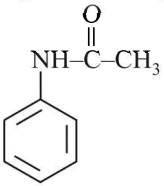
(D) Carboxylic acids.

Q1. What will be the IUPAC name of the following?

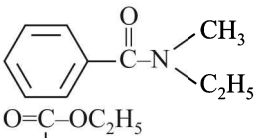
(i) $CH_3–C≡C–CH=CH–\overset{\overset{O}{||}}{C}–OH$ **(Delhi 2008C, Delhi 2011C, AI 2011C)**

(ii) 

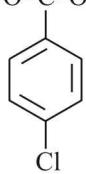
(AI 2011 C)

(iii) 

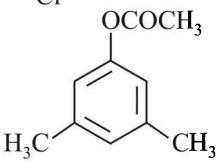
(Delhi 2012 C)

(iv) 

(Delhi 2008C)

(v) 

(AI 2009C)

(vi) 

(Delhi 2011C)

(E) Amines.

Q1. What will be the IUPAC name of the following?

(i) $H_2N–CH_2–CH_2–CH=CH_2$ **(Delhi 2010)**

(ii) $CH_2=CH–\underset{\underset{CH_3}{|}}{CH}–NH_2$ **(Delhi 2012 C)**

Q2. What will be the structure of the compound (s) given below?

(i) N, N-Ethylmethylamine. **(Delhi 2010 C)**

(ii) N-Methylethanamine. **(AI 2013)**

(iii) 2-Aminotoluene. **(AI 2013)**

(iv) Prop-2-en-1-amine. **(AI 2013)**

(A) Hydrocarbons and halogen derivatives.

Sol. 1

(i) 1-Bromo-2, 2-dimethylpropane.

(ii) 1-Bromoprop-2-ene.

(iii) 3-Bromo-2-methylpropene.

(iv) 4-Chloropent-1-ene.

(v) 4-Bromo-4-methylpent-2-ene.

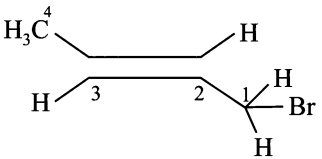
(vi) 2-Chloro-3-methylbutane.

(vii) 2-Chloro-3,3-dimethylbutane.

(viii) 2-Bromo-4-chloropentane.

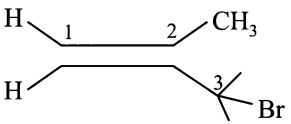
(ix) 2,5-Dichlorotoluene.

(x)



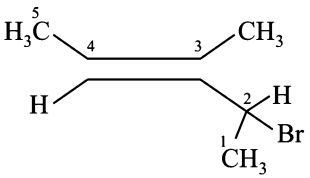
1-Bromobut-2-ene

(xi)



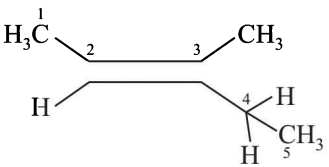
3-Bromo-2-methylprop-1ene

(xii)



2-Bromo-3-methylpent-3-ene

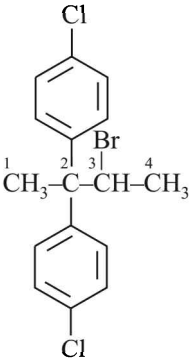
(xiii)



3-Methylpent-2-ene

(xiv) 1-Bromo-4-chlorobut-2-yne.

(xv) 1-Bromo-2-sec-butylbenzene.

(xvi) 

3-Bromo-2, 2-bis (4-chlorophenyl) butane

(xvii) 2-Bromo-3-methylbut-2-enol

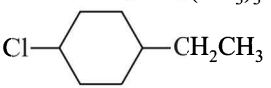
(xviii) 1-Ethyl-2-nitrocyclohexane

Sol. 2

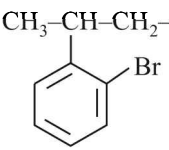
(i) $H_3\overset{1}{C}-\overset{2}{C}H(Cl)-\overset{3}{C}H(CH_3)-\overset{4}{C}H_2-\overset{5}{C}H_3$

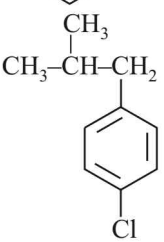
2-Chloro-3-methylpentane

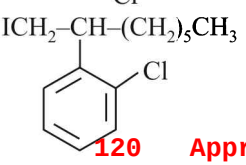
(ii) $H_3\overset{1}{C}-\overset{2}{C}H_2-\overset{3}{C}H(I)-\overset{4}{C}H(C(CH_3)_3)-\overset{5}{C}H_2-\overset{6}{C}H_2-\overset{7}{C}H_3$

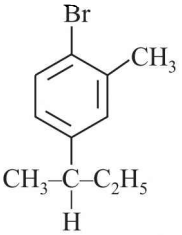
(iii) 

(iv) $BrCH_2-CH=CH-CH_2Br$

(v) 

(vi) 

(vii) 

(viii) 

(ix) $CH_3-\overset{\overset{O}{\|}}{C}-CH=\overset{\overset{CH_3}{|}}{C}-CH_3$

(B) Alcohols and Ethers.

Sol. 1

(i) Hex-4-en-3-ol.

(ii) Hex-1-en-3-ol.

(iii) 2, 5-Dimethylhexan-1, 3-diol.

(iv) 2, 5-Dimethylphenol.

(v) 1-Methoxy-2-methylbutane.

(vi) Cyclohexylmethanol.

(vii) 3, 3-Dimethylbutan-1-ol.

(viii) 4, 5-Dibromohexan-2-ol.

(ix) 2-Bromo-1,3,4-pentanetriol.

(x) 2-Ethoxynitrocyclohexane.

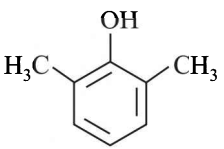
(xi) 1-Methoxy-2-methylpropane.

(xii) 2-Bromo-3-methylbut-2-en-1-ol.

Sol. 2

(i) $CH_3CH_2CH_2\underset{\underset{OH}{|}}{C}HCH=CH_2$

(ii) $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$

(iii) 

(iv) $C_6H_5-CH_2\overset{OH}{\overset{|}{C}}HCH_3$

(v) $CH_3-\overset{CH_3}{\overset{|}{\underset{OC_2H_5}{\underset{|}{C}}}}-CH_2CH_2CH_3$

(C) Aldehydes and ketones.

Sol. 1

(i) Pent-2-en-1-al.

(ii) 4-Methylpent-3-en-2-one.

(iii) 4-Hydroxy-4-methylpent-2-one.

(iv) 2, 5-Dimethylhexan-3-one.

(v) 4-Chloropent-2-one.

(vi) 2,4-Dimethylpentan-3-one.

(vii) Pentan-2,4-dione.

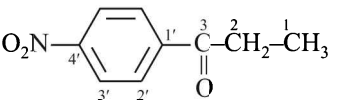
(viii) 3, 3, 5-Trimethylhexan-2-one.

(ix) 2-Chlorophenyl ethanone or *o*-Chloroacetophenone.

(x) 1-Phenylpropan-1-one.

(xi) 4, 4'-Dihydroxybenzophenone.

(xii) 4-Fluoroacetophenone or 1-(4-fluorophenyl) ethanone.

(xiii) 4′-Nitropropiophenone. 

(xiv) Cyclopentanecarbaldehyde.

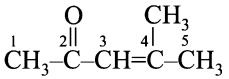
(xv) 3-Phenylprop-2-enal.

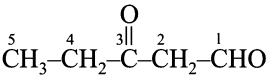
(xvi) 2-Methylcyclohexanone.

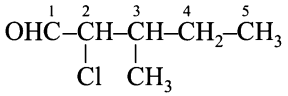
Sol. 2

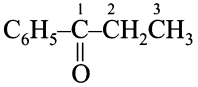
(i) $\overset{4}{C}H_3-\overset{3}{\overset{CH_3}{\overset{|}{C}}}H-\overset{2}{C}H_2-\overset{1}{C}HO$

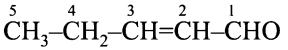
(ii) $\overset{1}{C}H_3-\overset{2}{\overset{O}{\overset{||}{C}}}-\overset{3}{C}H_2-\overset{4}{\overset{Cl}{\overset{|}{C}}}H-\overset{5}{C}H_3$

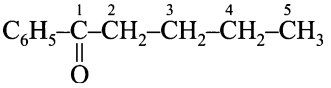
(iii) 

(iv) 

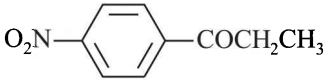
(v) 

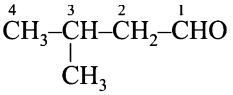
(vi) 

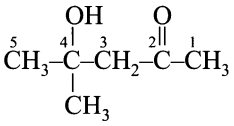
(vii) 

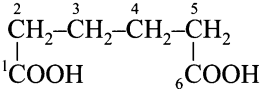
(viii) 

(ix)

(x) 

(xi) 

(xii) 

(xiii) 

(D) Carboxylic acids.

Sol. 1

(i) Hex-2-en-4-yn-1-oic acid.

(ii) 3-Bromo-5-chlorobenzoic acid.

(iii) N-Phenylethanamide.

(iv) N-Ethyl-N-methylbenzamide.

(v) Ethyl 4-chlorobenzoate.

(vi) Methyl 3, 5-dimethylbenzoate.

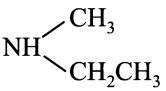
(E) Amines.

Sol. 1

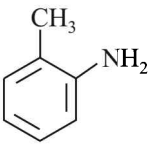
(i) But-3-en-1-amine.

(ii) 1-Methylprop-2-en-1-amine.

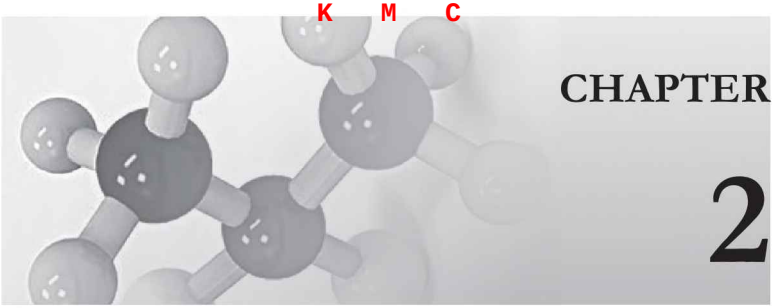
Sol. 2

(i) 

(ii) $CH_3CH_2NHCH_3$

(iii) 

(iv) $CH_2{=}CH{-}CH_2NH_2$



CHAPTER

2

How will you define the given reactions ?

Write chemical equations to illustrate the following name bearing reactions.

1. Friedel–Craft reactions. **(Delhi 2010)**
2. Friedel–Craft alkylation of anisole. **(AI 2011 C)**
3. Friedel–Craft acetylation of anisole **(Delhi 2011)**
4. Unsymmetrical ether **(AI 2009 C)**
5. Williamson synthesis
   (Delhi 2010, 2012 C, AI 2009 C, 2010 C, 2013)
6. Kolbe reaction **(Delhi 2010, 2012 C, AI 2009 C, 2011 C)**
7. Kolbe electrolytic method.
8. Aldol condensation **(AI 2013C)**
9. Cross aldol condensation **(Delhi 2008, 2012)**
10. Cannizzaro reaction
    (Delhi 2008, 2009, 2011, AI 2008, 2008 C, 2009, 2010, 2011, Foreign 2011, 2012)
11. Disproportionation **(AI 2009 C)**
12. Cross Cannizzaro reaction
13. Gattermann reaction **(Delhi 2009)**
14. Riemer–Tiemann reaction
    (Delhi 2010, 2011, 2012 C, AI 2009 C, 2010 C, 2011 C, 2013)

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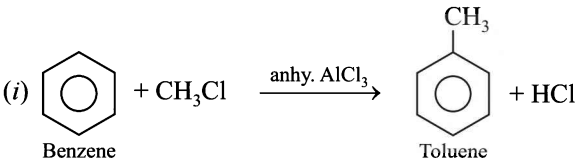
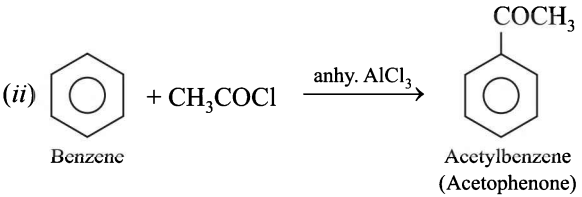
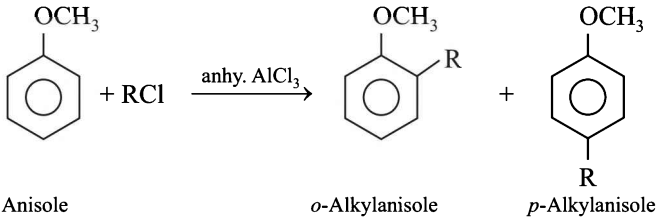
15. Clemmensen reduction K M C **(Delhi 2009, 2012, AI 2010, 2011)**
16. Wolf-Kishner reduction **(AI 2010, 2013C)**
17. Rosenmund reduction
18. Decarboxylation **(Delhi 2008, 2011, 2012, AI 2008, Foreign 2011)**
19. Hell-Volhard-Zelinsky reaction **(Delhi 2012, AI 2009, 2010, Foreign 2012)**
20. Gabriel phthalimide reaction **(Delhi 2009C, 2013C, AI 2008, 2013C, Foreign 2011)**
21. Hofmann bromamide reaction **(Delhi 2008C, 2009 2010C, AI 2008, 2012, Foreign 2011, 2012)**
22. Ammonolysis **(Delhi 2008C, 2009C)**
23. Acetylation **(Delhi 2008C, 2009C, 2010C, AI 2008)**
24. Benzoylation
25. Carbylamine reaction **(Delhi 2008C, 2009C, 2010C, AI 2012, Foreign 2012)**
26. Mustard oil reaction
27. Diazotisation **(Delhi 2008C)**
28. Sandmeyer reaction **(Delhi 2011C, AI 2012C)**
29. Coupling reaction **(Delhi 2008C, 2009, 2009C, 2011C, 2013C, AI 2012C, 2013C, Foreign 2011)**

1. **Friedel-Craft reactions:** Reaction of aromatic compounds with alkyl halide (R–X) or acyl halide (R–COCl) in presence of Lewis acid catalyst (e.g. anhydrous $AlCl_3$) to form alkylbenzene or acyl- benzene respectively is known as Friedel-Craft reaction. Examples are

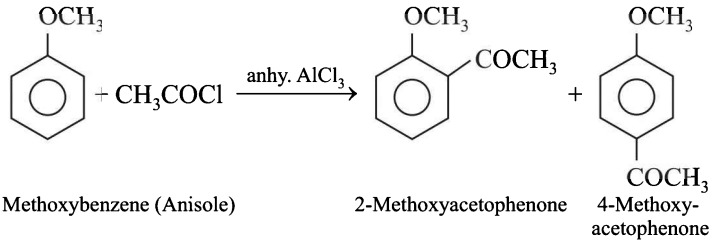




2. **Friedel-Craft alkylation of anisole:** Definition as above,



3. **Friedel-Craft acetylation of anisole:**



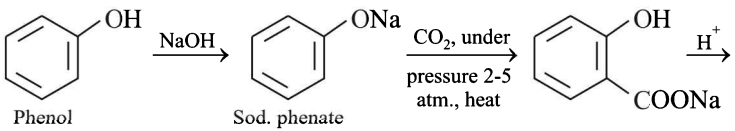
4. **Unsymmetrical ether:** When the two alkyl or aryl groups of an ether (R–O–R or Ar–O–Ar) are different, ethers are called unsymemtrical ethers. Examples

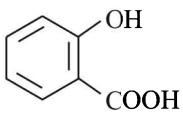
$C_2H_5-O-CH_3$	$CH_3-O-C_6H_5$	CH_3-O-CH_3	$C_6H_5-O-C_6H_5$
Ethyl methyl ether	Methyl phenyl ether	Dimethyl ether	Diphenyl ether
Unsymmetrical ethers		Simple ethers	

5. **Williamson synthesis of an ether:** Reaction of an alkyl halide and sodium alkoxide to form ether is known as Williamson synthesis. It is an example of S_{N^2} reaction.

$$\underset{\substack{\text{(Substrate)}\\ \text{Ethyl iodide}}}{CH_3CH_2I} + \underset{\substack{\text{(Nucleophile)}\\ \text{Sod. ethoxide}}}{C_2H_5O^-Na^+} \xrightarrow{S_{N^2}} \underset{\text{Diethyl ether}}{CH_3CH_2-O-C_2H_5}$$

6. **Kolbe's reaction or Kolbe-Schmidt reaction:** When sodium salt of phenol (sodium phenate) is heated with carbon dioxide gas under pressure, sodium salt of salicylic acid (*o*-hydroxybenzoic acid) is formed which on acidification gives salicylic acid. This reaction is known as Kolbe reaction or better Kolbe-Schmidt reaction.





Salicylic acid

7. **Kolbe electrolytic method:** When sodium or potassium salt of a carboxylic acid is electrolysed, hydrocarbons are formed. For example

(*i*) $\underset{\text{Sod. acetate}}{CH_3COO^-Na^+} \xrightarrow{\text{ionisation}} CH_3COO^- + Na^+$

At anode:

$$2CH_3COO^- - 2e^- \longrightarrow \underset{\text{Unstable}}{2CH_3COO} \longrightarrow \underset{\text{Ethane}}{CH_3-CH_3} + 2CO_2$$

At cathode: $2Na^+ + 2H_2O \longrightarrow 2NaOH + H_2\uparrow$

(*ii*) $\begin{array}{l} CH_2COONa \\ | \\ CH_2COONa \end{array} \longrightarrow \begin{array}{l} CH_2COO^- \\ | \\ CH_2COO^- \end{array} + 2\,Na^+$

At anode:

$$\begin{array}{l} CH_2COO^- \\ | \\ CH_2COO^- \end{array} - 2e^- \longrightarrow \underset{\text{Unstable}}{\begin{array}{l} CH_2COO \\ | \\ CH_2COO \end{array}} \longrightarrow \underset{\text{Ethylene}}{\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array}} + 2\,CO_2$$

At cathode: $2\,Na^+ + 2H_2O \longrightarrow 2\,NaOH + H_2\uparrow$

8. Aldol condensation: Condensation of two molecules of an aldehyde or a ketone having at least one α-hydrogen atom in presence of dilute solution of an alkali to form β-hydroxyaldehyde or β-hydroxyketone is known as **aldol condensation**. For example,

(*i*)

$$\underset{\text{Ethanal (2 molecules)}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}H + CH_3CHO} \xrightarrow{\text{dil. } OH^-} \underset{\beta\text{-Hydroxybutanal}}{{}^{4}CH_3-{}^{3}\overset{\overset{\displaystyle OH}{|}}{\underset{\beta}{C}}H-{}^{2}\underset{\alpha}{C}H_2-{}^{1}CHO}$$

(*ii*)

$$\underset{\text{Ethanone (2 molecules)}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3+CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} \xrightarrow{\text{dil. } OH^-} \underset{\text{4-Hydroxy-4-methylpentan-2-one (A β-hydroxyketone)}}{{}^{5}CH_3-{}^{4}\underset{\beta|}{\overset{\overset{\displaystyle OH}{|}}{C}}-{}^{3}\underset{\alpha}{C}H_2-{}^{2}\underset{\underset{\displaystyle O}{\|}}{C}-{}^{1}CH_3 \quad (CH_3)}$$

On heating, the product (β-hydroxyaldehyde or ketone) loses a molecule of water easily to form α, β-unsaturated aldehyde or ketone.

$$\underset{\beta\text{-Hydroxybutanal}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_2-CHO} \xrightarrow{\text{heat}} \underset{\substack{\text{But-2-enal}\\ \text{(Stable due to conjugation)}}}{CH_3-CH=CH-CHO} + H_2O$$

$$\underset{\substack{\text{4-Hydroxy-4-methylpentan-2-one}\\ \text{(A β-hydroxy ketone)}}}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} \xrightarrow{\text{heat}} \underset{\substack{\text{4-Methylpent-3-en-2-one}\\ \text{(Stable due to conjugated system}\\ \text{of double bonds)}}}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}=CH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + H_2O$$

9. Cross aldol condensation: Condensation between two different aldehydes or two different ketones or one aldehyde and one ketone, at least one component of which has at least one α-hydrogen atom in presence of alkali, is known as cross aldol condensation. For example,

(*i*)

$$\underset{\text{Methanal}}{H-\overset{\overset{\displaystyle O}{\|}}{C}-H} + \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{OH^-} \underset{\text{3-Hydroxypropanal}}{\overset{\overset{\displaystyle OH}{|}}{C}H_2-CH_2CHO}$$

(*ii*)

$$\underset{\text{Butanone}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-C_2H_5} + \underset{\text{Propanone}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} \xrightarrow{OH^-} CH_3-\underset{\underset{\displaystyle C_2H_5}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

(*iii*) $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{OH^-} {}^4CH_3-{}^3\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-{}^2CH_2-{}^1CHO$

Propanone — Ethanal as nucleophile — 3-Hydroxy-3-methylbutanal

or

$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{OH^-} CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

Ethanal — Propanone as nucleophile — 4-Hydroxypentan-2-one

10. **Cannizzaro reaction:** Condensation of two molecules of an aldehyde having no α-hydrogen atom in presence of conc. alkali to form a mixture of alcohol and carboxylic acid (in the form of salt) is known as **Cannizzaro reaction.** For example,

$$HCHO + HCHO \xrightarrow{\text{Conc. KOH}} \underset{\text{Methanol}}{CH_3OH} + \underset{\text{Pot. formate}}{HCOOK}$$

$$C_6H_5CHO + C_6H_5CHO \xrightarrow{\text{Conc. KOH}} C_6H_5CH_2OH + C_6H_5COOK$$

Note that here one molecule of an aldehyde is oxidised (to form carboxylic acid) and other is reduced (to form alcohol). Thus the reaction may said to be an example of **disproportionation**.

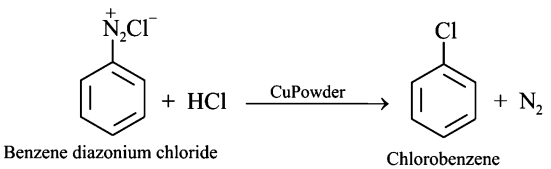
11. **Disproportionation:** See above

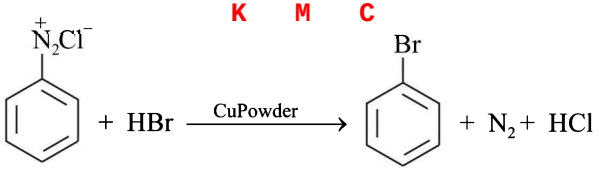
12. **Cross Cannizzaro reaction:** Condensation of two different aldehydes, none of which is having any α-hydrogen atom, in presence of conc. alkali to form a mixture of alcohol and carboxylic acid is known as cross Cannizzaro reaction.

$$\underset{\text{Methanal}}{HCHO} + \underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{\text{Conc. KOH}} \underset{\text{Pot. formate}}{HCOOK} + \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$$

Remember, when HCHO is one of the components, it is always oxidised and the other molecule is reduced.

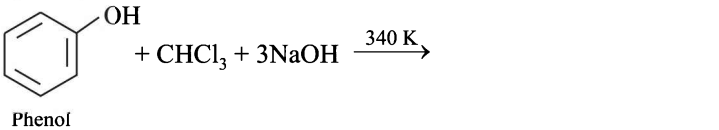
13. In this reaction, benzene diazonium chloride is treated with copper powder and halogen acid (HCl or HBr) to form the corresponding haloarene as the product.



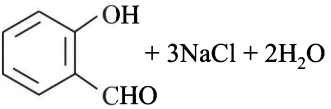


Bromobenzene

14. Riemer-Tiemann reaction: Reaction of phenol with chloroform in presence of aqueous NaOH at 340K to form salicylaldehyde (*o*-hydroxybenzaldehyde) is known as Riemer-Tiemann reaction.

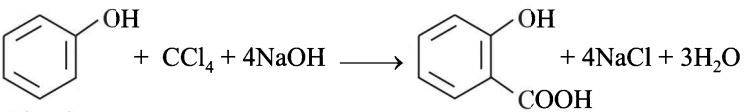


Phenol



Salicylaldehyde

In case, carbon tetrachloride is used in place of chloroform, the final product is salicylic acid (*o*-hydroxybenzoic acid). This is also an example of Riemer-Tiemann reaction.



Phenol

Salicylic acid

15. Clemmensen reduction: Reduction of carbonyl group (aldehydes and ketones) by means of amalgamated-zinc and conc. HCl to methylene group (hydrocarbons) is known as **Clemmensen reduction**.

(*i*) $CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow[\text{Conc. HCl}]{\text{Zn/Hg}} CH_3CH_2H$ or CH_3CH_3

Acetaldehyde Ethane

(*ii*) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{Conc. HCl}]{\text{Zn/Hg}} CH_3CH_2CH_3$

Acetone Propane

16. Wolf-Kishner reduction: Reduction of carbonyl group (aldehydes and ketones) by heating with hydrazine (H_2NNH_2) in presence of alkali (KOH or Me_3COK) in a high boiling solvent to methylene group (hydrocarbons) is called Wolf-Kishner reduction.

(*i*) $CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{NH_2NH_2} [CH_3CH=NNH_2] \xrightarrow[\text{glycol, 453–473 K}]{KOH} CH_3CH_3 + N_2$

Acetaldehyde, Hydrazone, Ethane

(*ii*) $CH_3COCH_3 \xrightarrow[\text{glycol, 453-473 K}]{NH_2NH_2} CH_3CH_2CH_3$

17. **Rosenmund reduction:** Reduction of acid chlorides with hydrogen in presence of palladium supported on barium sulphate to aldehydes is known as Rosenmund reduction. Examples are

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + H_2 \xrightarrow{Pd\text{-}BaSO_4} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

$$\underset{\text{Benzoyl chloride}}{C_6H_5COCl} + H_2 \xrightarrow{Pd\text{-}BaSO_4} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$$

Barium sulphate acts as a poison for palladium catalyst and prevents reduction of aldehydes to primary alcohols ($RCHO \rightarrow RCH_2OH$).

18. **Decarboxylation:** Heating of sodium salt of a carboxylic acid with soda lime (CaO + NaOH) to form hydrocarbon along with the removal of a carbon dioxide molecule in the form of sodium carbonate is known as decarboxylation.

$$\underset{\text{Sod. acetate}}{CH_3COONa} + NaOH \xrightarrow[\text{heat}]{CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

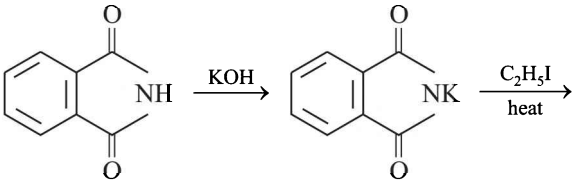
19. **Hell-Volhard-Zelinsky reaction (HVZ reaction):** Aliphatic carboxylic acids react with bromine or chlorine in presence of phosphorus (or a phosphorus halide) to give α-halo acids, the reaction is known as **Hell-Volhard-Zelinsky (HVZ) reaction**.

$$\overset{\beta}{CH_3}-\overset{\alpha}{CH_2}COOH \xrightarrow{Cl_2, P} \overset{\beta}{CH_3}-\overset{\alpha}{CH}(Cl)-COOH \xrightarrow{Cl_2, P} CH_3-C(Cl)_2-COOH$$

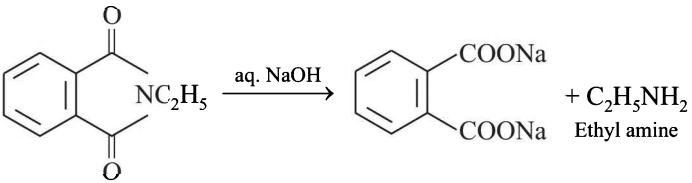
Remember that halogenation occurs specifically at the α-carbon.

20. **Gabriel phthalimide reaction:** Reaction of potassium phthalimide with alkyl halides (**not aryl halides**) followed by alkaline hydrolysis

to form primary aliphatic amines (not primary aromatic amines) is known as **Gabriel phthalimide reaction**.



Phthalimide Pot. phthalimide



N-Ethyl phthalimide

Primary aromatic amines can't be prepared by this method because aryl halides (ArX) do not undergo nucleophilic substitution with pot. phthalimide.

21. Hofmann bromamide reaction: Reaction of an acid amide with alkaline bromine to form a primary amine, with one carbon atom less, is known as Hofmann bromamide reaction.

$$(i)\ \underset{\substack{\text{Ethanamide (2C)}\\ \text{(Acetamide)}}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Methylamine (1C)}}{CH_3NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

$$(ii)\ \underset{\text{Benzamide}}{C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

22. Ammonolysis: Cleavage of alkyl halides (reaction of alkyl halides) with ammonia or its derivative (1°, 2° and 3° amines) is known as ammonolysis. Examples are

$$\underset{\text{Bromoethane}}{CH_3CH_2Br} + HNH_2 \xrightarrow[\text{heat}]{C_2H_5OH} \underset{\text{Ethanamine (1° amine)}}{CH_3CH_2NH_2} + HBr$$

K M C

$$CH_3CH_2Br + H_2NCH_2CH_3 \xrightarrow[\text{heat}]{C_2H_5OH} CH_3CH_2NHCH_2CH_3$$

Bromoethane Ethanamine N-Ethylethanamine (Diethylamine, 2° amine)

$$CH_3CH_2Br + HN(CH_2CH_3)_2 \xrightarrow[\text{heat}]{C_2H_5OH} (CH_3CH_2)_3N + HBr$$

Bromoethane N, N-Diethylethanamine (3°) (Triethylamine)

$$CH_3CH_2Br + N(CH_2CH_3)_3 \xrightarrow[\text{heat}]{C_2H_5OH} (CH_3CH_2)_4N^+Br^-$$

Bromoethane Tetraethyl ammonium bromide (quaternary ammonium salt)

23. Acetylation: Replacement of hydrogen atom of alcoholic group, phenolic group or amino (1° or 2°) group by an acetyl group ($-COCH_3$) by means of acetyl chloride (CH_3COCl) or acetic anhydride, $(CH_3CO)_2O$ to form corresponding ester or amide is known as acetylation. Examples are

(*i*) $CH_3CH_2OH + ClCOCH_3 \longrightarrow CH_3CH_2OCOCH_3$

Ethyl alcohol Ethyl acetate

(*ii*) $C_6H_5OH + ClCOCH_3 \longrightarrow C_6H_5OCOCH_3$

Phenol Phenyl acetate

(*iii*) $CH_3CH_2NH_2 + ClCOCH_3 \longrightarrow CH_3CH_2NHCOCH_3$

Ethyl amine N-Ethyl ethanamide

(*iv*) $(CH_3CH_2)_2NH + ClCOCH_3 \longrightarrow (CH_3CH_2)_2NCOCH_3$

N, N-Diethyl ethanamide

Acetylation is used to protect the $-OH$ or $-NH_2$ group.

24. Benzoylation: Reaction of amines (primary or secondary) with benzoyl chloride in presence of sodium hydroxide to form corresponding benzoyl derivative is known as **benzoylation** or **Schotten-Baumann reaction.**

$$CH_3CH_2NH_2 + ClOCC_6H_5 \xrightarrow{OH^-} CH_3CH_2NHOCC_6H_5$$

Ethyl amine Benzoyl chloride N-Ethyl benzamide

$$C_6H_5NH_2 + ClOCC_6H_5 \xrightarrow{OH^-} C_6H_5NHOCC_6H_5$$

Aniline N-Phenyl benzamide (Benzanilide)

$$(C_6H_5)_2NH + ClOCC_6H_5 \xrightarrow{OH^-} (C_6H_5)_2NOCC_6H_5$$

Diphenylamine N, N-Phenyl benzamide

25. Carbylamine reaction: Reaction of primary amines with alcoholic potassium hydroxide and chloroform to form isocyanides (also

known as carbylamines), having unpleasant odour, is known as carbylamine reaction.

(*i*) $\underset{\text{Ethyl amine}}{CH_3CH_2NH_2} + CHCl_3 + 3KOH(alc.) \longrightarrow \underset{\text{Ethyl isocyanide}}{CH_3CH_2N \overset{\rightarrow}{=} C} + 3KCl + 3H_2O$

(*ii*) $C_6H_5NH_2 + CHCl_3 + 3KOH(alc.) \longrightarrow \underset{\text{Phenyl isocyanide}}{C_6H_5N \overset{\rightarrow}{=} C} + 3KCl + 3H_2O$

26. Mustard oil reaction: Reaction of primary amines (aliphatic or aromatic) with alcoholic solution of carbon disulphide followed by heating with excess of mercuric chloride to form alkyl or aryl isothiocyanate, having mustard oil like smell, is known as mustard oil reaction (**test for 1° amines**).

$$CH_3CH_2NH_2 + S=C=S \longrightarrow S=C\begin{matrix} SH \\ NHCH_2CH_3 \end{matrix} \xrightarrow{HgCl_2} CH_3CH_2NCS + HgS + 2HCl$$

$$C_6H_5NH_2 + S=C=S \longrightarrow S=C\begin{matrix} SH \\ NHC_6H_5 \end{matrix} \xrightarrow{HgCl_2} C_6H_5NCS + HgS + 2HCl$$

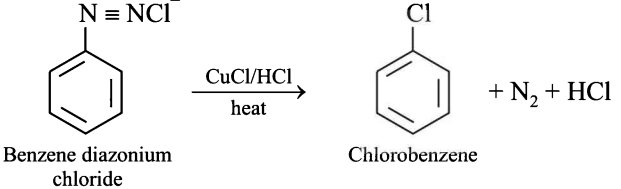
27. Diazotisation: Reaction of a primary aromatic amine with nitrous acid ($NaNO_2$ + HCl) in presence of dil HCl at low temperature (0° to 5°C) to form an aryl diazonium salt is known as diazotisation.

$$C_6H_5NH_2 + HONO \xrightarrow[273\text{–}278K]{\text{dil. HCl}} C_6H_5N_2Cl$$

Remember that aliphatic primary amines on such treatment give primary alcohols (not diazonium salts).

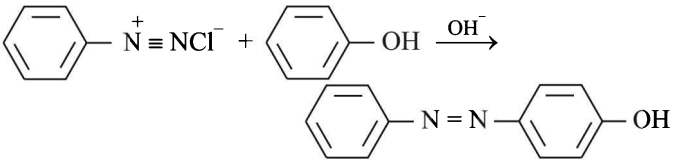
$$CH_3CH_2NH_2 + HONO \longrightarrow CH_3CH_2OH + N_2 + H_2O$$

28. Sandmeyer reaction: Conversion of aryl diazonium salts to chlorobenzene, bromobenzene or benzonitrile on treatment with CuCl/HCl, CuBr/HBr or CuCN/KCN respectively is called Sandmeyer reaction.



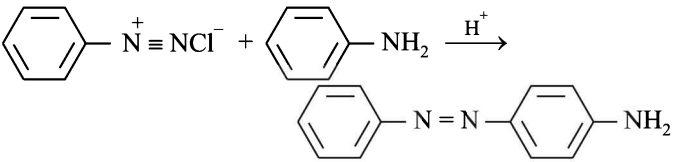
29. Coupling reaction: Reaction of aryl diazonium salts with phenol in presence of alkali (or with an aromatic amine, 1°, 2° or 3° in presence of acid) to form *p*-substituted azo dyes is known as coupling reaction.

(*i*)

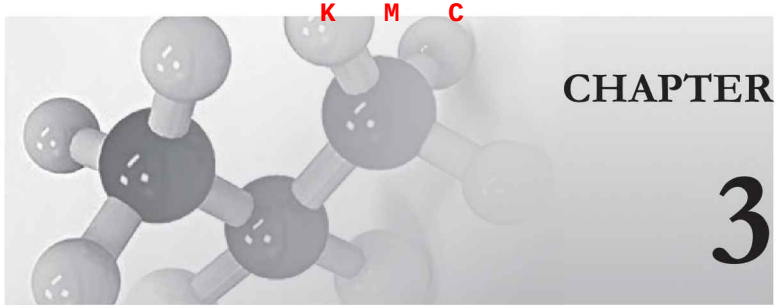


p-Hydroxyazobenzene (**Dye**)

(*ii*)



p-Aminoazobenzene (**Dye**)



CHAPTER

3

What happens when ...

What happens when

(A) Halogen derivatives

(i) Propene is treated with HBr in presence of benzoyl peroxide.

(ii) 2-Methylbromopropane is treated with sodium in presence of dry ether.

(iii) Chlorination of benzene in presence of UV light.

(iv) Chlorobenzene is subjected to hydrolysis.

(v) Chlorobenzene is treated with NaOH at 623 K under high pressure.

(vi) Butene-2 is heated with chlorine.

(vii) Ethylbenzene is heated with N–bromosuccinimide.

(viii) Silver acetate is heated with bromine.

(ix) Ethyl chloride is heated with sodium-lead alloy.

(x) Chloroform is oxidised by air. **(Delhi 2007)**

(xi) Chloroform reacts with chlorine. **(Delhi 2007)**

(xii) Chloroform is treated with acetone in alkaline solution.

(xiii) Chloroform is treated with ethylamine in presence of alcoholic potash.

(xiv) Iodoform is treated with silver powder. **(AI 2007)**

(xv) Chlorobenzene is heated with trichloroethanal (chloral) in presence of conc. H_2SO_4.

(xvi) Methyl bromide is treated with KCN. **(Delhi 2013)**

(xvii) Ethyl chloride is treated with aqueous KOH. **(Delhi 2013)**

(xviii) Bromine attacks on $CH_2{=}CH{-}CH_2{-}C{\equiv}CH$. **(AI 2012)**

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(B) Alcohols

(i) Isobutene is treated with dil. H_2SO_4.

(ii) Ethyl alcohol is heated with red phosphorus and HI.

(iii) Ethylene is treated with water gas in presence of cobalt carbonyl and the product is reduced with hydrogen in presence of Ni.

(iv) Propanol-1 is oxidised with alkaline $KMnO_4$ solution.

(v) 1-Methylcyclohexanol is treated with conc. H_2SO_4.

(vi) $CH_3CH_2CH_2CH_2OH$ is oxidised with excess of oxidising agent. **(Delhi 2012)**

(vii) 2-Butenol is oxidised with excess of oxidising agent. **(Delhi 2012)**

(viii) 2-Methyl-1-propanol is oxidised with excess of oxidising agent. **(Delhi 2012)**

(C) Phenols

(i) Phenol is treated with a solution of bromine in CCl_4 at low temperature.

(ii) Phenol is treated with dil. HNO_3.

(iii) Phenol is treated with chloroform in presence of NaOH.

(iv) Sodium phenoxide is treated with CO_2 at 413 K under 4–7 atm. pressure.

(D) Aldehydes and ketones

(i) Propanone is reacted with methylmagnesium bromide followed by hydrolysis. **(AI 2012C)**

(ii) Benzaldehyde is treated with

(a) Conc. NaOH **(Delhi 2011C)**

(b) HNO_3/H_2SO_4 (at 273 – 383 K) **(Delhi 2011C)**

(E) Carbohydrates

(i) D-Glucose is treated with

(a) HI and red P **(AI 2008, 2010C, 2012C)**

(b) Bromine water **(AI 2008, 2010 C, 2012C)**

(c) HNO_3 **(AI 2008, 2012)**

(d) Hydroxylamine **(AI 2012C)**

(e) Acetic anhydride **(AI 2012C)**

(ii) Sucrose is hydrolysed **(Delhi 2010, AI 2013, Foreign 2011)**

(iii) Lactose is hydrolysed **(AI 2010 C, Foreign 2011)**

(A) Halogen derivatives

(i) $CH_3CH{=}CH_2 + HBr \xrightarrow[\text{anti-Markow. addition}]{\text{Peroxide}} CH_3CH_2CH_2Br$

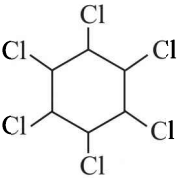
(ii) $2CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_2Br + 2Na \xrightarrow[\text{ether}]{\text{dry}} CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_2{-}CH_2{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_3$

2, 5-Dimethylhexane

This is an example of **Wurtz reaction**.

(iii)
Benzene

$+ 3Cl_2 \xrightarrow[\text{light}]{\text{UV}}$



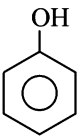
Benzene hexachloride

(iv) No Reaction

(v)

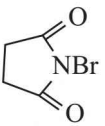
Chlorobenzene

$+ NaOH \xrightarrow[\text{high P}]{\text{623 K}}$

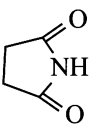


Phenol

(vi) $CH_3CH{=}CHCH_3 \xrightarrow[\text{heat}]{Cl_2} CH_3CH{=}CHCH_2Cl$ **(Chlorination)**

(vii) $C_6H_5CH_2CH_3 +$ 

(NBS)

$\xrightarrow[\text{bromination}]{\text{allylic}} C_6H_5\overset{\overset{Br}{|}}{C}HCH_3 +$ 

(viii) $CH_3COOAg + Br_2 \xrightarrow[\text{reaction}]{\text{Hunsdiecker}} CH_3Br + CO_2 + AgBr$

(ix) $4C_2H_5Cl + 4Na/Pb \longrightarrow (C_2H_5)_4Pb + 4NaCl + 3Pb$

Tetraethyl lead

(x) $2CHCl_3 + O_2 \longrightarrow 2COCl_2 + 2HCl$

Carbonyl chloride

(xi) $CHCl_3 + Cl_2\,(gas) \xrightarrow[\text{sunlight}]{\text{diffused}} CCl_4 + HCl$

(xii) $(CH_3)_2CO + HCCl_3 \xrightarrow{NaOH} (CH_3)_2C\begin{matrix}\diagup OH \\ \diagdown CCl_3\end{matrix}$

Chloritone (a hypnotic)

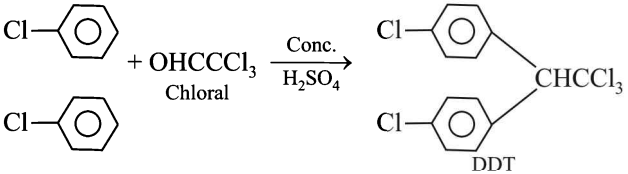
(xiii) $C_2H_5NH_2 + CHCl_3 + 3KOH \xrightarrow[\text{reaction}]{\text{Carbylamine}} C_2H_5NC + 3KCl + 3H_2O$

K M C

Ethyl carbylamine

(xiv) $HCI_3 + 6Ag + I_3CH \xrightarrow{\text{heat}} HC{\equiv}CH + 6AgI$

Acetylene

(xv) 

(xvi) $CH_3Br + KCN \longrightarrow CH_3CN + KBr$

Methyl bromide Methyl cyanide

(xvii) $CH_3CH_2Cl + KOH\ (aq) \longrightarrow CH_3CH_2OH + KCl$

Ethyl alcohol Ethyl alcohol

(xviii) $CH_2{=}CH{-}CH_2{-}C{\equiv}CH + Br_2 \xrightarrow[\text{addition}]{\text{anti}} CH_2{=}CH{-}CH_2{-}C{=}C(Br)(Br)H$

(B) Alcohols

(i) $CH_3{-}C(CH_3){=}CH_2 \xrightarrow[\text{(hydration)}]{H_2SO_4} CH_3{-}C(CH_3)(OH){-}CH_3$ **(Markownikoff addition)**

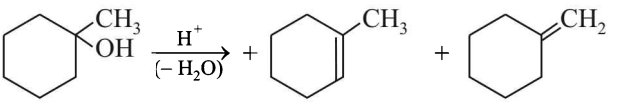
Isobutene 2-Methylpropanol-2

(ii) $C_2H_5OH + 2HI \xrightarrow{\text{red P}} C_2H_6 + I_2$ **(Reduction)**

(iii) $CH_2{=}CH_2 + \underbrace{CO + H_2}_{\text{water gas}} \xrightarrow{[Co\ (CO)_4]_2} CH_3CH_2CHO \xrightarrow{H_2/Ni} CH_3CH_2CH_2OH$

(iv) $CH_3CH_2CH_2OH \xrightarrow[\text{(oxidation)}]{\text{Alk. } KMnO_4} CH_3CH_2COOH$

Propanoic acid

(v) 

1-Methylcyclohexene (major) 1-Methylenecyclohexane

(vi) $CH_3CH_2CH_2CH_2OH \longrightarrow CH_3CH_2CH_2COOH$

Butanoic acid

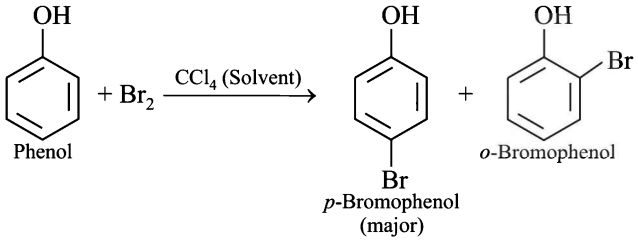
(vii) $CH_3CH{=}CH{-}CH_2OH \longrightarrow CH_3CH{=}CHCOOH$

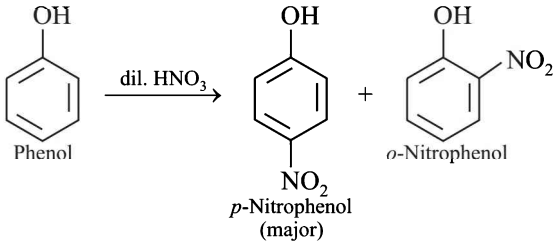
2-Butenol But-2-enoic acid

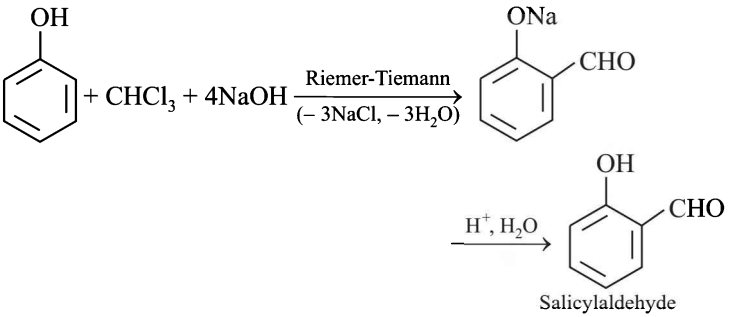
(viii) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH \xrightarrow{K} \overset{M}{CH_3}-\overset{C}{\underset{\underset{CH_3}{|}}{CH}}-COOH$

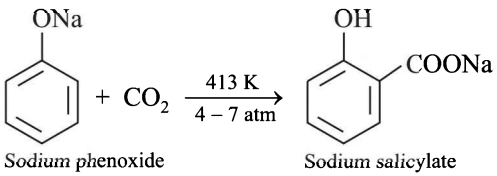
2-Methyl-1-propanol → 2-Methylpropanoic acid

(C) Phenols

(i) 

(ii) 

(iii) 

(iv) 

(D) Aldehydes and ketones

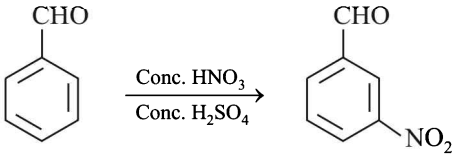
(i) $CH_3-\overset{\overset{O}{||}}{C}-CH_3 + CH_3MgBr \longrightarrow CH_3-\overset{\overset{OMgI}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \xrightarrow{H_2O} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

Propanone → 2-Methylpropanol-2

K M C

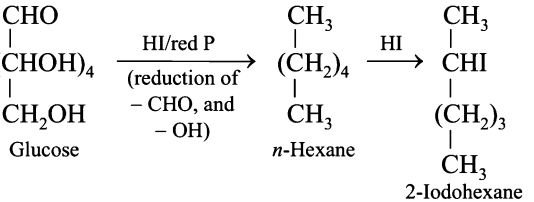
(ii) (a) $2C_6H_5CHO + 2NaOH \xrightarrow[\text{reaction}]{\text{Cannizzaro}} C_6H_5COONa + C_6H_5CH_2OH$

Sod. benzoate Benzyl alcohol

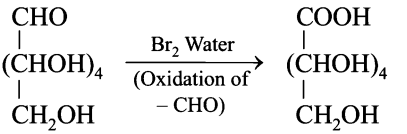
(b) 

Benzaldehyde *m*-Nitrobenzaldehyde

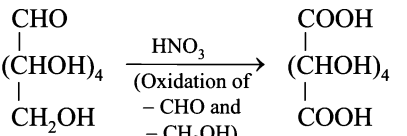
(E) Carbohydrates

(i) (a) 

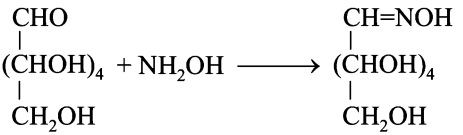
Glucose *n*-Hexane 2-Iodohexane

(b) 

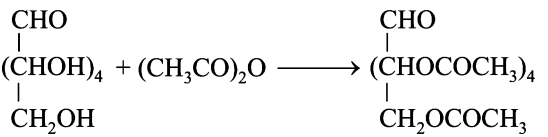
Glucose Gluconic acid

(c) 

Glucose Saccharic acid

(d) 

Glucose Glucose oxime

(e) 

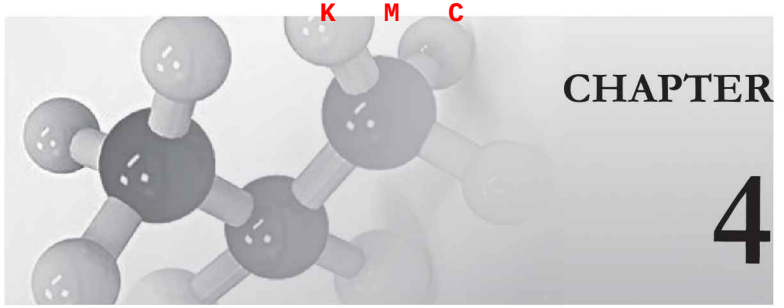
Glucose Glucose penta-acetate

(ii) $C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{or } H^+]{\text{invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$

Sucrose D-(+) –Glucose (D)-(–)-Fructose

(iii) $C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{or lactase}]{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

Lactose D-Glucose D-Galactose



CHAPTER

4

What are the missing compounds/ reagents ?

Q1. Complete the following :

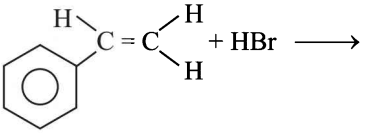
(A) Hydrocarbons and halogen derivatives.

(i) $CH_3CH_2CH = CH_2 + HBr \longrightarrow$ **(AI 2009, Foreign 2011)**

(ii) $CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{Peroxide}}$ **(Delhi 2008)**

(iii) $CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4}$ **(Delhi 2008, AI 2008)**

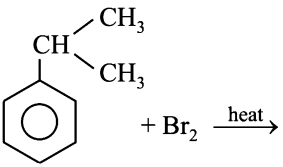
(iv) $C_6H_5N_2Cl + KI \longrightarrow$

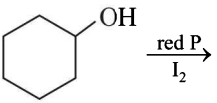
(v)  **(Foreign 2011)**

(vi) $(CH_3)_3CBr + H_2O \xrightarrow{\text{Heat}}$

(vii) $CH_3CH_2Cl + SbF_3 \xrightarrow{\text{Heat}}$

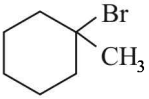
(viii) $CH_3CH_2C \equiv CNa + CH_2 = CHCH_2Br \xrightarrow{\text{Liq. } NH_3}$

(ix) 

(x) 

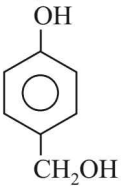
143 Approved: 0777 023 444

(xi) $CH_3CH_2Cl + KNO_2 \xrightarrow{K} \xrightarrow{M} \xrightarrow{C}$ Two products

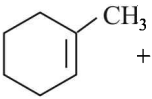
(xii) 

$\xrightarrow[C_2H_5OH]{C_2H_5ONa}$

(xiii) $+ Br_2 \xrightarrow[\text{light}]{\text{heat}}$ **(Delhi 2012C)**

(xiv) 

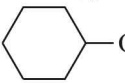
$- HCl \longrightarrow$

(xv) 

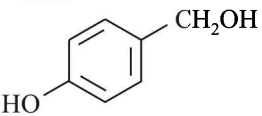
$+ HI \longrightarrow$ **(Delhi 2012C, AI 2009, Foreign 2011)**

(xvi) $CH_3CH = CHCH_2Cl + CN^- \longrightarrow (A) + (B)$ **(2012C)**

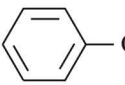
(B) Alcohols, phenols and ethers.

(i) 

$+ SOCl_2 \longrightarrow$ **(Delhi 2009)**

(ii) 

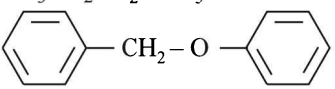
$+ HCl \longrightarrow$ **(Delhi 2009)**

(iii) 

$+ HBr \longrightarrow$ **(Foreign 2012)**

(iv) $(CH_3)_3C - O - C_2H_5 + HI \longrightarrow$ **(Foreign 2012)**

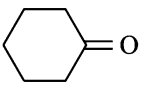
(v) $CH_3CH_2CH_2OCH_3 + HBr \longrightarrow$ **(Foreign 2012)**

(vi) 

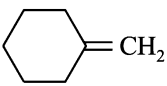
$+ HI \longrightarrow$

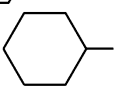
(C) Aldehydes, ketones and carboxylic acids.

(i) $CH_3C \equiv CH \xrightarrow[H_2SO_4]{Hg^{2+}}$ **(Delhi 2012)**

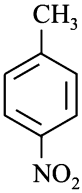
(ii) ..... $\xrightarrow[Zn - H_2O]{O_3}$ 2 

(Delhi 2008, AI 2011)

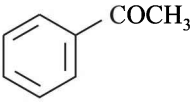
(iii) 

$\longrightarrow$ 

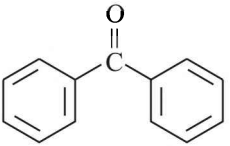
(Delhi 2008, AI 2011)

(iv) 

$\xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } CrO_2Cl_2}$ **(Delhi 2012)**

(v) + ... $\xrightarrow{\text{anhy. } AlCl_3}$ 

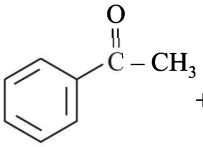
(Delhi 2009)

(vi) + ... $\xrightarrow{\text{.....}}$ 

(Delhi 2009)

(vii) + C_2H_5COCl $\xrightarrow[CS_2]{\text{anhy. } AlCl_3}$

(Delhi 2011C, 2012, AI 2012C)

(viii) 

+ $CH_3CH_2NH_2$ $\xrightarrow{H^+}$ **(AI 2011C)**

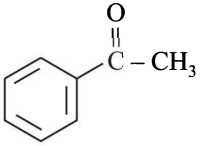
(ix) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$ **(AI 2011)**

(x) $2H-\underset{\underset{O}{\|}}{C}-H \xrightarrow{\text{Conc. KOH}}$ **(Delhi 2013)**

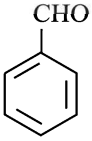
(xi) $C_6H_5CHO + C_6H_5COCH_3 \xrightarrow[293\text{ K}]{OH^-}$ **(Delhi 2011C)**

(xii) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[\text{Conc. HCl}]{\text{Zn–Hg}}$ **(AI 2013)**

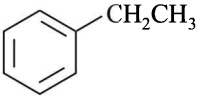
(xiii) $C_6H_5\text{–}COCl \xrightarrow[Pd\text{–}BaSO_4]{H_2}$ **(Delhi 2009A, 2011C, AI 2013)**

(xiv) 

$\xrightarrow{H_2CrO_4}$ **(AI 2011C)**

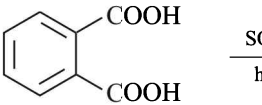
(xv) 

$\xrightarrow[273\text{-}283\text{ K}]{HNO_3/H_2SO_4}$ **(Delhi 2013)**

(xvi) 

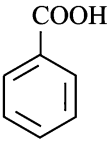
$\xrightarrow[\text{KOH, heat}]{KMnO_4}$ ..... **(Delhi 2008, 2011, Foreign 2011)**

(xvii)
$\xrightarrow[H_2SO_4\text{, heat}]{KMnO_4}$ **(AI 2011C)**

(xviii) 

$\xrightarrow[\text{heat}]{SOCl_2}$ **(Delhi 2011, AI 2011, Foreign, 2011)**

(xix) $CH_3COOH \xrightarrow{Br_2/P}$ **(Delhi 2013)**

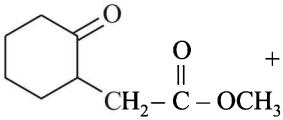
(xx) 

$\xrightarrow{Br_2/FeBr_3}$ **(AI 2013)**

(xxi) $R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[H_2O]{LiAlH_4}$ **(AI 2009)**

(xxii) $C_6H_5CONH_2 \xrightarrow[\text{heat}]{H_3O^+}$ **(AI 2009)**

(xxiii) $CH_3-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{Br_2 + NaOH}$ **(Delhi 2011, Foreign 2011)**

(xxiv) 

$+ NaBH_4 \longrightarrow$

(D) Amines.

(i) $C_2H_5NH_2 + C_6H_5SO_2Cl \longrightarrow$ **(AI 2009)**

(ii) $C_6H_5NH_2 + CH_3COCl \longrightarrow$ **(AI 2009)**

(iii) $C_2H_5NH_2 + HNO_2 \longrightarrow$ **(AI 2009)**

(iv) $RNH_2 + CHCl_3 + KOH \longrightarrow$ **(Delhi 2010, AI 2013)**

(v) $C_6H_5NH_2 + Br_2\ (aq.) \longrightarrow$ **(AI 2009, 2012, 2013, Foreign 2012)**

(vi) $C_6H_5NH_2 + HCl\ (aq.) \longrightarrow$ **(AI 2013)**

(vii) $C_6H_5N_2Cl + KI \longrightarrow$ ..... **(Delhi 2008)**

(viii) Diazonium group + $\longrightarrow$ –I **(Delhi 2008, AI 2008)**

(ix) $C_6H_5N_2Cl + H_3PO_2 + H_2O \xrightarrow{K} \xrightarrow{M} C$ **(AI 2009, 2012, Foreign 2012, AI 2013)**

(x) $C_6H_5N_2Cl + CH_3CH_2OH \longrightarrow$ **(Delhi 2010)**

(xi) $C_6H_5N_2Cl + C_6H_5NH_2 \xrightarrow{OH^-}$ **(Delhi 2010)**

(xii) $C_6H_5N_2^+Cl^- \xrightarrow[\text{room temp.}]{H_2O}$ **(AI 2013)**

Q2. Identify the missing compounds (reagents) in the following:

(i) $C_2H_5Cl \xrightarrow{NaCN} A \xrightarrow[Ni/H_2]{\text{Reduction}} B$ **(AI 2010)**

(ii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0°C]{HNO_2} C$ **(AI 2013)**

(iii) $C_6H_5NH_2 \xrightarrow[HCl]{NaNO_2} A \xrightarrow[OH^-]{C_6H_5NH_2} B$ **(AI 2010)**

(iv) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow[\text{heat}]{NH_3} C$ **(Delhi 2013)**

(v) $C_6H_5NO_2 \xrightarrow{Sn + HCl} A \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow[\text{heat}]{H_2O/H^+} C$ **(Delhi 2013)**

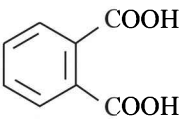
(vi) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOH + Br_2} B \xrightarrow[\text{alc. KOH}]{CHCl_3} C$ **(AI 2013)**

(vii) $CH_3CHO \xrightarrow[(ii)\ H_2O]{(i)\ C_2H_5MgCl} A \xrightarrow{\text{Conc. } H_2SO_4} B \xrightarrow[\text{peroxide}]{HBr} C$ **(Delhi 2011C)**

(viii) $A \xrightarrow{[O]} B \xrightarrow{Ca(OH)_2} C \xrightarrow[(-CaCO_3)]{\text{Distill}} D \xrightarrow{LiAlH_4} E \xrightarrow{HBr} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$ **(AI 2008C)**

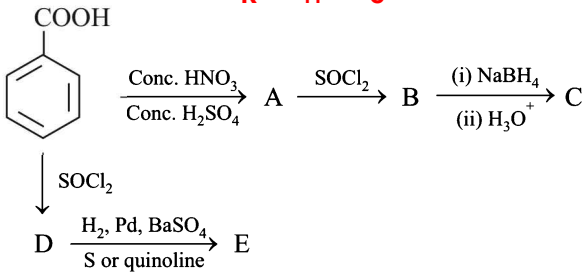
(ix) $CH_3CH_2COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{Br_2/KOH} B \xrightarrow{HONO} C \xrightarrow{O}$

$CH_3COOH \xrightarrow[\text{(ii) distill}]{\text{(i) } Ca(OH)_2} D \xrightarrow{LiAlH_4} E$ **(AI 2009C)**

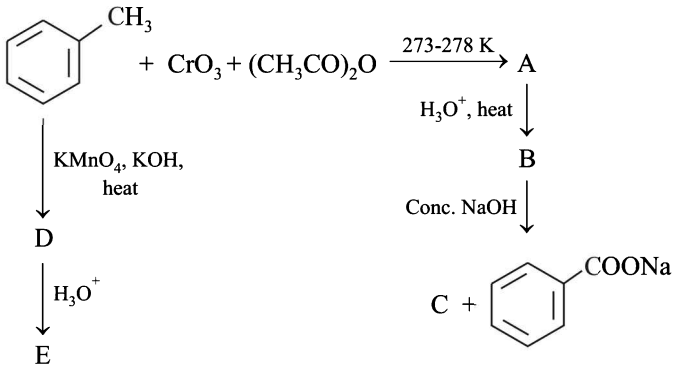
(x) 

$+ NH_3 \rightleftharpoons A \xrightarrow{\text{Heat}} B \xrightarrow[\text{heating}]{\text{strong}} C$ **(AI 2011C)**

(xi)



(xii)



(AI 2010C)

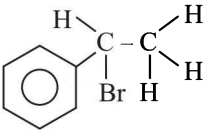
(A) Hydrocarbons and halogen derivatives.

1. (i) $CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{Mark. addition}} CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_3$

(ii) $CH_3CH_2CH = CH_2 + HBr \xrightarrow[\text{anti-markow. addition}]{\text{Peroxide}} CH_3CH_2CH_2CH_2Br$

(iii) $H_2C = CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2 - CH_2Br$

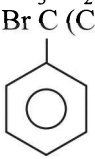
(iv) $C_6H_5N_2Cl + KI \longrightarrow C_6H_5I + N_2 + KCl$

(v) 

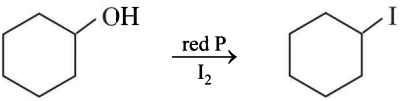
(vi) $(CH_3)_3COH$

(vii) $3CH_3CH_2Cl + SbF_3 \xrightarrow{\text{Heat}} 3CH_3CH_2F + SbCl_3$

(viii) $CH_3CH_2C \equiv CCH_2CH = CH_2$

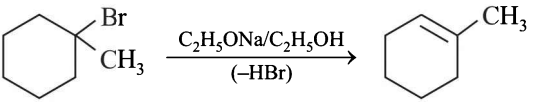
(ix) 

(Bromination takes place at α-position.)

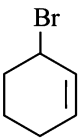
(x) 

(xi) $CH_3CH_2Cl + KNO_2 \longrightarrow CH_3CH_2-N{<}^{O}_{O} + CH_3CH_2-O-N=O$

Nitroethane Ethyl nitrite

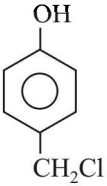
(xii) 

1-Methylcyclohexene

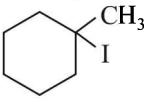
(xiii) 

3-Bromocyclohexene

In presence of heat and light, allylic bromination takes place, while in dark bromine adds on double bond to form dibromoderivative.

(xiv) 

HCl reacts with alcohols ($-CH_2OH$) and not with phenols.

(xv) 

HI adds according to Markownikof's rule.

(xvi) The reactant is allylic compound, so it can form two products.

$$CH_3-CH=CH-CH_2Cl \longrightarrow CH_3CH=CH-CH_2 + Cl^-$$

$$CH_3CH=CH-\overset{+}{C}H_2 \longleftrightarrow CH_3\overset{+}{C}H-CH=CH_2$$

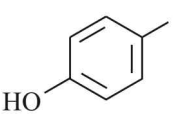
$$\downarrow CN^- \qquad\qquad \downarrow CN^-$$

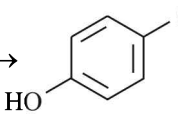
$$CH_3CH=CH-CH_2CN \qquad CH_3\underset{\underset{CN}{|}}{C}H-CH=CH_2$$

(B) Alcohols, phenols and ethers.

(i)

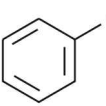
$+ SO_2 + HCl$

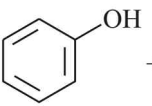
(ii) 

$+ HCl \longrightarrow$ 

$+ H_2O$

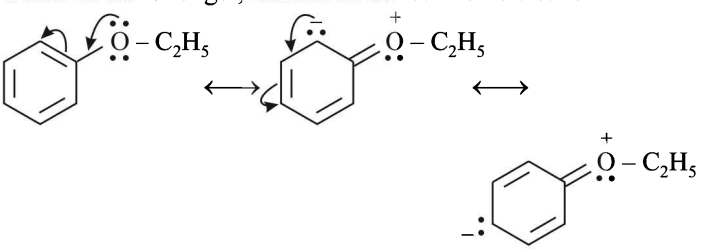
(Phenolic –OH is not easily replaced, hence does not react with HCl)

(iii) 

$+ HBr \longrightarrow$ 

$+ C_2H_5Br$

C_6H_5-O bond has some double bond character (see below), thus it is shorter and stronger, and hence difficult to be cleaved.



K M C

Moreover, $C_2H_5^+$ is more stable than $C_6H_5^+$.

$$C_6H_5OC_2H_5 \xrightarrow{H^+} C_6H_5O^+C_2H_5$$

$$C_6H_5^+ + HOC_2H_5 \longleftarrow \mathbf{C_6H_5O^+C_2H_5} \longrightarrow C_6H_5OH + \overset{+}{C_2}H_5$$

(less stable) **(more stable)**

$$C_6H_5^+ \xrightarrow{\times Br^-} C_6H_5Br \quad \text{(not formed)}$$

$$\overset{+}{C_2}H_5 \xrightarrow{Br^-} C_2H_5Br$$

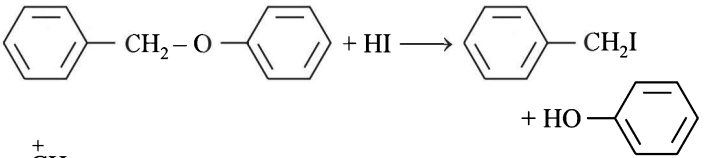
(iv) $(CH_3)_3C-O-C_2H_5 + HBr \longrightarrow (CH_3)_3CBr + C_2H_5OH$

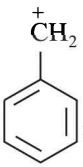
$(CH_3)_3C^+$ (a 3° carbocation) is more stable than the $C_2H_5^+$, hence it is easily formed.

(v) $CH_3CH_2CH_2OCH_3 + HBr \longrightarrow CH_3CH_2CH_2Br + CH_3OH$

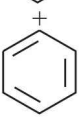
$CH_3CH_2\overset{+}{C}H_2$ is more stable than CH_3^+ due to inductive effect ($CH_3CH_2 \rightarrow CH_2^+$) as well as hyperconjugation.

(vi)





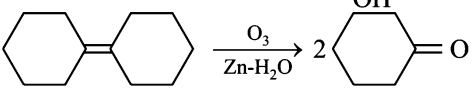
(benzyl carbocation) is more stable due to resonance than



(C) Aldehydes, ketones and carboxylic acids.

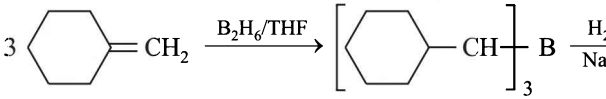
(i) $CH_3C\equiv CH \xrightarrow[\text{(hydration)}]{Hg^{2+},\ H_2SO_4} CH_3-\underset{\underset{OH}{|}}{C}=CH_2 \rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

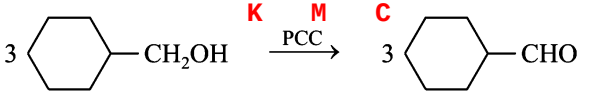
(ii)



In ozonolysis, $>C=C<$ is always cleaved to $>C=O + O=C<$.

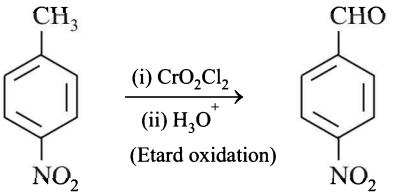
(iii)



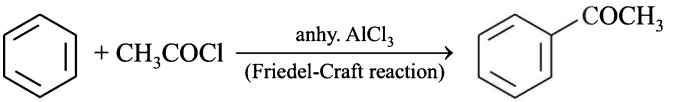


Cyclohexane carbaldehyde

(iv)

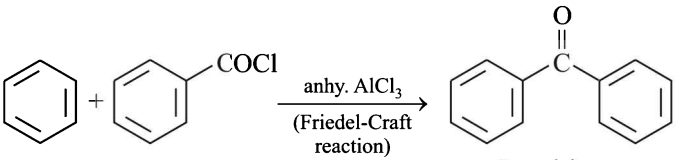


(v)



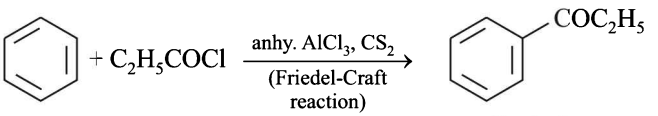
Acetophenone

(vi)



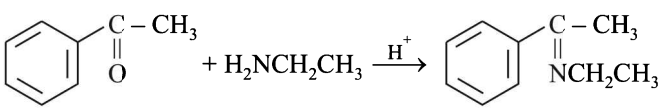
Benzolphenone

(vii)



Propiophenone

(viii)



Schiff's base

(ix) $C_6H_5CHO + H_2NNHCONH_2 \xrightarrow{H^+} C_6H_5CH=NNHCONH_2 + H_2O$

Benzaldehyde semicarbazone

Note that the $-NH_2$ end of $-CONH_2$ does not react because its

nucleophilic character is decreased due to resonance.

(x) $2H-\underset{\underset{O}{\|}}{C}-H \xrightarrow[\text{(Cannizzaro reaction)}]{\text{Conc. KOH}} CH_3OH + HCOONa$

Methanol Sod. methanoate

(xi) $C_6H_5CHO + H_3CCOC_6H_5 \xrightarrow[\text{crossed aldol condensation}]{OH^-,\ 293K} C_6H_5CH = CHCOC_6H_5$

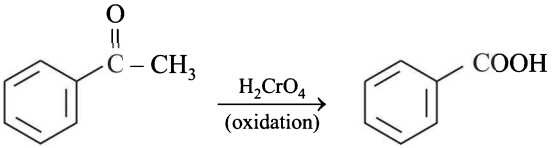
Benzaldehyde Acetophenone Benzal acetophenone

(xii) $CH_3COCH_3 \xrightarrow[\text{Clemmensen reduction}]{Zn\text{–}Hg/HCl} CH_3CH_2CH_3$

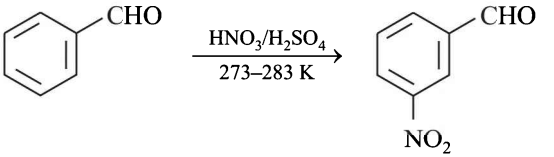
(xiii) $C_6H_5COCl \xrightarrow[\text{(Rosenmund reduction)}]{H_2\text{–}Pd\text{–}BaSO_4} C_6H_5CHO$

Benzaldehyde

(xiv)

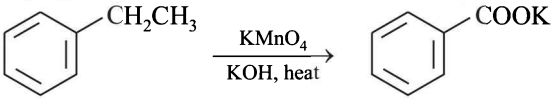


(xv)

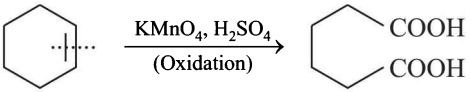


m-Nitrobenzaldehyde

(xvi) Alkyl group present on benzene ring is always oxidised to –COOH group, irrespective to its length, when oxidised by a strong oxidising agent.

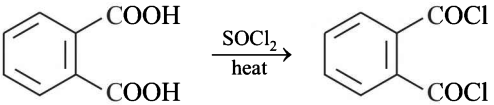


(xvii)



Cyclohexene Hexan-1, 6-dioic acid (Adipic acid)

(xviii)

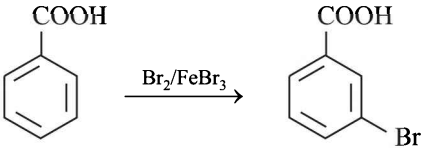


Phthaloyl chloride

(xix) $CH_3COOH \xrightarrow[\text{HVZ reaction}]{Br_2/P} BrCH_2COOH$

Acetic acid α-Bromoacetic acid

(xx)



(xxi) $R-\overset{\overset{\large O}{\|}}{C}-NH_2 \xrightarrow[\text{(reduction)}]{LiAlH_4,\ H_2O} R-CH_2-NH_2$

Alkanamide → Alkanamine

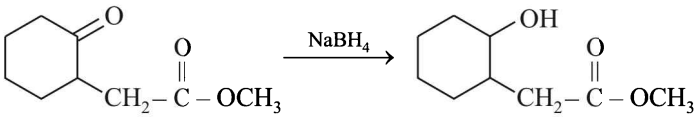
(xxii) $C_6H_5CONH_2 \xrightarrow[\text{(hydrolysis)}]{H_3O^+,\ heat} C_6H_5COOH + NH_3$

Benzamide → Benzoic acid

(xxiii) $CH_3-\overset{\overset{\large O}{\|}}{C}-NH_2 + Br_2 + 4NaOH \xrightarrow[\text{bromamide reaction}]{\text{Hofmann}}$

$CH_3NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$

(xxiv) Sodium borohydride ($NaBH_4$) is a weak reducing agent, hence it reduces only aldehydes/ketones, but not esters.



(D) *Amines.*

1. (i) $C_2H_5NH_2 + C_6H_5SO_2Cl \longrightarrow C_2H_5NHSO_2C_6H_5$

N-Ethyl benzenesulphonamide

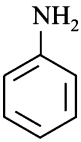
(ii) $C_6H_5NH_2 + CH_3COCl \longrightarrow C_6H_5NHCOCH_3$

Acetanilide

(iii) $C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2 + H_2O$

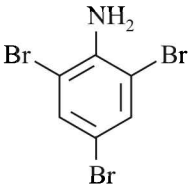
(iv) $RNH_2 + CHCl_3 + 3KOH \xrightarrow[\text{reaction}]{\text{Carbylamine}} R-N\overset{\rightleftharpoons}{\equiv}C + 3KCl + 3H_2O$

Alkyl isocyanide

(v) 

Aniline

$+ Br_2\,(aq.) \longrightarrow$

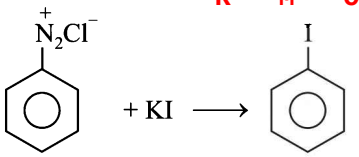


2, 4, 6-Tribromoaniline

($-NH_2$ group is highly activating and aqueous Br_2 solution is highly ionising to give Br^+ ions, hence tribromo product is formed)

(vi) $C_6H_5NH_2 + HCl\,(aq.) \longrightarrow C_6H_5NH_3^+Cl^-$

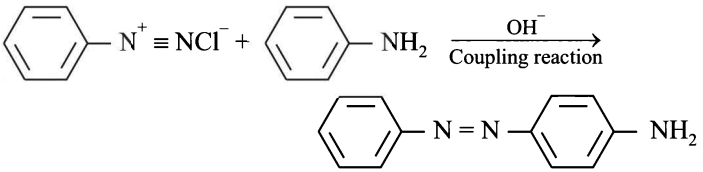
(vii) $C_6H_5N_2Cl + KI \longrightarrow C_6H_5I + N_2 + KCl$

(viii) 

Benzene diazonium chloride Iodobenzene

(ix) $C_6H_5N_2Cl + H_3PO_2 + H_2O \xrightarrow{\text{Reduction}} C_6H_6 + N_2 + H_3PO_3 + HCl$

(x) $C_6H_5N_2Cl + CH_3CH_2OH \xrightarrow{\text{Reduction}} \underset{\text{Benzene}}{C_6H_6} + CH_3CHO + N_2 + HCl$

(xi) 

p-Aminoazobenzene (azo dye)

(xii) $C_6H_5N_2^+Cl^- \xrightarrow[\text{room temp.}]{H_2O} C_6H_5OH + N_2 + HCl$

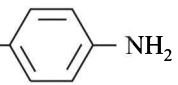
2.

(i) $C_2H_5Cl \xrightarrow{NaCN} \underset{(A)}{C_2H_5CN} \xrightarrow[Ni/H_2]{\text{Reduction}} \underset{(B)}{C_2H_5CH_2NH_2}$

(ii) $CH_3CH_2Br \xrightarrow{KCN} \underset{(A)}{CH_3CH_2CN} \xrightarrow{LiAlH_4} \underset{(B)}{CH_3CH_2CH_2NH_2}$

$\xrightarrow[0°C]{HNO_2} \underset{(C)}{CH_3CH_2CH_2OH}$

(iii) $C_6H_5NH_2 \xrightarrow[HCl]{NaNO_2} \underset{(A)}{C_6H_5N_2Cl} \xrightarrow[OH^-]{C_6H_5NH_2}$

$\underset{(B)}{C_6H_5N = N}$ 

(iv) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} \underset{\text{Benzonitrile (A)}}{C_6H_5CN} \xrightarrow{H_2O/H^+} \underset{(B)}{C_6H_5COOH} \xrightarrow{NH_3}$

$C_6H_5COONH_4 \xrightarrow{heat} \underset{\text{Benzamide (C)}}{C_6H_5CONH_2}$

K M C

(v) $C_6H_5NO_2 \xrightarrow{Sn + HCl} \underset{\text{Aniline (A)}}{C_6H_5NH_2} \xrightarrow[273\ K]{NaNO_2 + HCl} \underset{\text{(B)}}{C_6H_5N_2Cl}$

$\xrightarrow[\text{heat}]{H_2O/H^+} \underset{\text{Phenol (C)}}{C_6H_5OH}$

(vi) $CH_3COOH \xrightarrow{NH_3} CH_3COONH_4 \xrightarrow[(-H_2O)]{\Delta} \underset{\text{(A)}}{CH_3CONH_2}$

$\xrightarrow[\text{Hofmann bromamide reaction}]{NaOH + Br_2} \underset{\text{Methyl amine (B)}}{CH_3NH_2} \xrightarrow[\text{(Carbylamine reaction)}]{CHCl_3 + \text{alc. KOH}} \underset{\text{Methyl isonitrile (C)}}{CH_3N \overset{\rightarrow}{=} C}$

(vii) $CH_3CHO \xrightarrow[\text{(ii) } H_2O]{\text{(i) } C_2H_5MgCl} \underset{\text{(A)}}{CH_3 - \overset{OH}{\overset{|}{CH}} - C_2H_5} \xrightarrow{\text{Conc. } H_2SO_4}$

$\underset{\text{But-2-ene (B) (Major)}}{CH_3CH = CHCH_3} \xrightarrow[\textit{anti}\text{-Mark. addition}]{HBr + \text{peroxide}} \underset{\text{2-Bromobutane (C)}}{CH_3\overset{Br}{\overset{|}{C}}HCH_2CH_3}$

(viii) $\underset{\text{(A)}}{CH_3CHO} \xrightarrow[\text{Oxidation}]{[O]} \underset{\text{(B)}}{CH_3COOH} \xrightarrow{Ca(OH)_2} \underset{\text{(C)}}{(CH_3COO)_2Ca}$

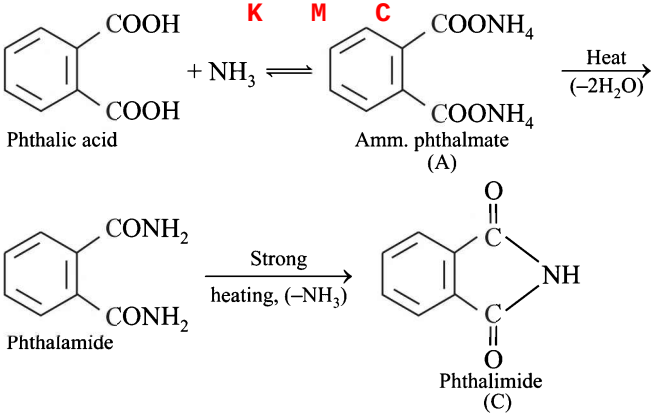
$\xrightarrow[(-CaCO_3)]{\text{Distill}} \underset{\text{(D)}}{CH_3COCH_3} \xrightarrow[\text{(reduction)}]{LiAlH_4} \underset{\text{(E)}}{CH_3\overset{OH}{\overset{|}{C}}HCH_3} \xrightarrow{HBr} CH_3\overset{Br}{\overset{|}{C}}HCH_3$

(ix) $CH_3CH_2COOH \xrightarrow[\Delta]{NH_3} \underset{\text{(A)}}{CH_3CH_2CONH_2} \xrightarrow[\text{(Hofmann bromamide reaction)}]{Br_2/KOH}$

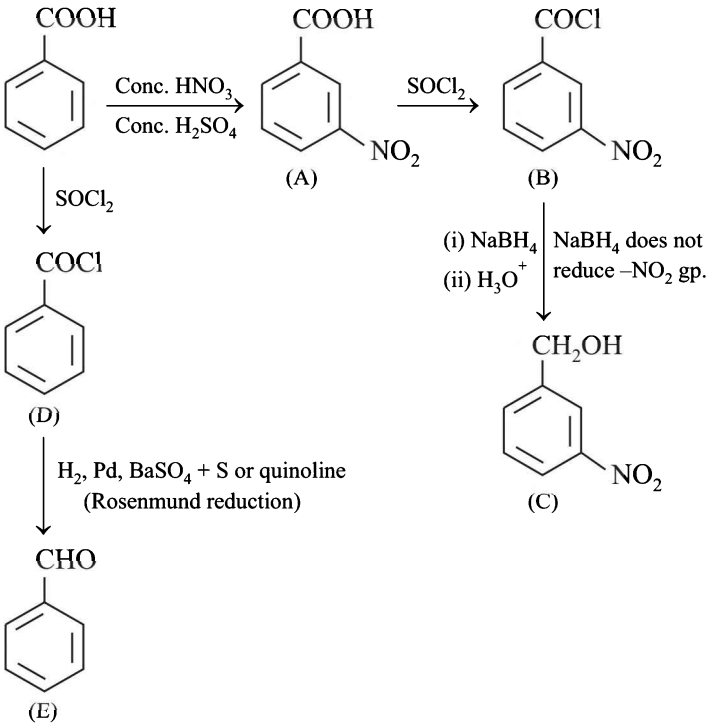
$\underset{\text{(B)}}{CH_3CH_2NH_2} \xrightarrow{HONO} \underset{\text{(C)}}{CH_3CH_2OH} \xrightarrow[\text{(Oxidation)}]{(O)} CH_3COOH$

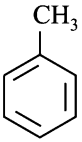
$\xrightarrow[\text{(ii) distill}]{\text{(i) } Ca(OH)_2} \underset{\text{(D)}}{CH_3COCH_3} \xrightarrow[\text{(reduction)}]{LiAlH_4} \underset{\text{(E)}}{CH_3\overset{OH}{\overset{|}{C}}HCH_3}$

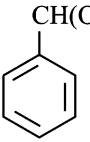
(x)


COOH
COOH
Phthalic acid
+ NH3
COONH4
COONH4
Amm. phthalmate
(A)
Heat
(–2H2O)
CONH2
CONH2
Phthalamide
Strong
heating, (–NH3)
O
C
NH
C
O
Phthalimide
(C)

(xi)


COOH
Conc. HNO3
Conc. H2SO4
COOH
NO2
(A)
SOCl2
COCl
NO2
(B)
SOCl2
COCl
(D)
(i) NaBH4
(ii) H3O+
NaBH4 does not reduce –NO2 gp.
CH2OH
NO2
(C)
H2, Pd, BaSO4 + S or quinoline
(Rosenmund reduction)
CHO
(E)

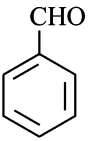
(xii) 

$+ CH_3 + (CH_3CO)_2O \xrightarrow[\text{(Etard reaction)}]{273\text{-}283\ K}$ 

Benzylidene diacetate

(A)

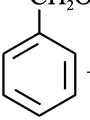
$\xrightarrow{H_3O^+, \Delta}$

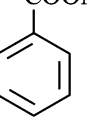


Benzaldehyde

(B)

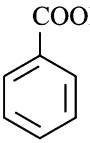
$\xrightarrow[\text{(Cannizzaro reaction)}]{\text{Conc. NaOH}}$



+ 

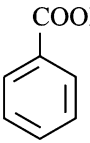
Benzyl alcohol

$\xrightarrow{KMnO_4, KOH, \text{heat}}$

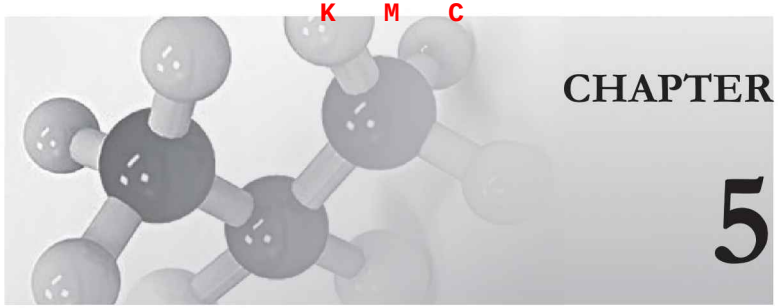


Pot benzoate (D)

$\xrightarrow{H_3O^+ \text{ (hydrolysis)}}$



Benzoic acid (E)



CHAPTER

5

How will you carry out the given Conversions ?

Q. How will you carry out following conversions?

(A) Halogen derivatives.

(i) Propene to allyl iodide.
(ii) Propene to allyl fluoride.
(iii) But-1-ene to 1-iodobutane.
(iv) 1-Bromopropane to 2-bromopropane.
(v) 2-Bromopropane to 1-bromopropane.
(vi) *ter*-Butyl bromide to isobutyl bromide.
(vii) But-1-ene to but-2-ene.
(viii) 2-Chloropropane to 1-propanol.
(ix) Cyclopentene to cyclopenta-1, 3-diene.
(x) Aniline to iodobenzene. **(Delhi 2011)**
(xi) Benzyl chloride to benzyl alcohol. **(Delhi 2010)**
(xii) Bromobenzene to benzoic acid. **(AI 2010)**
(xiii) Propene to propan-1-ol. **(Delhi 2013)**
(xiv) Bromobenzene to 1-phenylethanol. **(AI 2009)**
(xv) Methyl bromide to methyl isocyanide **(Delhi 2013C)**

(B) Alcohols

(i) Ethanol to ethene. **(AI 2011)**
(ii) Ethanal to propan-2-ol. **(Delhi 2011)**

159 Approved: 0777 023 444

(iii) Propene to propan-2-ol. K M C

(Delhi 2010, 2013, AI 2010, 2011, Foreign 2011)

(iv) 2-Methylpentene to 2-methylpentan-2-ol. **(AI 2012C)**

(v) 2-Methylpropene to 2-methylpropanol. **(Delhi 2011)**

(vi) Butan-2-one to butan-2-ol. **(Delhi 2008)**

(vii) Propanone to 2-methylpropan-2-ol. **(AI 2010)**

(viii) Methyl magnesium bromide to 2-methylpropan-2-ol.

(Delhi 2010, AI 2011, Foreign 2011)

(ix) Ethyl magnesium chloride to propan-1-ol.

(Delhi 2006C, 2010)

(x) A primary alcohol to an aldehyde. **(Delhi 2008)**

(xi) Cyclohexanol to cyclohexan-1-one. **(AI 2010)**

(xii) Propan-2-ol to propanone. **(Delhi 2013)**

(xiii) 2-Butene to ethanol. **(AI 2006 C)**

(xiv) Ethylene to *n*-propyl alcohol.

(xv) 2-Bromopropane to acetone. **(AI 2004 C)**

(xvi) Ethanol to 1,1-dichloroethane. **(Delhi 2005 C)**

(xvii) 1-Propanol to 1-chloro-2-propanol. **(Delhi 2004 C)**

(xviii) *n*-Propyl alcohol to hexane. **(Foreign 2003)**

(xix) 1-Propanol to 2-bromopropane.

(xx) 2-Propanol to 1-bromopropane.

(xxi) Ethanol to methanol.

(xxii) Ethanol to 2-propanol.

(xxii) Ethanol to acetone **(Delhi 2013C)**

(C) Phenols

(i) Phenol to *p*-benzoquinnone. **(AI 2010, 2011, Foreign 2011)**

(ii) Phenol to 2,4,6-tribromophenol. **(Delhi 2008, 2013)**

(iii) Phenol to picric acid. **(Delhi 2011)**

(iv) Phenol to salicylic acid. **(Delhi 2006)**

(v) Benzene to phenol. **(Delhi 2011)**

(vi) Phenol to phenyl ethanoate.
(vii) Aniline to phenol. **(AI 2004 C)**
(viii) Anisole to phenol. **(AI 2006 C)**
(ix) Phenol to salicylaldehyde. **(AI 2006 C)**
(x) Phenol to toluene. **(Delhi 2005 C)**
(xi) Phenol to aspirin.
(xii) Phenol to benzaldehyde. **(AI 2013C)**

(D) Aldehydes, ketones and carboxylic acids.

(i) Acetyl chloride to acetone. **(AI 2002 C)**
(ii) Propene to acetone.
(iii) Ethanol to propanone (acetone). **(Delhi 2008, AI 2001)**
(iv) Ethanol to 3-hydroxybutanal.
(AI 2009, Foreign 2009, 2010, 2012)
(v) Benzoyl chloride to benzaldehyde. **(Delhi 2013, AI 2001)**
(vi) Propanone to propane. **(Delhi 2013)**
(vii) Propanone to propan-2-ol. **(Al 2013)**
(viii) Propanone to propene.
(Delhi 2010, AI 2009, Foreign 2009, 2010)
(ix) Propanal to butanone
(x) Ethanal to but-2-enal (crotonaldehyde).
(Delhi 2010, 2011, 2013, AI 2001, Foreign 2011)
(xi) Ethanal to 2-butenol.
(xii) Ethanal to propan-2-ol. **(Delhi 2013)**
(xiii) Ethanal to 2-hydroxypropanoic acid. **(AI 2013)**
(xiv) Ethanal to but-2-enoic acid.
(xv) Toluene to benzaldehyde. **(Delhi 2009)**
(xvi) Benzene to acetophenone. **(Delhi 2008, AI 2002 C)**
(xvii) Benzaldehyde to benzophenone.
(AI 2009, Foreign 2009, 2010, 2012)
(xviii) Acetophenone to ethylbenzene.
(xix) Benzaldehyde to 3-phenylpropanol.
(xx) Toluene to benzoic acid. **(AI 2013, 2010)**
(xxi) Phenylethene to benzoic acid.
(xxii) Ethylbenzene to benzoic acid.
(Delhi 2009, 2011, AI 2010, 2011, Foreign 2011)
(xxiii) Bromobenzene to benzoic acid. **(AI 2010)**

(xxiv) Phenol to acetophenone. **(Delhi 2004 C, AI 2012 C)**
(xxv) Anisole to *p*-methoxyacetophenone. **(Delhi 2004)**
(xxvi) Acetylene to acetic acid. **(Delhi 2013C)**
(xxvii) Propanoic acid to acetic acid.
(xxviii) Ethanoic acid to propanoic acid.
(xxix) Ethanoic acid to ethane.
(xxx) Ethanoic acid to acetaldehyde.
(xxxi) Propanoic acid to propenoic acid.
(xxxii) Benzoic acid to benzaldehyde.
(Delhi 2008, 2010, AI 2009)
(xxxiii) Benzyl alcohol to phenylethanoic acid.
(xxxiv) Ethyl cyanide to ethanoic acid. **(Delhi 2012, AI 2010)**
(xxxv) Ethanoyl chloride to ethanonitrile. **(Delhi 2012 C)**
(xxxvi) Butan-1-ol to butanoic acid.
(Delhi 2011, 2012, AI 2010, 2011, Foreign 2011)
(xxxvii) Benzoic acid to *m*-bromobenzoic acid. **(Delhi 2012)**
(xxxviii) Benzoic acid to *m*-nitrobenzyl alcohol. **(Foreign 2012)**
(xxxix) 4-Methylacetophenone to benzene-1,4-dicarboxylic acid.
(Delhi 2012)
(xxxx) Toluene to *m*-nitrobenzoic acid. **(Delhi 2013C)**

(E) Amines.

(i) Ethanamine to ethanoic acid. **(Delhi 2011 C)**
(ii) Methanamine to iodomethane. **(Delhi 2011 C)**
(iii) Benzyl chloride to 2-phenylethanamine. **(Delhi 2012)**
(iv) $CH_3CH_2Cl \longrightarrow CH_3CH_2CH_2NH_2$ **(Delhi 2012 C)**
(v) Benzene to aniline **(Delhi 2011 C)**
(vi) Aniline to chlorobenzene. **(Delhi 2011 C)**
(vii) Aniline to nitrobenzene. **(Delhi 2011)**
(viii) Aniline to iodobenzene
(ix) Aniline to benzonitrile. **(Delhi 2001 C)**
(x) Aniline to benzoic acid. **(AI 2013C)**
(xi) Aniline to benzyl alcohol. **(Delhi 2012)**
(xii) Nitrobenzene to phenol. **(Delhi 2011 C)**
(xiii) Chlorobenzene to *p*-chloroaniline. **(Delhi 2011 C)**
(xiv) Nitrobenzene to benzoic acid. **(Delhi 2012)**
(xv) Aniline to *p*-hydroxyazobenzene. **(Delhi 2012 C)**

(A) Halogen derivatives.

(i) $\underset{\text{Propene}}{CH_3CH{=}CH_2} \xrightarrow{Cl_2,\ hv} ClCH_2CH{=}CH_2 \xrightarrow{NaI} \underset{\text{Allyl iodide}}{ICH_2CH{=}CH_2} + NaCl(s)$

Allyl chloride is readily converted to iodide with NaI in acetone because less soluble NaCl precipitates out and is removed by filtration. This drive the reaction to completion.

(ii) $\underset{\text{Propene}}{CH_3CH{=}CH_2} \xrightarrow{Cl_2,\ hv} ClCH_2CH{=}CH_2 \xrightarrow{AgF} \underset{\text{Allyl fluoride}}{FCH_2CH{=}CH_2} + AgCl(s)$

(iii) $\underset{\text{But-1-ene}}{CH_3CH_2CH{=}CH_2} \xrightarrow[\text{(anti-Markow. addition)}]{\text{HBr, peroxide}} CH_3CH_2CH_2CH_2Br$

$\xrightarrow[\text{(Finkelstein reaction)}]{\text{KI/acetone}} \underset{\text{1-Iodobutane}}{CH_3CH_2CH_2CH_2I}$

(iv) $\underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow[\text{(– HBr)}]{\text{KOH (alc.)}} CH_3CH{=}CH_2$

$\xrightarrow[\text{(Markownikov addition)}]{\text{HBr}} \underset{\text{2-Bromopropane}}{CH_3\overset{\overset{Br}{|}}{C}HCH_3}$

(v) $\underset{\text{2-Bromopropane}}{CH_3\overset{\overset{Br}{|}}{C}HCH_3} \xrightarrow[\text{(– HBr)}]{\text{KOH (alc.)}} CH_3CH{=}CH_2 \xrightarrow[\text{anti-Marko. addition}]{\text{HBr, peroxide}} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br}$

(vi) $\underset{\text{ter-Butyl bromide}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3} \xrightarrow[\text{(– HBr)}]{\text{KOH (alc.)}} CH_3-\overset{\overset{CH_3}{|}}{C}{=}CH_2 \xrightarrow[\text{anti-Marko. addition}]{\text{HBr, peroxide}} \underset{\text{Isobutyl bromide}}{CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2Br}$

(vii) $\underset{\text{But-1-ene}}{CH_3CH_2CH{=}CH_2} \xrightarrow{HBr} CH_3CH_2\overset{\overset{Br}{|}}{C}HCH_3 \xrightarrow[\text{(– HBr)}]{\text{KOH (alc.)}} \underset{\text{But-2-ene}}{CH_3CH{=}CHCH_3}$

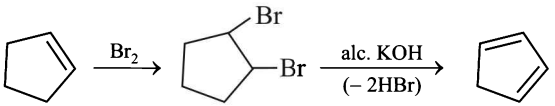
(Saytzeff product, more stable)

(viii) $CH_3-\underset{}{\overset{Cl}{CH}}-CH_3 \xrightarrow[(-HCl)]{KOH\ (alc.)} CH_3CH=CH_2 \xrightarrow[anti\text{-Mark. addition}]{HBr,\ peroxide}$

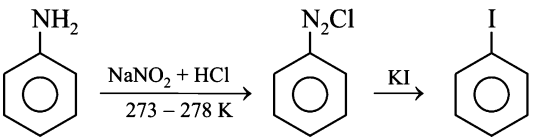
2-Chloropropane

$CH_3CH_2CH_2Br \xrightarrow{NaOH\ (aq.)} CH_3CH_2CH_2OH$

1-Propanol

(ix) 

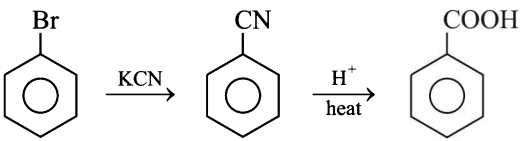
Cyclopentene Cyclopenta-1,3-diene

(x) 

Aniline Iodobenzene

(xi) $C_6H_5CH_2Cl \xrightarrow{aq.\ KOH} C_6H_5CH_2OH$

Benzyl chloride Benzyl alcohol

(xii) 

Bromobenzene Benzoic acid

(xiii) $CH_3CH=CH_2 \xrightarrow[(anti\text{-Markow. addition})]{HBr,\ peroxide} CH_3CH_2CH_2Br \xrightarrow{aq.\ KOH}$

Propene

$CH_3CH_2CH_2OH$

Propan-1-ol

(xiv) $C_6H_5Br + Mg \xrightarrow[ether]{dry} C_6H_5MgBr \xrightarrow{CH_3CHO} CH_3-\overset{OMgBr}{\overset{|}{CH}}-C_6H_5$

Bromobenzene

$\xrightarrow{H^+} CH_3\overset{OH}{\overset{|}{C}}HC_6H_5$

1-Phenylethanol

(xv) $CH_3Br + AgCN \longrightarrow CH_3N\overset{\rightarrow}{=}C + AgBr$

Methyl bromide Methyl isocyanide

(B) Alcohols

(i) $CH_3CH_2OH \xrightarrow{Conc.\ H_2SO_4} CH_2=CH_2$

Ethanol Ethene

(ii) $CH_3-\underset{\underset{H}{|}}{C}=O \xrightarrow{CH_3MgI} CH_3-\overset{\overset{OMgI}{|}}{\underset{\underset{H}{|}}{C}}-CH_3 \xrightarrow{H^+, (H_2O)} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_3$

Ethanal → Propan-2-ol

(iii) $CH_3CH=CH_2 + H_2SO_4 \xrightarrow[\text{boil}]{H_2O} CH_3-\overset{\overset{OH}{|}}{C}H-CH_3$

Propene → Propan-2-ol

$\downarrow$ HBr

$CH_3-\overset{\overset{Br}{|}}{C}H-CH_3 \xrightarrow{aq.\ KOH} CH_3-\overset{\overset{OH}{|}}{C}H-CH_3$

Propan-2-ol

(iv) $CH_3CH_2CH_2-\underset{\underset{CH_3}{|}}{C}=CH_2 + H_2SO_4 \xrightarrow{H_2O} CH_3CH_2CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

2-Methylpentene → 2-Methylpentan-2-ol

(v) $CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[\text{(Hydroboration)}]{BH_3} \left[CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2\right]_3 \xrightarrow[\text{(Oxidation)}]{H_2O_2, OH^-} 3CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2OH$

2-Methylpropene → 2-Methylpropanol

(vi) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_3 \xrightarrow[\text{or } Ni/H_2]{LiAlH_4,\ NaBH_4} CH_3-\overset{\overset{OH}{|}}{C}H-CH_2CH_3$

Butan-2-one → Butan-2-ol

(vii) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{CH_3MgI} CH_3-\overset{\overset{OMgI}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \xrightarrow{H^+, H_2O} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

Propanone → 2-Methylpropan-2-ol

(viii) Same as (vii)

(ix) $H-\overset{\overset{O}{\|}}{C}-H + C_2H_5MgCl \longrightarrow H-\overset{\overset{OMgCl}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-H \xrightarrow{H^+, H_2O} H-\overset{\overset{OH}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-H$

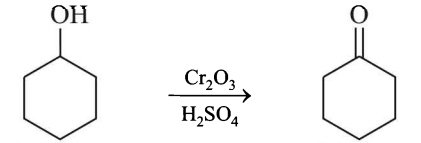
Ethyl mag. chloride → Propan-1-ol (Propanol) or $C_2H_5-CH_2OH$

(x) $CH_3CH_2CH_2OH \xrightarrow{PCC^*} CH_3CH_2CHO$

n-Propanol (1° alcohol) → Propanal (an aldehyde)

K M C

* PCC is pyridinium chlorochromate (a complex of Cr_2O_3 with pyridine and HCl). It does not oxidise C=C, if present.

(xi) 

Cyclohexanol (a 2° alcohol) — Cyclohexanone

(xii) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[\text{Conc. } H_2SO_4]{K_2Cr_2O_7} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

Propan-2-ol — Propanone

(xiii) $CH_3CH{=}CHCH_3 \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3} 2CH_3CHO \xrightarrow{LiAlH_4} 2CH_3CH_2OH$

But-2-ene

(xiv) $CH_2{=}CH_2 + CO + H_2 \xrightarrow{[Co(CO)_4]_2} CH_3CH_2CHO \xrightarrow{LiAlH_4,\ \text{Ethanol}} CH_3CH_2CH_2OH$

(xv) $CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow{\text{aq. KOH}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[573\text{ K}]{Cu} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

2-Bromopropane — Acetone

(xvi) $CH_3CH_2OH \xrightarrow[573\text{ K}]{Cu} CH_3CHO \xrightarrow{PCl_5} CH_3CHCl_2$

Ethanol — 1,1-Dichloroethane

(xvii) $CH_3CH_2CH_2OH \xrightarrow[443\text{ K}]{\text{Conc. } H_2SO_4} CH_3CH{=}CH_2 \xrightarrow{HOCl} CH_3\underset{\underset{OH}{|}}{C}HCH_2Cl$

1-Propanol — 1-Chloro-2-propanol

(xviii) $CH_3CH_2CH_2OH + PCl_5 \longrightarrow CH_3CH_2CH_2Cl + POCl_3 + HCl$

n-Propyl alcohol

$CH_3CH_2CH_2Cl + 2Na + ClCH_2CH_2CH_3 \xrightarrow[\text{Wurtz reaction}]{\text{dry ether}} CH_3CH_2CH_2CH_2CH_2CH_3$

n-Hexane

(xix) $CH_3CH_2CH_2OH \xrightarrow[443\text{ K}]{\text{Conc. } H_2SO_4} CH_3CH{=}CH_2 \xrightarrow[\text{Mark. addition}]{HBr} CH_3\underset{\underset{Br}{|}}{C}H-CH_3$

1-Propanol — 2-Bromopropane

(xx) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[\text{heat}]{\text{Conc. } H_2SO_4} \overset{K}{CH_3CH}=\overset{M}{CH_2} \xrightarrow[\text{anti-Mark. addition}]{\text{HBr, Peroxide}} \overset{C}{CH_3CH_2CH_2Br}$

2-Propanol 1-Bromopropane

(xxi) $CH_3CH_2OH \xrightarrow[\text{(oxidation)}]{KMnO_4/H_2SO_4} CH_3COOH \xrightarrow[\text{heat}]{NH_3} CH_3CONH_2$

$\xrightarrow{Br_2/KOH} CH_3NH_2 \xrightarrow{HNO_2} CH_3OH$

Ethanol Methanol

(xxii) $CH_3CH_2OH \xrightarrow[573\text{ K}]{Cu} CH_3CHO \xrightarrow{CH_3MgBr} CH_3-\underset{\underset{OMgBr}{|}}{CH}-CH_3$

$\xrightarrow{H^+, H_2O} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

Ethanol 2-Propanol

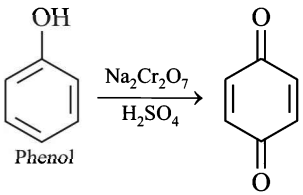
(xxiii) $CH_3CH_2OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH \xrightarrow{Ca(OH_2)} (CH_3COO)_2Ca$

$\xrightarrow{\text{distill}} (CH_3)_2CO$

Ethanol Acetone

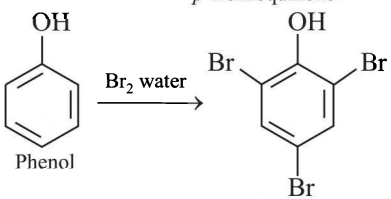
(C) Phenols

(i)



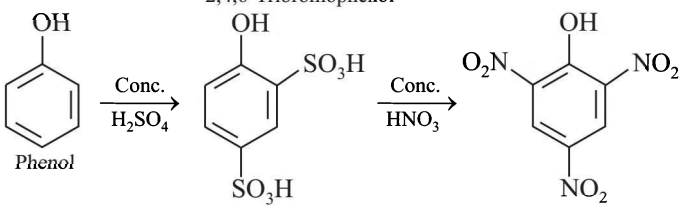
p-Benzoquinone

(ii)

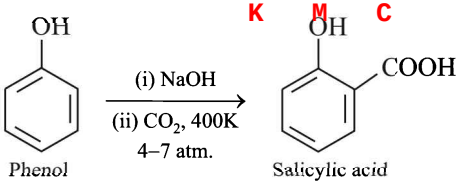


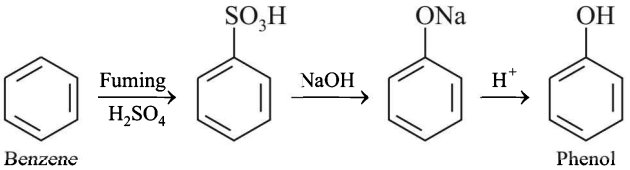
2,4,6-Tribromophenol

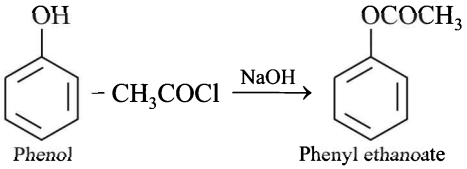
(iii)



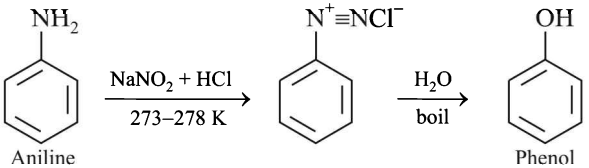
Picric acid

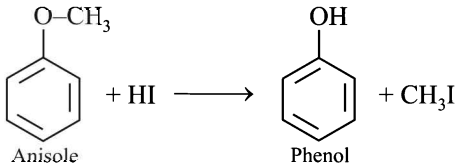
(iv) 

(v) 

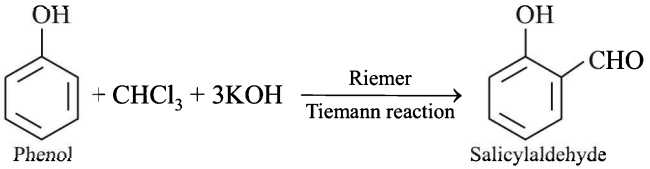
(vi) 

Remember, if anhy. $AlCl_3$ is used in place of NaOH, electrophilic substitution takes place forming *p*- and *o*-hydroxyacetophenone.

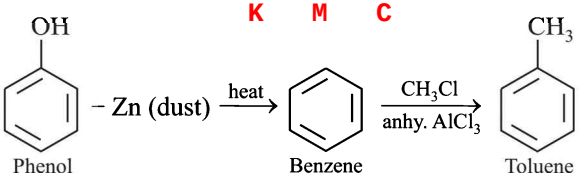
(vii) 

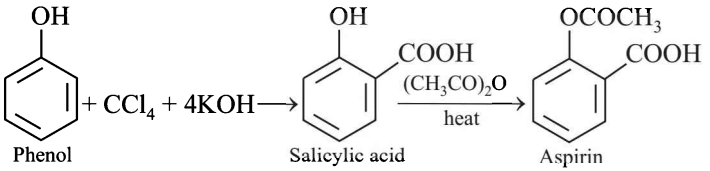
(viii) 

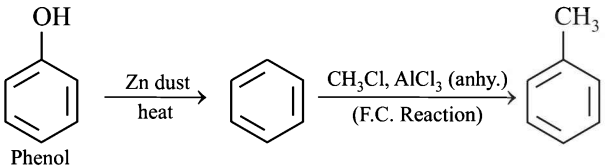
Remember that C–O bond is stronger than O–C bond because of resonance in former case which leads to partial double bond character to C–O bond.

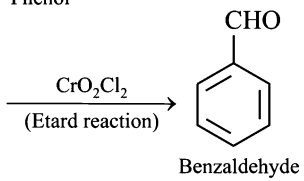
(ix) 

Remember if we take CCl_4 in place of $CHCl_3$, salicylic acid would be formed (–COOH in place of –CHO in the product).

(x) 

(xi) 

(xii) 



(D) Aldehydes, ketones and carboxylic acids.

(i) $CH_3-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

Acetyl chloride → Acetone

$2CH_3COCl + (CH_3)_2Cd \longrightarrow 2CH_3COCH_3 + CdCl_2$

Acetyl chloride → Acetone

(ii) $CH_3CH{=}CH_2 \longrightarrow CH_3COCH_3$

Propene → Acetone

$CH_3CH{=}CH_2 + H_2O \xrightarrow[H_2SO_4]{Hg^{2+}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[573K]{Cu} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

Propene → Acetone

(iii) $CH_3CH_2OH \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

Ethanol → Propanone

$CH_3CH_2OH \xrightarrow[\text{dil. } H_2SO_4]{KMnO_4} CH_3COOH \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca \xrightarrow[(-\,CaCO_3)]{\text{dry distill}} CH_3COCH_3$

Ethanol → Acetone (propanone)

(iv) $CH_3CH_2OH \longrightarrow CH_3\overset{K}{C}H(OH)\overset{M}{C}H_2\overset{C}{C}HO$

Ethanol → 3-Hydroxybutanal

$$CH_3CH_2OH \xrightarrow{PCC} CH_3CHO \xrightarrow[\text{(aldol conden.)}]{\text{dil. NaOH}} CH_3CH(OH)CH_2CHO$$

Ethanol → CH3CHO → 3-Hydroxybutanal

(v) $C_6H_5COCl \xrightarrow[\text{(Rosenmund reduction)}]{H_2 - Pd/BaSO_4} C_6H_5CHO$

Benzoyl chloride → Benzaldehyde

(vi) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{(Clemmensen reduction)}]{Zn - Hg/HCl} CH_3-CH_2-CH_3$

Propanone → Propane

(vii) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{(reduction)}]{LiAlH_4} CH_3-\overset{OH}{\overset{|}{C}H}-CH_3$

Propanone → Propan-2-ol

(viii) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{LiAlH_4} CH_3-\overset{OH}{\overset{|}{C}H}-CH_3 \xrightarrow{\text{Conc. } H_2SO_4} CH_3CH=CH_2$

Propanone → Propene

(ix) $CH_3CH_2CHO \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$

Propanal → Butanone

$$CH_3CH_2CHO + CH_3MgI \xrightarrow{H_3O^+} CH_3-CH_2-\overset{OH}{\overset{|}{C}H}CH_3$$

Propanal

$$\xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3$$

Butanone

(x) $CH_3CHO \longrightarrow CH_3CH=CHCHO$

Ethanal → But-2-enal

$$CH_3CHO \xrightarrow[\text{(aldol conden)}]{OH^-} CH_3\overset{OH}{\overset{|}{C}H}CH_2CHO \xrightarrow{-H_2O} CH_3CH=CHCHO$$

Ethanal → But-2-enal

(xi) $CH_3CHO \longrightarrow CH_3CH=CHCH_2OH$

Ethanal → But-2-enol

$$CH_3CHO \xrightarrow{\text{as in (x)}} CH_3CH=CHCHO \xrightarrow[\text{(C=C is not reduced)}]{NaBH_4} CH_3CH=CHCH_2OH$$

Ethanal → But-2-enal → But-2-enol

(xii) $CH_3CHO \longrightarrow CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCH_3$

Ethanal — Propan-2-ol

$$CH_3CHO + CH_3MgI \longrightarrow CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OMgI}{|}}{C}}-H \xrightarrow{H^+} CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-H$$

Ethanal — Propan-2-ol

(xiii) $CH_3CHO \longrightarrow CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCOOH$

Ethanal — 2-Hydroxypropanoic acid

$$CH_3CHO \xrightarrow{HCN} CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCN \xrightarrow{H_3O^+} CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCOOH$$

Ethanal — 2-Hydroxypropanoic acid

(xiv) $CH_3CHO \longrightarrow CH_3CH{=}CHCOOH$

Ethanal — But-2-enoic acid

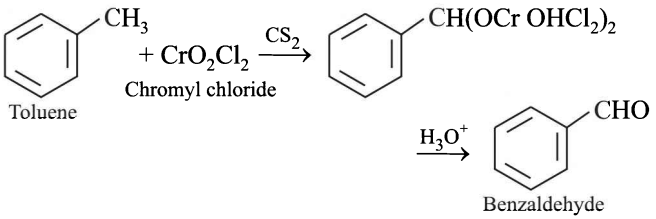
$$CH_3CHO \xrightarrow{\text{as in (x)}} CH_3CH{=}CHCHO \xrightarrow[\text{Tollen's reagent}]{[Ag(NH_3)_2]^+} CH_3CH{=}CHCOOH$$

Ethanal — But-2-enoic acid

Note: Tollen's reagent is a mild oxidising agent and does not oxidise C=C linkage

(xv) $C_6H_5CH_3 \longrightarrow C_6H_5CHO$

Toluene — Benzaldehyde



(xvi) $C_6H_6 + CH_3COCl \xrightarrow[\text{Friedel-Craft}]{\text{anhy. } AlCl_3} C_6H_5COCH_3$

Benzene — Acetophenone

(xvii) $C_6H_5CHO \longrightarrow C_6H_5COC_6H_5$

Benzaldehyde — Benzophenone

K M C

$$C_6H_5CHO \xrightarrow{(Oxid.)} C_6H_5COOH \xrightarrow{Ca(OH)_2} (C_6H_5COO)_2Ca$$

Cal. benzoate

distillation

$$C_6H_5COC_6H_5$$

Benzophenone

C_6H_5MgBr

$C_6H_5COOH \xrightarrow{NaOH/CaO,\ heat} C_6H_6$

Benzene

$C_6H_6 \xrightarrow[anhy.\ AlCl_3]{C_6H_5COCl}$ Benzophenone

$$C_6H_5CH(OH)C_6H_5 \xrightarrow{(O)} C_6H_5COC_6H_5$$

Benzophenone

(xviii) $C_6H_5COCH_3 \xrightarrow[\text{Clemmensen reduction}]{Zn/Hg,\ HCl} C_6H_5CH_2CH_3$

Acetophenone — Ethylbenzene

(xix) $C_6H_5CHO \longrightarrow C_6H_5CH_2CH_2CH_2OH$

Benzaldehyde — 3-Phenylpropanol

$$C_6H_5CHO + CH_3CHO \xrightarrow[\text{cross aldol cond.}]{dil.\ OH^-} C_6H_5CH(OH)CH_2CHO \xrightarrow[-H_2O]{heat}$$

$$C_6H_5CH{=}CHCHO \xrightarrow[\text{(Both C=C and – CHO are reduced)}]{H_2/Ni} C_6H_5CH_2CH_2CH_2OH$$

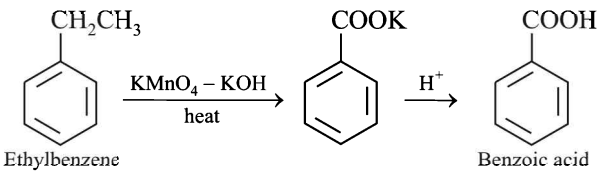
3-Phenylprop-2-enal (Cinnamaldehyde) — 3-Phenylpropanol

(xx) $C_6H_5CH_3 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} C_6H_5COOK \xrightarrow{H^+} C_6H_5COOH$

Toluene — Benzoic acid

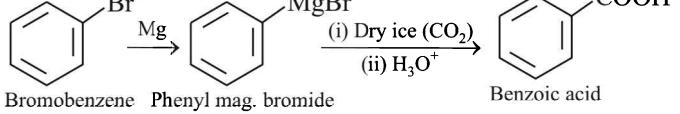
(xxi) $C_6H_5CH{=}CH_2 \xrightarrow[(-\ HCOOK)]{KMnO_4/KOH} C_6H_5COOK \xrightarrow{H^+} C_6H_5COOH$

Phenylethene — Benzoic acid

(xxii) 

Ethylbenzene — Benzoic acid

Remember that alkyl group attached to benzene, when oxidised with strong oxidising agent, is always oxidised to –COOH group, whatever may be the length of the chain, viz. $-CH_3$, $-CH_2CH_3$, $-CH(CH_3)_2$; but not $-C(CH_3)_3$ which is resistant to oxidation.

(xxiii) 

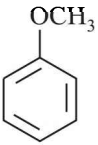
Bromobenzene — Phenyl mag. bromide — Benzoic acid

(xxiv) $C_6H_5OH \longrightarrow C_6H_5COCH_3$ K M C

Phenol → Acetophenone

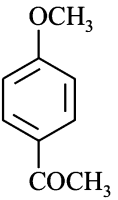
$$C_6H_5OH \xrightarrow[\text{heat}]{\text{Zn dust}} C_6H_6 \xrightarrow[\text{anhy. } AlCl_3]{CH_3COCl} C_6H_5COCH_3$$

Phenol → Benzene → Acetophenone

(xxv) 

Anisole

$$+ CH_3COCl \xrightarrow[\text{(F.C. Reaction)}]{\text{anhy. } AlCl_3}$$



p-Methoxyacetophenone

(xxvi) $CH{\equiv}CH \xrightarrow[H_2SO_4]{Hg^{2+}} CH_3CHO \xrightarrow{\text{Oxidation}} CH_3COOH$

Acetylene → Acetic acid

(xxvii) $CH_3CH_2COOH \longrightarrow CH_3COOH$

Propanoic acid → Acetic acid

$$CH_3CH_2COOH \xrightarrow[\text{(ii) heat}]{\text{(i) } NH_3} CH_3CH_2CONH_2 \xrightarrow[\text{Hofmann bromamide reaction}]{Br_2/KOH}$$

Propanoic acid → Propanamide

$$CH_3CH_2NH_2 \xrightarrow{HONO} CH_3CH_2OH \xrightarrow[\text{dil. } H_2SO_4]{KMnO_4} CH_3COOH$$

Ethanol → Acetic acid

(xxviii) $CH_3COOH \longrightarrow CH_3CH_2COOH$

Ethanoic acid → Propanoic acid

$$CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{PCl_5} CH_3CH_2Cl \xrightarrow{KCN}$$

Ethanoic acid

$$CH_3CH_2CN \xrightarrow{H^+} CH_3CH_2COOH$$

Propanoic acid

(xxix) $CH_3COOH \xrightarrow[\text{(reduction)}]{\text{Red P/HI}} CH_3CH_3$

Ethanoic acid → Ethane

(xxx) $CH_3COOH \longrightarrow CH_3CHO$

Ethanoic acid → Acetaldehyde

$$CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow[\text{(oxidation)}]{PCC} CH_3CHO$$

Ethanoic acid → Acetaldehyde

(xxxi) $CH_3CH_2COOH \longrightarrow CH_2{=}CHCOOH$

Propanoic acid → Propenoic acid

$$CH_3CH_2COOH \xrightarrow[\text{(HVZ reaction)}]{P/Cl_2} CH_3\underset{\underset{Cl}{|}}{C}HCOOH \xrightarrow{\text{alc. KOH}} CH_2{=}CHCOOH$$

Propanoic acid → Propenoic acid

(xxxii) $C_6H_5COOH \longrightarrow C_6H_5CHO$ K M C

Benzoic acid — Benzaldehyde

$$C_6H_5COOH \xrightarrow{LiAlH_4} C_6H_5CH_2OH \xrightarrow{PCC} C_6H_5CHO$$

Benzoic acid — Benzyl alcohol — Benzaldehyde

$$C_6H_5COOH \xrightarrow{PCl_5} C_6H_5COCl \xrightarrow[\text{(Rosenmund reduction)}]{H_2\text{-Pd-}BaSO_4} C_6H_5CHO$$

Benzoyl chloride

(xxxiii) $C_6H_5CH_2OH \longrightarrow C_6H_5CH_2COOH$

Benzyl alcohol — Phenylethanoic acid

$$C_6H_5CH_2OH \xrightarrow{PCl_5} C_6H_5CH_2Cl \xrightarrow{KCN} C_6H_5CH_2CN \xrightarrow{H^+} C_6H_5CH_2COOH$$

Benzyl alcohol — Phenylethanoic acid

(xxxiv) $CH_3CH_2CN \longrightarrow CH_3COOH$ **(Degradation by one carbon)**

$$CH_3CH_2CN \xrightarrow{H^+} CH_3CH_2COOH \xrightarrow[\text{(ii) heat}]{\text{(i) } NH_3} CH_3CH_2CONH_2$$

Ethyl cyanide

$$\xrightarrow[\text{Hofmann brom-amide reaction}]{Br_2 + NaOH} CH_3CH_2NH_2 \xrightarrow{HONO} CH_3CH_2OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH$$

Ethanoic acid

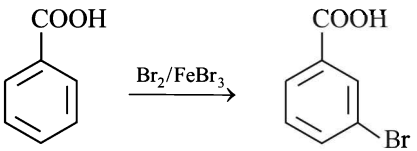
(xxxv) $CH_3COCl \xrightarrow{NH_3} CH_3CONH_2 \xrightarrow[\text{heat}]{P_2O_5} CH_3CN + H_2O$

Ethanoyl chloride — Ethanonitrile

(xxxvi) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{Jone's reagent}]{CrO_3 - H_2SO_4} CH_3CH_2CH_2COOH$

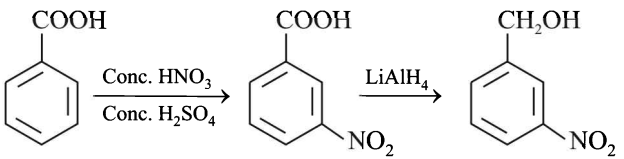
Butan-1-ol — Butanoic acid

(xxxvii)



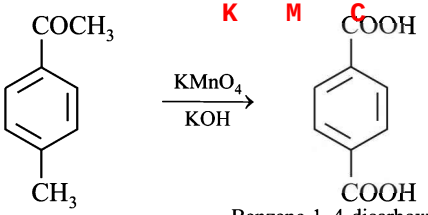
Benzoic acid — *m*-Bromobenzoic acid

(xxxviii)

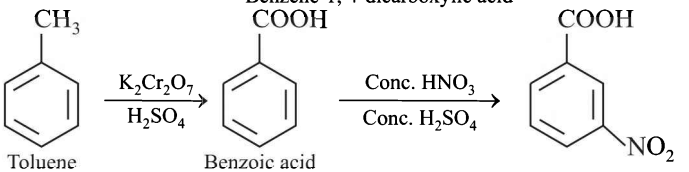


m-Nitrobenzyl alcohol

Note that $LiAlH_4$ does not reduce $-NO_2$ group.

(xxxix) 

Benzene-1, 4-dicarboxylic acid

(xxxx) 

Toluene Benzoic acid

(E) Amines

(i) $CH_3CH_2NH_2 \xrightarrow{HONO} CH_3CH_2OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH$

Ethanamine Ethanol Ethanoic acid

(ii) $CH_3NH_2 \xrightarrow{HONO} CH_3OH \xrightarrow{P + I_2} CH_3I$

Methanamine Iodomethane

(iii) $C_6H_5CH_2Cl \xrightarrow{KCN} C_6H_5CH_2CN \xrightarrow[H_2/Ni]{LiAlH_4} C_6H_5CH_2CH_2NH_2$

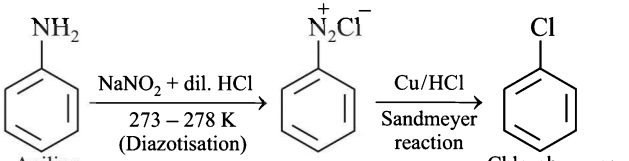
Benzyl chloride Benzylmethanamine (2-Phenylethanamine)

(iv) $CH_3CH_2Cl \xrightarrow{KCN} CH_3CH_2CN \xrightarrow[H_2/Ni]{LiAlH_4} CH_3CH_2CH_2NH_2$

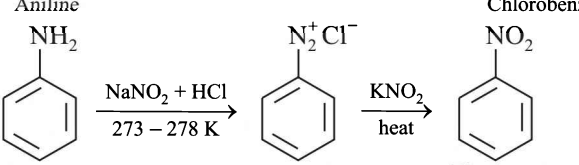
Ethyl chloride

(v) $C_6H_6 \xrightarrow[Conc.\ H_2SO_4]{Conc.\ HNO_3} C_6H_5NO_2 \xrightarrow[(reduction)]{Sn + HCl} C_6H_5NH_2$

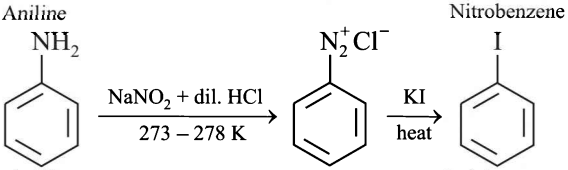
Benzene Aniline

(vi) 

Aniline Chlorobenzene

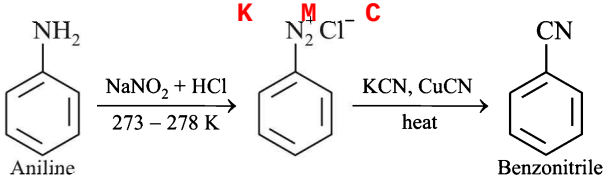
(vii) 

Aniline Nitrobenzene

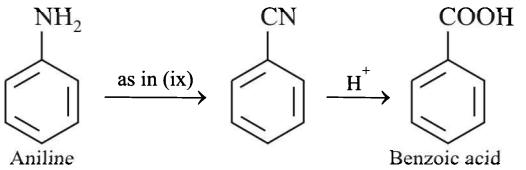
(viii) 

Aniline Iodobenzene

(ix)



(x)



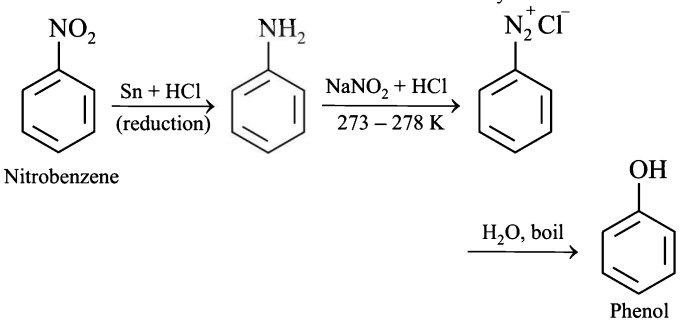
(xi) $C_6H_5NH_2 \xrightarrow[273-278\ K]{NaNO_2 + HCl} C_6H_5N_2Cl \xrightarrow[\text{(reduction)}]{H_3PO_2,\ H_2O} C_6H_6 \xrightarrow[\text{anhy. } AlCl_3]{CH_3Cl}$

Aniline

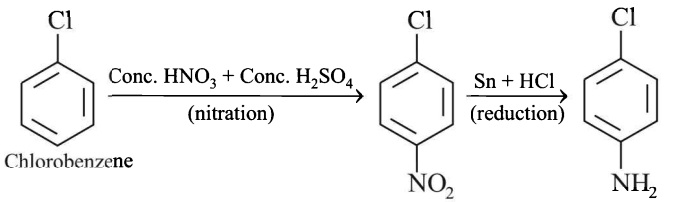
$C_6H_5CH_3 \xrightarrow[hv]{Cl_2} C_6H_5CH_2Cl \xrightarrow{\text{aq. KOH}} C_6H_5CH_2OH$

Benzyl alcohol

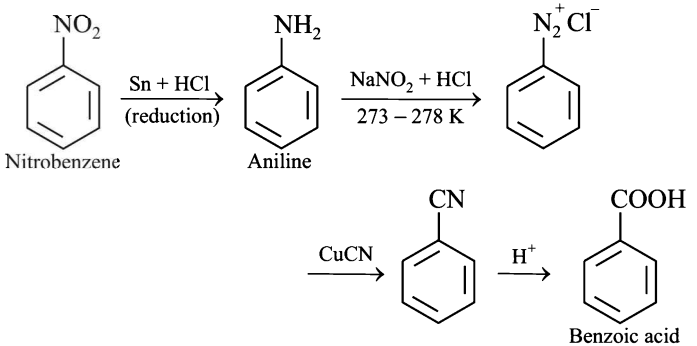
(xii)



(xiii)



(xiv)



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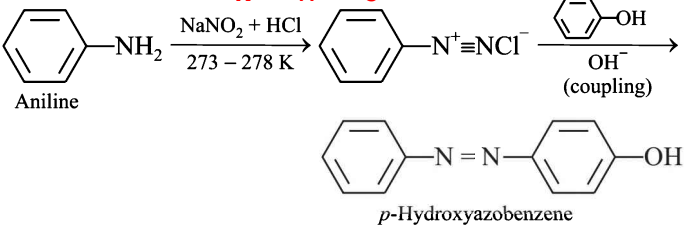
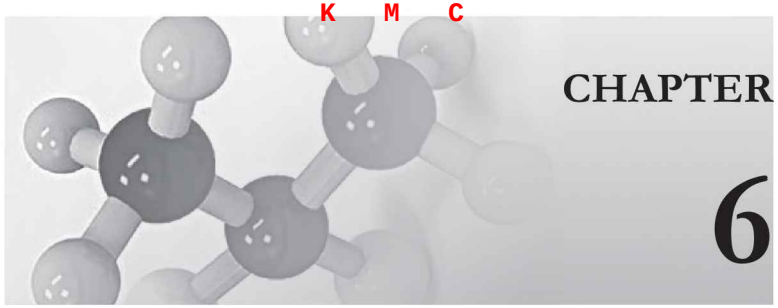
(xv) 
NH2
Aniline
NaNO2 + HCl
273 – 278 K
N+≡NCl−
OH
OH−
(coupling)
N = N
OH
p-Hydroxyazobenzene



CHAPTER

6

How will you distinguish the given pair of compounds ?

How will you distinguish the following compounds in each pair ? Give one characteristic test.

(A) Halogen derivatives.

(i) C_2H_5Br and C_6H_5Br **(AI 2012C)**
(ii) Ethyl chloride and vinyl chloride
(iii) Vinyl chloride and allyl chloride
(iv) Chlorobenzene and benzyl chloride **(AI 2011C, 2013C)**
(v) *o*-Chlorotoluene and benzyl chloride
(vi) Chloroform and carbon tetrachloride **(AI 2011C, 2013C)**

(B) Alcohols, phenols and ethers.

(i) Methyl alcohol and ethyl alcohol
(ii) 1-Propanol and 2-propanol
(Delhi 2008C, 2009C, 2010C, AI 2008)
(iii) 1-Propanol and 2-methyl-2-propanol
(iv) Methanol and phenol **(AI 2013C)**
(v) Ethanol and phenol **(Delhi 2008C, 2012C, AI 2009, 2010C)**
(vi) 2-Pentanol and 3-pentanol **(Delhi 2012C, AI 2013C)**
(vii) Diethyl ether and propanol

(C) Aldehydes, ketones and carboxylic acids.

(i) Ethanal and propanal
(Delhi 2008, 2010, 2011, 2012C, 2013, AI 2008, 2013)

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(ii) Formaldehyde and acetaldehyde

(iii) Acetaldehyde and benzaldehyde **(Delhi 2008)**

(iv) Ethanal and ethanol

(v) Ethanal and propanone

(vi) Propanal and propanone

(Delhi 2007, 2011, 2012, 2012C, AI 2008, 2009, 2011)

(vii) Propanol and propanone **(Delhi 2008, AI 2008, 2012)**

(viii) Pentan-2-one and pentan-3-one **(Delhi 2012, AI 2013)**

(ix) Benzaldehyde and acetophenone

(Delhi 2011, 2012, AI 2005C, 2006C, 2011, 2012, 2012C, Foreign 2011)

(x) Acetophenone and benzophenone **(Delhi 2012, AI, 2008, 2009)**

(xi) Ethanol and propanal **(AI 2009)**

(xii) Phenol and benzoic acid

(Delhi 2009C, 2012C, 2010, 2012, 2013, AI 2008, 2009, 2012C)

(xiii) Benzoic acid and ethyl benzoate **(AI 2009, 2011)**

(xiv) Methyl acetate and ethyl acetate **(Delhi 2007, AI 2012C)**

(xv) Benzaldehyde and benzoic acid **(AI 2005C, 2006C)**

(xvi) Propanoic acid and propanoyl chloride.

(xvii) Benzamide and 4-aminobenzoic acid. **(AI 2012C)**

(D) Amines

(i) Ethyl amine and aniline

(Delhi 2013C, AI 2008C, 2009C, 2010, 2010C, 2011)

(ii) Aniline and N-methylaniline **(AI 2008C, 2010)**

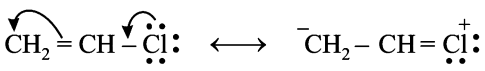
(iii) Methylamine and dimethylamine

(Delhi 2013C, AI 2009C, 2010, 2010C)

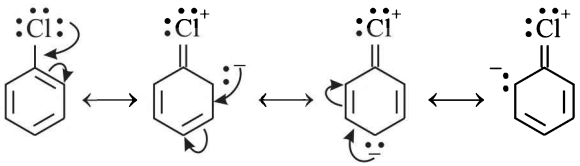
(iv) Aniline and benzylamine **(AI 2010)**

(A) Halogen derivatives.

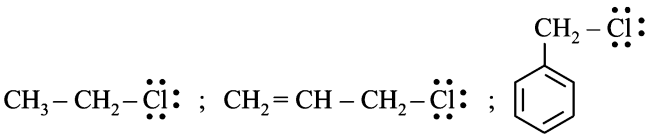
General. Halogen atom attached to sp^2-hybridised carbon (as in =CHCl, ArCl, etc.) is relatively inert to nucleophiles, hence can't be replaced easily. The reason for this is resonance which leads to C–Cl bond to some double bond character, which, being shorter, is stronger.



(–C=Cl is shorter and stronger)



(–C=Cl bond is shorter than the usual –C–Cl bond and hence stronger and difficult to replace)



Ethyl chloride ; Allyl chloride ; Benzyl chloride

(Resonance not possible, hence –C–Cl is lengthier and weaker, thus can be replaced by nucleophile easily).

Thus compounds having $-\overset{sp^3}{C}-Cl$ (e.g. alkyl halides, allyl halides and aryl compounds having –X on the side chain, viz. $C_6H_5CH_2Cl$) easily undergo nucleophilic substitution and hence give precipitate of silver halide on treatment with silver nitrate solution, while compounds having $=\overset{sp^2}{C}-Cl$ (e.g. $CH_2=CHCl$, C_6H_5Cl) do not give precipitate of silver halide on treatment with $AgNO_3$ solution. These facts can be applied on each pair of compound.

(i) $C_2H_5Br + NaOH\ (aq.) \longrightarrow C_2H_5OH + Na^+\ Br^-$

$Br^- + AgNO_3 \longrightarrow AgBr\downarrow + Ag^+$

$C_6H_5Br + NaOH\ (aq.) \not\rightarrow$ No NaBr is formed, hence no precipitate will be formed with $AgNO_3$ solution.

(ii) $CH_3CH_2 - Cl \xrightarrow[\text{solution}]{AgNO_3} AgCl\downarrow$

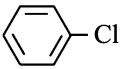
Ethyl chloride — White ppt

$CH_2 = CHCl + AgNO_3$ solution $\longrightarrow$ No white ppt.

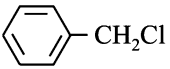
Vinyl chloride

(iii) Allyl chloride ($CH_2{=}CHCH_2Cl$) gives white precipitate with $AgNO_3$ solution, while vinyl chloride ($CH_2{=}CHCl$) does not do so.

(iv)

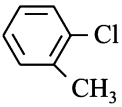


Chlorobenzene
(no ppt. with $AgNO_3$solution)

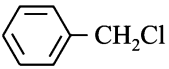


Benzyl chloride
(gives white ppt. with $AgNO_3$ solution)

(v)



o-Chlorotoluene
(No ppt. with $AgNO_3$ solution)



Benzyl chloride
(White ppt. with $AgNO_3$ solution)

(vi) Chloroform when heated with aniline in presence of alcoholic KOH gives offensive smelling phenyl isocyanide (**carbylamine reaction**); carbon tetrachloride does not give this reaction.

$$C_6H_5NH_2 + CHCl_3 + 3KOH\ (alc.) \xrightarrow{heat} C_6H_5N \overset{\rightarrow}{=} C + 3KCl + 3H_2O$$

Phenyl isocyanide

(B) Alcohols, phenols and ethers.

(i) CH_3OH — Methyl alcohol; CH_3CH_2OH — Ethyl alcohol

Ethyl alcohol, when heated with alkaline iodine, undergoes iodoform reaction to give yellow precipitate of iodoform.

$$CH_3CH_2OH + NaOI\ (NaOH + I_2) \xrightarrow{Oxi.} CH_3CHO + NaI + H_2O$$

$$CH_3 - \overset{\overset{O}{\|}}{C} - H + 3NaOI \longrightarrow HCOONa + CHI_3\downarrow + 2NaOH$$

(yellow ppt.)

Methyl alcohol does not undergo iodoform test.

Iodoform test. Ethanal (CH_3CHO), ketones having $-COCH_3$ group ($R-COCH_3$), ethanol (CH_3CH_2OH) and secondary alcohols having $-CHOHCH_3$ group ($R-CHOHCH_3$) when heated with alkaline iodine (or chlorine or bromine) gives iodoform (or chloroform or bromoform). **Iodoform is yellow crystalline compound**, hence can

be easily detected, while chloroform and bromoform are liquids, hence difficult to detect.

$$-COCH_3 + 3NaOI \longrightarrow CHI_3\downarrow + -COONa + 2NaOH$$

(ii) $CH_3CH_2CH_2OH$ (1-Propanol) $\qquad CH_3-\underset{}{\overset{OH}{\overset{|}{C}H}}-CH_3$ (2-Propanol)

Only 2-propanol gives yellow precipitate with alkaline iodine (sodium hypoiodite).

$$\underset{\text{2-Propanol}}{CH_3-\underset{OH}{\underset{|}{CH}}-CH_3} + NaOI \xrightarrow{\text{Oxi.}} \underset{\text{Acetone}}{CH_3-\underset{O}{\underset{||}{C}}-CH_3} + NaI + H_2O$$

$$CH_3-\underset{O}{\underset{||}{C}}-CH_3 + 3NaOI \xrightarrow[\text{reaction}]{\text{Iodoform}} CH_3COONa + \underset{\textbf{(yellow)}}{CHI_3\downarrow} + 2NaOH$$

(iii) $CH_3CH_2CH_2OH$ (1-Propanol (1° alcohol)) $\qquad CH_3-\underset{OH}{\overset{CH_3}{\overset{|}{\underset{|}{C}H}}}-CH_3$ (2-Methyl-2-propanol (3° alcohol))

2-Methyl-2-propanol, being 3° alcohol, gives milkiness immediately when treated with $ZnCl_2$ in presence of conc. HCl (Luca's reagent); while **1-propanol** does not give any milkiness.

(iv) CH_3OH (Methanol) $\qquad C_6H_5OH$ (Phenol)

Phenol gives violet colour with neutral $FeCl_3$ solution and also turns blue litmus solution to red; while **methyl alcohol** does not respond either of the two tests.

(v) Ethanol (C_2H_5OH) and phenol (C_6H_5OH). Same as above

(vi) $CH_3-\overset{OH}{\overset{|}{C}H}-CH_2CH_2CH_3$ (2-Pentanol) $\qquad CH_3CH_2-\overset{OH}{\overset{|}{C}H}-CH_2CH_3$ (3-Pentanol)

2-Pentanol has $-\overset{OH}{\overset{|}{C}H}CH_3$ group so it undergoes haloform reaction, while 3-pentanol does not.

(vii) $C_2H_5-O-C_2H_5$ (Diethyl ether) $\qquad CH_3CH_2CH_2OH$ (Propanol)

Only propanol when treated with metallic sodium evolves hydrogen gas.

$$CH_3CH_2CH_2OH + Na \longrightarrow CH_3CH_2CH_2ONa + \frac{1}{2}H_2\uparrow$$

Diethyl ether does not react with metallic sodium. However, when heated with HI at high temperature, it gives C_2H_5I which when heated with $AgNO_3$ solution gives yellow precipitate of AgI.

$$C_2H_5-O-C_2H_5 \xrightarrow[\text{heat}]{2HI} 2C_2H_5I \xrightarrow[\text{heat}]{AgNO_3} AgI\downarrow \quad \textbf{(yellow)}$$

(C) Aldehydes, ketones and carboxylic acids.

(i) CH_3CHO (Ethanal) CH_3CH_2CHO (Propanal)

Ethanal (CH_3CHO) when heated with alkaline iodine gives yellow precipitate of iodoform (**iodoform test**), while **propanal** (CH_3CH_2CHO) does not undergo iodoform test.

$$CH_3CHO + 3I_2 + 4NaOH \longrightarrow HCOONa + \underset{\text{Iodoform (yellow ppt.)}}{CHI_3\downarrow} + 3NaI + 3H_2O$$

(ii) Formaldehyde (HCHO) does not undergo iodoform test, while acetaldehyde (CH_3CHO) gives iodoform test.

(iii) Only acetaldehyde (CH_3CHO) gives iodoform test, but benzaldehyde (C_6H_5CHO) not.

(iv) CH_3CHO (Ethanal) CH_3CH_2OH (Ethanol)

Only **ethanal** (being aldehyde) gives silver mirror with Tollen's reagent and red precipitate with Fehling solution (For reactions, consult next question). Remember that both of these compounds give iodoform test.

(v) $CH_3-\underset{\underset{O}{\|}}{C}-H$ (Ethanal) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3$ (Propanone)

Ethanal reduces Tollen's reagent to form silver mirror.

$$\underset{\text{Ethanal}}{CH_3CHO} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+} + 3OH^- \longrightarrow CH_3COO^- + 4NH_3 + \underset{\textbf{Silver mirror}}{2Ag\downarrow} + 2H_2O$$

It also reduces Fehling solution to give red colour of Cu_2O (***Fehling test***). None of the two tests is given by propanone. Note that both of the compounds respond iodoform test.

$$\underset{\text{Ethanal}}{CH_3CHO} + \underbrace{2AgNO_3 + 2NH_4OH}_{\text{Tollen's reagent}} \longrightarrow CH_3COOH + 2NH_4NO_3 + H_2O + 2Ag\downarrow$$

$$CH_3CHO + \underbrace{2CuSO_4 + 4NaOH}_{\text{Fehling solution}} \longrightarrow CH_3COOH + 2Na_2SO_4 + \underset{\textbf{Red}}{Cu_2O\downarrow} + 2H_2O$$

(vi) **Propanal** (CH_3CH_2CHO) does not give iodoform test, while **propanone** (CH_3COCH_3) does so. Alternatively, propanal (being aldehyde) gives red ppt. with Fehling solution, while propanone does not.

(vii) **Propanol** ($CH_3CH_2CH_2OH$) does not give iodoform test, while **propanone** (CH_3COCH_3) does so.

(viii) $CH_3-\underset{\underset{O}{\|}}{C}-CH_2CH_2CH_3$ $\quad$ $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_2CH_3$

Pentan-2-one $\quad$ Pentan-3-one

Only **pentan-2-one**, having $-COCH_3$ group, gives iodoform test.

(ix) Only **benzaldehyde** (C_6H_5CHO) but not **acetophenone** ($C_6H_5COCH_3$) reduces Tollen's reagent to give silver mirror. Secondly, acetophenone gives iodoform test, while benzaldehyde not.

(x) **Acetophenone** ($C_6H_5COCH_3$) undergoes iodoform test, but benzophenone not.

$$C_6H_5COCH_3 + 3NaOI \longrightarrow C_6H_5COONa + \underset{\textbf{(yellow ppt.)}}{CHI_3\downarrow}$$

(xi) C_2H_5-OH $\quad$ CH_3CH_2CHO

Ethanol $\quad$ Propanal

Ethanol undergoes iodoform reaction.

$$CH_3CH_2OH \xrightarrow{NaOI} CH_3CHO \xrightarrow{NaOH + I_2} CHI_3\downarrow$$

Propanal, being aldehyde, forms silver mirror with Tollen's reagent.

(xii) **Benzoic acid**, when treated with $NaHCO_3$ gives brisk effervescences of carbon dioxide, whereas **phenol** (being weak acid) does not give this reaction.

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaHCO_3 \longrightarrow C_6H_5COONa + H_2O + CO_2\uparrow$$

$$\underset{\text{Phenol}}{C_6H_5OH} + NaHCO_3 \longrightarrow \text{No reaction}$$

(xiii) (*a*) **Benzoic acid** (but not ethyl benzoate) gives brisk effervescenses of CO_2 with $NaHCO_3$.

(*b*) **Ethyl benzoate** on boiling with excess of NaOH solution gives ethyl alcohol and sodium benzoate.

$$\underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5} + NaOH \xrightarrow{M} \underset{\text{Sod. benzoate}}{C_6H_5COONa} + C_2H_5OH$$

The product, ethyl alcohol, is heated with NaOH and iodine, when yellow precipitate of iodoform is formed (**iodoform reaction**).

$$\underset{\text{Acetaldehyde}}{CH_3CH_2OH} \xrightarrow[\text{(oxidation)}]{I_2} CH_3CHO$$

$$\downarrow \text{Sod. hypoiodite, NaOI (from NaOH + } I_2\text{)}$$

$$HCOONa + CHI_3\downarrow + 2NaOH + 2H_2O$$

Benzoic acid does not show this test. **Alternatively**, benzoic acid gives brisk effervescences of CO_2 with $NaHCO_3$ solution.

(xiv)

$$\underset{\text{Methyl acetate}}{CH_3-\overset{O}{\overset{||}{C}}-OCH_3} \qquad \underset{\text{Ethyl acetate}}{CH_3-\overset{O}{\overset{||}{C}}-OC_2H_5}$$

Both are treated with NaOH to give acid and alcohol as follows.

$$\underset{\text{Methyl acetate}}{CH_3-\overset{O}{\overset{||}{C}}-OCH_3} \xrightarrow{NaOH} \underset{\text{Sod. acetate}}{CH_3-\overset{O}{\overset{||}{C}}-ONa} + \underset{\text{Methyl alcohol}}{HOCH_3}$$

$$\underset{\text{Ethyl acetate}}{CH_3-\overset{O}{\overset{||}{C}}-OC_2H_5} \xrightarrow{NaOH} \underset{\text{Sod. acetate}}{CH_3-\overset{O}{\overset{||}{C}}-ONa} + \underset{\text{Ethyl alcohol}}{HOC_2H_5}$$

The products of the two are treated with alkaline iodine, when only ethyl alcohol (obtained from ethyl acetate) gives yellow precipitate of iodoform (**iodoform test**).

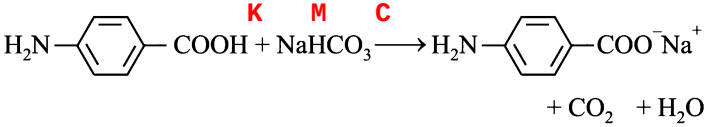
(xv) Only **benzoic acid** (not benzaldehyde) will give brisk effervescences of CO_2 with $NaHCO_3$. Further, only **benzaldehyde** reduces Tollen's reagent and Fehling solution.

(xvi) Only **propanoic acid** (not propanoyl chloride, CH_3CH_2COCl) will give brisk effervescences of CO_2 with $NaHCO_3$.

(xvii) Benzamide (not 4-aminobenzoic acid) when heated with NaOH solution gives smell of ammonia.

$$C_6H_5CONH_2 + NaOH \xrightarrow{heat} C_6H_5COONa + NH_3\uparrow$$

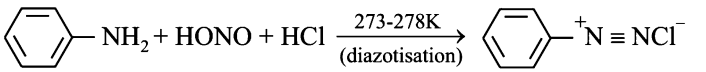
Alternatively, 4-aminobenzoic acid (but not benzamide) gives effervescences of CO_2 on treatment with $NaHCO_3$ solution.



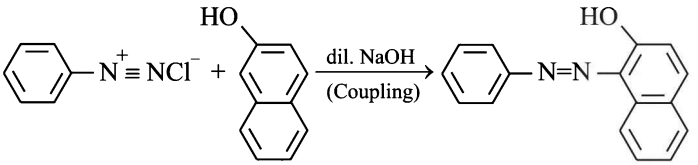
(D) Amines.

(i) $C_2H_5NH_2$ — Ethyl amine; $C_6H_5NH_2$ — Aniline

Aniline, a primary aromatic amine, when treated with a solution of sodium nitrite in dil. HCl at 273–278K followed by treatment with an alkaline solution of β-naphthol gives an orange coloured dye (**azo dye test**).



Benzene diazonium chloride



β-Naphthol — 1-Phenylazo-2-naphthol (**orange dye**)

Ethyl amine, ***a primary aliphatic amine***, when treated with a solution of $NaNO_2$ in dil. HCl gives a primary alcohol along with a brisk evolution of N_2 gas.

$$C_2H_5NH_2 + HONO \xrightarrow{273\text{-}278K} C_2H_5OH + N_2\uparrow + H_2O$$

(ii) $C_6H_5NH_2$ — Aniline; $C_6H_5NHCH_3$ — N-Methylaniline

Aniline gives *azo dye test* (as mentioned above). Moreover, aniline like any other primary amine (aliphatic or aromatic), when heated with an alcoholic solution of KOH and $CHCl_3$ gives foul smell of phenyl isocyanide (**carbylamine test**)

$$\underset{\text{Aniline}}{C_6H_5NH_2} + CHCl_3 + 3KOH \xrightarrow{heat} \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3KCl + 3H_2O$$

N-Methylaniline, a 2° amine, gives neither of the above two tests.

(iii) CH_3NH_2 — Methyl amine; $(CH_3)_2NH$ — Dimethyl amine

Methyl amine, being a primary amine, undergoes carbylamine reaction (see aniline in above question). **Dimethyl amine**, a secondary amine does not respond carbylamine reaction.

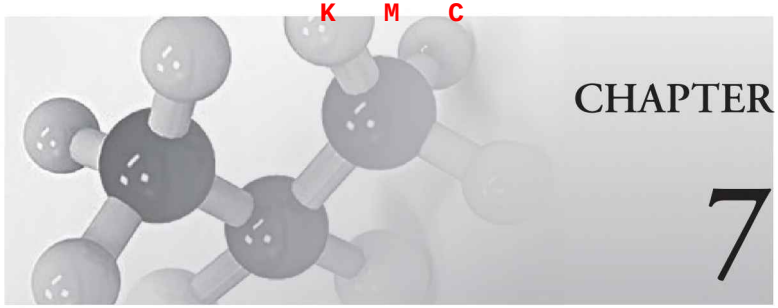
(iv) $C_6H_5NH_2$ K M C $C_6H_5CH_2NH_2$

Aniline Benzylamine

(1° aromatic amine) (1° aryl substituted aliphatic amine).

Aniline gives azo dye test (see aniline), while benzyamine gives alcohol and N_2 (see $C_2H_5NH_2$).

$$C_6H_5CH_2NH_2 + HONO \longrightarrow C_6H_5CH_2OH + N_2\uparrow + H_2O$$



CHAPTER

7

What will be the Mechanism of the given Reactions?

1. $S_N{}^1$ reactions. **(Delhi 2008C)**
2. n–BuBr + KCN $\xrightarrow[H_2O]{C_2H_5OH}$ n–BuCN **(Delhi 2009C, 2011C, AI 2008C)**
3. Acid catalysed hydration of an alkene to form corresponding alcohol. **(Delhi 2009, AI 2010C, 2011C, 2012, Foreign 2009, 2010)**
4. $CH_3CH_2OH \xrightarrow[443\ K]{H^+} CH_2{=}CH_2 + H_2O$ **(AI 2013)**
5. Acid catalysed dehydration of ethanol to yield ethene. **(Delhi 2008C, 2009, AI 2009, 2010C, 2011C, Foreign 2010)**
6. $2CH_3CH_2OH \xrightarrow{Conc.\ H_2SO_4} CH_3CH_2OCH_2CH_3$ **(Delhi 2013)**
7. Alcohols acting both as nucleophiles as well as electrophiles in their reactions. **(Foreign 2008)**
8. Reaction of 3-methylbutan-2-ol with HBr.
9. Reaction of HI with methoxymethane. **(Delhi, 2009, AI 2011C, Foreign 2012)**
10. Nucleophilic attack on a carbonyl group. **(Delhi 2010)**
11. Addition of Grignard's reagent to the carbonyl group of a compound forming an adduct followed by hydrolysis. **(Delhi 2009, Foreign 2012)**
12. Esterification of carboxylic acids. **(Delhi 2012C)**
13. Give mechanism of preparation of ethoxyethane from ethanol. **(Delhi 2013C)**

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Solution

1. Mechanism of S_{N^1} reactions

$$(CH_3)_3C{-}Br \xrightarrow[\text{(1st step)}]{\text{slow}} (CH_3)_3C^+ + Br^-$$

ter-Butylchloride

$$(CH_3)_3C^+ + :\ddot{O}H_2 \xrightarrow[\text{(2nd step)}]{\text{fast}} (CH_3)_3C{-}\overset{+}{\ddot{O}}H_2$$

$$(CH_3)_3C{-}\overset{+}{\ddot{O}}{<}^{H}_{H} \xrightarrow[\text{(3rd step)}]{\text{fast}} (CH_3)_3C{-}OH + H^+$$

ter-Butyl alcohol

S_{N^1} mechanism is mainly given by *ter*-alkyl halides

2. KCN ionises to give CN^- which is ambident nucleophile and thus can attack on the carbon of alkyl halide through its carbon or nitrogen. However, since the C–C bond is stronger than the C–N bond, attack occurs through carbon to form *n*–BuCN.

$$:\bar{C}{\equiv}N: \longleftrightarrow :C{\equiv}\ddot{N}:^-$$

$$:\bar{C}{\equiv}N: + CH_3CH_2CH_2\overset{\delta+}{C}H_2{-}\overset{\delta-}{Br} \xrightarrow{S_N2} CH_3CH_2CH_2CH_2{-}CN + Br^-$$

3. Acid catalysed hydration of alkenes.

(a) $$CH_2{=}CH_2 \xrightarrow{H^+} CH_3{-}\overset{+}{C}H_2 \xrightarrow{H_2\ddot{O}:} CH_3CH_2\overset{+}{\ddot{O}}{-}H \xrightarrow{-H^+} CH_3CH_2OH$$

(b) $$CH_3CH{=}CH_2 \xrightarrow{H^+} CH_3\overset{+}{C}HCH_3 \xrightarrow{H_2\ddot{O}:} CH_3{-}CH(\overset{+}{\ddot{O}}{-}H)-CH_3 \xrightarrow{-H^+} CH_3{-}CH(OH){-}CH_3$$

2° Carbocation
(more stable)

Note that $CH_3{-}CH{=}CH_2 \xrightarrow{H^+} CH_3{-}CH_2{-}\overset{+}{C}H_2$ is not favourable because it leads to formation of **less stable** primary carbocation, $CH_3{-}CH_2{-}\overset{+}{C}H_2$.

4. $$CH_3CH_2\ddot{O}H + H^+ \rightleftharpoons CH_3CH_2{-}\overset{+}{\ddot{O}}H_2 \xrightarrow{(-H_2O)} CH_3\overset{+}{C}H_2 \xrightarrow{H^+} CH_2{=}CH_2$$

Ethanol — Ethene

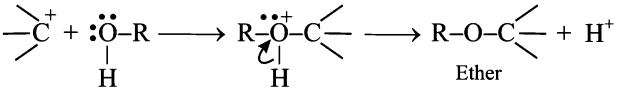
5. Same as (iv)

6. $CH_3CH_2OH \xrightarrow{H^+} CH_3CH_2\overset{+}{O}H_2 \xrightarrow[(-H_2O)]{} CH_3\overset{+}{C}H_2 \xrightarrow[\text{(2nd molecule)}]{CH_3CH_2OH}$

$CH_3CH_2-\overset{+}{O}(H)-CH_2CH_3 \xrightarrow[(-H^+)]{} CH_3CH_2-O-CH_2CH_3$

Diethyl ether

7. Alcohols as nucleophiles (attack on electron deficient species).



Alcohols as electrophiles (attack on electron rich species).

$R-CH_2OH \xrightarrow{H^+} R-CH_2\overset{+}{O}H_2 \xrightarrow{-H_2O} R-\overset{+}{C}H_2 \xrightarrow{Br^-} R-CH_2Br$

8. $CH_3-CH(CH_3)-CH(OH)-CH_3 \xrightarrow{H^+} CH_3-CH(CH_3)-CH(\overset{+}{O}H_2)-CH_3 \xrightarrow[(-H_2O)]{}$

3-Methylbutan-2-ol

$CH_3-C(CH_3)(H)-\overset{+}{C}H-CH_3 \xrightarrow[\text{shift}]{\text{1, 2-Hydride}} CH_3-\overset{+}{C}(CH_3)-CH_2-CH_3 \xrightarrow{Br^-}$

2° Carbocation (less stable) 3° Carbocation (more stable)

$CH_3-C(Br)(CH_3)-CH_2-CH_3$

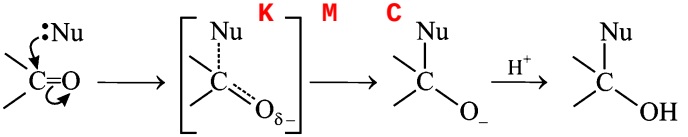
2-Bromo-2-methylbutane

9. $CH_3-\ddot{O}-CH_3 \xrightarrow[(-I^-)]{} CH_3-\ddot{O}^+-CH_3 \xrightarrow{S_{N^2}} CH_3I + HOCH_3$

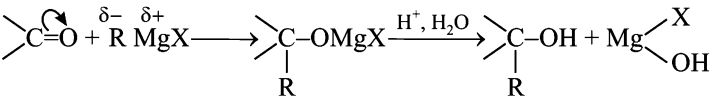
When HI is taken in excess, it further reacts with CH_3OH (formed as product) to form second molecule of CH_3I.

$CH_3-\ddot{O}-H \xrightarrow{-I^-} CH_3-\ddot{O}^+-H \xrightarrow{S_{N^2}} CH_3I + H_2O$

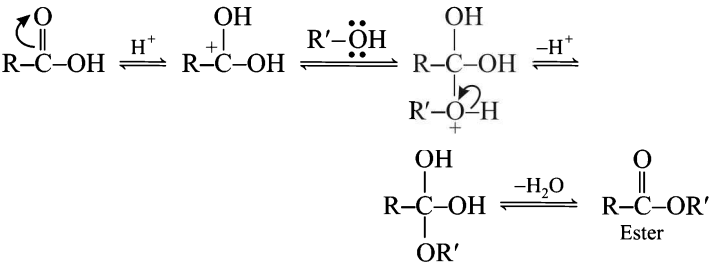
K M C

10. 

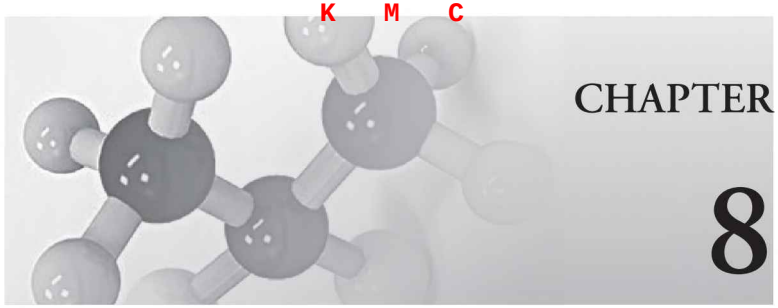
Carbonyl group (Trigonal) | Transition state (Trigonal) | Tetrahedral | Addition product

11. 

Adduct

12. 

Ester



CHAPTER

8

Why do the following happens ?

Explain the following:

(A) Halogen derivatives.

1. Alkyl halides are polar yet they are immiscible with water.
   (Delhi 2010C, 2013C, AI 2010C, 2012C, 2013C, Foreign 2012)
2. Haloalkanes easily dissolve in organic solvents.
   (Delhi 2011, Foreign 2012)
3. Chlorobenzene has lower dipole moment than cyclohexyl chloride.
   (Delhi 2010C, 2011C, 2013C, AI 2010C, 2012C, 2013C, Foreign 2012)
4. Reaction of alkyl chlorides with aqueous KOH leads to alcohols while with alcoholic KOH, alkenes are major products.
   (Delhi 2008C, AI 2000C)
5. Alkyl halides react with KCN to form mainly alkyl cyanides (RCN) with some alkyl isocyanides (RNC), while with AgCN they form exclusively isocyanides.
6. Methyl chloride reacts with silver nitrite to form mainly nitromethane, while with potassium nitrite it forms methyl nitrite along with some nitromethane.
7. Alkyl halides (R–X) are more reactive than aryl halides (Ar–X) towards nucleophilic substitution.
   (Delhi 2008, AI 2008, 2011C, 2013)
8. Phosphoric acid (but not sulphuric acid) is used for preparing alkyl iodides from alcohols and potassium iodide.

$$CH_3CH_2OH + KI \xrightarrow[\text{(not } H_2SO_4)]{H_3PO_4} CH_3CH_2I + KOH$$

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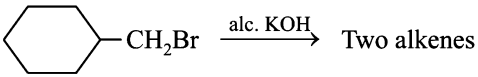
9. Methylene chloride, CH_2Cl_2, having two chlorine has more dipole moment than chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4) having three and four chlorine respectively.

10. *p*-Dichlorobenzene has higher melting point and lower solubility than the *o*-and *m*-isomers. **(Delhi 2013, AI 2009C)**

11. Nucleophilic substitution of primary alkyl chlorides with sodium acetate is catalysed by sodium iodide.

12. *neo*-Pentyl bromide, Me_3CCH_2Br, a 1° alkyl bromide reacts with aqueous NaOH to form 3° alcohol, $(CH_3)_2C(OH)CH_2CH_3$.

13. 

14. 3-Bromocyclohexene is more reactive than 4-bromocyclohexene towards hydrolysis with aqueous NaOH.

15. Vinyl chloride is unreactive towards nucleophilic substitution reactions.

16. *p*-Methoxybenzyl bromide is more reactive than *p*-nitrobenzyl bromide with ethanol to form ether.

17. Although chlorine is highly electronegative, it undergoes electrophilic aromatic substitution in *o*- and *p*- position.

(Delhi 2012)

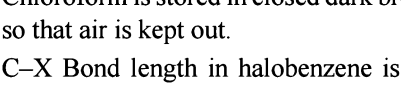
18. Carbon tetrachloride does not give precipitate with $AgNO_3$ solution, while $SiCl_4$ does so.

19. Chlorobenzene (a haloarene) is extremely less reactive towards a nucleophilic substitution reaction than chloroethane (a haloalkane).

(Delhi 2008, 2013, AI 2009C)

20. Chloroform is stored in closed dark brown bottles, completely filled so that air is kept out. **(Delhi 2010C, 2013)**

21. C–X Bond length in halobenzene is smaller than the C–X bond length in CH_3–X. **(Delhi 2013, AI 2013)**

22. 

reacts faster than **(Delhi 2008C)**

23. Order of reactivity of haloalkanes is RI > RBr > RCl.

(Delhi 2009C)

24. Neopentyl chloride, $(CH_3)_3CCH_2Cl$ does not follow S_{N^2} mechanism. **(Delhi 2009C)**

25. Grignard reagents are prepared strictly under anhydrous conditions. **(Delhi 2010C, 2013C, AI 2012C, Foreign 2012)**

26. Haloalkanes undergo nucleophilic substitution whereas haloarenes undergo electrophilic substitution. **(Delhi 2012C)**

(B) Alcohols, ethers and phenols

1. Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.

(Delhi 2008C, AI 2008C, 2012)

2. Lower alcohols are soluble in water, while higher alcohols are not so.
3. Propanol has higher boiling point than butane.

(Delhi 2008C, 2011C)

4. Alcohols act as weak bases. **(Delhi 2008C)**
5. Boiling point of ethanol is higher than that of methanol.

(Delhi 2011C, AI 2008, 2009)

6. Boiling points of alcohols decrease with increase in branching of the alkyl chain. **(Delhi 2011C)**
7. (±)–2–Butanol is optically inactive. **(Delhi 2011C)**
8. Methanol boils at higher temperature than methyl amine.
9. Methanol is miscible with water while iodomethane is not.
10. Boiling point of ethers are lower than isomeric alcohols.
11. Ethers have low boiling points.

(Delhi 2009C, 2011C, AI 2009, Delhi)

12. Ethanol has higher b.p. than methoxymethane.

(Delhi 2008C, AI 2009)

13. Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method.

(Delhi 2008C, 2011C, AI 2008C)

14. Phenyl methyl ether reacts with HI to give phenol and methyl iodide.

(Delhi 2010C, 2011C)

15. The alkoxy group in aryl alkyl ethers directs the incoming substituents to *ortho* and *para*-positions in benzene ring.
16. Phenol has a smaller dipole moment than methanol. **(Delhi 2002)**
17. *p*-Dichlorobenzene has zero dipole moment, while *p*-dihydroxy benzene has definite dipole moment.
18. *p*-Isomer of a compound is less soluble in a given solvent than the *m*- and *o*-isomers.

19. Phenol is a stronger acid than alcohol. **(Delhi 2011C, AI 2008C, 2009)**
20. Phenol is more acidic than ethanol. **(AI 2009)**
21. Phenol does not give protonation reaction readily. **(Delhi 2011C, AI 2008)**
22. *o*-Nitrophenol has lower boiling point than *p*-nitrophenol. **(Delhi 2002C, 2013C)**
23. The C–O bond is much shorter in phenol than in ethanol. **(Delhi 2012C)**
24. Although phenoxide ion has more resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. **(Delhi 2013)**
25. *o*-Nitrophenol is more acidic than *ortho*- methoxyphenol. **(Delhi 2011C, AI 2012, 2012C, 2013C)**
26. *o*- and *p*-nitrophenols are more acidic than phenol. **(AI 2009)**
27. *m*-Aminophenol is a stronger acid than *o*-aminophenol. **(Delhi 2008C)**
28. The –OH group attached to a carbon in the benzene ring activates the benzene ring towards electrophilic substitution. **(AI 2005)**

(C) Aldehydes, ketones and carboxylic acids

1. Aldehydes and ketones have lower boiling points than the corresponding alcohols. **(AI 2012C)**
2. The boiling points of aldehydes and ketones are lower than that of the corresponding carboxylic acid. **(Delhi 2008)**
3. Ethanal is soluble in water. **(AI 2013)**
4. Aldehydes and ketones undergo a number of addition reactions. **(Delhi 2008)**
5. Aldehydes are more reactive than ketones towards nucleophiles. **(Delhi 2008, AI 2013C)**
6. Cyclohexanone forms cyanohydrin in good yield but 2, 4, 6 – trimethylcyclohexanone does not. **(Delhi 2012)**
7. Formaldehyde does not take part in aldol condensation. **(AI 2012C)**
8. There are two $-NH_2$ groups in semicarbazide. However, only one such group is involved in the formation of semicarbazones. **(Delhi 2012)**

K M C

9. Carboxylic acids do not give characteristic reactions of the carbonyl group. **(Delhi 2012C, AI 2013C)**
10. Ethanoic acid is a weaker acid than benzoic acid. **(Delhi 2008)**
11. Monochloroethanoic acid has a higher pK_a value than dichloroethanoic acid. **(Delhi 2008)**
12. Electrophilic substitution in benzoic acid takes place at meta position. **(Delhi 2012C, AI 2013C)**
13. Ester hydrolysis is slow in the beginning and becomes faster after some time. **(Delhi 2010C)**
14. Chloroacetic acid is stronger than acetic acid. **(Delhi 2013C)**
15. pH of reaction should be carefully controlled while preparing ammonia derivatives of carbonyl compounds. **(Delhi 2013C)**

(D) Amines.

1. Ethyl amine is soluble in water, whereas aniline is not soluble in water. **(Delhi 2009C, AI 2010C, 2011)**
2. Primary amines have higher boiling points than tertiary amines. **(Delhi 2008C, AI 2011)**
3. Alkyl amines (methylamine) are more basic than ammonia. **(Delhi 2008C, 2009, 2011, AI 2008C, Foreign 2011)**
4. Aliphatic amines are stronger bases than aromatic amines. **(AI 2008, 2009C, 2010C, 2011C)**
5. Aniline is a weaker base than cyclohexylamine. **(AI 2012C)**
6. Amines are less acidic than alcohols of comparable masses. **(AI 2009C)**
7. Amines are more basic than alcohols of comparable masses. **(AI 2011C)**
8. pK_b value for aniline is more than that of methylamine. **(Delhi 2008, 2009C, AI 2008, 2010C, 2011, 2011C)**
9. Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide. **(Delhi 2008, AI 2008, 2010C, 2012C)**
10. Ethanamide (CH_3CONH_2) is a weaker base than ethanamine ($CH_3CH_2NH_2$). **(AI 2012C, 2013C)**
11. Gabriel phthalimide is preferred for synthesizing primary amines. **(AI 2010C)**

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K M C

12. Primary aromatic amines cannot be prepared by Gabriel phthalimide synthesis. **(AI 2011C)**
13. Silver chloride dissolves in methylamine solution. **(AI 2008C)**
14. Electrophilic substitution in case of aromatic amines takes place more readily than benzene. **(Delhi 2010C, AI 2012C, 2013C)**
15. Aniline does not undergo Friedel-Craft reaction. **(Delhi 2008, AI 2008C, 2010C, 2011C)**
16. Diazonium salts of aromatic amines are more stable than those of aliphatic amines. **(AI 2011C)**
17. Nitro compounds have high boiling points in comparison with other compounds of same molecular mass.

(E) Biomolecules and soaps

1. Carbohydrates are generally optically active. **(Delhi 2008C)**
2. Glucose is soluble in water but cyclohexane is not. **(Delhi 2010C)**
3. Aldehyde group is absent in the pentaacetate of D-glucose. **(Delhi 2010C)**
4. The use of the sweetner *aspartame* is limited in cold foods and drinks. **(Foreign 2012)**
5. During electrolysis of amino acids in acidic solution, they migrate towards the cathode, while during electrolysis in alkaline solution they migrate towards the anode. **(Delhi 2008C)**
6. Vitamin A is essential for us. **(Delhi 2010C)**
7. The two strands of DNA are not identical, but complimentary. **(Delhi 2009C, 2010C AI 2011C)**
8. When DNA is hydrolysed, the molar ratio between cytosine to guanine is same and similarly adenine to thymine is also same.
9. When RNA is hydrolysed, there is no relationship among the quantities of different bases. **(Delhi 2008C)**
10. Soaps do not work in hard water. **(Delhi 2011, Foreign 2011, 2012)**
11. Bithional is added to soap. **(Delhi 2013)**
12. Synthetic detergents are better than soaps. **(Foreign 2011)**

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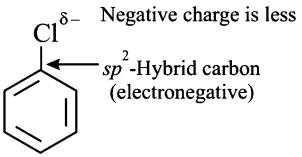
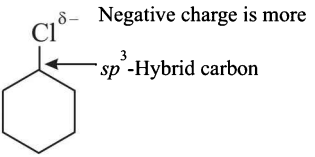
(A) Halogen derivatives.

1. Forces of attraction between alkyl halide-alkyl halide and also between water-water molecules are *stronger* than that between alkyl halide and water molecules.
2. Interactions between (a) haloalkane – organic solvent, (b) haloalkane-haloalkane, and (c) organic solvent-organic solvent are almost similar. Hence molecules of the haloalkane gradually mix with the molecules of the organic solvent.
3. Since sp^2-hybrid carbon is more electronegative than an sp^3 hybrid carbon, the former has smaller tendency to release electrons to Cl than the sp^3-hybrid carbon. Hence the –Cl attached to sp^2- carbon, has lesser negative charge than the –Cl attached to sp^3-hybrid carbon.

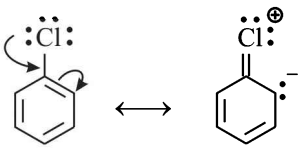


Chlorobenzene



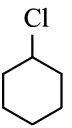
Cyclohexyl chloride

Moreover, delocalisation of lone pairs of electrons in chlorobenzene causes the C–Cl bond to have some double bond character which is shorter than the single C–Cl bond in cyclohexyl chloride.



Chlorobenzene (note the presence of C = Cl^+ bond)

etc.,



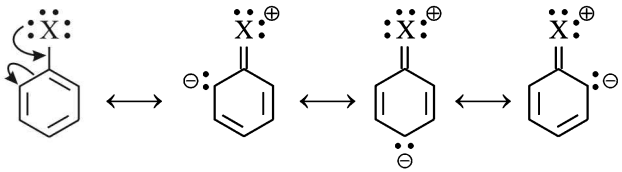
Cyclohexyl chloride
(It has only C – Cl bond)

Thus dipole moment (μ = distance × charge) of chlorobenzene having lesser charge and shorter C–Cl bond will be lower than that of cyclohexyl chloride.

4. In aqueous solution, KOH is almost completely ionised to give OH^- ions which being a strong nucleophile leads to substitution reaction to form alcohols. Further, OH^- ions are highly solvated which reduces the basic character of OH^- ions and hence elimination reaction is avoided.

In case of alcoholic solution of KOH ($C_2H_5OH + KOH \rightarrow C_2H_5O^- + K^+$), alkoxide ($RO^-$) ions are present which being much stronger base than OH^- ions causes elimination of a molecule of HCl leading to alkenes.

5. KCN is predominently ionic and thus gives cyanide ions ($^-C \equiv \ddot{N}$) in solution of which both C and N can donate electrons to form R–CN and R–NC respectively. However, attack takes place mainly through carbon atom because the resulting C–C bond is more stable than the C–N bond, formed when attack takes place through N. However, $AgC\ddot{N}$ is mainly covalent and hence only N is free to donate electrons forming $R - N \overset{\rightarrow}{=} C$.
6. Same as above.
7. Resonance in aryl halides leads to partial double bond character in C–X bond with the result C–X bond length becomes shorter and hence stronger.



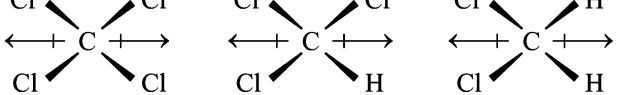
Resonance is not possible in alkyl halides (R–X), hence the C–X bond is lengthier and thus weaker than the $C = X^+$ bond. Moreover, in aryl halides, C bearing halogen is sp^2 hybridised and thus more electronegative (due to greater *s*-character) and hence holds the electrons of C–X bond more tightly than the sp^3 hybridised carbon of alkyl halides.

8. Sulphuric acid is an oxidising agent and will oxidise HI, produced during the reaction between KI and H_2SO_4, to iodine.

$$2\,KI + H_2SO_4 \longrightarrow 2KHSO_4 + 2\,HI$$
$$2\,HI + H_2SO_4 \longrightarrow H_2O + I_2 + SO_2$$

To avoid oxidation of HI, non-oxidising acid (like H_3PO_4) is used.

9. Let us draw three dimensional structures of the three compounds.



CCl_4 ($\mu = 0$ D) $CHCl_3$ ($\mu = 1.03$ D) CH_2Cl_2 ($\mu = 1.62$ D)

Carbon tetrachloride is symmetrical, hence the resultant of the two

K M C

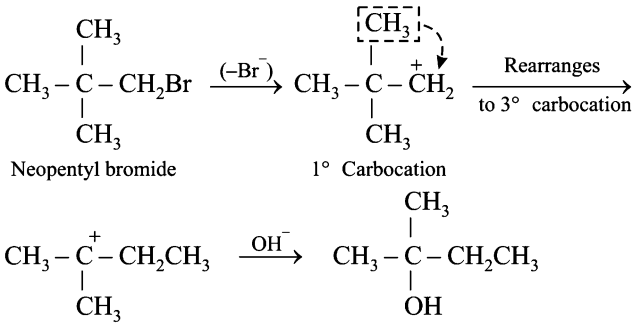
C–Cl dipoles is cancelled by the resultant of the two C–Cl bonds in opposite direction. In $CHCl_3$, the resultant of the two C–Cl dipoles is opposed by the resultant of the C–Cl and C–H bonds in the opposite direction which of course is smaller in magnitude and thus the net dipole moment of $CHCl_3$ will have a significant value.

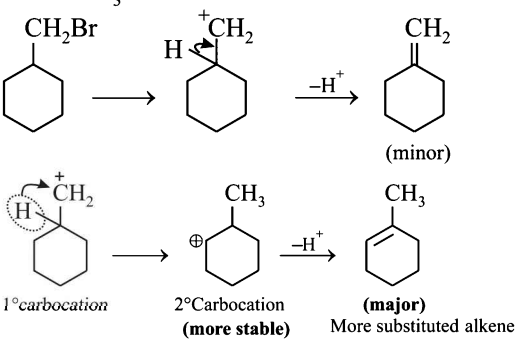
In CH_2Cl_2, the resultant of the two C–Cl dipoles is opposed by the resultant of the two C–H bonds in opposite direction which is very small in magnitude. Thus the dipole moment of CH_2Cl_2 will be more than that of $CHCl_3$.

10. *p*-Dichlorobenzene, being symmetrical, fits tightly in its crystal lattice. Thus the intermolecular forces of attraction in the *p*-isomer are stronger than those in the *o*-and *p*- isomers; hence it requires larger amount to energy to melt or dissolve the *p*-isomer than the *o*- and *m*-isomers. Consequently, the melting point of the *p*-isomer will be higher and its solubility lower than the corresponding *o*- and *m*-isomers.

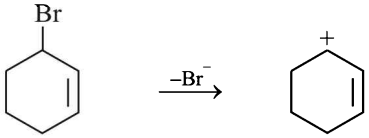
11. A primary alkyl chloride reacts with sodium iodide to form primary alkyl iodide which is more reactive than the alkyl chloride.

$$R-Cl \xrightarrow{NaI} \underset{\text{More reactive than R–Cl}}{R-I} \xrightarrow{CH_3COONa} CH_3COOR$$

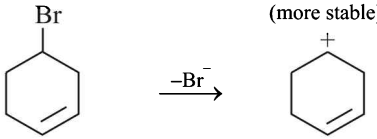
12. 

13. 

14. 3-Bromocyclohexene forms the stable allyl carbocation, while 4-bromocyclohexene forms less stable 2° carbocation as intermediate.

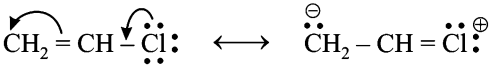


3-Bromocyclohexene — Allylic carbocation (more stable)

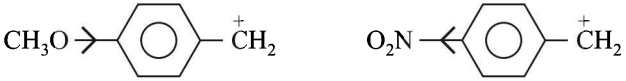


4-Bromocyclohexene — 2° Carbocation (less stable)

15. Vinyl chloride (like halobenzenes, ArCl) is unreactive towards nucleophilic substitution because of partial double bond character between C and Cl due to resonance.



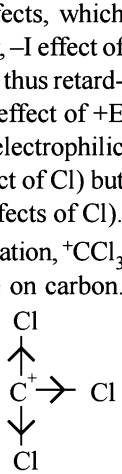
16. Benzyl halides react with ethanol via S_N1 reaction because the intermediate benzyl carbocation is highly stable. Further, higher the stability of the carbocation more will be its reactivity.



More stable due to dispersal of +ive charge — Less stable due to accumulation of +ive charge

17. Chlorine in chlorobenzene undergoes +E and +M effects, which increase electron density in *o*- and *p*-positions. However, –I effect of chlorine decreases electron density on benzene nucleus, thus retarding electrophilic substitution. However, the combined effect of +E and +M is greater than the –I effect of Cl with the result electrophilic substitution in chlorobenzene is difficult (due to –I effect of Cl) but takes place in *o*- and *p*-positions (due to +E and +M effects of Cl).

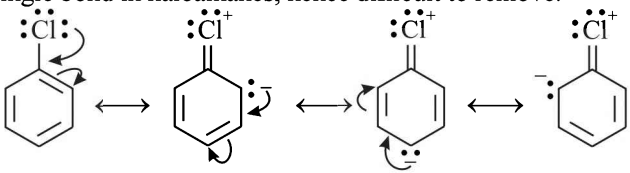
18. CCl_4 is inert in S_N1 reactions with Ag^+ because the carbocation, $^+CCl_3$ is destabilized due to accumulation of positive charge on carbon. Other reason for destability of the $^+CCl_3$ is the disparity of the size of the 2*p* AO of C and 3*p* AO of Cl. CCl_4 is also inert by S_N2 because the three remaining chlorines on C sterically hinder the approach of OH^-. However, Si, in $SiCl_4$, has available empty *d* AO's, it



readily adds H_2O molecule to give the unstable intermediate, $Cl_4Si^-\overset{+}{O}H_2$, which loses HCl. The resulting product accepts another H_2O molecule and then again loses HCl. This stepwise addition of H_2O and elimination of HCl, ultimately, leads to the replacement of the four Cl's by four OH's.

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

19. Resonance in chlorobenzene leads to partial double bond character to C–Cl bond which, being shorter, is stronger, than the usual C–Cl single bond in haloalkanes, hence difficult to remove.



Secondly, benzene and its derivatives, except those having electronegative groups like $-NO_2$, are electron rich species, hence not easily attacked by nucleophiles.

20. Chloroform is stored in dark coloured bottles to cut off light which would otherwise oxidise $CHCl_3$ to carbonyl chloride, also known as **phosgene**, a poisonous gas.

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} 2\,COCl_2 + 2HCl$$

21. The C–X bond in halobenzene acquires partial double bond character which is shorter than the C–X single bond in CH_3–X, where resonance is not possible. **Secondly**, in haloarenes, the halogen atom is attached to sp^2-hybridized carbon which is more electronegative than the sp^3-hybridized carbon in CH_3–X. Higher electronegativity of the sp^2-hybridized carbon shortens the C–X bond length.

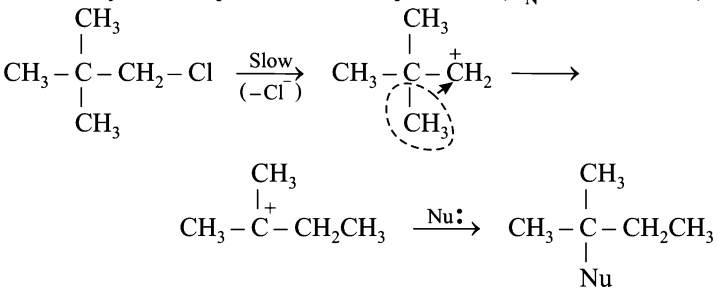
22. 3° Alkyl halide (former one) reacts faster than the 2° alkyl halide (latter one) due to greater stability of 3° carbocations over 2° carbocations.

23. For a given alkyl group, the order of reactivity is R–I > R–Br > R–Cl > R–F. This is due to C–X bond energy, C–I bond dissociation enthalpy is minimum, while the C–F bond dissociation enthalpy is maximum. Hence R – I is most reactive, while R–F is least reactive.

24. In neopentyl chloride, carbon bearing chlorine is sterically hindered due to bulky $(CH_3)_3C$– group, hence not attacked easily by nucleophile to form transition state (S_{N^2} mechanism).

$$(CH_3)_3C{-}CH_2{-}Cl \xrightarrow[S_{N^2}]{Nu:} \text{Transition state, not formed}$$

However, neopentyl chloride ionises to give carbocation (1°) which rearranges to the highly stable 3° carbocation. Hence formation of carbocation takes place easily; which is then attacked by nucleophile to form product (S_{N1} mechanism).



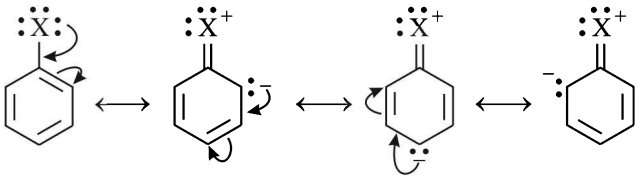
25. Grignard reagents are very reactive. They react with moisture present in the apparatus or the starting materials, i.e. alkyl halide, magnesium and solvent (ether or THF).

$$\overset{\delta-}{R}-\overset{\delta+}{Mg}-\overset{\delta-}{X} + HOH \longrightarrow RH + Mg(OH)X$$

26. In haloalkanes, carbon bearing halogen is electron-deficient due to –I character of the halogen, hence such carbon is easily attacked by electron rich species (nucleophiles).

$$\overset{\delta+}{R}-\overset{\delta-}{X} + Nu: \longrightarrow R-Nu + X^-$$

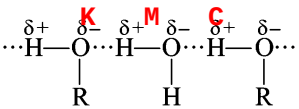
However, in haloarenes, carbon-halogen has partial double bond character due to resonance, hence the C–Cl bond in haloarenes is stronger and not easily broken i.e. they are not easily replaced by nucleophiles. On the other hand, resonance in haloarenes increases the electron density in *o*- and *p*-positions (due to + E and + M effects) on which electron deficient species (electrophiles) easily attack



Resonance in haloarenes (note the *o*- and *p*-positions have high electron density).

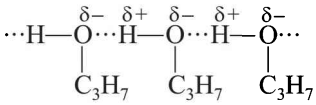
(B) *Alcohols, ethers and phenols.*

1. Alcohols have polar group, hence they can form H –bonds with water, the H–bond between –OH group of alcohols and H–O–H is stronger than the H–bonds between water–water and between alcohol–alcohol, hence alcohols (essentially lower) easily become miscible with water molecules.



Hydrocarbons have no polar group, hence can't form H–bond with water and thus remain insoluble in water.

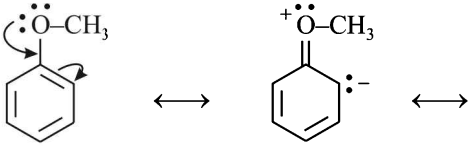
2. Lower alcohols can form H–bonds with water, but as the alkyl group becomes larger in size, i.e. greater than C_4H_9 –, the alkyl group starts dominating and the effect of –OH group in forming H–bond becomes less important and thus solubility of alcohols in water starts decreasing with increase in alkyl group.
3. Propanol (C_3H_7OH) molecules are held together by *strong* intermolecular H–bonds, while butane (C_4H_{10}) molecules are held together by *weak* van der Waal's forces of attraction.



Stronger the intermolecular interactions, higher will be the b.p.

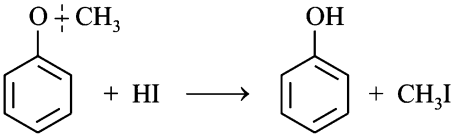
4. Due to presence of lone pair of electrons on oxygen, alcohols behave as Bronsted base (proton acceptors).
5. More the number of carbon atoms of a homologous species (e.g. $C_2H_5OH > CH_3OH$), greater will be van der Waal's forces and hence higher will be the boiling point.
6. Increase in branching of the alkyl group restricts the alcohol-alcohol H-bonding, hence association of molecules does not occur leading to lower boiling point.
7. (±)-2-Butanol is optically inactive because the two enantiomers, (+)-and (–)-2-butanol, are present in equal amounts (remember that each of the individual enantiomer is optically active and when the two enantiomers are present in unequal amounts, the mixture is also optically active).
8. Methanol has stronger intermolecular H-bonding than methyl amine because oxygen is more electronegative than nitrogen.
9. Methanol can form H-bond with water, becuase –OH group is polar, while iodomethane cannot form H–bond with water because C–I bond is not sufficiently polar.
10. Alcohol molecules are capable of forming H–bonds with each other. On the other hand ether molecules do not form H–bonds and thus they do not exhibit association, hence their boiling points are lower than the isomeric alcohols.

11. Consult Question 10.
12. Consult Question 10.
13. On dehydration, secondary and tertiary alcohols give alkenes as the major product due to stability of 2° and 3° carbocations.
14. The C–O bond between carbon of phenyl group and oxygen is stronger than the O–C bond between O and carbon of methyl group due to resonance,



(C = O bond is stronger)

hence cleavage occurs at O–C bond rather than the stronger C–O bond.



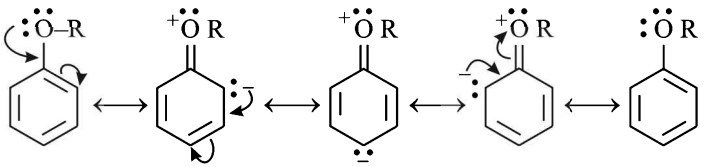
Secondly, $C_6H_5–O–CH_3$ on protonation gives $C_6H_5–\overset{+}{O}(H)–CH_3$ which can break up in two ways:

$$C_6H_5-OH + \underset{\textbf{(stable)}}{\overset{+}{C}H_3} \longleftarrow \mathbf{C_6H_5-\overset{+}{O}(H)-CH_3} \longrightarrow \underset{\textbf{(unstable)}}{\overset{+}{C}_6H_5} + HOCH_3$$

Since, $\overset{+}{C}H_3$ is more stable than $C_6H_5^+$, hence $^+CH_3$ will be formed as intermediate.

$$C_6H_5-\overset{+}{O}(H)-CH_3 \longrightarrow C_6H_5-OH + \overset{+}{C}H_3 \xrightarrow{I^-} CH_3I$$

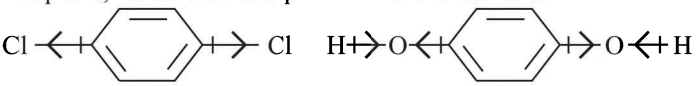
15. Consult Q. 28



16. In phenol, negative charge on oxygen is delocalised due to resonance leading to decrease in charge and hence in dipole moment; whereas resonance is not possible in CH_3OH.

17. In *p*-dichlorobenzene, both –Cl groups are in the same plane, and the dipoles from the two –Cl groups are equal and opposite leading to zero net dipole moment.

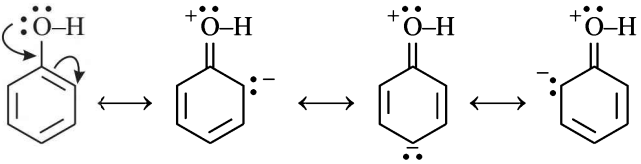
However, in *p*-dihydroxybenzene, the two –OH groups are not in same plane, hence the net dipole moment is not zero.



$\mu = 0D$ $\mu \neq 0D$

18. *p*-Isomer is symmetrical and hence fits into crystal more tightly, thus it has high lattice energy and less solubility than the corresponding *o*- and *m*-isomers.

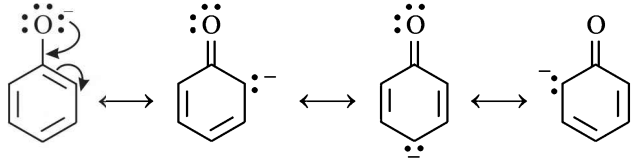
19. Greater acidity of phenol than an alcohol is due to possibility of resonance in phenol which leads to electron-deficient oxygen atom. Presence of electron-deficient oxygen atom (see structures II, III and IV) in turn weakens the $-\overset{+}{O}\longleftarrow H$ bond, and thus facilitates release of proton.



I II III IV

Such structures are not possible in alcohols.

Once hydrogen atom is removed from phenol, the ion (phenoxide) is very much stabilized due to delocalization of its negative charge.



V VI VII VIII

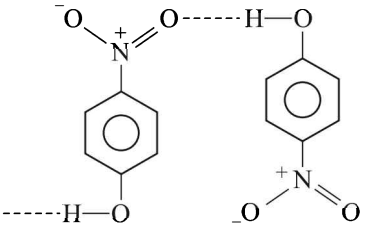
Resonance in phenoxide ion (note that structures VI to VIII are equivalent)

Remember that phenoxide ion is much more stable than the parent compound phenol because phenoxide ion does not involve charge separation, while in phenol three equivalent resonanting structures (II to IV) involve charge separation.

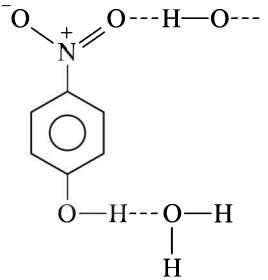
20. Refer above Question 19.

21. Due to positive charge on resonating structures of phenol (Q. 19), it does not undergo protonation easily.

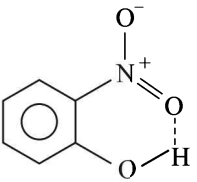
22. *p*-Nitrophenol is capable of forming intermolecular H–bond between themselves, hence it has high higher m.p. Further it can also form H-bond with water and hence it is more soluble in water. *m*-Nitrophenol also behaves in the same way.



p-Nitrophenol (intermolecular H-bond between two *p*-nitrophenol molecules)



(intermolecular H-bond with water)

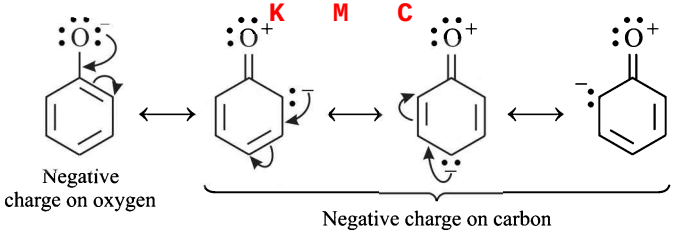


o-Nitrophenol (intramolecular H-bond restricts intermolecular H-bonds)

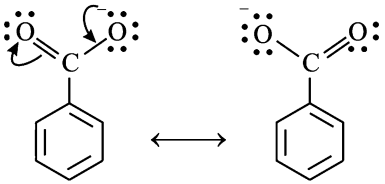
However, *o*-nitrophenol is capable of forming intramolecular H-bond because the newly formed ring will be 6-membered. Due to intramolecular H-bonding, it does not form intermolecular H-bond neither with its second molecule nor with water. Hence *o*-nitrophenol has low m.p. and low solubility in water than the corresponding *m*- and *p*-isomers.

23. Carbon of C–O bond of phenol is sp^2 hybridised, while C–O bond of ethanol is sp^3 hybridised. Since sp^2 hybridised carbon is more electronegative than the sp^3 hybridised carbon, hence the former causes the contraction of the C–O bond. **Secondly,** phenol shows resonance in which C–O bond acquires partial double bond character leading to shortening of the C–O bond (See Q 19). Resonance is not possible in ethanol.

24. All resonating structures of phenoxide ion are not equivalent, while the resonating structures of carboxylate ion are equivalent.



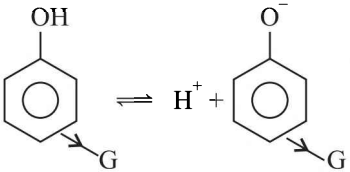
Resonating structures of phenoxide ion



Resonating structures of carboxylate ion

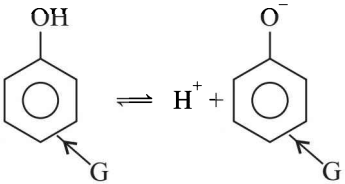
Resonance is more important where all resonating structures are equivalent, hence carboxylate ion is more stable than the phenoxide ion.

25. Electron-withdrawing substituents increase the acidity of phenols; while electron-releasing substituents decrease acidity. Thus substituents affect acidity of phenols in the same way as they affect acidity of carboxylic acids; it is of course, opposite to the way these groups affect basicity of amines.



G withdraws electrons, thus disperses the –ve charge of the ion due to – I, – R or both effects, stabilises it and hence increases ionization of the parent phenol.

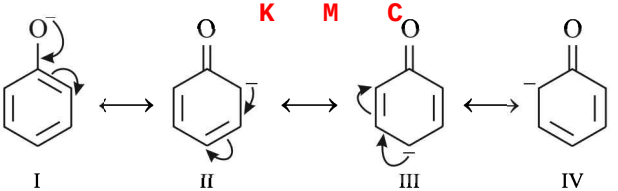
(where G = $-NO_2$, –CN, – CHO, –COOH, – $^+NR_3$, –X)



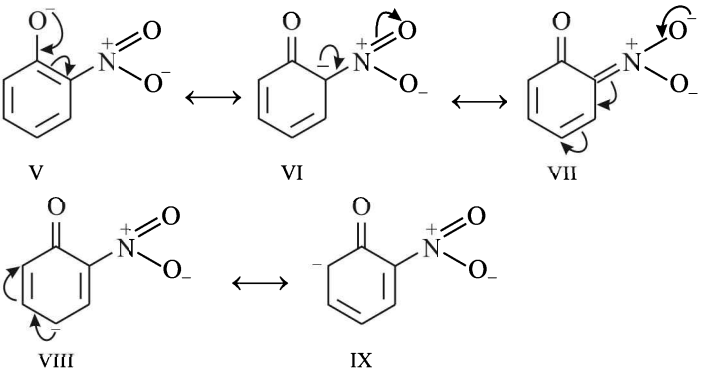
G releases electrons, thus intensifies the –ve charge of the ion due to +I, +R or both effects, destabilises it and hence decreases ionization of the parent phenol.

(where G = –R, OR, NR_2)

26. $-NO_2$ is electron withdrawing group (–R and –I effect), so it increases stability of *o*- and *p*-phenoxide ion as compared to phenoxide ion from phenol.



Resonating structures of phenoxide ion

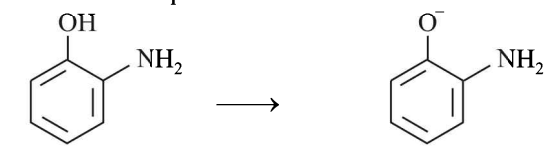


Resonating structures of *o*-nitrophenoxide ion

(Note that an additional structure, (vii) is possible here, hence *o*-nitrophenoxide ion is more stable than phenoxide ion)

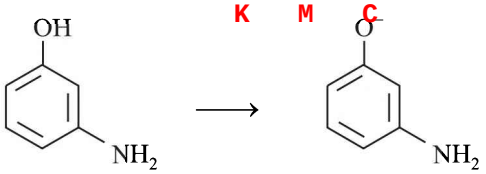
Similarly, five resonating structures are possible for *p*-nitrophenoxide ion.

27. Amino group, being electron releasing, intensifies the negative charge if present at *ortho* and *para* positions (but not *meta* position) and thus makes the phenoxide less stable and thus the parent phenol (*o*-amino phenol) less acidic than phenol. However, when present at *meta* position, it is not involved in the intensification of charge and thus has no additional effect on stability of the corresponding phenoxide ion and hence on acidity of the corresponding phenol (*m*-amino phenol), i.e. it is as acidic as phenol and hence more acidic than *o*-aminophenol.



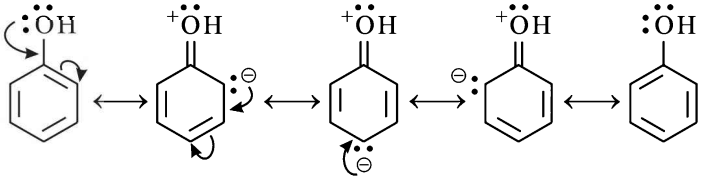
o-Aminophenol

o-Aminophenoxide ion
(It shows +R effect, intensifies –ve charge on oxygen, destabilises the ion)



m-Aminophenol *m*-Aminophenoxide ion
(It does not show + R effect)

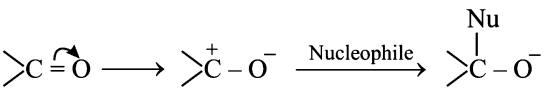
28. An –OH group present on benzene nucleus undergoes +R effect and increases the electron density especially on the *ortho*- and *p*-positions.



Now since electron density on benzene ring increases, the electrophilic substitution takes place easily as compared to benzene and thus –OH group is said to be **activating group** towards electrophilic **substitution**. Further, the electron density increases on *ortho*- and *para*-positions, electrophilic substitution will be taking place at these positions, and thus –OH group is said to be *o*, *p*-directing.

(C) Aldehydes, ketones and carboxylic acids.

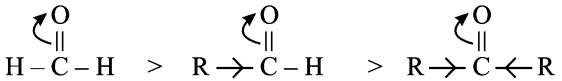
1. Alcohol molecules undergo strong association due to strong H–bond between alcohol molecules hence boil at higher temperatures; while association between aldehyde/ketone molecules is weak due to weak dipole-dipole interactions; hence they boil at lower temperatures.
2. Consult above question (1) Carboxylic acids, like alcohols also undergo association due to strong H-bond.
3. Ethanal is soluble in water due to H–bonding between the polar carbonyl group and water molecules.
4. Polarity of carbonyl group develops positive charge on carbon and negative charge on oxygen.



Where, Nu = Nucleophile, e.g. CN^- from HCN.

5. Nucleophiles (nucleus loving reagents) attack on nucleus (site where electron density is minimum) i.e. atom which bears positive charge.

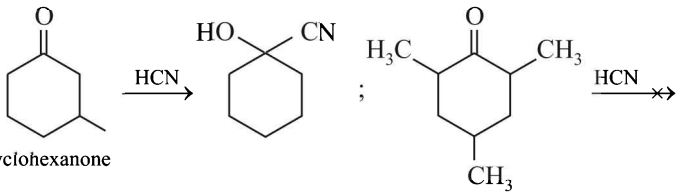
Thus any factor or group which increases positive charge on carbonyl carbon (i.e. group showing –I effect) will increase nucleophilic addition and a group which decreases positive charge (i.e. group showing +I effect) on carbonyl carbon will decrease nucleophilic addition. Thus reactivity follows:



Formaldehyde (having max. +ve charge)	>	Aldehydes (carbon having less +ve charge)	>	Ketones (C having least +ve charge)

In aldehydes, positive charge on carbonyl carbon (due to polarity of carbon group) is decreased by electropositive character (+I effect) of the alkyl group, hence these are less reactive towards nucleophiles than formaldehyde. In ketones, positive charge on carbon is more decreased due to +I effect of the two alkyl groups, hence ketones are less reactive towards nucleophiles than aldehydes.

6.



Cyclohexanone

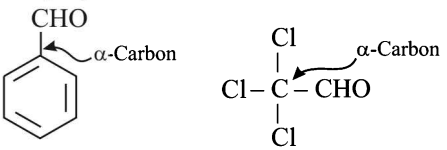
2, 4, 6-Trimethylcyclohexanone

This may be explained in two ways.

(a) Presence of three $-CH_3$ groups decreases positive charge on carbon of C=O group due to +I effect.

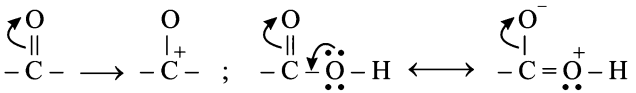
(b) Steric hindrance by $-CH_3$ groups in *ortho*-positions does not allow the nucleophile (CN^-) to attack on the carbonyl carbon.

7. Aldol condensation is given by aldehydes or ketones having α-hydrogen atom, since $H-\underset{\underset{O}{\|}}{C}-H$ does not have any α-hydrogen atom it does not undergo aldol condensation. Other such compounds are benzaldehyde, trichloroacetaldehyde, etc.



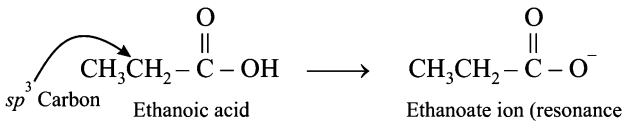
8. Lone pair of electrons on the $-NH_2$ group adjacent to the $>C=O$ group is involved in resonance leading to decrease in its nucleophilic character, and hence it can't take part in reaction with the carbonyl group.

9. Carboxylic acids exhibit resonance due to which its carbon bears no positive charge, i.e. it is less electrophilic than the carbonyl carbon.

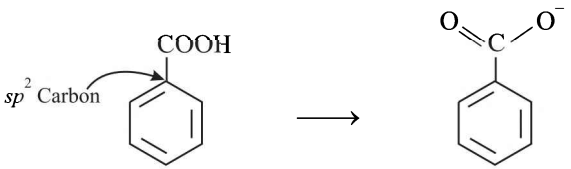


Carbonyl group (carbon has +ve charge, i.e. it is electrophilic) ; Carboxylic acids (Note that carbon is less electrophilic, i.e. it does not have +ve charge)

10. Higher the stability of a carboxylate ion, more will be the acidic character of the parent acid (i.e. deprotonation of the parent carboxylic acid). Observe the statement in the two acids.



Ethanoic acid — Ethanoate ion (resonance not possible)

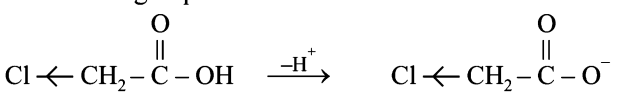


Benzoic acid — Benzoate ion (resonance possible due to benzene ring)

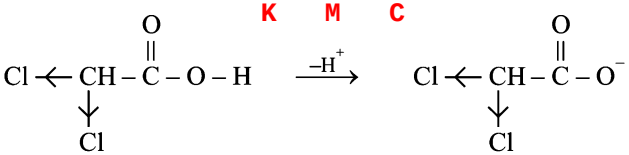
Benzoate ion shows extensive resonance due to benzene ring hence it is more stable and thus benzoic acid is more acidic than ethanoic acid.

Alternatively, in benzoic acid, –COOH group is attached to sp^2 hybridised carbon which makes it acidic while in ethanoic acid, –COOH group is attached to sp^3 hybridised carbon.

11. Monochloroethanoic acid is weaker acid than dichloroethanoic acid because former has one electronegative group (–Cl) while the latter has two –Cl groups.



Monochloroethanoic acid (–I effect of –Cl weakens the O–H bond) — Monochloroethanoate ion (–ve charge on oxygen dispersed due to –I effect of –Cl)

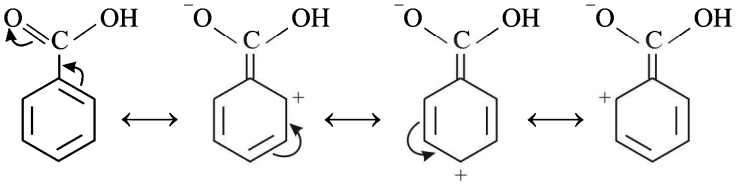


Dichloroethanoic acid (–I effect of two –Cl makes O–H bond more weaker)

Dichloroethanoate ion (–I effect of two –Cl disperses the charge on O, hence stabilises the ion)

Thus dichloroethanoate ion is more stable, and dichloroethanoic acid is more acidic than monochloroethanoic acid. Now we know that higher the pK_a (or lower the K_a) value of an acid, lower will be its acidic character. Thus monochloroethanoic acid, a weaker acid, will have high pK_a value than dichloroethanoic acid, a stronger acid.

12. Carboxylic group is electron withdrawing and withdraws electrons from the ortho and para positions of the benzene ring due to –M and –I effects.



Mesomeric (–M) effect in benzoic acid

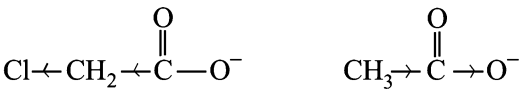
Thus *meta* positions, which are not affected by –M effect, are relatively electron rich than the *o*- and *p*-positions causing electrophilic substitution at meta position .

13. Ester hydrolysis is initiated by the addition of a small amount of dilute sulphuric acid to form a carboxylic acid and an alcohol. The

$$\underset{\text{Ester}}{RCOOR'} \xrightarrow{\text{dil. } H_2SO_4} \underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{Alcohol}}{R'OH}$$

carboxylic acid self ionises to give proton (H^+) which acts as a catalyst and fastens the reaction (hydrolysis of ester).

14. Chloroacetic acid is a stronger acid than acetic acid and has higher value of dissociation constant K_a than that of acetic acid. This is because Cl group is electron withdrawing and chloroacetate ion is more stabilised than acetate ion (as methyl group is electron releasing).



15. Formation of ammonia derivatives (oximes, hydrazones, semicarbazones, etc.) proceeds via the attack of carbonyl carbon with proton to form the conjugate acid.

$$>C=\ddot{O}+H^+ \longrightarrow >C=\overset{+}{O}H \longleftrightarrow >\overset{+}{C}-OH$$

Therefore, presence of an acid is a must for preparing these derivatives. However, in strongly acidic medium, the proton attacks the unshared pair of electrons on nitrogen to form the species $\overset{+}{R}NH_3$ which cannot attack the carbonyl carbon.

$$H^+ + :NH_2R \longrightarrow \overset{\oplus}{N}H_3R$$

In basic medium, there is no protonation of carbonyl group, and hence no reaction. $>C=O \xrightarrow{\text{Basic medium}}$ No protonation, No reaction

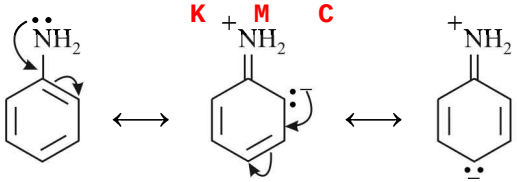
Therefore, preparation of ammonia derivatives requires slightly acidic medium and its careful control is essential.

(D) Amines.

1. Ethylamine ($C_2H_5NH_2$) is soluble in water due to its capability to form hydrogen bond with water, while aniline ($C_6H_5NH_2$) is insoluble in water because it does not form hydrogen bond owing to larger (bulkyl) hydrocarbon part.
2. Primary amines (RNH_2) have two H–bonds, hence undergo extensive intermolecular H–bonding (association), while tertiary amines (R_3N) don't have any H–atom on N–atom, hence do not form H–bonding, i.e. their molecules do not associate.
3. The +I effect of the alkyl ($-CH_3$) group increases electron density on the nitrogen atom of the $-NH_2$ group which can donate electron more easily than NH_3 (having no +I group) and thus acts as a stronger base than ammonia.
4. In aliphatic amines ($R-NH_2$), the +I effect of the alkyl group increases the electron density on the N-atom due to which they act as Lewis base. On the other hand, in aromatic amines ($Ar-NH_2$), the electron density on the N-atom decreases due to delocalization of the lone pair of electrons over the benzene ring, hence they act as weak bases.

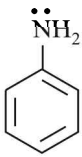
$$R \rightarrow \ddot{N}H_2$$

+I effect in aliphatic amines increases electron density on N-atom

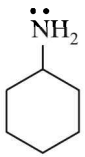


+M effect in aniline decreases electron density on N-atom

5. In aniline, the lone pair of electrons on the N-atom is delocalised over the benzene ring, hence it is less available for protonation and thus acts as a weak base (also consult Q. 4) However, in cyclohexylamine, the lone pair of electrons on N-atom is not delocalised and hence easily available for protonation and thus it acts as a strong base than aniline.



Aniline
(resonance possible)



Cyclohexylamine
(resonance not possible)

6. Acids are those compounds which undergo deprotonation to form an anion. Higher the stability of the anion formed, more will be the acidic character of the parent compound. Now observe this statement of amines and alcohols.

$$\underset{\text{Amine}}{R-NH_2} \rightleftharpoons \underset{\text{Imide ion (less stable)}}{R-NH^- + H^+}$$

$$\underset{\text{Alcohol}}{R-OH} \rightleftharpoons \underset{\text{Alkoxide ion (more stable)}}{R-O^- + H^+}$$

Since O is more electronegative than N, the RO^- (formed from ROH) can accommodate the negative charge easily than the RNH^- (from RNH_2).

7. Refer above question. Alternatively, bases are those compounds which can easily accept proton, and higher the stability of the protonated species, more will be the basic character of the parent compound. Observe this statement on amines and alcohols.

$$R-\ddot{N}H_2 \xrightleftharpoons{H^+} R-\overset{+}{N}H_3$$

Amine — Protonated amine (more stable)

$$R-\ddot{O}H \xrightleftharpoons{H^+} R-\overset{+}{O}H_2$$

Alcohol — Protonated alchol (less stable)

8. Lower the basicity, higher is pK_b value. Since methylamine is more basic (due to +I effect of $-CH_3$ group) than aniline due to delocalization of the lone pair of electrons on N atom over the benzene ring, pK_b value of CH_3NH_2 will be less than that of aniline.
9. Methylamine, being more basic than water, takes a proton from water liberating free OH^- ions which react with Fe^{3+} ions to form brown precipitate of ferric hydroxide or hydrated ferric oxide.

$$CH_3\ddot{N}H_2 + HOH \longrightarrow CH_3\overset{+}{N}H_3 + OH^-$$

$$2Fe^{3+}\text{ (from } FeCl_3) + 6OH^- \longrightarrow 2Fe(OH)_3 \text{ or } Fe_2O_3\cdot 3H_2O\downarrow$$

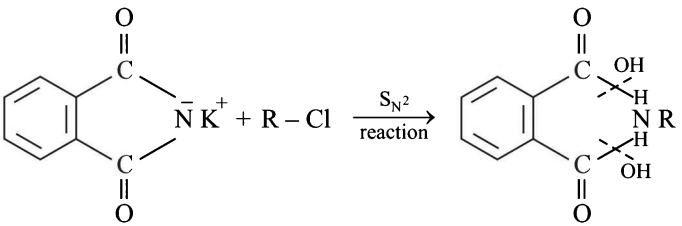
Brown precipitate

10. In ethanamide (CH_3CONH_2), the lone pair of electrons on N-atom is delocalised, hence lesser available for protonation, i.e. it is a weak base,

$$CH_3-\overset{\overset{\curvearrowleft O}{\|}}{C}-\ddot{N}H_2 \longleftrightarrow CH_3-\overset{\overset{O^-}{|}}{C}=\overset{+}{N}H_2 \;;\; CH_3CH_2-\ddot{N}H_2$$

while the lone pair of electrons in ethanamine $(CH_3CH_2\ddot{N}H_2)$ is localised, hence easily available for protonation.

11. Gabriel phthalimide reaction gives primary amines in good yield without any contamination of secondary and tertiary amines.



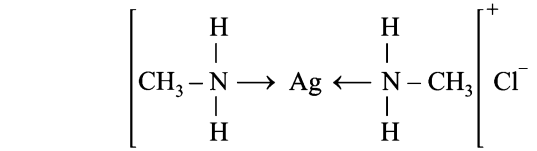
12. In aromatic halides (Ar–X), halogen is not reactive, hence aromatic halides (Ar–X) do not undergo S_{N^2} reaction (see first step in above reaction) with potassium phthalimide.

13. Silver chloride dissolves in aqueous methylamine solution due to formation of a soluble complex.

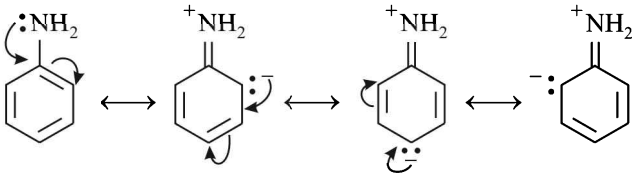
$$AgCl + 2\,CH_3NH_2 \longrightarrow [(CH_3NH_2)_2Ag]^+\,Cl^-$$

bis-(Methylamine) silver (I) chloride

or



14. Amino group ($-NH_2$) is a strong activating group due to +M and +E effects. This leads to increase in electron density on the *ortho* and *para* positions of the benzene ring causing electrophilic substitution very easy as compared to benzene which is not having any activating group

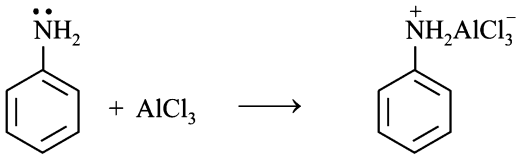


+ M and + E effects in aniline

15. Aniline, being a Lewis base, reacts with the Lewis acid ($AlCl_3$, catalyst for Friedel-Craft reaction) to form a salt.

$$\underset{\text{Lewis base}}{C_6H_5NH_2} + \underset{\text{Lewis acid}}{AlCl_3} \longrightarrow \underset{\text{Salt}}{C_6H_5\overset{+}{N}H_2AlCl_3^-}$$

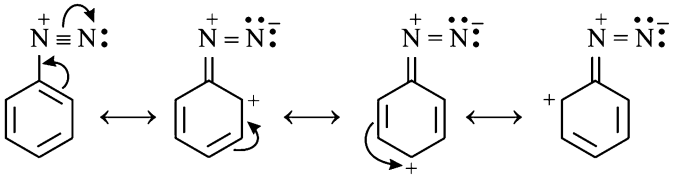
Thus the catalyst $AlCl_3$ is consumed. Moreover, the product has positive charge on N, which is deactivating.



Aniline (having activating $-\ddot{N}H_2$ group)

Salt (having deactivting $-\overset{+}{N}H_2AlCl_3^-$ group)

16. Diazonium salts of aromatic amines are more stable due to resonance (dispersal of positive charge over the benzene ring).

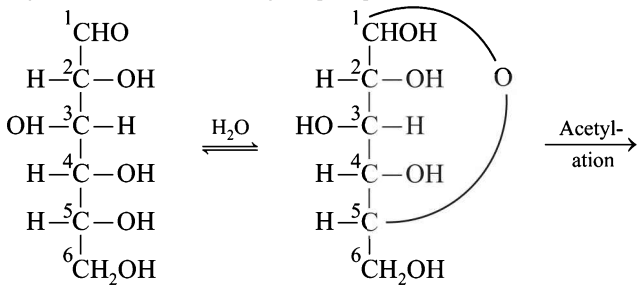


However, resonance is not possible in diazonium salts of aliphatic amines ($C_2H_5–N^+≡N$), hence these are less stable.

17. Nitro compounds are polar in nature and hence exhibit dipole-dipole interaction.

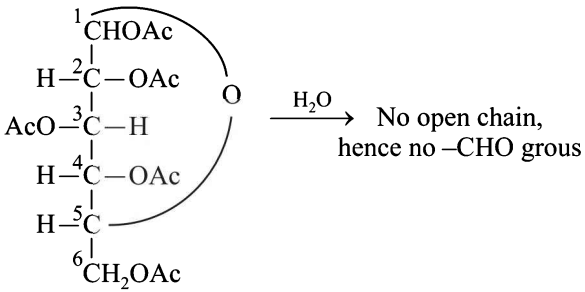
(E) Biomolecules and soaps.

1. Carbohydrate molecules are chiral due to the presence of chiral carbon.
2. Glucose is a polar molecule and contains five –OH groups, hence forms extensive intermolecular H–bonding with water molecules, hence it dissolves in water very easily. Cyclohexane is a non-polar molecule and can't form H–bond with water, hence it is insoluble in water.
3. Glucose penta-acetate does not contain –OH group at C–1, hence it can't get converted in aqueous solution to the open chain structure only which has free aldehyde group.



Open chain structure of glucose

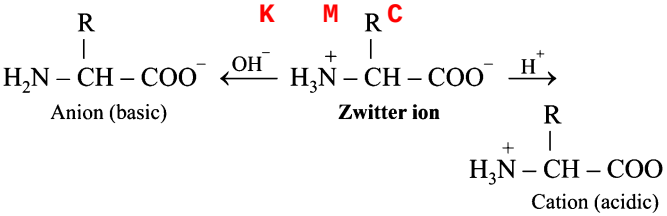
Cyclic structure of glucose



Glucose pentaacetate

4. Aspartame is unstable at cooking temperature, hence it is used only in cold foods and drinks.
5. Amino acids have zwitterion structure. However, in presence of strong acids they exist as cations (and hence migrate towards cathode during electrolysis), and in presence of alkalies they

K M R C



exist as anions (and hence migrate towards anode on electrolysis).

6. Deficiency of vitamin A causes xerophthalmia (hardening of cornea of eye) and night blindness.
7. The two strands of DNA (polynucleotides) are held together by hydrogen bonds between purine base of one strand and pyrimidine base of the other and vice versa. Further due to different sizes and geometries of the bases, the only possible pairing in DNA are between **(i)** Guanine (G) and Cytosine (C) through three H–bonds (G ≡ C) and **(ii)** adenine (A) and thymine (T) through two H–bonds (A = T). Due to this specific base pairing, the two strands of DNA are not identical but complimentary.
8. Due to specific base-pairing between G and C, DNA on hyrolysis will always give equal molecules of G and C; similar is the case for A and T molecules.
9. It is due to the fact that unlike DNA, RNA exists as a single strand and hence there is no base-pairing in RNA molecules and thus there is no relationship between the number of molecules of the four bases (A, G, C and U).
10. Hard water contains insoluble calcium and magnesium chlorides which form insoluble precipitate (scum) with soap. This causes wastage of soap and further the insoluble scum cannot be rinsed off easily.
11. Bithional acts as a deodorant in soaps and thus reduces the odours produced by bacterial decomposition of organic matter on the skin. Bithional is also antiseptic.
12. Unlike soaps, synthetic detergents can be used with soft as well as hard water.

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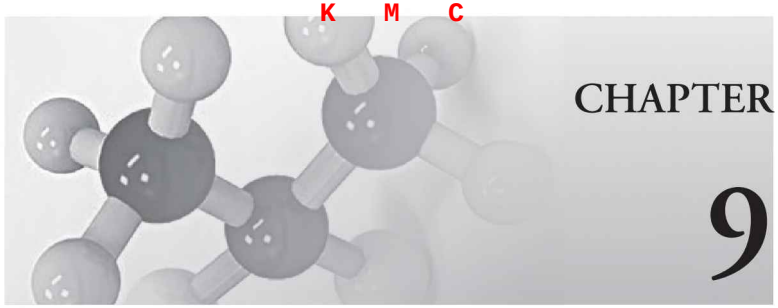


CHAPTER

9

What is the correct Increasing/Decreasing Order?

(A) *Halogen derivatives*

1. Which reaction (S_N1, S_N2, E1, E2) is favoured in each of the following reactions; more than one symbol may be used.

   (i) $2° \text{ RCl} + I^- \xrightarrow{\text{acetone}}$

   (ii) $2° \text{ RCl} + OH^- \xrightarrow{\text{HCOOH}}$

   (iii) $2° \text{ RCl} + C_2H_5ONa \xrightarrow{C_2H_5OH}$

   (iv) *ter*-BuBr + $CN^- \longrightarrow$

   (v) *ter*-BuBr + $C_2H_5OH \longrightarrow$

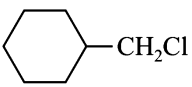
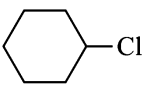
   (vi) *ter*-BuBr $\xrightarrow[CH_3COONa]{CH_3COOH}$

2. Which compound in each of the following pairs will react fast with regard to S_N2 reaction?

   (i) CH_3Cl or $(CH_3)_3CCl$ **(Delhi 2008, AI 2010 C)**

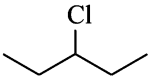
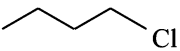
   (ii) $C_6H_5CH_2Cl$ or $C_6H_5CH(Cl)C_6H_5$

   (iii) CH_3Br or CH_3I **(Delhi 2008, AI 2012, 2013)**

   (iv)  or  **(Delhi 2009)**

   (v) $CH_3-CH_2-\underset{\underset{CH_3}{|}}{C}HCH_2Br$ or $CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_2CH_2Br$

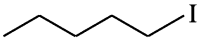
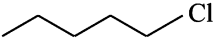
221 Approved: 0777 023 444

(vi)  or  **(Delhi 2008, AI 2008)**

(vii) $CH_3CHClCH_2CH_3$ or $CH_3CH_2CH_2CH_2Cl$ **(Delhi 2010)**

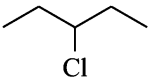
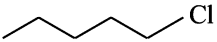
(viii) 1-Bromopentane or 2-bromopentane.
(Delhi 2010, Foreign 2011)

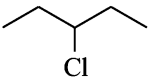
(ix) 1-Bromo-2-methylbutane or 2-bromo-2-methylbutane.
(Delhi 2010)

(x)  or  **(Delhi 2009)**

3. Which one is more reactive in S_N^1 substitution reaction?

(i) $C_6H_5CH(CH_3)Br$ (I) or $C_6H_5CH(C_6H_5)Br$(II) **(Delhi 2011)**

(ii)  or 
(Delhi 2010 C, AI 2009, 2012)

(iii) or 
(Delhi 2010 C, 2012 C, 2013, AI 2009)

4. What is the correct order of each of the following sets in order of decreasing reactivity towards S_N^2 displacement?

(a) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(b) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane.

(c) 1-Bromobutane, 1-Bromo-2, 2-dimethylpropane, 1-Bromo-2-methylbutane. **(AI 2001)**

5. Which alkyl halide would you expect to react more rapidly by an S_N^2 mechanism?

(a) $CH_3CH_2CH_2Br$ or $(CH_3)_2CHBr$

(b) $CH_3CH_2CH_2CH_2Cl$ or $CH_3CH_2CH_2CH_2I$

(c) $(CH_3)_2CHCH_2Cl$ or $CH_3CH_2CH_2CH_2Cl$

(d) C_6H_5Br or $CH_3(CH_2)_4CH_2Cl$

(e) $(CH_3)_2CHCH_2CH_2Cl$ or $CH_3CH_2CH(CH_3)CH_2Cl$

6. Which S_N^2 reaction of each pair would you expect to take place more rapidly in a protic solvent?

(a) $CH_3CH_2CH_2Cl + CH_3CH_2OH^- \xrightarrow{K\ M\ C} CH_3CH_2CH_2OCH_2CH_3 + Cl^-$

or $CH_3CH_2CH_2Cl + CH_3CH_2OH \longrightarrow CH_3CH_2CH_2OCH_2CH_3 + HCl$

(b) $CH_3CH_2CH_2Cl + CH_3CH_2O^- \longrightarrow CH_3CH_2CH_2OCH_2CH_3 + Cl^-$

or $CH_3CH_2CH_2Cl + CH_3CH_2S^- \longrightarrow CH_3CH_2CH_2SCH_2CH_3 + Cl^-$

(c) $CH_3CH_2CH_2Br + Ph_3N \longrightarrow CH_3CH_2CH_2N^+Ph_3 + Br^-$

or $CH_3CH_2CH_2Br + Ph_3P \longrightarrow CH_3CH_2CH_2P^+Ph_3 + Br^-$

(d) $CH_3CH_2CH_2Br\ (1.0M) + CH_3O^-\ (1.0M) \longrightarrow CH_3CH_2CH_2OCH_3 + Br^-$

or $CH_3CH_2CH_2Br\ (1.0M) + CH_3O^-\ (2.0M) \longrightarrow CH_3CH_2CH_2OCH_3 + Br^-$

7. Which of the reactants of each pair will undergo S_N^1 reaction more rapidly?
   (a) $(CH_3)_3CCl + H_2O$ **or** $(CH_3)_3CBr + H_2O$
   (b) $(CH_3)_3CCl + H_2O$ **or** $(CH_3)_3CCl + CH_3OH$
   (c) $(CH_3)_3CCl\ (1.0M) + CH_3CH_2O^-\ (1.0M)$
   or $(CH_3)_3CCl\ (2.0M) + CH_3CH_2O^-\ (1.0M)$
   (d) $(CH_3)_3CCl\ (1.0M) + CH_3CH_2O^-\ (1.0M)$
   or $(CH_3)_3CCl\ (1.0\ M) + CH_3CH_2O^-\ (2.0M)$
8. Isopropylmethyl ether, $CH_3OCH(CH_3)_2$ can better be prepared by which reaction?
   (I) $(CH_3)_2CHONa + CH_3I \longrightarrow CH_3OCH(CH_3)_2$
   (II) $CH_3ONa + (CH_3)_2CHI \longrightarrow CH_3OCH(CH_3)_2$
9. Which of the two reactions is more faster?

$$CH_3CH_2CH_2Br + NaCN \xrightarrow[\text{as solvent}]{C_2H_5OH} CH_3CH_2CH_2CN$$

$$CH_3CH_2CH_2Br + NaCN \xrightarrow[\text{as solvent}]{DMF} CH_3CH_2CH_2CN$$

10. What is the correct arrangement for the decreasing reactivity towards reactions (mentioned against them) in each of the following?
   (a) 1-Bromobutane (I), 1-bromo-2-methylbutane (II), 1-bromo-3-methylbutane (III), 1-bromo-2, 2-dimethylpropane towards S_N^2 reactions **(AI 2011)**

(b) $C_6H_5CH_2Br$, $C_6H_5CH(CH_3)Br$, $C_6H_5CH(C_6H_5)Br$, $C_6H_5C(CH_3)(C_6H_5)Br$ towards S_N^1 reactions. **(Delhi 2011, 2012 C)**

(c) The four isomeric chlorobutanes towards S_N^1 reactions. **(Delhi 2012 C)**

(d) $ClCH_2CH{=}CHCH_2CH_3$ (I), $CH_3CH{=}CHCH_2CH_2Cl$ (II),

$CH_3CH{=}CH\overset{\overset{Cl}{|}}{C}HCH_3$ (III), $CH_3\underset{\underset{Cl}{|}}{C}{=}CHCH_2CH_3$ (IV)

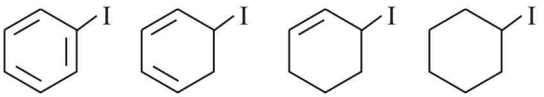
towards S_N^1 reactions.

(e) The two alcohols, $CH_2{=}CHCH_2OH$ and $CH_2{=}CHCH_2CH_2OH$ with conc. HCl in presence of $ZnCl_2$. **(Foreign 2012)**

11. What is the correct order for dehydrohalogenation (– HX) reaction of the following alkyl halides?

(i) $(CH_3)_2CHCH_2Br$, $(CH_3)_2CHCH_2Cl$, $CH_3CH_2CH_2CH_2Cl$, $CH_3CH(Br)CH_2CH_3$, $(CH_3)_3CBr$

(ii) $CH_3CH_2CH_2Br$, $CH_3CH(Br)CH_3$, $(CH_3)_2CHCH_2Br$, $(CH_3)_3CBr$

(iii) 

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

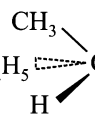
12. What you would expect the main path (S_N^1, S_N^2, E1 or E2) in each of the following reactions?

(a) $CH_3CH_2CH_2Br + CH_3O^- \xrightarrow[50^\circ C]{CH_3OH}$

(b) $CH_3CH_2CH_2Br + (CH_3)_3CO^- \xrightarrow[50^\circ C]{(CH_3)_3COH}$

(c) $(CH_3CH_2)_3CBr + OH^- \xrightarrow[50^\circ C]{CH_3OH}$

(d) $(CH_3CH_2)_3CBr \xrightarrow[25^\circ C]{CH_3OH}$

(e) 

$+ HS^- \xrightarrow[50^\circ C]{CH_3OH}$

(f) $CH_3(CH_2)_3CH_2Br + CH_3CH_2O^- \xrightarrow{CH_3CH_2OH}$

(g) $CH_3(CH_2)_3CH_2Br + (CH_3)_3CO^- \xrightarrow{(CH_3)_3COH}$

K M C

(h) $(CH_3)_3CBr + CH_3O^- \xrightarrow{CH_3OH}$

(i) $CH_3CH_2CH(Cl)CH_2CH_3 + CH_3O^- \xrightarrow{CH_3OH}$

(j) $CH_3CH_2CH(Cl)CH_2CH_3 + CH_3COO^- \xrightarrow{CH_3COOH}$

(k) $(R)\text{–}CH_3CH(Br)CH_2CH_3 \xrightarrow{25^\circ C}$

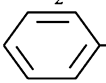
(l) $(S)\text{–}CH_3CH(Br)(CH_2)_5CH_3 + I^- \xrightarrow{CH_3OH}$

(m) $(S)\text{–}CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}\text{–}CH_2CH_2CH_3 \xrightarrow{CH_3OH}$

(B) Alcohols, aldehydes, ketones and carboxylic acids

1. Rearrange the following compounds in the increasing order of their boiling points.
   CH_3CHO, CH_3CH_2OH and $CH_3CH_2CH_3$ **(AI 2013)**

2. Arrange the following in increasing order of their reactivity towards hydrogen cyanide.
   Acetaldehyde, acetone, methyl *ter*-butyl ketone.

3. Which acid of each pair shown here would you expect to be stronger?
   (i) FCH_2COOH **or** $ClCH_2COOH$ **(AI 2013)**
   (ii)  –OH **or** CH_3COOH **(AI 2013)**

4. Arrange the following compounds in increasing order of their acidic character.
   (i) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ **(AI 2009, 2012)**
   (ii) $(CH_3)_2CHCOOH$, $CH_3CH_2CH(Br)COOH$, $CH_3CHBrCH_2COOH$ **(Delhi 2008)**
   (iii) Benzoic acid, 4-nitrobenzoic acid, 3, 4-dinitrobenzoic acid, 4-methoxybenzoic acid. **(AI 2009, 2012)**

(C) Amines

1. Arrange the following compounds in an increasing order of their solubility in water.
   $C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5H_2$ **(Delhi 2011, AI 2011C)**

2. Rearrange the following compounds as directed below

(i) in increasing order of basic strength.

(a) $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2 **(Delhi 2010)**

(b) $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_6H_5)_2NH$ and CH_3NH_2 **(Delhi 2010)**

(ii) in decreasing order of basic strength

Aniline, *p*-nitroaniline and *p*-toluidine **(Delhi 2010)**

(iii) in an increasing order of pK_b values

$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$ **(Delhi 2010)**

(iv) in an increasing order of basic strength in gas phase.

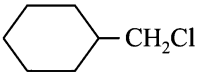
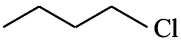
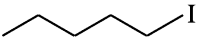
$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and CH_3NH_2 **(AI 2008)**

3. Arrange the following compounds in increasing order of basic strength in their aqueous solutions.

(i) NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ **(AI 2009)**

(ii) $C_6H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3 **(Delhi 2012, 2013, AI 2008)**

(A) Halogen derivatives

1. (i) S_N^2 (ii) S_N^1
   (iii) E2, S_N^2 (iv) E2
   (v) S_N^1, very little E1 (vi) S_N^1, E1
2. Remember that in S_N^1 reactions carbocations are formed as intermediate, so the alkyl halide whose intermediate carbocation is more stable will undergo S_N^1 path. In S_N^2 reaction, transition state is formed, so alkyl halide whose halogen is less sterically hindered will follow preferably S_N^2 path. Thus answer in each case can be written as below.
   (i) CH_3Cl (ii) $C_6H_5CH_2Cl$
   (iii) Here alkyl group is same, hence iodide, being larger in size than bromide, is a better leaving group.
   (iv) 
   (v) $(CH_3)_2CHCH_2CH_2Br$
   (vi) 
   (vii) $CH_3CH_2CH_2CH_2Cl$
   (viii) $CH_3CH_2CH_2CH_2CH_2Br$ (1-Bromopentane) > $CH_3CH_2CH_2\overset{Br}{\overset{|}{C}}HCH_3$ (2-Bromopentane)
   (ix) $CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2Br$ (1-Bromo-2-methylbutane) > $CH_3-\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_2-CH_3$ (2-Bromo-2-methylbutane)
   (x)  , consult (iii)
3. (i) Since carbocation, $C_6H_5\overset{+}{C}HC_6H_5$ from II is more stable because it has two phenyl groups hence more resonance stabilized than the carbocation, $C_6H_5\overset{+}{C}HCH_3$, from I. Hence $C_6H_5CH(C_6H_5)Br$ will react faster.
   (ii) **Former** because it forms more stable (2°) carbocation than the 1° carbocation from the latter.
   (iii) **Former** because it forms more stable (3°) carbocation than the 2° carbocation from the latter.
4. Greater the steric hindrance around Br, lesser will be the reactivity of the alkyl halide towards S_N^2 reaction.

(a) $CH_3CH_2CH_2CH_2CH_2Br$ > $CH_3CH_2CH_2\overset{\overset{Br}{|}}{C}HCH_3$ >

1-Bromopentane 2-Bromopentane

$CH_3CH_2-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

2-Bromo-2-methylbutane

(b) $CH_3-\overset{\overset{CH_3}{|}}{C}HCH_2CH_2Br$ > $CH_3-\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{Br}{|}}{C}H-CH_3$ > $CH_3CH_2\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

1-Bromo-3-methyl-butane (–Br is least hindered) | 3-Bromo-2-methyl-butane | 2-Bromo-2-methyl-butane (–Br is most hindered)

(c) Consult Q 10(a).

5. (a) $CH_3CH_2CH_2Br$ (1° alkyl halide)
   (b) $CH_3CH_2CH_2CH_2I$ (I^- is a better leaving group than Cl)
   (c) $CH_3CH_2CH_2CH_2Cl$ (carbon bearing Cl is less sterically hindered)
   (d) $CH_3(CH_2)_4CH_2Cl$ (1° alkyl halide, while C_6H_5Br is aryl halide)
   (e) $(CH_3)_2CHCH_2CH_2Cl$ (carbon bearing Cl is less sterically hindered)
6. (a) **Former** because ethoxide ion is a stronger nucleophile than ethanol.
   (b) **Latter** because ethyl sulphide ion ($C_2H_5S^-$) is a stronger nucleophile than the ethoxide ion in a protic solvent. Due to larger size of sulphur than oxygen, $C_2H_5S^-$ is less solvated and hence more polarizable.
   (c) **Latter** because phosphorus is larger, hence less solvated and thus more reactive than nitrogen.
   (d) **Latter** because here concentration of the nucleophile is twice than that in the former reaction (remember that in S_N2 reactions, Rate $\propto$ [Substrate] [Nucleophile].
7. (a) $(CH_3)_3CBr + H_2O$ because Br^- ion is a better leaving group.
   (b) $(CH_3)_3CCl + H_2O$ because H_2O is a more polar solvent than CH_3OH (remember that S_N1 reactions take place faster in more polar solvents).
   (c) $(CH_3)_3CCl$ (2.0M) + $CH_3CH_2O^-$ (1.0M) because the concentration of the substrate is twice than in the former (1.0M).

(d) Both reactions would take place at the same rate, because S_N^1 reactions are independent of the concentration of the nucleophile, i.e. Rate $\propto$ [Substrate].

8. Reaction I because the substrate (CH_3I) is primary alkyl iodide and undergoes S_N^2 reaction, while in reaction II substrate, $(CH_3)_2CHI$, is secondary iodide and would undergo E2 reaction in presence of CH_3O^-, a strong base.

9. The reaction is an S_N^2 reaction. In presence of DMF, $HCONMe_2$, (a polar aprotic solvent), the nucleophile CN^- is relatively unencumbered by solvent molecules, and therefore it will be more reactive than in ethanol.

10. (a) As mentioned earlier, reactivity of alkyl halides towards S_N^2 reactions is affected by steric hindrance around the halogen; greater the steric hindrance around halogen, smaller will be reactivity towards S_N^2 reaction.

$CH_3CH_2CH_2CH_2Br$
1-Bromobutane (I)
(–Br least sterically hindered)

$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}H–CH_2Br$
1-Bromo-2-methylbutane (II)
(–Br and branched alkyl gp. are separated by one $–CH_2$ gp.)

$CH_3–\overset{\overset{\displaystyle CH_3}{|}}{C}H–CH_2CH_2Br$
1-Bromo-3-methylbutane (III)
(–Br and branched alkyl group are separated by two $–CH_2–$ groups)

$CH_3–\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}–CH_2Br$
1-Bromo-2, 2-dimethylpropane (IV)
(–Br most sterically hindered)

I > III > II > IV

(b) S_N^1 Reactions involve carbocation as intermediate, so higher the stability of the carbocation formed from the alkyl halide, more will be its reactivity. Carbocations formed from the four alkyl bromides are

$C_6H_5\overset{+}{C}H_2$
I
Least stable

$C_6H_5\overset{+}{\underset{\underset{\displaystyle CH_3}{|}}{C}}H$
II
2° Carbocation more stable than I

$C_6H_5\overset{+}{\underset{\underset{\displaystyle C_6H_5}{|}}{C}}H$
III
2° Carbocation with 2 C_6H_5 gps. more stable than II

$C_6H_5–\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{\overset{+}{C}}}$
IV
3° Carbocation with 2 C_6H_5 gps. (most stable)

Thus order of reactivity towards S_N1 reactions is

$$\underset{\text{IV}}{C_6H_5-\overset{\overset{CH_3}{|}}{\underset{\underset{C_6H_5}{|}}{C}}-Br} > \underset{\text{III}}{C_6H_5-\underset{\underset{C_6H_5}{|}}{CH}-Br} > \underset{\text{II}}{C_6H_5-\underset{\underset{CH_3}{|}}{CHBr}} > \underset{\text{I}}{C_6H_5CH_2Br}$$

(c) Four isomeric chlorobutanes are

$$CH_3CH_2CH_2CH_2Cl \qquad CH_3CH_2\overset{\overset{Cl}{|}}{C}HCH_3$$

$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2Cl \qquad CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl$$

Thus stability of carbocations formed from the above chlorobutanes is

$$\underset{\substack{\text{I}\\ 3^\circ\text{ Carbocation}\\ \text{(most stable)}}}{(CH_3)_3\overset{+}{C}} > \underset{\substack{\text{II}\\ 2^\circ\text{ Carbocation}\\ \text{(more stable)}}}{CH_3CH_2\overset{+}{C}HCH_3} > \underset{\substack{\text{III}\\ 1^\circ\text{ Carbocation}}}{(CH_3)_2CH\overset{+}{C}H_2}$$

$$> \underset{\substack{\text{IV}\\ 1^\circ\text{ Carbocation}}}{CH_3CH_2CH_2\overset{+}{C}H_2}$$

Note: III is more stable than IV because $(CH_3)_2CH-$ group in III has greater +I effect than the $CH_3CH_2CH_2-$ group in IV.

Thus order of S_N1 reactivity is

$$(CH_3)_3CCl > CH_3CH_2\overset{\overset{Cl}{|}}{C}HCH_3 > (CH_3)_2CHCH_2Cl$$

$$> CH_3CH_2CH_2CH_2Cl$$

(d) The concerned carbocations are

$$\underset{\text{From I}}{\overset{+}{C}H_2CH=CHCH_2CH_3} \qquad \underset{\text{From II}}{CH_3CH=CHCH_2\overset{+}{C}H_2}$$

$$\underset{\text{From III}}{CH_3CH=CH\overset{+}{C}HCH_3} \qquad \underset{\text{From IV}}{CH_3-\overset{+}{C}=CHCH_2CH_3}$$

The order of stability of the four is

K M C

$CH_3CH{=}C\overset{+}{H}CH_3$ > $\overset{+}{C}H_2CH{=}CHCH_2CH_3$ >

From III — most stable 2° carbocation with conjugated system

From I — more stable 1° carbocation with conjugated system

$CH_3CH{=}CHCH_2\overset{+}{C}H_2$ > $CH_3\overset{+}{C}{=}CHCH_2CH_3$

From II

From IV — least stable, +ve charge present on doubly bonded C atom

Thus order of reactivity towards S_N1 reactions is
III > I > II > IV

(e) $CH_2{=}CHCH_2OH$ will react faster than $CH_2{=}CHCH_2CH_2OH$.
Alcohol reacts with HCl to form carbocation, so more the stability of the carbocation, higher will be reactivity of the parent alcohol.

$$CH_2{=}CHCH_2OH \xrightarrow[(-H_2O)]{H^+} CH_2{=}CH\overset{+}{C}H_2$$

Allyl carbocation (**more stable**)

$$CH_2{=}CHCH_2CH_2OH \xrightarrow[(-H_2O)]{H^+} CH_2{=}CHCH_2\overset{+}{C}H_2$$

Ordinary 1° carbocation (less stable)

11. Remember following points.
(a) Order of dehydrohalogenation is 3° > 2° > 1° alkyl halides.
(b) Among alkyl halides having similar alkyl group, the one carrying larger halogen will undego dehydrohalogenation easily. Thus order will be R–I > R–Br > R–Cl
(c) Dehydrohalogenation of alkyl halides leads to alkenes, so more the stability of the product (alkene), higher will be the reactivity (dehalogenation) of the alkyl halide. Further, remember that greater the number of alkyl groups attached on doubly bonded carbon atoms, higher is the stability of the alkene.

(i) $(CH_3)_3CBr$ > $CH_3{-}\overset{Br}{\overset{|}{C}H}{-}CH_2CH_3$ > $(CH_3)_2CHCH_2Br$ >

3° bromide — 2° bromide — 1° bromide

$(CH_3)_2CHCH_2Cl$ > $CH_3CH_2CH_2CH_2Cl$

1° chloride (giving more stable alkene) — 1° chloride (giving less stable alkene)

$$(CH_3)_2CHCH_2Cl \xrightarrow{-HCl} (CH_3)_2C{=}CH_2$$

Dialkylsubstituted alkene (more stable)

$$CH_3CH_2CH_2CH_2Cl \xrightarrow[-HCl]{} CH_3CH_2CH{=}CH_2$$

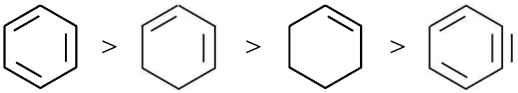
K M C

Monoalkylsubstituted alkene (less stable)

(ii) $(CH_3)_3CBr$ > $CH_3{-}\underset{|}{\overset{Br}{C}H}{-}CH_3$ > $(CH_3)_2CHCH_2Br$ > $CH_3CH_2CH_2Cl$

3° Bromide, 2° Bromide, 1° Bromide, 1° Chloride

(iii) Stability of the product follows the order.



From (B) > From (C) > From (D) > From (A)

Thus the correct order of dehalogenation is

B > C > D > A

12. (a) The substrate is a 1° halide and the base/nucleophile (CH_3O^-) is a strong base (but not hindered) and a good nucleophile. Hence main reaction will be S_N2 forming $CH_3CH_2CH_2OCH_3$ and minor reaction will be E2 forming $CH_3CH{=}CH_2$.

(b) The substrate is a 1° halide, but the base/nucleophile $(CH_3)_3CO^-$, is a strong hindered base. Thus the major product would be $CH_3CH{=}CH_2$ by E2 pathway, with a minor product, $CH_3CH_2CH_2OC(CH_3)_3$ by S_N2 pathway.

(c) Although OH^- is a strong base and a strong nucleophile, the substrate is a 3° halide which undergoes mainly E2 reaction forming $(CH_3CH_2)_2C{=}CHCH_3$.

(d) Here the solvent CH_3OH is a weak base (therefore, E2 reaction is not possible) and a poor nucleophile. The substrate is 3° halide (therefore, no S_N2 reaction) and hence the major reaction would be S_N1 leading to $(CH_3CH_2)_3COCH_3$ along with some minor E1 reaction forming $(CH_3CH_2)_2C{=}CHCH_3$.

(e) The reactant is an optically active 2° halide, while the reagent (HS^-) is a strong nucleophile but a weak base. Thus the main reaction will be S_N2 forming optically active compound with opposite configuration.

(f) to (m)

	Nature of substrate	Nature of reagent	Reaction
(f)	1°	Nucleophile-base is not hindered	Major S_N2 Minor E2
(g)	1°	Sterically hindered strong base	Major E2, Minor S_N2
(h)	3°	Strong base	E2
(i)	2°	Strong base	Major E2, Minor S_N2
(j)	2°	Weak base	Major S_N2, Minor E2
(k)	2° optically active	Strong base	Major E2, Minor S_N2 (S-product)
(l)	2° (S–) optically active	Weak base	S_N2 (R-configuration)
(m)	3° (S–) optically active	Only solvent (weak base)	Major S_N1 (±-Product), Minor E1.

(B) Alcohols, aldehydes, ketones and carboxylic acids

1. Increasing order of boiling points.

$CH_3CH_2CH_3$ < CH_3CHO < CH_3CH_2OH

Very weak vander Waals forces — Weak dipole–dipole interaction — Form strong intermolecular H-bond

2. $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-C(CH_3)_3$ < $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ < $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H$

Methyl ter-butylketone — Acetone — Acetaldehyde

For explaination, consult chapter 8, Q.10 in Aldehydes, Ketones and Carboxlic acids.

3. **General discussion about relative acidic character**

Relative acidic character of compound is affected by following.

Inductive effect: Remember that the presence of –I groups (e.g. $-NO_2$, –X, –CN) increases acidic character; while presence of +I groups (e.g. –R, $-OCH_3$) decreases acidic character. Further, stronger the inductive effect (–I or +I), higher will be its magnitude. Thus, acidic strength of the compounds follows the order:

(a) $O_2N \leftarrow CH_2-COOH$ > $Cl \leftarrow CH_2-COOH$

(–I effect of $-NO_2$ > – Cl)

(b) $F \leftarrow CH_2-COOH$ > $Cl \leftarrow CH_2-COOH$

(–I effect of – F > – Cl)

(c) H–COOH > $CH_3 \rightarrow COOH$ (+I effect of $-CH_3$ > – H)

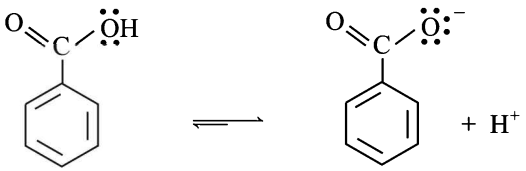
(d) $(CH_3)_2CH \rightarrow COOH$ > $(CH_3)_3C \rightarrow COOH$

(+I effect of $-C(CH_3)_3$ > $-CH(CH_3)_2$)

Moreover, farther the group from the –COOH group, lesser will be its effect in increasing or decreasing the acidic character. Thus

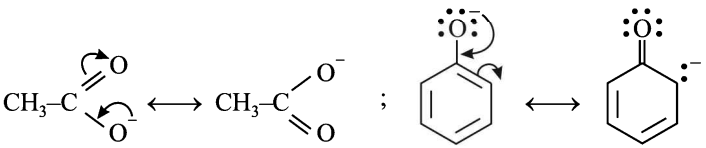
$CH_3CH_2\overset{Cl}{\overset{|}{C}}HCOOH$ > $CH_3\overset{Cl}{\overset{|}{C}}HCH_2COOH$ > $ClCH_2CH_2CH_2COOH$

Resonance: Remember that resonance (delocalisation of electrons) increases the stability of the species. Thus, when the deprotonated species shows significant resonance, it means it is more stable than the parent compound and hence the latter will have a tendency to lose proton, i.e. it will be acidic in nature For example,



Benzoic acid (Resonance insignificant) ⇌ Benzoate ion (Resonance significant)

When the resonating structures are equivalent, resonance is more important and thus the species is more stable than that in which resonating structures are not equivalent. Thus



Equivalent structures of acetate ion (–ve charge is present on O in both structures) ; Non-equivalent structures of phenoxide ion (–ve charge is present on O and C)

(i) FCH_2COOH is more acidic than $ClCH_2COOH$ because F is more electronegative (i.e. it has strong –I effect) than Cl.

(ii) CH_3COOH is more acidic than phenol (C_6H_5OH) because the acetate ion is more stable (due to equivalent resonating structures) than phenoxide ion ($C_6H_5O^-$).

4. (i) $(CH_3)_2CH \rightarrow COOH$ < $CH_3CH_2 \rightarrow COOH$ <

More +I effect of $(CH_3)_2CH$–group

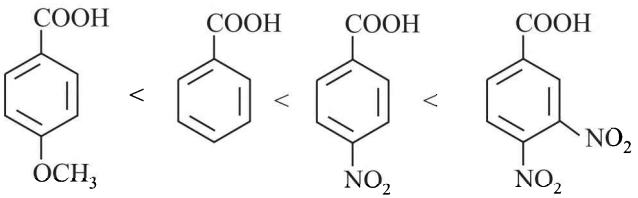
Less +I effect of CH_3CH_2–group

CH_3CHCH_2COOH (Br) < $CH_3CH_2CHCOOH$ (Br)

Less –I effect of Br due to increased distance

More –I effect of Br due to less distance

(ii) $(CH_3)_2CH \rightarrow COOH$ < CH_3CHCH_2COOH (Br) < $CH_3CH_2CHCOOH$ (Br)

(iii) 

4-Methoxybenzoic acid; Least acidic due to $-OCH_3$ (+I) group

Benzoic acid (neither +I nor –I group is present)

4-Nitrobenzoic acid Lesser acidic due to one $-NO_2$ (–I) group

3, 4-Dinitrobenzoic acid Most acidic due to two $-NO_2$ (–I) groups

(C) Amines

1. Primary and secondary amines are soluble in water because these can form H–bond with water. The solubility order will be

$C_6H_5NH_2$ < $(C_2H_5)_2NH$ < $C_2H_5NH_2$

Least soluble because it has very large C_6H_5- group

Lesser soluble because it has one H, and bulky alkyl groups

Most soluble because it has two H'S

2. (i) (a) $C_6H_5\ddot{N}H_2$ < $C_6H_5\ddot{N}(CH_3)_2$ < $CH_3\ddot{N}H_2$ < $(C_2H_5)_2\ddot{N}H$

Electron pair delocalised over benzene ring

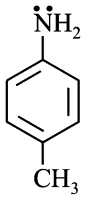
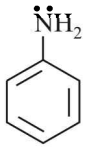
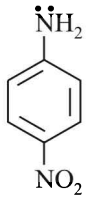
Two +I groups, but electron pair delocalised over benzene ring

Lesser +I effect of $-CH_3$ group

More +I effect of $-C_2H_5$ group

(b) $(C_6H_5)_2\ddot{N}H$ < $C_6H_5\ddot{N}H_2$ < $C_6H_5\ddot{N}(CH_3)_2$ < $CH_3\ddot{N}H_2$

$(C_6H_5)_2\ddot{N}H$	$C_6H_5\ddot{N}H_2$	$C_6H_5\ddot{N}(CH_3)_2$	$CH_3\ddot{N}H_2$
Electron pair delocalised over two benzene rings	Electron pair delocalised over benzene ring	+I effect of 2 $-CH_3$ gps., but electron pair delocalised over benzene ring	+I effect of $-CH_3$ group

(ii)  >  > 

+I Effect of CH_3 gp. increases basic character	No other group is present	–M and –I effects due to $-NO_2$ gp. decreases basicity

(iii) Stronger a base, lower is its pK_b value. Thus

$(C_2H_5)_2NH$ < $C_2H_5NH_2$ < $C_6H_5NHCH_3$ < $C_6H_5NH_2$

Strongest base (lowest pK_b)			Weakest base (highest pK_b)

(iv) CH_3NH_2 < $C_2H_5NH_2$ < $(C_2H_5)_2NH$ < $(C_2H_5)_3N$

Least +I effect due to CH_3 group	Lesser +I effect due to 1 ethyl group	Lesser +I effect due to 2 ethyl groups	Max. +I effect due to 3 ethyl groups

3. Remember that **order of basicity of amines in aqueous solution is somewhat different** from that in gas phase. The altered order is due to **solvation effect** which is absent in gas phase. Solvation (formation of H–bond between protonated base and the solvent, H_2O) stabilizes the protonated base (i.e. conjugate acid) and hence increases basic strength of the amine. Thus higher the possibility of forming H–bond between protonated base and water, higher will be its stability and more will be the basic character of the parent amine. This can better be explained as below.

$$CH_3\ddot{N}H_2 \xrightarrow{H^+} CH_3\overset{+}{N}H_3$$

Methylamine Base → Conjugate acid

$$(CH_3)_2\ddot{N}H \xrightarrow{H^+} (CH_3)_2\overset{+}{N}H_2$$

Dimethylamine → Conjugate acid

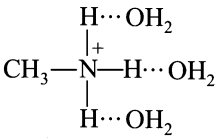
$$(C\ddot{H}_3)_3N \xrightarrow{H^+} (CH_3)_3\overset{+}{N}H$$

Trimethylamine → Conjugate acid

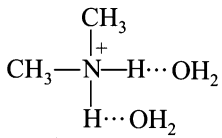
$$\ddot{N}H_3 \xrightarrow{H^+} NH_4^+$$

Ammonia → Conjugate acid

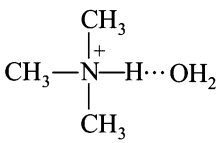
The above four conjugate acids can form H–bonds with water (solvent) as below.



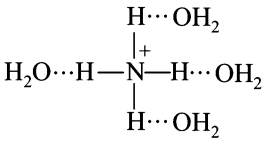
$CH_3\overset{+}{N}H_3$ form 3 H–bonds



$(CH_3)_2\overset{+}{N}H_2$ form 2 H–bonds



$(CH_3)_3\overset{+}{N}H$ form 1 H–bond



NH_4^+ form 4 H–bonds

Thus according to solvation effect, order of stability of the four conjugate acids should be

$$\overset{+}{N}H_4 > CH_3\overset{+}{N}H_3 > (CH_3)_2\overset{+}{N}H_2 > (CH_3)_3\overset{+}{N}H$$

However, stability of the above conjugate acids is also influenced by **inductive effect**. More is the dispersal of positive charge (by alkyl groups), greater will be stability of the conjugate acid. Thus according to inductive effect, order of stability should be

$(CH_3)_3\overset{+}{N}H$	>	$(CH_3)_2\overset{+}{N}H_2$	>	$CH_3\overset{+}{N}H_3$	>	$\overset{+}{N}H_4$
Three +I ($-CH_3$) groups		Two +I groups		One +I group		No +I group

However, the net stability is determined by the combined effect of the two effects (**solvation and inductive**).

Secondary amines possess the best combination and thus its conjugate acid is more stable than that of primary as well as that of tertiary amines. On the basis of the above discussion, the given questions should have following answers.

(i) Stability of the corresponding conjugate acids.

$(CH_3)_2\overset{+}{N}H_2$	>	$CH_3\overset{+}{N}H_3$	>	$(CH_3)_3\overset{+}{N}H$	>	NH_4^+
Most stable due to solvation as well as inductive (2 CH_3 gps) effects		Less stable due to one +I gp.		Lesser stable due to less solvation		**Least stable** due to absence of +I gp.

Thus the relative basic strength of the four parent compounds is

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$$

K M C

(ii) Stability of the corresponding conjugate acids.

$$(C_2H_5)_2 \rightarrow \overset{+}{N}H_2 \;>\; (C_2H_5)_3 \rightarrow \overset{+}{N}H \;>\; NH_4^+ \;>\; C_6H_5 \leftarrow \overset{+}{N}H_3$$

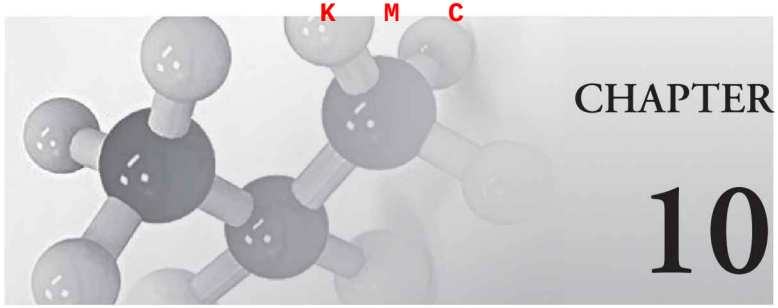
Most stable due to best combination of the solvation and inductive effects

No destabilising group is present

Least stable because the substituent (C_6H_5–) group destabilizes the conjugate acid

Thus the relative basic strength of the four parent compounds will be

$$(C_2H_5)_2NH \;>\; (C_2H_5)_3N \;>\; NH_3 \;>\; C_6H_5NH_2$$



CHAPTER

10

How to Solve Analytical Problems?

Problem 1. An organic compound contains 69.77% carbon, 11.63% hydrogen and the rest is 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 a positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acids. Deduce the possible structure of the organic compound.

(Delhi 2008, 2009, AI 2008, 2009, 2012C *modified*)

Problem 2. A compound A (C_2H_6O) on oxidation by PCC gave B, which on treatment with aqueous alkali and subsequent heating furnished C. B on oxidation by $KMnO_4$ forms a monobasic carboxylic acid with molar mass 60 g mol^{-1}. Deduce the structures of A, B and C. **(AI 2011C)**

Problem 3. An organic compound (A) on treatment with acetic acid in the presence of sulphuric acid produces an ester (B). (A) on mild oxidation gives (C). (C) with 50% KOH followed by acidification with dil. HCl generates (A) and (D). (D) with PCl_5 followed by reaction with ammonia gives (E). (E) on dehydration produces hydrocyanic acid. Identify the compounds (A), (B), (C), (D), and (E). **(Delhi 2009C)**

Problem 4. Compound A ($C_7H_6Cl_2$) on treatment with NaOH solution gives another compound B (C_7H_6O). B, on oxidation gives an acid C ($C_7H_6O_2$) which on treatment with a mixture of concentrated HNO_3 and H_2SO_4 gives a compound D ($C_7H_5NO_4$). B on treatment with conc. NaOH gives a compound E (C_7H_8O) and C_6H_5COONa. Deduce the structures of A, B, C, D and E. **(Delhi 2008C)**

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Problem 5. An organic compound A (C_3H_6O) is susceptible to oxidation and forms compound B (C_3H_8O) on reduction. B reacts with HBr to form the compound C. C with Mg forms Grignard reagent D which reacts with A to form a product which on hydrolysis gives E. Identify A to E.

(AI 2008C)

Problem 6. A ketone A (C_4H_8O), which undergoes a haloform reaction, gives compound B on reduction. B on heating with sulphuric acid gives a compound C which forms mono-ozonide D. D on hydrolysis in presence of Zn dust gives only acetaldehyde E. Identify A, B, C, D and E. Write the reactions involved. **(Delhi 2010C)**

Problem 7. An organic compound with molecular formula $C_9H_{10}O$ forms 2, 4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro's reaction. On vigorous oxidation it gives benzene-1, 2- dicarboxylic acid. Identify the compound. **(Delhi 2012, AI 2012, 2012C)**

Problem 8. An organic compound A, having the formula C_3H_8O on treatment with copper at 573 K, gives B. B does not reduce Fehling solution but gives a yellow precipitate of the compound C with I_2/NaOH. Deduce the structures of A, B and C. **(Delhi 2011C)**

Problem 9. 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. **(Delhi 2012C, AI 2013C)**

Problem 10. Compound (A), $C_6H_{12}O_2$ on reduction with $LiAlH_4$ yields two compounds (B) and (C). The compound (B) on oxidation gave (D) which on treatment with aqueous alkali and subsequent heating furnished (E). The latter on catalytic hydrogenation gave (C). The compound (D) on further oxidation gave CH_3COOH. Deduce the structures of (A), (B), (C), (D) and (E). **(AI 2009C)**

Problem 11. 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 produced (B). (C) on dehydration gives but-1-ene. Write chemical equations for the reactions involved. **(Delhi 2008C, 2010, AI 2009)**

Problem 12. An organic compound (A) with molecular formula C_8H_8O forms an orange red precipitate with DNP reagent and gives yellow

K M C

precipitate on heating with I_2 and NaOH. It neither reduces Tollen's reagent nor Fehling reagent nor does it decolorize bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula $C_7H_6O_2$. Identify the compounds (A) and (B) and explain the reactions involved. **(Delhi 2012C)**

Problem 13. An organic compound (A) on treatment with ethyl alcohol gives a carboxylic acid (B) and compound (C). Hydrolysis of (C) under acidified conditions gives (B) and (D). Oxidation of (D) with $KMnO_4$ also gives (B). (B) on heating with $Ca(OH)_2$ gives (E) having molecular formula C_3H_6O. (E) does not give Tollen's test and does not reduce Fehling solution but forms a 2, 4-dinitrophenylhydrazone. Identify (A), (B), (C), (D) and (E). **(AI 2010C)**

Problem 14. Two moles of an organic compound 'A' on treatment with a strong base gives two compounds 'B' and 'C'. Compound 'B' on dehydrogenation with Cu gives 'A' while acidification of 'C' yields carboxylic acid 'D' with molecular formula of CH_2O_2. Identify the compounds A, B, C and D and write all chemical reactions involved. **(Delhi 2013C)**

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Solution 1: Calculation of molecular formula

Element	%	Relative No. of atoms	Simplest whole ratio
C	69.77	69.77/12 = 5.88	5.88/1.16 = 5
H	11.63	11.63/1 = 11.63	11.63/1.16 = 10
O	18.60	18.60/16 = 1.16	1.16/1.16 = 1

∴ Empirical formula of the compound = $C_5H_{10}O$

Empirical formula mass = (5 × 12) + (10 × 1) + 16 = 86

∴ $$n = \frac{\text{Empirical formula mass}}{\text{Molar mass}} = 1$$

∴ Molecular formula of the compound = $(C_5H_{10}O)_1 = C_5H_{10}O$

Determination of structure. Since the compound forms an addition compound with $NaHSO_3$, it may be either an aldehyde or a ketone. However, the compound does not reduce Tollen's reagent, it must be a ketone. Further the compound undergoes iodoform reaction, the ketone should contain $-COCH_3$ group, i.e. it should be

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \quad \text{or} \quad C_3H_7-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Lastly the nature of C_3H_7- (i.e. $CH_3CH_2CH_2-$ or $(CH_3)_2CH-$) is assessed by its oxidation to give ethanoic acid (CH_3COOH) and propanoic acid (CH_3CH_2COOH).

$$CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[\text{oxidation}]{\text{Vigorous}} \underset{\text{Propanoic acid}}{CH_3CH_2COOH} + \underset{\text{Ethanoic acid}}{CH_3COOH}$$

Solution 2: Summary of the given facts.

$$\underset{(C_2H_6O)}{A} \xrightarrow[\text{(oxidation)}]{\text{PCC}} B \xrightarrow[\text{(ii) heat}]{\text{(i) aq. alkali}} C$$

$$B \xrightarrow[\text{(oxidation)}]{KMnO_4} \underset{(\text{molar mass} = 60\text{g mol}^{-1})}{\text{Monocarboxylic acid}}$$

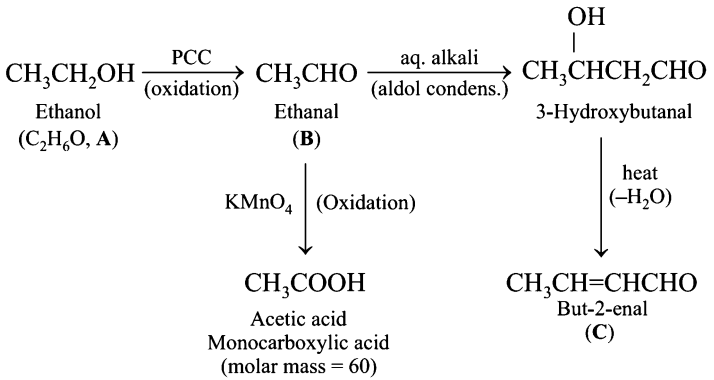
Conclusions:

(i) Molar mass of 60 for the carboxylic acid (R–COOH) indicates that the value of R is CH_3 since molar mass of the acidic group (–COOH)

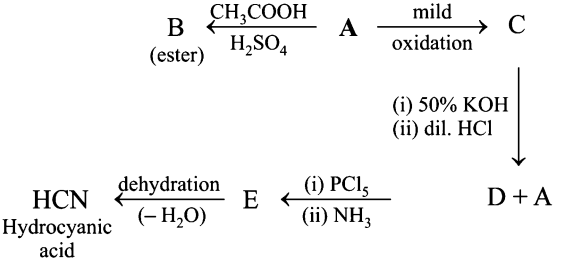
is 45, hence the molar mass of the alkyl group should be 15 which matches with the $-CH_3$ group.

(ii) PCC is an oxidising agent which oxidises $-CH_2OH$ group to $-CHO$, hence A (C_2H_6O) should be CH_3CH_2OH.

(iii) Thus B should be CH_3CHO.



Solution 3: Summary of the given facts.

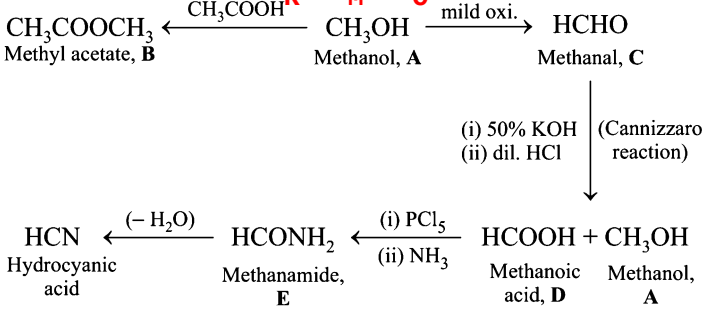


Conclusions:

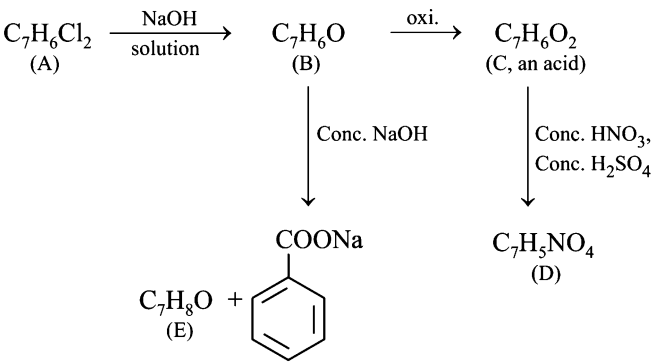
(i) Compound (A) reacts with acetic acid to form an ester (B) indicates that (A) is an alcohol.

(ii) Formation of hydrocyanic acid (HCN) by dehydration of (E) indicates that (E) should be HCN + H_2O, i.e. $HCONH_2$.

(iii) Since E ($HCONH_2$) has one carbon atom, its parent compound D and hence C as well as A should also have one carbon atom. Thus the compound A (already established as an alcohol) should be CH_3OH which explains all the given reactions.



Solution 4: Let us summarise the given facts in the following format.

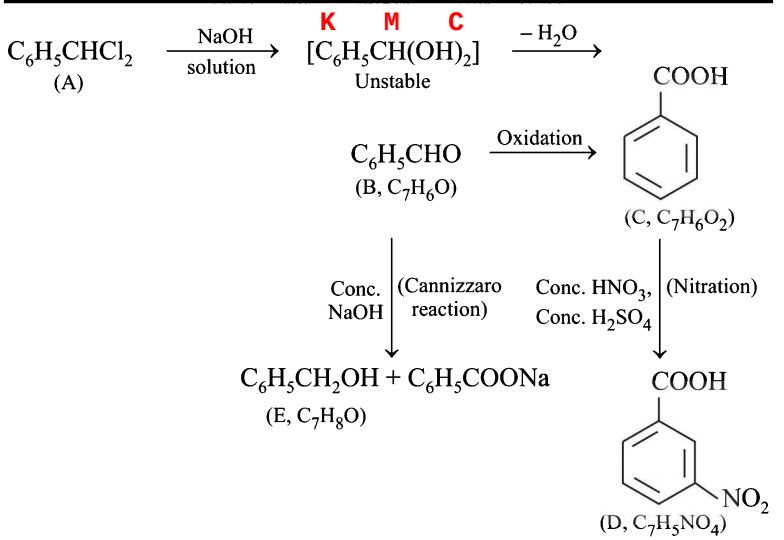


The above statements lead to following conclusions.

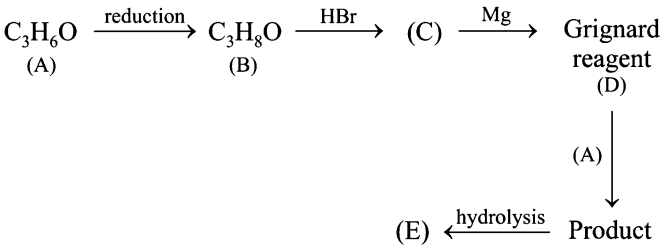
(i) Oxidation of B to form an acid, C indicates that B is an –CHO.

(ii) Reaction of B to form C_6H_5COONa indicates that B should have a phenyl (C_6H_5 –) group. Hence B (C_7H_6O) can be written as C_6H_5CHO.

Nature of B as C_6H_5CHO explains its formation from A and all other given reactions as below.



Soution 5: Summary of the given facts.

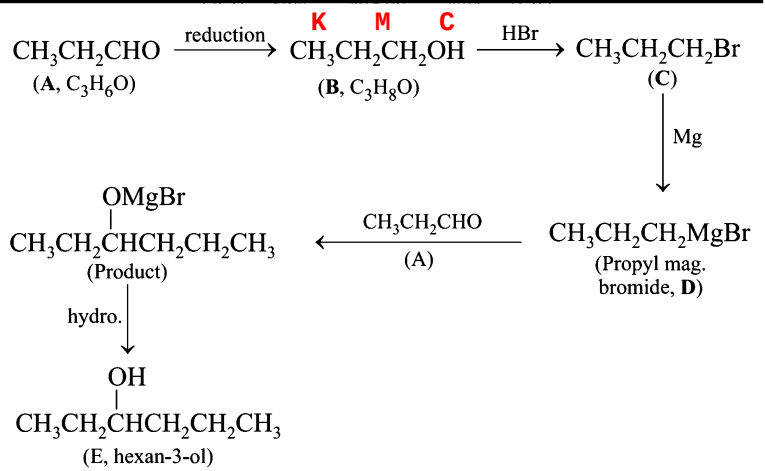


Conclusions:

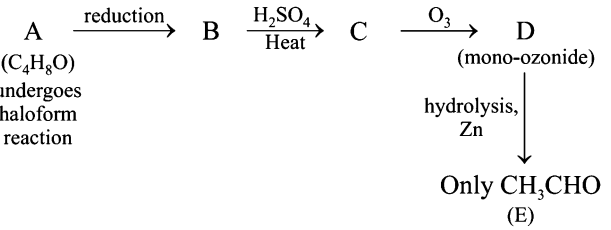
(i) Formation of Grignard reagent (D) from (C) with Mg indicates that (C) is an alkyl bromide.

(ii) Since (C) an alkyl bromide is formed by the reaction of (B) with HBr, (B) should be an alcohol and hence (A) should be an aldehyde (–CHO), i.e. C_2H_5CHO.

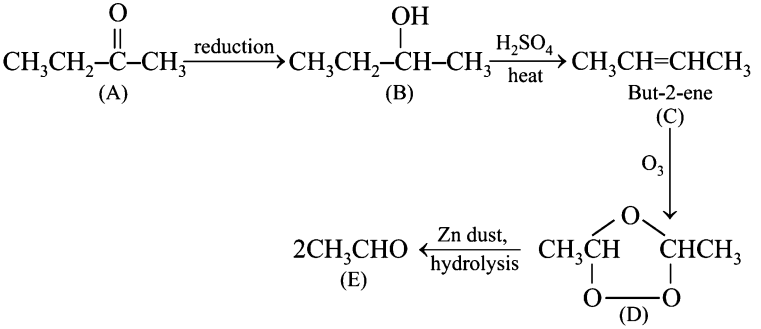
Nature of (A) as CH_3CH_2CHO explains all the given reactions as below.



Solution 6: Summary of given facts.



Conclusion: Since A (C_4H_8O) undergoes haloform reaction, it must contain $-COCH_3$ group; hence it can be written as $C_2H_5COCH_3$ which can explain all the given reactions.

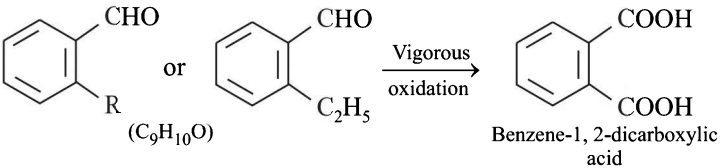


Solution 7: Conclusions from the given statements.

(i) Given reactions of the compound ($C_9H_{10}O$) indicates that it has an aldehydic group.

(ii) Vigorous oxidation of the compound to form benzene-1, 2-dicarboxylic acid indicates that it is a benzene derivative having two

substituents in 1, 2-positions. Further one of the substituents is –CHO (as indicated in (i) point), the other substituent must be an alkyl group (R). Thus the compound ($C_9H_{10}O$) can be written as below.



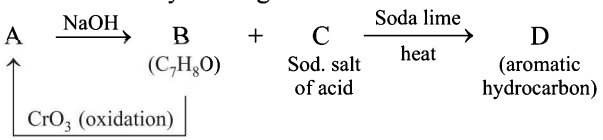
Remember that an alkyl group present on benzene ring is always oxidised to –COOH group, whatever might be the nature (length) of the alkyl group.

Solution 8: (i) Since the compound B does not reduce Fehling solution, but gives yellow precipitate of C with I_2/NaOH (iodoform reaction), it must contain $-COCH_3$ group.

(ii) Further B (a ketone having $-COCH_3$ group) is produced from A (C_3H_8O) by reaction with reduced copper at 573 K, A must be a secondary alcohol with $-CHOHCH_3$ group, i.e. it is $RCHOHCH_3$ or $CH_3CHOHCH_3$ which explains all the given reactions as below.

$$\underset{(\mathbf{A},\ C_3H_8O)}{CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3} \xrightarrow[\text{(Oxidation)}]{\text{Cu, 573 K}} \underset{(\mathbf{B})}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} \xrightarrow{I_2\ /\ NaOH} \underset{(\text{yellow, }\mathbf{C})}{CHI_3\downarrow} + CH_3COONa$$

Solution 9: Summary of the given facts.



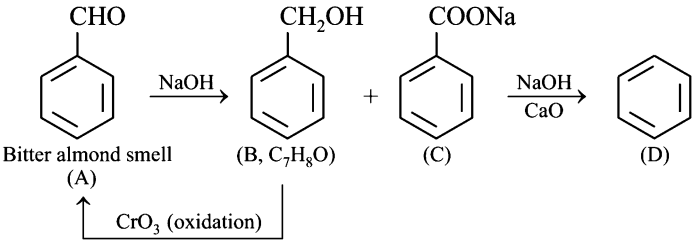
Conclusions:

(i) Since C (sodium salt of an acid) and B (C_7H_8O) are formed by the reaction of A with NaOH, the reaction seems to be an example of Cannizzaro reaction and hence A is an aldehyde with no α-hydrogen atom.

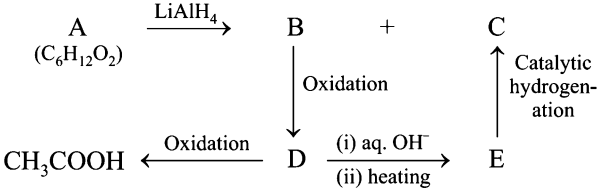
(ii) The other product of Cannizzaro reaction (B, C_7H_8O) should be a primary alcohol ($-CH_2OH$), hence it is $C_6H_5-CH_2OH$.

(iii) Reaction of C with soda lime gives aromatic hydrocarbon, hence C is sodium salt of an aromatic acid.

Thus compound A is C_6H_5CHO which explains all the given reactions.



Solution 10: Summary of the given facts.



Conclusions:

(i) Compound (A) on reduction with $LiAlH_4$ gives two products (B) and (C), hence (A) should be an ester and both (B) and (C), should be alcohol.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR \xrightarrow{LiAlH_4} RCH_2OH + ROH$$

(ii) Observe that the final product (CH_3COOH, a compound having 2 carbon atoms) is obtained by two steps oxidation of B through D. Hence going backward from CH_3COOH, D should be CH_3CHO and hence B should be CH_3CH_2OH.

$$\underset{}{CH_3COOH} \xleftarrow{\text{Oxidation}} \underset{D}{CH_3CHO} \xleftarrow{\text{Oxidation}} \underset{B}{CH_3CH_2OH}$$

(iii) The compound (D) CH_3CHO reacts with aq. alkali in the following way to form (E) which on catalytic hydrogenation gives (C).

$$2CH_3CHO \xrightarrow[\text{(aldol conden.)}]{\text{aq. } OH^-} \underset{\text{Aldol}}{CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCH_2CHO} \xrightarrow[(-H_2O)]{\text{heat}}$$

$$\underset{\substack{\text{Crotonaldehyde}\\(E)}}{CH_3CH{=}CHCHO} \xrightarrow[H_2]{\text{catalyst}} \underset{(C)}{CH_3CH_2CH_2CH_2OH}$$

Thus (C) should be butanol. Hence compound (A) can be

$$\underset{\text{Ethyl butyrate, (A)}}{CH_3CH_2CH_2-\overset{O}{\overset{||}{C}}-OCH_2CH_3} \quad \textbf{or} \quad \underset{\text{Butyl acetate, (A)}}{CH_3-\overset{O}{\overset{||}{C}}-OCH_2CH_2CH_2CH_3}$$

$$\downarrow LiAlH_4 \qquad\qquad \downarrow LiAlH_4$$

$$\underset{(C)}{CH_3CH_2CH_2CH_2OH} + \underset{(B)}{HOCH_2CH_3} \quad \underset{(B)}{CH_3CH_2OH} + \underset{(C)}{HOCH_2CH_2CH_2CH_3}$$

Solution 11: Summary of the given statements.

$$\underset{C_8H_{16}O_2}{(A)} \xrightarrow[\text{hydrolysis}]{\text{dil. } H_2SO_4} \underset{(B)}{\text{Carboxylic acid}} + \underset{(C)}{\text{Alcohol}}$$

$$\text{Carboxylic acid} \xrightarrow{CrO_3 \text{ (Oxidation)}} \text{Alcohol}$$

$$\underset{(C)}{\text{Alcohol}} \xrightarrow[(-H_2O)]{\text{dehydration}} \text{But-l-ene}$$

Conclusions:

(i) Formation of carboxylic acid (B) and an alcohol (C) by the action of dil. H_2SO_4 on (A), $C_8H_{16}O_2$ indicates that (A) is an ester.

(ii) Dehydration of (C) to form butene-1 indicates that the alcohol (C) is $CH_3CH_2CH_2CH_2OH$, but not $CH_3CH_2CH(OH)CH_3$ because the latter on dehydration gives but-2-ene as the major product.

$$\underset{\text{Butanol-1}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[(-H_2O)]{\text{dehydration}} \underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2}$$

$$\underset{\text{Butanol-2}}{CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_3} \xrightarrow[(-H_2O)]{\text{dehydration}} \underset{\text{But-2-ene (Major)}}{CH_3CH=CHCH_3}$$

(iii) Oxidation of (C), butanol-1 with chromic acid, a strong oxidising agent to form (B), further indicates that (B) is $CH_3CH_2CH_2COOH$. Thus (A), an ester should be butyl butyrate which explains all the given reactions.

$$CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-OCH_2CH_2CH_2CH_3 \xrightarrow[\text{(hydrolysis)}]{\text{dil. } H_2SO_4}$$

Butyl butyrate, **A** ($C_8H_{16}O_2$)

$$CH_3CH_2CH_2COOH + HOCH_2CH_2CH_2CH_3$$

(B), Carboxylic acid **(C)**, Butanol

$$CH_3CH_2CH_2CH_2OH \xrightarrow[\text{(oxidation)}]{CrO_3} CH_3CH_2CH_2COOH$$

Butanol, **C** Butanoic acid, **B**

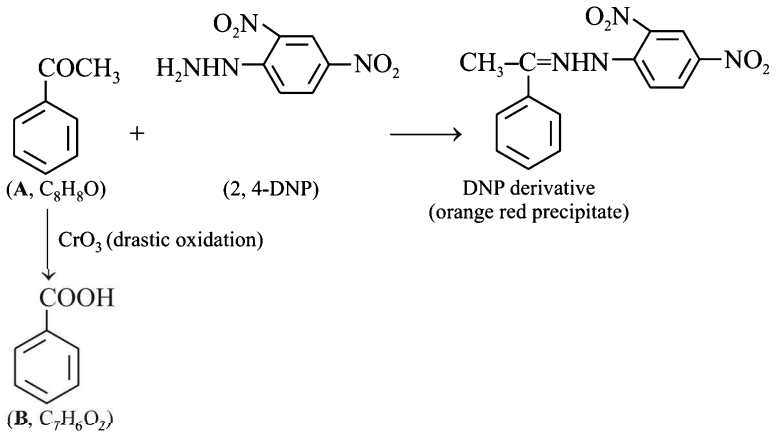
$$CH_3CH_2CH_2CH_2OH \xrightarrow[(-H_2O)]{\text{dehydration}} CH_3CH_2CH{=}CH_2$$

Butanol, **C** But-1-ene

Solution 12: *Conclusions from the given statements.*

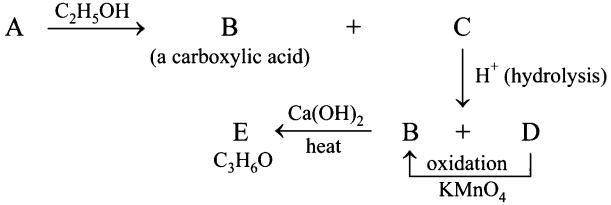
(i) Compound (A) gives orange red precipitate with DNP (dinitro phenylhydrazine), a reagent for carbonyl group (–CHO or >CO), indicates that the compound has an aldehydic or a ketonic group. However, (A) neither reduces Tollen's reagent nor react with Fehling solution (characteristic reactions of –CHO group), hence it is a ketone.

(ii) The compound (A) gives yellow precipitate with iodine and NaOH (iodoform reaction), indicating that it (A) contains $-COCH_3$ group, hence C_8H_8O (A) should be $C_6H_5COCH_3$ which explains all given reactions.



Since (A) does not have carbon-carbon double bond it does not decolorise bromine water and Baeyer's reagent.

Solution 13: Summary of the given facts.



Conclusions:

(i) Since compound (E) reacts with 2, 4-dinitrophenylhydrazine to form 2, 4-dinitrophenylhydrazone, but does not give Tollen's and Fehling tests, it must contain a ketonic group and hence can be written as below.

$$\underset{(E,\ C_3H_6O)}{R-\overset{\overset{O}{\|}}{C}-R} \quad \text{or} \quad \underset{(E,\ C_3H_6O)}{H_3C-\overset{\overset{O}{\|}}{C}-CH_3}$$

(ii) Since (E), ketone (acetone), is formed by heating the compound (B) with $Ca(OH)_2$, (B), should be acetic acid (recall the method of preparation of ketones).

$$\underset{(B)}{2CH_3COOH} \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca \xrightarrow[(-CaCO_3)]{heat} \underset{(E)}{CH_3COCH_3}$$

(iii) Further (B) i.e. CH_3COOH is formed by the oxidation of (D) with $KMnO_4$, (D) can be CH_3CH_2OH or CH_3CHO. However, (D) is also obtained by the acidic hydrolysis of (C),

$$\underset{(D)}{CH_3CH_2OH} \xrightarrow[\text{oxidation}]{KMnO_4} \underset{(B)}{CH_3COOH}$$

possibility of (D) as CH_3CHO is discarded by the fact that (D) is also formed along with CH_3COOH (B) by the acidic hydrolysis of (C). Actually (C) is an ester which on hydrolysis gives CH_3CH_2OH (D) and CH_3COOH (B).

$$\underset{(C)}{CH_3COOCH_2CH_3} \xrightarrow[\text{(hydrolysis)}]{H^+} \underset{(B)}{CH_3COOH} + \underset{(D)}{HOCH_2CH_3}$$

(iv) Thus the compound (A) is an anhydride which reacts with ethyl alcohol and gives acetic acid (a carboxylic acid) and an ester (C).

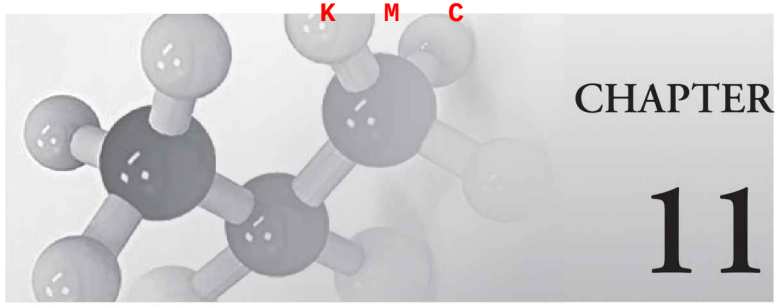
$$\underset{(\textbf{A},\ \text{Acetic anhydride})}{\begin{matrix} CH_3CO \diagdown \\ CH_3CO \diagup \end{matrix} O} \xrightarrow{CH_3CH_2OH} \underset{(\textbf{B},\ \text{acetic acid})}{CH_3COOH} + \underset{(\textbf{C},\ \text{Ethyl acetate})}{CH_3COOCH_2CH_3}$$

Solution 14: Molecular formula of the carboxylic acid D is CH_2O_2, therefore, D is HCOOH. D is obtained by acidification of C which is obtained along with B when two moles of A react with strong base (like NaOH). Therefore, B and C are CH_3OH and HCOONa respectively. The compound A is therefore, HCHO (formaldehyde).

$$\underset{\substack{\text{Formaldehyde}\\(A)}}{2HCHO} + NaOH \xrightarrow[\text{reaction}]{\text{Cannizzaro}} \underset{\substack{\text{Methyl alcohol}\\(B)}}{CH_3OH} + \underset{\substack{\text{Sodium formate}\\(C)}}{HCOONa}$$

$$\underset{(B)}{CH_3OH} \xrightarrow[573\ K, -H_2]{Cu, \Delta} \underset{(A)}{HCHO}$$

$$\underset{(C)}{HCOONa} \xrightarrow[-NaCl]{\text{dil. HCl}} \underset{\substack{(D)\\\text{Formic acid}}}{HCOOH}$$



CHAPTER

11

Miscellaneous Questions

(A) Biomolecules

(i) Carbohydrates.

1. Define carbohydrates.
2. How the carbohydrates are classified into two broad types ?
3. What are homopolysaccharides ? Give one example.
4. What are monosaccharides ? Classify sugars on the basis of number of monosaccharide units present in one molecule ?
(Delhi 2009C, 2011C, AI 2010)
5. (a) Define reducing sugars. Give one example,
(b) What are non-reducing sugars ? Give one example,
(Delhi 2009C, 2011C, AI 2010)
6. What are aldoses ? Give two examples.
7. Give two main functions of carbohydrates in plants.
(AI 2008, 2012C)
8. How the presence of carbohydrates can be detected in laboratory ?
9. Define photosynthesis.
10. Mention the important types of functional groups present in glucose molecule. Also mention the number of chiral carbon atoms, a glucose molecule has.
11. List the reactions of glucose which cannot be explained by its open chain structure. **(Delhi 2008, 2012, AI 2009, 2010C, 2011, 2011C, Foreign 2012)**

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12. Describe pyranose structure of glucose. **(AI 2011, 2012, Foreign 2011)**

13. What is essential difference between α- and β- forms of glucose ? **(Delhi 2011, AI 2012)**

14. Draw open chain and ring structures of fructose.

15. Discuss invert sugar. **(Foreign 2012)**

16. Arrange the following sugars according to their decreasing sweetening power : Glucose, fructose, lactose, sucrose, maltose and invert sugar.

17. Give the name of the constituent monosaccharides in each of the following.

    (a) Sucrose (b) Maltose (c) Lactose

18. What is glycogen ? how is it different from starch ? How is starch structurally different from cellulose ? **(Foreign 2012)**

(ii) Amino-acids and proteins.

1. Explain the following terms.

(i) Acidic, basic and neutral α-amino acids.

(ii) Essential and non-essential α-amino acids. **(Delhi 2012C, AI 2008C, 2010, 2013C)**

(iii) Zwitter ion **(AI 2011C)**

(iv) Amphoteric behaviour of α-amino acids. **(AI 2008)**

(v) Polypeptides **(Foreign 2012)**

(vi) Primary structure of proteins. **(Delhi 2011, AI 2008, Foreign 2011)**

(vii) Secondary structure of proteins **(Delhi 2011, Foreign 2011)**

(viii) Tertiary structure of proteins.

(ix) Denaturation **(Delhi 2008, AI 2008C, 2009, 2012)**

(x) Biocatalysis **(Delhi 2012)**

(xi) Enzymes **(Delhi 2010, 2011, 2012, AI 2010, Foreign 2012)**

2. Differentiate between fibrous proteins and globular proteins. What is meant by denaturation of proteins ? **(Delhi 2010C, AI 2010)**

3. Name the forces involved in holding the substrate molecules to the active site of enzymes. **(AI 2008C)**

4. Which type of linkage is present in the following ?

(i) Peptide linkage **(Delhi 2008, 2009, 2011, 2012, AI 2008, 2011, 2012, 2013, Foreign 2011)**

(ii) Primary structure of proteins **(Delhi 2011, AI 2008, 2008C, 2012, Foreign 2011)**

(iii) Cross linking of polypeptide chains **(AI 2008C)**

(v) Secondary structure of proteins **(Delhi 2011, Foreign 2011)**

(iv) α-Helix formation **(Dehi 2010C, 2013, AI 2008C)**

(vi) β-Sheet structure **(Delhi 2013, AI 2008C)**

(vii) Glycosidic linkage **(Delhi 2009, 2011, 2013, AI 2008, 2012)**

(iii) Vitamins

1. What are vitamins ? Deficiency of which vitamins causes
   (a) pernicious anaemia (b) convulsions **(AI 2010C)**
2. How are vitamins classified ? Mention the chief sources of vitamins A and C. **(AI 2008)**
3. What are provitamins ? Give one example.
4. What are the main sources for different vitamins ?
5. What is deficiency disease ? List the deficiency disease caused by different vitamins.
6. Name two water soluble vitamins, their sources and diseases caused due to their deficiency in the diet. **(Delhi 2009)**
7. Name two fat soluble vitamins, their sources and the diseases caused due to their deficiency in diet. **(AI 2009)**
8. Name a water soluble vitamins which is a powerful antioxidant. Give its one natural source. **(Delhi 2012C)**
9. Name the deficiency disease resulting from the lack of vitamin A in the diet. **(Delhi 2011C)**
10. Name the only vitamin which can be synthesised in our body. Name one disease that is caused due to the deficiency this vitamin. **(AI 2012C, 2013C)**
11. Which member of vitamin B complex is destroyed during cooking?
12. Name the deficiency disease resulting from lack of vitamins A and E in the diet. **(Delhi 2013C)**

(iv) Nucleic acids

1. What are nucleic acids ?
2. Summarise the hydrolysis products of nucleic acids in different steps.

3. What is the structural difference between a nucleoside and a nucleotide ? **(Delhi 2009C, AI 2013C)**
4. Write the full forms of the two types of nucleic acids, i.e. DNA and RNA. **(Foreign 2012)**
5. What are important purine and pyrimidine bases found to be present in the hydrolysate (hydrolysis product) of nucleic acids.
6. Name the four bases present in DNA. Which one of these is not present in RNA ? **(AI 2009, Foreign 2012)**
7. Name the bases present in RNA. Which one of this is not present in DNA ? **(Delhi 2011, Foreign 2012)**
8. Mention the names of the bases produced on hydrolysis of DNA. **(Delhi 2009C)**
9. Name the bases which are common to both DNA and RNA.
10. Of type two bases, thymine and uracil, which one is present in DNA ? **(Delhi 2012)**
11. What are the products of hydrolysis of a nucleotide from DNA containing thymine ? **(AI 2010C)**
12. Name the chemical components which constitute nucleotides. Write any four functions of nucleotides in a cell. **(Delhi 2009C)**
13. Mention important differences between DNA and RNA.
14. Write the important structural difference between DNA and RNA. **(Delhi 2009C, 2012, 2013C, AI 2011)**
15. What are the different types of RNA found in cells of organisms ? State the functions of each type. **(Delhi 2012C, 2013)**
16. What are complimentary bases ?
17. What are structural and functional differences between DNA and RNA ? **(Delhi 2013C)**

(B) Every Day Chemistry

(i) Polymers.

1. Define the term polymerisation. **(AI 2008)**
2. Define the term homopolymerisation, giving an example. **(Delhi 2012)**
3. What is meant by copolymerisation ? Give two examples of copolymers and the reactions for their preparation. **(AI 2010, 2012C)**
4. Distinguish between homopolymers and copolymers and give an example of each class. **(Delhi 2008C, AI 2008)**
5. Is $-(CH_2-CH(C_6H_5))_n-$ a homopolymer or copolymer. **(Delhi 2008C)**

6. Is $\left(CH_2-\underset{\underset{Cl}{|}}{CH}\right)_n$ a homopolymer or copolymer ? **(AI 2013)**

7. Differentiate between condensation and addition polymerisation. Give one example each of the resulting polymers. **(AI 2009)**

8. Distinguish between addition polymers and condensation polymers. Classify the following into addition and condensation polymers.
   (i) Polythene (ii) PTFE (iii) Polybutadiene (iv) Bakelite
   (AI 2011C)

9. What is step growth polymerisation ? Explain the steps involved in this process. **(AI 2008C)**

10. What are addition polymers ? How are the two types of addition polymers different from each other ? Give one example of each type.
    (Foreign 2011)

11. Which polymer is obtained when free radical polymerisation of chloroprene occurs ? Write the structure of the polymer thus obtained.
    (Foreign 2011)

12. Give one example each of
    (a) addition polymers **(Delhi 2010)**
    (b) codensation polymers **(Delhi 2010, AI 2013)**
    (c) copolymers. **(Delhi 2010)**

13. Classify the polymers into various classes on the basis of molecular forces.

14. Name the sub groups into which polymers are classified on the basis of magnitude of intermolecular forces.

15. Classify the polymers on the basis of their structure. **(Delhi 2011)**

16. What is the difference between elastomers and fibres ? Give one example of each. **(AI 2008C)**

17. What are the thermoplastic and thermosetting resins ? Give one example of each. **(Delhi 2010, 2012C, AI 2008, 2012, 2013)**

18. Explain the following terms giving a suitable example for each.
    (a) Elastomers **(Delhi 2009, AI 2012)**
    (b) Condensation polymers **(AI 2012)**
    (c) Addition polymers **(AI 2012)**

19. What are biodegradable polymers ? Give an example of such a polymer and mention its uses. **(Delhi 2009C, AI 2013)**

20. Write chemical equations to form the following:
    (i) Polythene **(AI 2009C)** (ii) Teflon
    (iii) PVC (iv) Orlon

(v) Neoprene (vi) Buna-S
(vii) Buna-N (viii) Terylene **(AI 2009C)**
(ix) Nylon-6 **(AI 2009C)** (x) Nylon-6, 6 **(AI 2009C)**
(xi) Nylon-6, 10 (xii) Bakelite **(AI 2009C)**

21. What does the part '6,6' means in the name nylon-6, 6 ?
(Delhi 2009, 2011, AI 2009, 2010, Foreign 2011)

22. What is the difference between two notations : nylon-6 and nylon-6,6 ? **(AI 2008C)**

23. Mention two important uses of each of the following :
(a) Bakelite **(AI 2011)**
(b) Nylon-6 **(Delhi 2011)**
(c) PVC **(AI 2011)**
(d) Nylon-6,6 **(AI 2011)**

24. Give the monomer(s) of the following polymers.
(i) Buna-S **(Delhi 2008, 2010, 2011C, 2013, AI 2011)**
(ii) Buna-N
(iii) Neoprene
(Delhi 2008, 2010, 2010C, 2011C, 2012, 2013, AI 2011, Foreign 2012,)
(iv) Polypropene **(Delhi 2011C, 2012)**
(v) Polythene **(Delhi 2009, 2013, AI 2009C, 2011)**
(vi) Teflon **(Delhi 2009, 2010, 2010C, 2013, AI 2010, AI 2011, Foreign 2012)**
(vii) Polystyrene **(Delhi 2013)**
(viii) Bakelite **(Delhi 2013, AI 2009C, 2010, AI 2010C, 2013C)**
(ix) Nylon-6 **(Delhi 2008, 2012, 2013, AI 2010, Foreign 2012)**
(x) Nylon-6,6 **(Delhi 2010C, 2013)**
(xi) Terylene (Dacron) **(Delhi 2010C, 2011C, 2013, AI 2009C, AI 2011, 2011C, 2013)**
(xii) PVC **(Delhi 2010C, 2011C, AI 2010, 2010C, 2011)**
(xiii) Urea formaldehyde resin **(AI 2010C)**
(xiv) Glyptal **(Delhi 2011C)**
(xv) Natural rubber **(AI 2013C)**

(ii) Food preservatives

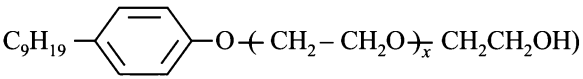
1. What are food preservatives ?
(Delhi 2009, 2011, 2012, AI 2010, 2011, 2012)
2. How does sodium benzoate is removed through urine ?
3. How does potassium metabisulphite act as a food preservative in jams and squashes ?

K M C

4. What are artificial sweetening agents ?
(Delhi 2009C, AI 2009, 2011, Foreign 2011)
5. Arrange the following artificial sweeteners according to their sweetness value.
6. What are antioxidants ? Name two examples. **(AI 2013C)**

(iii) Detergents

1. What are synthetic detergents ?
(Delhi 2011, 2012, AI 2010, 2011, 2012C)
2. What are biodegradable and non-biodegradable detergents ?
3. What are cationic detergents ? Give one example
(Delhi 2008C, 2009, 2010, 2013C, AI 2009, 2010C)
4. What are anionic detergents ? Give one example.
(Delhi 2009C, 2013C, AI 2010C)
5. What are non-ionic detergents ? **(Delhi 2009, AI 2009, 2010C)**
6. Label the hydrophilic and hydrophobic parts of the following molecule of a non-ionic detergent.



Identify the functional group(s) present in the molecule.
(Delhi 2010C)
7. Explain the cleansing action of soap. Why do soaps not work in hard water ? **(AI 2012)**

(iv) Drugs

1. Explain the term chemotherapy with one example. **(AI 2010C)**
2. What are analgesic medicines ? How are they classified and when are they commonly recommended for use ? **(Delhi 2010, AI 2010)**
3. Explain the following types of drugs giving one suitable example for each case.
   (i) Analgesics **(Delhi 2009, 2011, AI 2010C, 2012C)**
   (ii) Narcotic analgesics **(AI 2012C)**
   (iii) Tranquillisers **(Delhi 2008C, AI 2010C, 2012C)**
   (iv) Antiseptics **(Delhi 2009, AI 2010, 2010C, Foreign 2011)**
   (v) Disinfectants **(Delhi 2012, AI 2009)**
   (vi) Antacids **(Delhi 2009, 2011, 2012, AI 2009C, 2011, Foreign 2011)**

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(vii) Antihistamines **(Delhi 2012C, AI 2008C, 2009C)**
(viii) Antifertility drugs **(Delhi 2010)**
(ix) Antibiotics **(AI 2009C, 2010, 2010C, 2012C)**
(x) Antimicrobials.
(xi) Antipyretics **(AI 2013C)**

4. How do antiseptics differ from disinfectants ? Give one example of each type. **(Delhi 2009, 2011, 2012C, AI 2011, 2012)**

5. Name a substance that can be used as an antiseptic as well as disinfectant. **(Delhi 2008)**

6. Name the constituents of dettol. **(Delhi 2010C)**

7. What is tincture of iodine and what is it used for ? **(AI 2008, 2011)**

8. What are bactericidal and bacteriostatic antibiotics ?

9. Classify the following into bactericidal and bacteriostatic antibiotics.
Tetracycline, penicillin **(AI 2008C)**

10. Define the terms Gram-positive and Gram-negative bacteria.

11. What are broad spectrum antibiotics ? Name a broad spectrum antibiotic and state two diseases for which it is prescribed. **(Delhi 2012C, AI 2009C, 2010C, 2012C, 2013C)**

12. What is meant by 'narrow spectrum antibiotics' ? **(Foreign 2012)**

13. What are antibiotics ? Distinguish between narrow spectrum and broad spectrum antibiotics. **(AI 2008C)**

14. What are limited spectrum antibiotics ? Give one example. **(Delhi 2013C)**

15. Mention one use for each of the following drugs.
(i) Ranitidine (ii) Paracetamol (iii) Tincture of iodine **(AI 2008C)**

16. Mention the action of the following on the human body in bringing relief from a disease. **(AI 2011C)**
(i) Brompheniramine (ii) Aspirin (iii) Equanil

(C) Value Based Questions

1. After watching a programme on TV about the adverse effects of junk food and soft drinks on the health of school children, Sonali, a student of Class XII, discussed the issue with the school principal. Principal immediately instructed the canteen contractor to replace the fast food with the fibre and vitamins rich food like sprouts, salad, fruits etc.

K M C

This decision was welcomed by the parents and the students. After reading the above passage, answer the following questions.

[Delhi 2013]

(a) What values are expressed by Sonali and the principal of the school?

(b) Give two examples of water-soluble vitamins.

2. Shanti, a domestic help of Mrs. Anuradha, fainted while mopping the floor. Mrs. Anuradha immediately took her to the nearby hospital where she was diagonised to be severely 'anaemic'. The doctor prescribed an iron rich diet and multivitamins supplement to her. Mrs. Anuradha supported her financially to get the medicines. After a month, Shanti was diagonised to be normal.

[AI 2013]

After reading the above passage, answer the following questions :

(i) What values are displayed by Mrs. Anuradha?

(ii) Name the vitamin whose deficiency causes 'pernicious anaemia'.

(iii) Give an example of a water soluble vitamin.

3. Mrs. Gupta read a topic on diabetes. For self concern she visited chemist and asked for a sugar free tablets. The chemist advised her to check sugar level first and then only use sugar free tablets.

(a) What are contents of sugar free?

(b) Give some examples of sugar free sweetners?

(c) What values are shown by the chemist.

4. We all know how terrible plastic bags are for the environment? They choke wild life, they don't break down in land fills and they aren't easy to recycle, which is the biggest reason why 90 percent of plastic bags in the U.S. are not recycled. Delhi government has also taken some serious steps against it but still many of us are not following it.

(a) What can be the other polymers that can replace them?

(b) What properties of these polymers make it suitable for environment?

(c) What is our moral responsibilities towards environment?

5. Reena went to her village during summer holidays. There she noticed that her grandmother is following very traditional way of cooking using earthen wares and copper utensils. She suggested her to replace the entire kitchen utensils with teflon coated ones.

(a) In your opinion why should she replace her cooking pots with teflon coated ones?

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(b) What is the monomer of teflon? What is its structure?
(c) What are the values displayed by Reena?

6. Rohan and Ryan went to their native place to attend a family function. When they reached, due to long journey Rohan started suffering from hyperacidity and he was not even able to enjoy the party. His friend, Ryan offered him 'soda water' (aqueous $NaHCO_3$), while Ratan, another friend, wanted Rohan to take 'gelusil' (aluminium hydroxide gel).

(a) Should Rohan follow Ryan's advice or Ratan's?
(b) What are the values associated with friend giving correct advice?

7. Jagjit was bitten by honey-bee during an excursion trip. His collegue immediately approached a local resident and asked for baking soda.

(a) What chemical is present in honey bee sting? Why did the collegue use baking soda for its treatment?
(b) Which personality trait of the collegue is reflected by this?

8. A teacher was discussing 'carbylamine test' of 1° amines in the class and the precautions to be taken when carrying out this test. She discussed about the Bhopal gas tragedy of 1984 and the gas responsible for it i.e. methylisocyanate (MIC).

(a) What is the structure of methyl isocyanate?
(b) Why we should take precautions while carrying 'carbylamine test'?
(c) What social issues are carried by the Bhopal Disaster of 1984?

9. While doing a research on uses of insecticides Rohit found that, a farmer is cultivating his land near the village pond and also drawing water from it for irrigation. He is using insecticide excessively to protect his crops and improve the harvest. Over a period of time his agricultural growth improved vastly, but the pond lost its aquatic life.Rohan suggested him to avoid excessive use of insecticide as it has high toxicity towards fishes and other aquatic animals.

(a) Draw the structure and write IUPAC name of the compound used as an insecticide but not a pesticide..
(b) What values got expressed in Rohan's suggestion?

10. An anaesthetic bottle was left on the window side of the operation theatre for a few days. It was exposed to sun and rain. A doctor used the same bottle on one of his patient and found the patient having severe vomiting and stomach poisoning.

K M C

(a) Identify the anaesthetic compound. Give relevant equation as to its action.

(b) What are the values to be kept in mind while using drugs?

11. Ramendra is working in a coal mine and from few days he is complaining about pain in his bones especially in his legs and arms. His supervisor asked to him to take leave for some days and go to sunny place for some days.

(a) Which vitamin deficiency may be there in Ramendra?

(b) Why his supervisor suggested him to go to a sunny place?

(c) What are the values associated with Ramendra's supervisor?

12. While standing on the bus stand, Ganga saw a hoarding which said, 'Don't mix drinking with driving' and 'say NO to alcohol'. On reading this, she enquired her father about it. Based on the above information, answer the following questions.

(a) Which alcohol is used for drinking purpose?

(b) What are the harmful effects of drinking alcohol?

(c) What values does the slogan shows ?

13. Lt. Ramesh used to drink from a local wine shop. He complained of blurred vision, started losing his eyesight slowly and died in a couple of days.

(a) Give IUPAC name of the main component of wine.

(b) Which constituent of wine was responsible for the death of Ramesh?

(c) What values can be derived from the sad incident?

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(A) Biomolecules

(i) Carbohydrates

1. **Carbohydrates:** At one time, carbohydrates were defined as **hydrates of carbon**, i.e. $C_x(H_2O)_y$. Examples are

   $C_6H_{12}O_6$ or $C_6(H_2O)_6$ $C_{12}H_{22}O_{11}$ or $C_{12}(H_2O)_{11}$

   Glucose and fructose Sucrose

   $(C_6H_{10}O_5)_n$ or $[C_6(H_2O)_5]_n$

   Cellulose and starch

   However, later on it was found that certain

   (a) carbohydrates do not correspond to the formula $C_x(H_2O)_y$, e.g.

   $C_6H_{12}O_5$ $C_7H_{14}O_6$

   Rhamnose Rhamnohexose

   (b) compounds, although correspond to the formula, $C_x(H_2O)_y$, they are not carbohydrates, e.g.

   CH_2O $C_2H_4O_2$ or $C_2(H_2O)_2$ $C_3H_6O_3$ or $C_3(H_2O)_3$

   Formaldehyde Acetic acid Lactic acid

   Hence **carbohydrates are defined as the optically active polyhydroxyaldehydes or ketones or substances which give these on hydrolysis.**

2. **Classification of carbohydrates. 1 Sugars:** Sugars are sweet, crystalline substances and soluble in water. Their molecular weights are known and fixed for a particular compound. Examples are glucose, fructose, sucrose, maltose etc.

2. **Non-sugars or polysaccharides:** These are usually tasteless, amorphous solids and are either insoluble in water or form colloidal suspension. They have high and variable molecular weights (similarity with polymers). They are themselves tasteless, but on hydrolysis with dilute acids, they yield sweet monosaccharide molecules. Examples are cellulose, starch and glycogen.

$$\underset{\text{Cellulose, Starch or Glycogen (tasteless)}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[H^+]{\text{hydrolysis}} \underset{\text{Glucose (sweet)}}{nC_6H_{12}O_6}$$

3. **Classification of polysaccharides:** Polysaccharides which have only one type of monosaccharides are known as **homopolysaccharides,**

e.g. starch, cellulose, glycogen, and inulin all of which are composed of only glucose units. Polysaccharides which have different types of monosaccharide units are called **heteropolysaccharides**, e.g. gum.

4. **Classification of sugars:**

1 monosaccharides. These are polyhydroxyaldehydes or ketones which can't be hydrolysed further, to simpler sugars. Examples are glucose, fructose, mannose etc.

2 Oligosaccharides. They yield two to ten molecules of monosaccharides on hydrolysis; those yielding two molecules are called *disaccharides* (e.g. sucrose, maltose, lactose etc), those yielding three molecules are called trisaccharides (e.g. raffinose), and so on.

5. **(a), (b). Classification of sugars as reducing and non-reducing sugars:** Sugars which reduce Fehling solution, Benedict solution and Tollen's reagent are called **reducing sugars**. Examples are all monosaccharides (e.g. glucose, mannose, fructose etc) and nearly all disaccharides (except sucrose), viz. maltose, lactose, etc. Sugars which do not reduce Fehling solution, Benedict solution and Tollen's reagents are called **non-reducing sugars**, e.g. sucrose (a disaccharide) and all polysaccharides (e.g. starch, cellulose, glycogen etc).

6. **Classification of monosaccharides:** Monosaccharides may be classified on the basis of *carbonyl group* and *the number of carbon atoms* in a molecule, those bearing aldehydic group (–CHO) are called **aldoses**, while those bearing ketonic group ($-\overset{\overset{\displaystyle O}{\|}}{C}-$) are called **ketoses**. Aldoses as well as ketoses may be *trioses* (having three carbon atoms in a molecules), *tetroses* (4 carbon atoms), pentoses (5 carbon atoms), *hexoses* (6 carbon atoms) and *heptoses* (7 carbon atoms). Aldohexoses (e.g. glucose, mannose) and ketohexoses (e.g. fructose) are most important and common examples of monosaccharides.

7. **Functions of carbohydrates:**

(i) Sugars (e.g. glucose, sucrose, lactose etc.) serve as source of energy.

(ii) Glycogen serves as store of energy in animals.

(iii) Sugars are used for preparing alcohol.

(iv) Cellulose and its derivatives are used in making cotton, linen, jute, paints, explosives etc.

(v) Ribose and deoxyribose (both are aldopentoses) are components of nucleic acids.

(vi) Starch is the major reserve food material in seeds of plants.

(vii) Sugars make fruits sweet.

(viii) Cellulose acts as the main structural material of the plant cell walls.

(ix) Certain carbohydrates (e.g. chitin) form the major constituent of the shells of crabs and lobsters.

8. Test of carbohydrates: Carbohydrates when treated with **Molisch reagent** (1% alcoholic solution of α-naphthol) in presence of conc. H_2SO_4 form violet ring (**Molisch test**).

9. Photosynthesis: Reaction of carbon dioxide with water in presence of light and chlorophyll to form carbohydrates is known as **photosynthesis**.

$$x\,CO_2 + x\,H_2O \xrightarrow[\text{Chlorophyll}]{\text{Light}} \underset{\text{Carbohydrate}}{(CH_2O)_x} + O_2$$

10. Open chain structure of glucose indicates that it has an

$$OHC.^*CHOH.^*CHOH.^*CHOH.^*CHOH.CH_2OH$$

aldehydic group, four secondary alcoholic groups and a primary alcoholic group. It has four chiral (asymmetric) carbon atoms (marked by asterisk, *), hence it can exist in $2^4 = 16$ optically active forms, i,e. eight enantiomeric pairs.

11. Open chain structure of glucose (see above, question 10) does not explain following reactions.

(a) It does not explain certain reactions of –CHO group, viz.

(i) it does not react with $NaHSO_3$ to form a bisulphite.

(ii) it does not react with ammonia to form aldehyde-ammonia compound.

(iii) it does not restore Schiff's reagent colour.

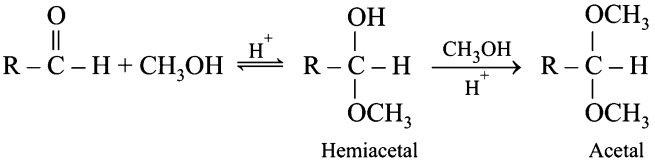
(b) It forms two isomeric penta-acetates neither of which reacts with none of the carbonyl reagents.

(c) Glucose when dissolved in water, its specific rotation changes until it reaches a constant value. This phenomenon is known as mutarotation and is shown by almost all reducing sugars. This is due to existence of glucose in two isomeric forms (α-and β-) which can't be explained by open chain structure.

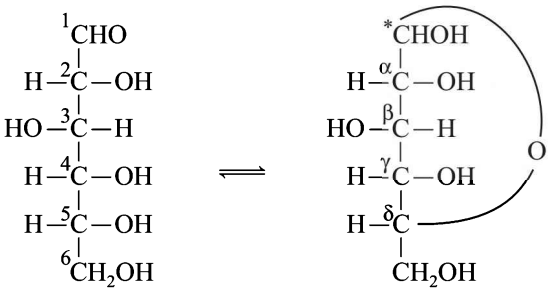
(d) Glucose reacts with one molecule of methanol in presence of hydrogen chloride to form two isomeric compounds.

$$\text{D (+)- Glucose} + CH_3OH \xrightarrow{HCl} \text{Two isomeric methyl glucosides}$$

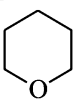
Remember that a normal aldehyde reacts with methanol in presence of hydrogen chloride in the following manner.



12. Pyranose structure of glucose: Since open chain of glucose (having a free aldehydic group) could not explain its certain (mentioned in Q. 11) properties, it was found that glucose actually exists as a ring structure in which free –CHO group is not present.

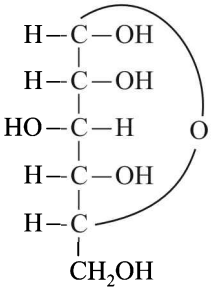


In formation of ring, –CHO group has reacted with –OH group on C_5 to form stable δ-oxide ring structure. Since the δ-oxide ring or six membered ring is analogous to **pyran**, a well known and stable

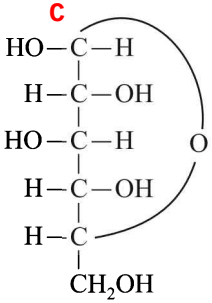


compound), the structure is commonly called pyranose structure of glucose.

13. Since in the ring structure, the new chiral carbon (C_1, marked by asterisk in Q 12) has developed, the ring structure of glucose may have two different arrangements, viz. α- and β-. In α- form of the D-glucose, the hydroxyl group is attached to the right and hydrogen to left, while in β-form –OH group is present on the left side, and H on the right side.



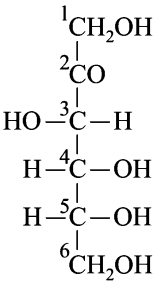
α-D-Glucose or
α-D-Glucopyranose



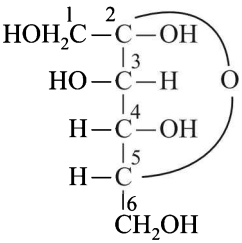
β-D-Glucose or
β-D-Glucopyranose

Note that α- and β- glucoses differ from each other in the configuration of carbon atom involved in ring formation. Such stereoisomeric pairs are known as **anomers** and the carbon as anomeric carbon.

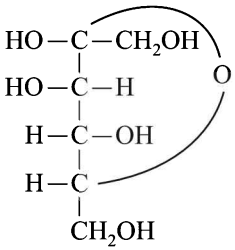
14.



Open chain structure
of fructose



α-Fructofuranose
Five membered ring structure of fructose



β-Fructofuranose

α- and β- fructoses are anomers of each other.

15. Invert sugar: Sucrose, on hydrolysis with mineral acid or by the enzyme **invertase**, gives equal amounts of glucose and fructose.

$$\underset{\substack{\text{Sucrose}\\ [\alpha]_D = +66.5^\circ\\ (\textit{dextro-})}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{or invertase}]{H^+} \underbrace{\underset{\substack{\text{Glucose}\\ [\alpha]_D = +52.5^\circ\\ (\textit{dextro-})}}{C_6H_{12}O_6} + \underset{\substack{\text{Fructose}\\ [\alpha]_D = -92^\circ\\ (\textit{laevo-})}}{C_6H_{12}O_6}}_{\substack{\text{Invert sugar, } [\alpha]_D = -20^\circ\\ (\textit{laevo-})}}$$

Note that during hydrolysis, *dextro*-rotatory compound (sucrose) has changed into laevorotatory product (mixture of glucose and fructose), i.e. inversion in optical activity has occurred, hence hydrolysis of sucrose is known as **optical inversion** and the hydrolysis product is known as **invert sugar**.

16. Sweetening power of common sugars

Fructose > Invert sugar > Sucrose > Glucose > Maltose > Lactose

17. **(a)** Sucrose molecule is composed of one glucose and one fructose molecule

$$\underset{\text{Sucrose}}{CH_{12}H_{22}H_{11}} + H_2O \xrightarrow{\text{hydrolysis}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(b) Each maltose molecule has two glucose molecules.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{hydrolysis}} \underset{\text{Glucose}}{2\,C_6H_{12}O_6}$$

(c) Lactose molecule has one glucose and one galactose molecule.

$$\underset{\text{Lactose}}{CH_{12}H_{22}H_{11}} + H_2O \xrightarrow{\text{hydrolysis}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}$$

18. **Glycogen**, also called **animal starch**, is the **reserve food** in **animals**. **Starch** is found exclusively **in plants** as stored food. **Starch** is a mixture of two components, namely **amylose** which is water soluble and **amylopectin** which is water insoluble. Amylose is a linear polymer of α-D-glucose, while amylopectin and glycogen are branched polymers of α-D-glucose.

Cellulose is the chief constituent of cell walls. It is the major food material for cattles because cattles have **cellulases** (digestive enzymes for cellulose) in their digestive tract. Starch is the major food material for human beings.

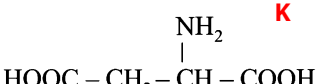
(ii) Amino-acids and proteins

1. (i) Amino acids which contain a carboxyl group and an amino group in α- position to each other are called **neutral amino acids**, e.g. glycine, alanine, etc.

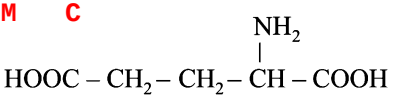
$$\underset{\text{Glycine (Gly)}}{H_2N{\cdot}CH_2{\cdot}COOH \text{ or } H_3N^+CH_2COO^-}$$

$$\underset{\text{Alanine (Ala)}}{H_2N-\overset{\overset{\displaystyle CH_3}{|}}{CH}-COOH \quad \text{or} \quad H_3\overset{+}{N}-\overset{\overset{\displaystyle CH_3}{|}}{CH}-COO^-}$$

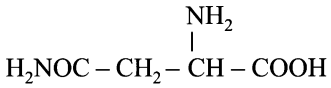
In addition to the carboxyl and amino groups alpha to each other, some α- amino acids contain a second carboxyl group or a *potential carboxyl group* in the form of carboxamide. These α-amino acids are called **acidic amino acids**. Examples are



Aspartic acid (Asp)

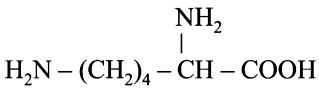


Glutamic acid (glu)

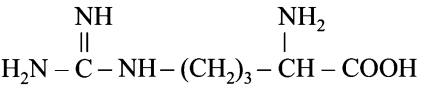


Asparagine (Asn)

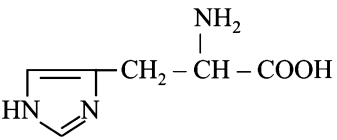
Similarly, there are some **basic amino acids** which contain an additional basic group in the form of an amino group (e.g. lysine), a guanido group (e.g. arginine) or an imidazole ring (e.g. histidine and tryptophan).



Lysine (Lys)



Arginine (Arg)

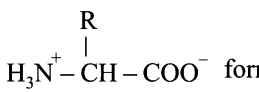
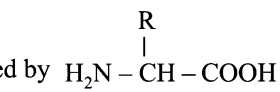


Histidine (His)

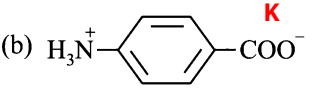
(ii) Proteins are found to contain **twenty two** different α-amino acids. Out of 22 α-amino acids, human body is capable of synthesising only 12 α-amino acids, hence these may or may not be present in the diet, hence called as **non-essential or dispensable amino acids**. Examples are glycine, alanine etc.

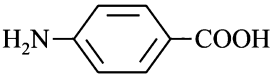
The human body cannot synthesise certain amino acids (about 10 in number), hence these must be supplied in diet, these are called **essential or indispensable amino acids**. Examples are valine, leucine, isoleucine, tryptophan etc.

(iii) **Zwitter ion.** The dipolar ion formed by the neutralisation of acidic and basic groups present in the same molecule is called dipolar ion or zwitter ion. For example,

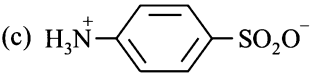
(a)  formed by 

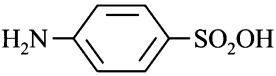
α-Amino acids

(b) 

formed by 

Anthranilic acid

(c) 

formed by 

Sulphanilic acid

(iv) **Amphoteric behaviour of amino acids.** Amino acids exist in the form of zwitter ions (dipolar ions) which show **amphoteric** behaviour as it reacts with acids as well as alkalies.

$$H_3\overset{+}{N}-\underset{}{\overset{R}{\overset{|}{C}H}}-COOH \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} \underset{\text{(acidic gp.)}}{H_3\overset{+}{N}}-\overset{R}{\overset{|}{C}H}-\underset{\text{(basic gp.)}}{COO^-}$$

Zwitter ion

$$\Downarrow OH^- \quad H^+$$

$$H_2N-\overset{R}{\overset{|}{C}H}-COO^-$$

(v) **Polypeptides.** When more than ten α-amino acids are linked together by peptide linkages (more than 9), peptides formed are known as polypeptides.

(vi) **Primary structure of proteins** refers to the number, nature and sequence of amino acid residues present in polypeptide chain(s) of a protein.

(vii) **Secondary structure of proteins** refers to the conformation of polypeptide chain(s) present in a protein molecule.

(viii) **Tertiary structure** of a protein refers to its three-dimensional structure, i.e. the coiling (folding) of the long peptide chain and thus it gives an exact account of molecular shape of the protein molecule.

(ix) **Denaturation.** Globular proteins (soluble in water) are converted into fibrous proteins (insoluble in water) under the influence of change in temperature, pH etc. the phenomenon is known as **denaturation**. During denaturation, 2° and 3° structures (but not 1°) of proteins are destroyed and their biological activity is lost, e.g. boiling of egg (remember that boiled egg can't be hatched to produce chickens).

(x) **Biocatalysts.** Biocatalysts (biological catalysts) are the catalysts which increase the rate of metabolism of biochemical reactions.

(xi) **Enzymes.** See above (biocatalysts are enzymes).

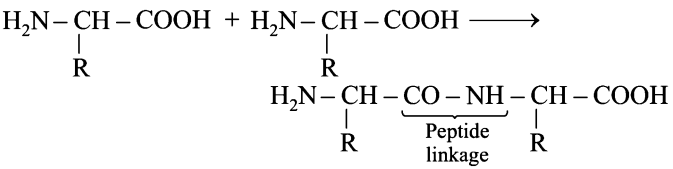
2.

	Globular proteins		Fibrous proteins
(a)	Their molecules are folded to almost spheroidal shape	(a)	They are long and thread like and tend to lie side by side to form fibres.
(b)	Intermolecular forces are weak	(b)	They are held together by hydrogen bonds (strong forces).
(c)	These are soluble in water	(c)	These are insoluble in water
(d)	They are sensitive to small changes of temperature and pH thus they undergo denaturation on heating or treatment with acids/bases.	(d)	They are stable to moderate changes of temperature and pH
(e)	They possess biological activity. Examples are enzymes (invertase), hormones (insulin), haemoglobin, antibodies, etc.	(e)	They serve as the chief structural material of animal tissues. Examples are keratin (in skin, hair, nails), collagen (in tendons), fibroin (in silk) etc.

For denaturation of proteins, consult Q.1, (ix)

3. Hydrogen bonding, dipole-dipole interactions, vander Waals interactions and ionic bonding.

4. (i) **Peptide linkage.** It is an amide type of linkage, $-\overset{\overset{\displaystyle O}{\|}}{C}-NH-$ formed between –COOH group of one α-amino acid and the $-NH_2$ group of the other α-amino acid. This type of linkage is found in polypeptides and proteins.



(ii) Primary structure of proteins have peptide linkages.

(iii) Cross linking of polypeptide chains have peptide linkage.

(iv) Secondary structure of proteins have hydrogen bonds.

(v) α-Helix formation has intramolecular hydrogen bonds between $>C=O$ group of one amino acid and –NH group of the fourth amino acid.

(vi) β-Pleated sheet structure is due to intermolecular hydrogen bonds between two neighbouring polypeptide chains.

(vii) Glycosidic linkage. An ether or oxide type of linkage formed between the –CHO or $>$CO group of a monosaccharide and an alcohol (CH_3OH) or –OH group (alcoholic group) of the other monosaccharide molecule.

(iii) Vitamins

1. **Vitamins:** Vitamins are the organic compounds which are required (in addition to carbohydrates, proteins, fats, mineral salts and water) by the animals for the maintenance and normal growth of life.
   (a) Pernicious anaemia is caused by deficiency of vitamin B_{12}.
   (b) Convulsions is caused by deficiency of vitamin B_6.
2. **Classification of vitamins:** Vitamins are classified as water soluble (e.g. vitamin B complex and vitamin C) and fat soluble (e.g. vitamins A, D, E and K). Sources of vitamins A and C, consult Q 4 and 5, table.
3. **Provitamins** are compounds which are similar in structure to vitamins but inactive biologically. They are known as provitamins because they are converted easily into active vitamins in vivo. Examples are β-carotene and ergosterol which are provitmins for the vitamins A and D respectively.

4 and 5. Sources of vitamins and their deficiency diseases.

Vitamin	Sources	Deficiency disease
Vitamin A or Retinol	Milk, cod liver oil, green leaves, carrots, egg, butter	Night blindness (nyctalopia), xerophthalmea
Vitamin B_1 or Thiamine	Pulses, nuts, egg, whole cereals, tomatoes, yeast	Beriberi and loss of apetite.
Vitamin B_2 or Riboflavin	Milk, meat, green vegetables and yeast	Inflammation of tongue and cracking of lips
Vitamin B_6 or Pyridoxin	Rice bran, meat, egg yolk, fish, yeast, maize	Anaemia
Vitamin B_{12} or Cyanocobalamine	Milk, egg, liver, kidney	Pernicious anaemia

K M C

Vitamin C or Ascorbic acid	Citrus fruits (lemon, oragne, black currants), sprouted pulses, germinated grains, amla	Scurvy (bleeding into skin), bleeding gums and fragile bones
Vitami D or Ergocalciferol or Sunshine vitamin	Fish liver oil, milk, cod liver oil	Rickets (rachitis), osteomalacia
Vitamin E or Tocopherols	Egg, milk, fish, cotton seed oil	Loss of sexual and reproduction power.
Vitamin K or Phylloquinones	Cabbage, spinach and carrot tops	Haemorrhage, delayed blood clotting

6. Two water soluble Vitamins are vitamin B_2 and vitamin C. For their deficiency disease, consult Table, Q 4 and 5.
7. Vitamins A and D are fat soluble. For their deficiency disease, consult Table, Q. 4 and 5.
8. Vitamin C is a powerful antioxidant. Its most important natural source is **amla**.
9. Night blindness and xerophthalmea (hardening of cornea).
10. Vitamin D is synthesised in our body by the action of sunlight on ergosterol (a provitamin).
11. Vitamin B is destroyed by heat, while other members of vitamin B complex are stable to heat.
12. Deficiency of vitamin A results in night blindness. Deficiency of vitamin E results in sterility.

(iv) Nucleic acids

1. Nucleic acids are biomolecules present in the nuclei of all living cells in the form of proteins known as nucleoproteins. Chemically, these are polymers of nucleotides (monomers).
2. Nucleic acids $\xrightarrow{\text{aq. } NH_3}$ Nucleotides $\xrightarrow[448\text{ K}]{\text{aq. } NH_3}$

   Nucleosides + Phosphoric acid (H_3PO_4)

   Nucleosides $\xrightarrow[\text{or dil. } H_2SO_4]{\text{dil. HCl}}$ Bases (Purines/Pyrimidines) + Sugar (Ribose/2-Deoxyribose)
3. A **nucleotide** is the first hydrolysis product of a nucleic acid. Structurally, it consists of three components:

   (a) a heterocyclic base which may be a purine or pyrimidine,

K M C

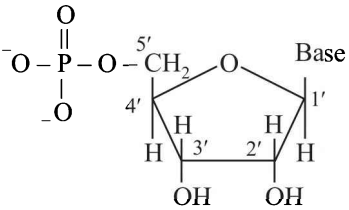
(b) a sugar which may be ribose or 2-deoxyribose, and
(c) phosphoric acid.

Base —Sugar—Phosphate

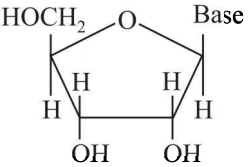
A **nucleoside** is the hydrolysis product of nucleotide. Structurally, it consists of two components:

(a) a heterocyclic base which may be a purine or pyrimidine, and
(b) a sugar which may be ribose or 2-deoxyribose.

Base—Sugar



Nucleotide

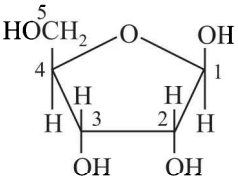


Nucleoside

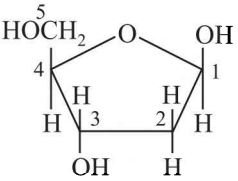
4. Boradly, nucleic acids are of two types.

(a) RNA (Ribonucleic acids). They contain ribose (an aldopen tose) as sugar.

(b) DNA (Deoxyribonucleic acids). They contain 2-deoxyribose (an aldopentose) as sugar.



Ribose



2-Deoxyribose

5. Nucleic acids contain mainly two purine bases (adenine and guanine) and three pyrimidine bases (cytosine, thymine and uracil).

6. Bases present in DNA are

(i) Adenine (A) (ii) Guanine (G)
(iii) Cytosine (C) (iv) Thymine (T).

Thymine (T) is not present in RNA, it is replaced by uracil (U) in RNA.

7. Bases present in RNA are

(i) Adenine (A) (ii) Guanine (G)
(iii) Cytosine (C) (iv) Uracil (U).

Uracil is not present in DNA, its place is taken by thymine (T).

8. DNA, on hydrolysis, gives four nitrogenous bases, namely adenine, guanine, cytosine and thymine.

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9. Adenine, guanine (both purine bases) and cytosine (pyrimidine base) are common in DNA and RNA.
10. Thymine is present in DNA.
11. Structurally, a nucleotide consists of three components;
    (a) a base (purine or pyrimidine),
    (b) a sugar (ribose or 2-deoxyribose), and
    (c) phosphoric acid, i.e. a nucleotide is base–sugar–phosphoric acid. On complete hydrolysis, a nucleotide gives a base, a sugar and a phosphoric acid molecule.

    Thus a nucleotide from DNA (deoxyribonucleic acid) containing thymine, on hydrolysis, will give thymine (base), deoxyribose (sugar) and phosphoric acid (H_3PO_4).
12. Chemical compounds of nucleotides are
    (a) a nitrogenous base (purine or pyrimidine),
    (b) a pentose sugar (ribose or 2-deoxyribose), and
    (c) a phosphoric acid group.

    Functions of nucleotides:
    (a) Nucleotides are precursors of nucleic acids in the cell.
    (b) They are source of chemical energy, viz. ATP (adenosine triphosphate) and ADP (adenosine diphosphate).
    (c) Some nucleotides (e.g. ATP, ADP, DPN, TPN etc.) are compo nents of coenzymes.
13. **Deoxyribonucleic acids** (DNA) occur in the nucleus of the cell. They have 2-deoxyribose as pentose sugar. They contain adenine, guanine (both are purine bases) and cytosine and **thymine** both are (pyrimidine bases). They transfer heredity character from parents to offsprings. They have a double stranded α-helix structure. They replicate.

    Ribonucleic acids (RNA) occur in the cytoplasm of the cell. They contain ribose as pentose sugar. The bases present in RNA are adenine, guanine, cytosine and **uracil**. They control synthesis of proteins. They have a single stranded α-helix structure. They do not replicate.
14. Important structural differences between DNA and RNA

	DNA		RNA
(a)	DNA have A, G, C and T as bases	(a)	RNA have A, G, C and U as bases
(b)	They have 2-deoxyribose as sugar	(b)	They have ribose as sugar

K M C

(c)	They have double stranded structure.	(c)	They have single stranded structure.
(d)	They have large molecular mass which varies from 6×10^6 to 16×10^6 u.	(d)	They have relatively low molecular mass which may vary from 20,000 to 40,000 u.

15. There are three types of RNAs.

(a) Messenger RNA (*m* RNA). They carry the message of DNA for specific protein synthesis.

(b) Ribosomal RNA (*r* RNA). They provide the site for protein synthesis.

(c) Transfer RNA (*t* RNA). They transfer amino acids to the site of protein synthesis.

16. The arrangement of heterocyclic bases present in one strand of DNA are not identical with that of the other strand, but the base present in one strand of DNA forms H-bond with the specific base in other strand, such pairs of bases are called **complimentary bases**. Because of different sizes and geometries of the bases, two possible pairing in DNA are thymine (T) with adenine (A) through two hydrogen bonds (A = T) and cytosine (C) with guanine (G) through three H-bonds (C ≡ G).

17. Structural differences between DNA and RNA, consult Q. 14. DNA controls hereditary effects, while RNA controls synthesis of proteins.

(B) Every Day Chemistry

(i) Polymers

1. **Polymerisation:** The process in which simple (same or different types) and reactive molecules (called **monomers**) combine together to form macromolecules of high molecular mass, called **polymers** is known as polymerisation.
2. **Homopolymerisation:** Polymer formed by the polymerisation of infinite number of the same monomeric species is called homopolymerisation. Examples are polythene, PVC, polypropylene etc.
3. **Copolymerisation:** Polymer formed by the polymerisation of two or more different monomers, is called copolymerisation. For example, **(a)** buna-S is a copolymer formed by the polymerisation of 1, 3-butadiene and styrene, **(b)** buna-N is a copolymer of 1, 3-butadiene and acrylonitrile.

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(a) $n\,CH_2 = CH - CH = CH_2 + n\,C_6H_5CH = CH_2 \longrightarrow$

1, 3-Butadiene Styrene

$$\left[CH_2 - CH = CH - CH_2 - CH_2 - \underset{}{\overset{C_6H_5}{\overset{|}{CH}}}\right]_n$$

Buna-S

(b) $n\,CH_2 = CH - CH = CH_2 + n\,CH_2 = CHCN \longrightarrow$

1, 3-Butadiene Acrylonitrile

$$\left[CH_2 - CH = CH - CH_2 - CH_2 - \overset{CN}{\overset{|}{CH}}\right]_n$$

Buna-N

4. Polymers which are formed by the polymerisation of a single type of monomers, and thus they have only one type of repeating units, are known as **homopolymers**. Examples are polyethene, PVC, teflon etc. Polymers which are formed by the polymerisation of two or more types of monomer molecules, and thus they have two or more types of repeating structural units, are known as **copolymers**. Examples are buna-S, buna-N, nylon-6, 6 etc.

5. $-(CH_2 - CH(C_6H_5))_n-$ is a homopolymer since it is obtained from the polymerisation of styrene ($CH_2 = CHC_6H_5$) and has only one type of structural repeating unit.

6. $-(CH_2 - \underset{Cl}{\underset{|}{CH}})_n-$ is a homopolymer as it is made up of same monomer units i.e. $CH_2 = \underset{Cl}{\underset{|}{CH}}$ (Vinyl chloride)

7. **Condensation or step growth polymerisation.** The process in which two or more molecules, each having two functional groups, undergo a series of independent condensation reactions with the elimination of simple molecules like H_2O, HCl, NH_3 etc. to form macromolecules is called *condensation polymerisation*; and the product formed is called *condensed polymer*. For example, nylon-6,6 is formed by the condensation polymerisation of hexamethylenediamine and adipic acid.

$$n\,HOOC.(CH_2)_4.COOH + H_2N - (CH_2)_6 - NH_2 \xrightarrow{525\ K}$$

Adipic acid Hexamethylenediamine

$$\left[C - (CH_2)_4 - \overset{O}{\overset{||}{C}} - NH - (CH_2)_6 - NH\right]_n + n\,H_2O$$

Nylon-6, 6

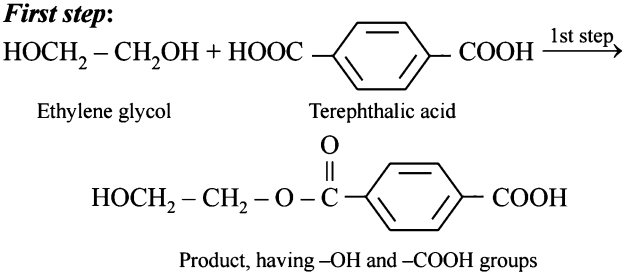
K M G

Addition or chain growth polymerisation. The process in which same or different molecules simply add on one another to form a macromolecule without elimination of a small molecule like H_2O, HCl etc. is called addition polymerisation, and the product formed is called addition polymer. For example, polythene is formed by polymerisation of ethene.

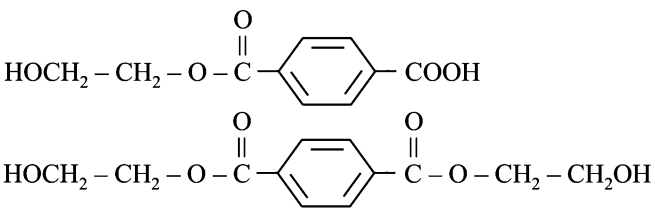
$$\underset{\text{Ethene}}{n\,CH_2 = CH_2} \longrightarrow \underset{\text{Polyethene}}{\left[CH_2 - CH_2 \right]_n}$$

8. **Addition polymers** are formed by the repeated addition of a large number of same or different monomers having double or triple bonds. Condensation polymers are obtained by the repeated condensation of a large number of same or different monomers (each having at least two functional groups).
   (i) Polyethene is addition polymer
   (ii) PTFE (polytetrafluoroethylene) is addition polymer.
   (iii) Polybutadiene is addition polymer.
   (iv) Bakelite is condensation polymer.
9. Step growth polymerisation or condensation polymerisation. For definition, consult Q 7. The reaction taken place in steps, i.e. the polymer grows stepwise, hence the name **step growth polymerisation**. For example, the two monomers, each having two functional groups, condense to form a product still having two functional groups (first step).

***First step*:**



***Second step*:**



Or

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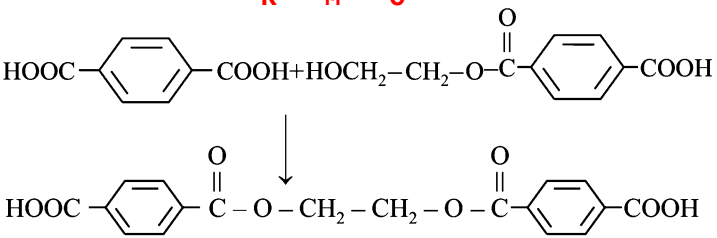


Thus each step gives a product which has two functional groups either of which may further react to form still higher product. The reaction goes on till a polymer is formed.

10. **Addition polymers:** Polymers which are formed by the repeated addition of a large number of same or different monomers having double or triple bond as the functional group are called addition polymers. The two types of addition polymers are
    (a) *Free radical polymers.* These are formed via free radical intermediates, e.g. polythene.
    (b) *Ionic polymers.* These are formed via ionic mechanism, e.g. PVC (polyvinyl chloride).
11. Free radical polymerisation of chloroprene (2-chloro-1,3-butadiene) gives neoprene.

$$n\,CH_2=\underset{\underset{Cl}{|}}{C}-CH=CH_2 \xrightarrow{O_2 \text{ or peroxides}} \left[CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2\right]_n$$

Chloroprene Neoprene

12. (a) Addition polymers: Polythene, PVC, neoprene
    (b) Condensation polymers: Nylon 6, 6
    (c) Copolymers: Buna-N, Buna-S.
13. **Classification on the basis of molecular forces present between polymer chains:**
    (a) *Elastomers.* The polymers in which polymer chains are held together by weakest forces, i.e. vander Waal's forces are called elastomers. Due to weak forces, polymer chains can be stretched and when the stretching force is withdrawn, polymers return to its original position. Examples are buna-S, buna-N, natural rubber, vulcanised rubber etc.
    (b) *Fibres.* The polymers in which polymer chains are held together by strong forces, like hydrogen-bonding and dipole-dipole interactions, are known as fibres. Examples are nylon, orlon, polyesters etc. They don't possess elasticity.

K M C

(c) *Thermoplastic polymers* are those in which polymer chains are held together by such intermolecular forces which are intermediate between those of elastomers and fibres. Examples are polythene, polypropylene, PVC etc. These are formed by addition as well as condensation polymerisations. These are linear in structure and can be easily moulded by heating.

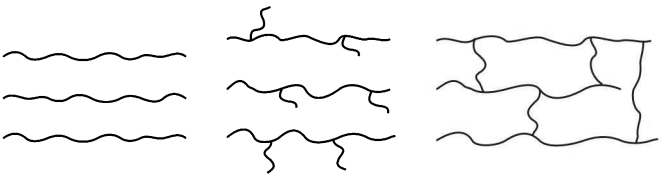
(d) *Thermosetting polymers* are those which have cross linked structures. These are formed by condensation reactions. On heating, these are permanently set into a solid, i.e. become hard and can't be remelted and re-worked. Examples are bakelite, melamine etc.

14. (a) Elastomers
(b) Fibres
(b) Thermoplastic polymers
(d) Thermosetting polymers.

15. Classification of polymers on the basis of structure:

(a) *Linear polymers*. They have long straight polymer chains. The different polymer chains are stacked over one another to give a close packed structure due to which they have high melting points, high densities and high tensile strengths. Examples are nylon, polyesters, high density polythene (HDPE) etc.

(b) *Branched chain polymers*. They have branched polymer chains. Due to branches, these polymers do not pack well and hence they have low melting points, low densities and low tensile strengths than the linear polymers. Examples are low density polythene (LDPE), glycogen, amylopectin etc.



Linear polymers Branched chain polymers Cross linked polymers

(c) *Three dimensional network polymers*. They have polymer chains which are joined together through two or more cross links, hence also known as cross linked polymers. They are hard, rigid and brittle. Examples are bakelite, urea-formaldehyde, melmac etc.

16. Refer Q, 13

17. Refer Q, 13.

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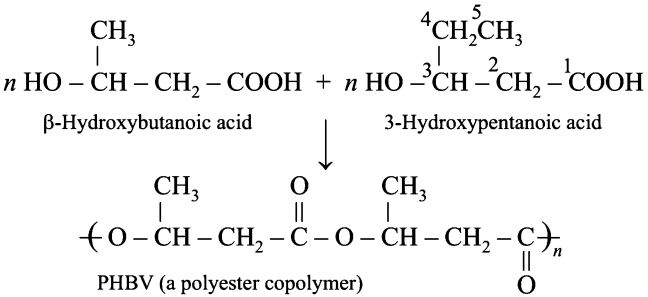
18. (a) **Elastomers:** These are rubber-like solids with elastic properties The polymer chains are held together by the weakest intermolecular forces so they can be stretched. Examples are buna-S and buna-N.

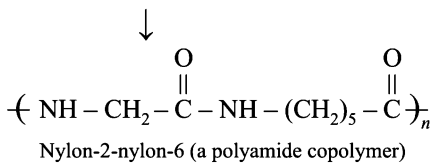
(b) **Condensation polymers:** Consult Q. 8. Example : nylon-6, 6.

(c) **Addition polymers:** Consult Q. 8. and Q. 10. Example polythene.

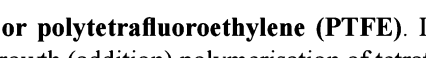
19. **Biodegradable polymers** are those which are decomposed by microorganisms. These polymers degrade, in biological systems, mainly by enzymatic hydrolysis and to some extent by oxidation. Examples are poly-β-hydroxybutyrate-Co-β-hydroxyvalerate (PHBV) and nylon-2-nylon-6.

PHBV is used in packaging, orthopaedic devices and in controlled release of drugs.

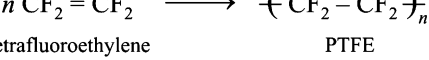




20. (i) **Polythene:** It is formed by addition polymerisation of ethene.



(ii) **Teflon or polytetrafluoroethylene (PTFE)**. It is formed by chain growth (addition) polymerisation of tetrafluoroethylene.



(iii) **Polyvinyl chloride (PVC).** It is a chain growth polymer of vinyl chloride.

$$n\,CH_2 = CHCl \longrightarrow \left(CH_2 - \underset{}{\overset{Cl}{\overset{|}{CH}}} \right)_n$$

Vinyl chloride PVC

(iv) **Orlon or polyacrylonitrile (PAN).** It is obtained by the addition (chain growth) polymerisation of acrylonitrile

$$n\,CH_2 = CHCN \longrightarrow \left(CH_2 - \overset{CN}{\overset{|}{CH}} \right)_n$$

Acrylonitrile PAN

(v) **Neoprene or duprene.** It is a polymer of chloroprene (2-chloro-1, 3-butadiene), formed by addition polymerisation

$$n\,CH_2 = \overset{Cl}{\overset{|}{C}} - CH = CH_2 \longrightarrow \left(CH_2 - \overset{Cl}{\overset{|}{C}} = CH - CH_2 \right)_n$$

Chloroprene Neoprene

(vi) **Buna-S or Styrene-butadiene rubber (SBR).** It is a copolymer of butadiene (1, 3-butadiene) and styrene (vinylbenzene). It is formed by addition polymerisation.

$$n\,CH_2 = CH - CH = CH_2 + n\,C_6H_5CH = CH_2 \longrightarrow$$

1, 3-Butadiene Styrene

$$\left(CH_2 - CH = CH - CH_2 - \overset{C_6H_5}{\overset{|}{CH}} - CH_2 \right)_n$$

(vii) **Buna-N.** It is a copolymer of butadiene and acrylonitrile (vinyl cyanide), formed by addition polymerisation.

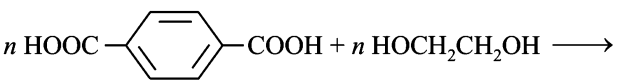
$$n\,CH_2 = CH - CH = CH_2 + n\,CH_2 = CHCN \longrightarrow$$

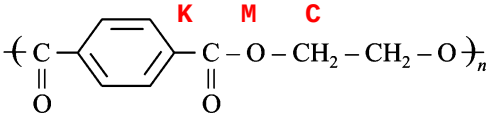
1, 3 – Butadiene Acrynonitrile

$$\left(CH_2 - CH = CH - CH_2 - CH_2 - \overset{CN}{\overset{|}{CH}} \right)_n$$

Buna-N

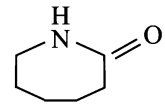
(viii) **Terylene or Dacron.** It is a step growth linear polyester fibre, formed by condensation polymerisation of ethylene glycol and terephthalic acid.





Terylene

(ix) **Nylon-6 or Perlon.** It is formed by the prolonged heating of caprolactam at 533–543 K. Caprolactam is first converted into 6-aminohexanoic acid which then undergoes condensation polymerisation to form nylon-6.



Caprolactam

$$\xrightarrow{533\text{-}543\ K} H_3\overset{+}{N}-(CH_2)_5-COO^-$$

6-Aminohexanoic acid

$$\longrightarrow \left(\overset{H}{N}-(CH_2)_5-\overset{O}{\overset{\|}{C}}\right)_n$$

Nylon-6

Since the starting material has *six carbon atoms*, nylon formed is known as **nylon-6**.

(x) **Nylon-6, 6.** It is obtained by condensation polymerisation of hexamethylene diamine and adipic acid. Thus it is a step growth polyamide copolymer.

$$n\,HOOC(CH_2)_4COOH + n\,H_2N(CH_2)_6NH_2 \longrightarrow$$

Adipic acid (a six carbon compound) — Hexamethylene diamine (a six carbon compound)

$$\left(\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH\right)_n$$

Nylon-6, 6

Since each of the starting material has six carbon atoms, nylon is named as nylon 6, 6.

(xi) **Nylon-6, 10.** It is obtained by condensation polymerisation of hexamethylene diamine (a six carbon monomer) and sebacic acid (a ten carbon monomer).

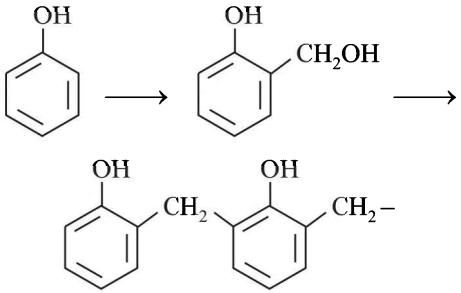
$$HOOC(CH_2)_8COOH + H_2N(CH_2)_6NH_2 \longrightarrow$$

Sebacic acid — Hexamethylene diamine

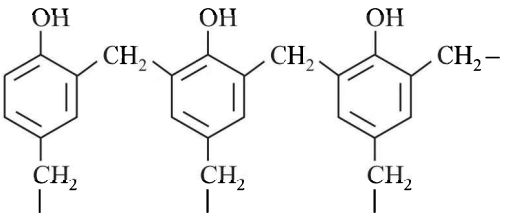
$$\left(\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH\right)$$

Nylon-6, 10

(xii) **Bakelite or Phenol-formaldehyde resin.** It is obtained by step growth polymerisation of phenol and formaldehyde. The initial product is linear and called **novolac** (used in paints), while the final product is highly branched thermosetting copolymer, and called bakelite.



Novolac



Bakelite

21. Nylon-6, 6 means that each of its two monomers contains six carbon atoms. For details, consult Q. 20 (x).

22. Nylon-6 means that it is formed only from one monomer which has six carbon atoms (caprolactam). Nylon-6, 6 means that it is a copolymer of two monomers, each of which has six carbon atoms, namely adipic acid and hexamethylene diamine (consult Q 20, ix and x)

23. (a) Bakelite is used in making electrical switches and switch boards.

(b) Nylon-6 fibres are used in making fabrics, carpets, ropes, tyre cords etc.

(c) PVC is used in making sheets, pipes, rain coats, table cloth, floor covering and electrical insulating coating on electrical cables.

(d) Nylon-6, 6: Consult uses of nylon-6.

24. Monomers of

(i) Buna-S : $CH_2 = CH - CH = CH_2$ and $C_6H_5CH = CH_2$

1, 3-Butadiene Phenylethene (Styrene)

(ii) Buna-N : $CH_2 = CH - CH = CH_2$ and $CH_2 = CHCN$

1, 3-Butadiene Acrylonitrile (Vinyl cyanide)

(iii) Neoprene : $CH_2 = \overset{\overset{Cl}{|}}{C} - CH = CH_2$

2-Chloro-1, 3-butadiene (Chloroprene)

(iv) Polypropene : $CH_3CH = CH_2$ (Propene)

(v) Polyethene : $CH_2 = CH_2$ (Ethylene or ethene)

(vi) Teflon : $CF_2 = CF_2$ (Tetrafluoroethylene), a addition polymer

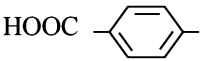
(vii) Polystyrene : $C_6H_5CH = CH_2$ (Styrene)

(viii) Bakelite : C_6H_5OH (Phenol) and HCHO (Formaldehyde), condensation polymer

(ix) Nylon-6 : Caprolactam

(x) Nylon-6, 6 : $H_2N(CH_2)_6NH_2$ (Hexamethylenediamine), and $HOOC(CH_2)_4COOH$ (Adipic acid)

(xi) Terylene : Ethylene glycol ($HOCH_2CH_2OH$) and

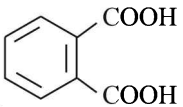


(Terephthalic acid)

(xii) PVC : $CH_2 = CH\,Cl$ (Vinyl chloride)

(xiii) Urea–formaldehyde resin : H_2NCONH_2 (Urea) and HCHO (formaldehyde)

(xiv) Glyptal : $HOCH_2CH_2OH$ (Ethylene glycol) and



(Phthalic acid)

(xv) Natural rubber : $CH_2 = \overset{\overset{CH_3}{|}}{C} - CH = CH_2$ (Isoprene) Addition polymer

(ii) Food preservatives

1. **Food preservatives:** Chemical substances which are added to protect food against decomposition (spoilage) by micro-organisms (bacteria, yeast and moulds) are called **food preservatives**. The most important preservative is sodium benzoate followed by potassium metabisulphite ($K_2S_2O_5$). Other examples are propionic acid, sorbic acid, table salt etc.
2. Sodium benzoate metabolizes to hippuric acid ($C_6H_5CONH\,CH_2COOH$) which is ultimately excreted through urine.

3. Potassium metabisulphite ($K_2S_2O_5$) is used in jams, squashes, pickles etc. Its preservative action is due to its decomposition by weak acid like carbonic acid (H_2CO_3) to SO_2 which dissolves in water to form sulphurous acid which inhibits the growth of micro-organisms.
4. Sweetening agents. Chemical substances which are sweet in taste but do not provide any calorie to our body are called artificial sweetening agents. These are excreted as such through urine. Examples are saccharin, aspartame, L-glucose etc.
5. Sweetness values as compared to sucrose are

   Alitame (2000) > Sucralose (650) > Saccharin (600) > Dulcin (500) > Aspartame (160)
6. Antioxidants. Chemicals used to prevent oxidation of fats in processed foods like potato chips, biscuits, breakfast serials are called antioxidants. Examples are butylated hydroxytoluene (**BHT**) and butylated hydroxyanisole (BHA). BHA is added to butter for increasing its storage time from months to years.

(iii) Detergents

1. **Synthetic detergents.** These are sodium sulphates of higher primary alcohols (e.g. lauryl alcohol, $C_{12}H_{25}OH$) or sodium salts of linear alkyl substituted benzene sulphonic acid. Common examples are

   $CH_3(CH_2)_{10}CH_2OSO_2O^-Na^+$ $CH_3(CH_2)_{10}CH_2-C_6H_4-SO_2O^-Na^+$

   Sodium lauryl sulphate Sodium *p*-lauryl benzene sulphonate

   In these detergents, active portion is negatively charged, hence these are commonly known as **anionic detergents.**
2. **Biodegradable detergents.** Detergents which are easily decomposed (degraded) by microorganisms are called biodegradable detergents. Detergents having a normal (straight) chain alkyl group, viz. sodium lauryl sulphate and sodium *p*-lauryl benzene sulphonate are biodegradable detergents.

   Non-biodegradable detergents. These detergents are not easily decomposed by microorganisms because they have branched chain alkyl group. Common example is sodium *p*-(1,3,5,7—tetramethyloctyl) benzene sulphonate.

   The above molecule has either and 1° alcoholic groups.
3. **Cationic detergents.** These are quaternary ammonium salts of amines with acetates, chlorides or bromides. Thus here long

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hydrocarbon chain has a positive charge, and hence called as cationic detergents. Example is

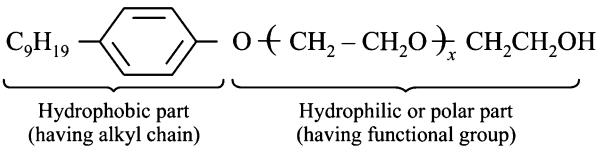
$$\left[CH_3(CH_2)_{15} - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N}} - CH_3 \right]^+ Br^- \quad \text{Cetyltrimethylammonium bromide}$$

4. **Anionic detergents.** Those detergents in which large part (hydrocarbon chain) of the molecule is anions are called anionic detergents. Examples are sodium lauryl sulphate and sodium *p*-lauryl sulphate.

5. **Non-ionic detergents.** These are esters of higher molecular mass alcohols with higher fatty acids. Example is

$$\underbrace{CH_3(CH_2)_{16}\,COO}_{\text{Stearic acid part}}\underbrace{\left(CH_2CH_2O\right)_n CH_2CH_2OH}_{\text{higher alcohol}}$$

Polyethyleneglycol stearate

6. 

The above molecule has ether and 1° alcoholic groups.

7. **Cleansing action of soap.** Cleansing action of soap is due to the fact that soap moecules form micelles around the oil droplets in such a way that hydrophobic part of stearate ions is in the oil droplet and hydrophilic part projects out of the oil droplet like the bristles. Since the polar groups can interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface. Thus soap helps in emulsification and washing away of oils and fats.

   Hard water contains Ca^{2+} and Mg^{2+} ions. These ions form **insoluble** calcium and magnesium soaps when sodium or potassium soaps are dissolved in hard water.

(iv) Drugs

1. Treatment of diseases by chemicals which selectively inhibit the growth of parasitic organisms is known as **chemotherapy**. For example, aspirin (an analgesic) is used for relieving pain, chloronycetin (an antibiotic) is used for typhoid fever etc.

2. **Analgesics.** Analgesics are drugs used to reduce or abolish pain. They are of two types

(a) Non-narcotic (non-additive). These are not habit forming. Examples are aspirin and ibuprofen.

(b) Narcotic (additive). These are habit forming and also produce sleep, e.g. morphine and heroin.

3. (i) Analgesics. Refer Q. 2.

(ii) **Narcotic analgesics.** Consult Q. 2.

(iii) **Tranquillizers.** Drugs which are used for the treatment of stress, fatigue, mild and severe mental diseases are called *tranquillizers*. Examples are equanil, veronal, meprobamate, iproniazid, etc.

(iv) **Antiseptics.** Chemical substances which prevent the growth of microorganisms and may even kill them, but safe to be applied on living tissues are called antiseptics. Examples are tincture of iodine, iodoform, *n*-hexylresorcinol, acriflavine etc.

(v) **Disinfectants.** Chemical substances which kill microorganisms but are not safe when applied on living tissues are called disinfectants. Examples are phenol, chlorine etc.

(vi) **Antacids.** Those substances which neutralize the excess acid and raise the pH to an appropriate level in stomach are called *antacids*. Examples are sodium bicarbonate, $Mg(OH)_2 + Al(OH)_3$, ranitidine etc.

(vii) **Antihistamines.** Antihistamines are amines used as drugs to control the allergy effects produced by histamines. Examples are cetrizine, brompheniramine, benadryl (diphenhydramine), antergan, trimeton (avil) etc.

(viii) **Antifertility drugs.** Chemical substances used to check pregnancy in women are called antifertility drugs or birth control pills or oral contraceptives. These control the female menstrual cycle and ovulation. Examples are ethinyl oestradiol, norethindrone, mestranol etc.

(ix) **Antibiotics.** Antibiotics are substances produced completely or partially by chemical synthesis, and when given in low concentrations inhibit the growth or kill the microorganisms by intervening in their metabolic activities. Examples are penicillin, chloramphenicol, streptomycin, amoxycillin etc.

(x) **Antimicrobials.** Those drugs which kill microbes (microorganisms) are called antimicrobials e.g. penicillin, erythromycin, tetracycline etc.

(xi) **Antipyretics.** Chemicals which are used to bring down the body temperature during high fever are called antipyretics. Examples are *aspirin, paracetamol, phenacetin* etc.

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4.

	Antiseptics		Disinfectants
(a)	They prevent the growth of microorganisms or may kill them	(a)	They kill the microorganisms
(b)	They are safe to the living tissues	(b)	They are not safe to living tissues, e.g. phenol causes burning sensations
(c)	They are generally applied on cuts, wounds, ulcers and diseased skin surfaces.	(c)	They are used to kill micro-organisms present in drains, floors etc.
(d)	Examples; Tincture of iodine, dettol, savlon etc.	(d)	Examples: Phenol (≥ 1.0% solution) and chlorine (0.2 to 0.4 ppm.)

5. Phenol. A 0.2% solution of phenol acts as antiseptic, while its 1% solution acts as disinfectant.
6. Dettol is a mixture of chloroxylenol (a phenol) and α-terpineol in a suitable solvent.
7. Tincture of iodine is 2-3% solution of iodine in alcohol and water. It is used as a powerful antiseptic on wounds.
8. Antibiotics, which prevent the growth and multiplication of bacteria are called **bacteriostatic** e.g. chloramphenicol, tetracycline, erythromycin etc. (*static*-inhibitory); while those which kill the bacteria are called **bactericidal** (*cidal*-killing), e.g. penicillin, ofloxacin etc.
9. Tetracycline is bacteriostatic; penicillin is bactericidal.
10. In medicinal chemistry, bacteria are mainly divided into two types depending upon their staining characteristics. Bacteria which retain the violet stain of **Gram's reagent** (crystal violet + iodine) are known as **Gram positive bacteria**, while those which do not retain the violet colour of Gram's reagent are known as **Gram negative**.
11. **Broad spectrum antibiotics.** Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are called *broad spectrum antibiotics*, e.g. chloramphenicol which is used for typhoid, dysentery, acute fever, urinary infections etc. Other broad spectrum antibiotics are tetracyclines, ampicillin and neomycin.
12. **Narrow spectrum antibiotics.** Antibiotics which are effective mainly against Gram positive or Gram-negative bacteria are called narrow spectrum antibiotics. Penicillins and erythromycin are

effective against Gram-positive bacteria; while streptomycin and gentamycin are used against Gram-negative bacteria.

13. For definition of antibiotics, refer Q 3 (ix).

	Broad spectrum antibiotics		Narrow spectrum antibiotics
(i)	Definition, refer Q 11	(i)	Definition, refer Q. 12
(ii)	Sensitivity test is not required.	(ii)	Sensitivity test is required
(iii)	They can be absorbed rapidly.	(iii)	They are absorbed slowly.

14. Antibiotics which are effective against only a few harmful bacteria are called limited **spectrum antibiotics**. Example is penicillin.

15. (i) Ranitidine is an antacid and used to prevent acidity in stomach.

(ii) *Paracetamol* is a non-narcotic analgesic used to reduce fever and body ache.

(iii) *Tincture of iodine* is an antiseptic and applied on wounds.

16. (i) *Brompheniramine* is an antihistamine and used for treatment of sneezing, hay fever etc.

(ii) *Aspirin* (Acetylsalicylic acid) is a non-narcotic analgesic and used for releiving pain.

(iii) *Equanil* is a tranquillizer and used for releiving tension (de pression).

(C) Value Based Questions

1. (a) This action shows Sonali's concern for the health and well-being of her fellow students and her alert and helping nature.

The principal has shown promptness in taking action that shows she is duti bound and is concerned about the health of the students.

(b) The two water soluble vitamins are vitamin B_2 (riboflavin) and vitamin C (ascorbic acid).

2. (i) The incident shows the caring nature of Mrs. Anuradha. She values human life irrespective of who it is.

(ii) Deficiency of Vitamin B_{12} causes pernicious anaemia.

(iii) Water soluble vitamin : Vitamin B_2 (riboflavin).

3. (a) Sugar free contains artificial sweetening agents.

(b) Saccharin, aspartame, alitame, etc.

(c) The chemist is helpful, (not greedy) and concerned for others health.

4. (a) PHBV and nylon-2-nylon-6.

(b) These polymers are biodegradable, hence these are suitable for environment.

(c) We should prefer to use eco-friendly modern technologies. The new eco-friendly modern technologies are beneficial for our environment as well as for us.

5. (a) This is because teflon is non-sticky, chemically inert, oleophobic, hydrophobic and possesses fairly high heat resistance.

(b) Tetrafluoroethylene is the monomer of teflon; $F_2C = CF_2$

(c) Expresses opinion, sensitive and supportive towards others, knowledgable, awareness etc. are some values displayed by Reena.

6. (a) Rohan should follow Ratan's advice as gelusil's composition suggests that it is a weak base which neutralizes the excess acid.

(b) Helping and caring behaviour, awareness, decision making,etc. are some values displayed by Ratan.

7. (a) Sting of the honey bee contains methanoic acid. Baking soda is sodium bicarbonate which is a mild base and is thus used for the treatment of honey bee bite..

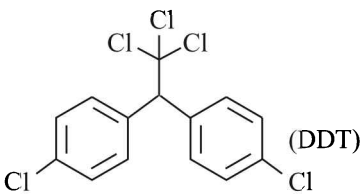
(b) The colleague was quick to respond and had a knowledge about the infection and its treatment.

8. (a) $CH_3 - N = C = O$

(b) Carbylamine test produces isocyanide gas which has very pungent and suffocating odour. Thus, precautions are necessary.

(c) The Bhopal gas tragedy raises concern over the precautionary measures taken in industries. A plant which is using such harmful chemicals should follow all the guide lines very strictly so that not a single loop hole is left which can result in damage to lives and properties.

9. (a)



(DDT)

IUPAC name of DDT:

2, 2-bis (4-chlorophenyl)–1, 1, 1-trichloroethane.

(b) Sensitivity towards environment, awareness about uses of chemicals, concern about nature etc. are some values shown by Rohan.

10. (a) The compound is chloroform.

$$\underset{\text{Air}}{2CHCl_3 + O_2} \xrightarrow{\text{light}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

(b) Sensitivity towards others health, perfection, profession awareness, knowledge about products and their uses etc.

11. (a) Vitamin D

(b) This is because sunlight is a richest source of vitamin D.

(c) Awareness towards health, helpful to others, presence of mind, understand his moral duty etc. are some values displayed by Ramendra's supervisor.

12. (a) Alcohol used for drinking purpose is ethanol.

(b) Continuous use of alcohol damages liver.

(c) Awareness of the bad effects of 'drink and drive' concern for well being of people etc.

13. (a) Ethanol.

(b) Methanol

(c) We must make purchasing from a standard shop.

PART A

Physical Chemistry

CHAPTER 1

Write the definition/ example(s)/type(s) of ...

(A) *The Solid State*

1. Define the following:

(i) Ferromagnetism

(ii) Paramagnetism **[Delhi Comptt. 2010, 2012]**

(iii) Schottky defect

(iv) Interstitial defect **[Delhi Comptt. 2010]**

(v) Doping **[Delhi Board 2012]**

(vi) Frenkel defect

(vii) F-centres

(viii) Ferrimagnetism

2. Give example(s) for the following :

(i) An ionic compound which shows Frenkel defect. **[Outside Delhi Comptt. 2010]**

(ii) Amorphous solids.

(iii) A ferroelectric solid

(iv) Anti-ferroelectric solid.

(v) Hydrogen bonded crystals.

(vi) Metallic crystal with low melting point of about 100 °C.

3. What is a semiconductor? What are the two main types of semiconductors? **[Delhi Comptt. 2012]**

4. What type of stoichiometric defect is shown by AgCl? **[Delhi Board 2013]**

5. (i) What type of non-stoichiometric defect is responsible for pink colour of LiCl?

(ii) What type of stoichiometric defect is shown by NaCl? **[Outside Delhi 2014]**

6. (i) Write the type of magnetism observed when the magnetic moments are oppositely aligned and cancel out each other.

(ii) Which stoichiometric defect does not change the density of the crystal? **[Outside Delhi 2014]**

7. What type of substances show antiferromagnetism? **[Delhi Board 2008]**

8. What type of interactions hold the molecules together in a polar molecular solid? **[Outside Delhi 2010]**

9. What type of defect arises when a solid is heated? **[Outside Delhi Comptt. 2012]**

10. (a) What type of semiconductor is obtained when silicon is doped with boron?

    (b) What type of magnetism is shown in the following alignment of magnetic moments?

    ↑ ↑ ↑ ↑ ↑ ↑

    (c) What type of point defect is produced when AgCl is doped with $CdCl_2$? **[Delhi Board 2013]**

11. What type of substances would make better permanent magnets, Ferromagnetic or Ferrimagnetic? **[Delhi Board 2013]**

12. What type of stoichiometric defect in crystals increases the density of a solid? **[Delhi Board 2011, Outside Delhi 2012]**

13. Which type of crystals exhibits piezoelectricity?

(B) Solutions

1. Define the following:

   (i) Mole fraction

   (ii) van't Hoff factor

   (iii) Molality of solution **[Outside Delhi 2009]**

   (iv) Osmotic pressure **[Delhi Comptt. 2009, Delhi Board 2011, Outside Delhi 2010, 2013]**

   (v) Osmosis **[Outside Delhi 2010, Delhi Board 2011]**

   (vi) Reverse osmosis **[Outside Delhi 2011]**

   (vii) Ideal solution **[Outside Delhi 2013, Delhi 2014]**

   (viii) Henry's law

   (ix) Boiling point elevation constant for a reaction **[Outside Delhi 2012, 2014]**

   (x) Isotonic solutions. **[Delhi Board 2012, 2014]**

   (xi) Azeotropes **[Delhi Board 2014]**

2. Give example(s) for the following : K M C

(i) Minimum boiling point azeotrope

(ii) Maximum boiling point azeotrope

(iii) A solution that contains a gas dissolved in a liquid

(iv) A solution containing a liquid solute in a solid solvent

3. State Raoult's law for solutions of volatile solutes.

[Delhi 2014, 2013C, 2012C, 2009C, 2008; Outside Delhi 2008]

4. State Henry's law correlating the pressure of a gas and its solubility in a solvent and mention two applications for the law.

[Delhi Board 2008, 2014]

5. What type of intermolecular attraction exists in each of the following pairs of compounds?

(i) *n*-Hexane and *n*-octane

(ii) Methanol and acetone **[Delhi Comptt. 2010]**

6. What types of membranes are used in reverse osmosis ? Name one such membrane.

7. What type of azeotrope is formed an mixing nitric acid with water?

8. What type of liquids from ideal solutions?

C. *Electrochemistry*

1. Define the following

(i) Molar conductivity **[Delhi Board 2009, 2012]**

(ii) Faraday's first law of electrolysis. **[Delhi Board 2014]**

(iii) Limiting molar conductivity

(iv) Secondary batteries **[Outside Delhi 2014]**

2. What is a primary cell? Give an example. **[Delhi Board 2008]**

3. State Kohlrausch law of independent migration of ions. How can the degree of dissociation of acetic acid in a solution be calculated from its molar conductivity data? **[Outside Delhi Comptt. 2012]**

(D) *Chemical kinetics*

1. Define the following :

(i) Order of reaction :

[Delhi Board 2008, 2010, Delhi Comptt. 2009, Outside Delhi 2010]

(ii) Rate of reaction **[Delhi, 2010]**

(iii) Activation energy of a reaction **[Outside Delhi 2011]**

(iv) Molecularity of a reaction **[Outside Delhi Comptt. 2011, Outside Delhi 2010]**

(v) Rate determining step of a reaction

(vi) Pseudo first order reaction. **[Outside Delhi Comptt. 2011, Delhi Board 2014]**

(vii) Half-life of a reaction **[Outside Delhi 2014]**

(viii) Photosensitisation?

2. Give example(s) of the following :

(i) zero order reaction.

(ii) Reaction whose order of reaction is fractional.

(iii) First order reaction.

(iv) Reaction, where order and molecularity are same.

3. What is meant by the 'rate constant, *k*' of a reaction? If the concentration is expressed in mol L^{-1} and time in seconds, what will be the units of rate constant *k* for (i) zero order reaction (ii) first order reaction? **[Delhi Board 2008]**

(E) Surface chemistry

1. Define the following :

(i) Electrophoresis **[Outside Delhi 2008, Outside Delhi Comptt. 2009, 2010, 2011]**

(ii) Tyndall effect. **[Delhi Board 2009, Outside Delhi Comptt. 2009, 2010, 2011]**

(iii) Coagulation process **[Outside Delhi 2009, 2010, Outside Delhi Comptt. 2010]**

(iv) Shape-selective catalysis **[Outside Delhi Comptt. 2009, Outside Delhi 2001, 2012]**

(v) Dialysis. **[Outside Delhi Comptt. 2009, 2011]**

(vi) Peptization **[Outside Delhi 2012]**

(vii) Reversible sols **[Outside Delhi 2010]**

(viii) Chemisorption **[Delhi Board Comptt. 2011]**

(ix) Micelles

(x) Aerosol **[Delhi Board 2012, Outside Delhi 2012]**

2. Give example(s) for the following : K M C

(i) Oil in water

(ii) Water in oil emulsion **[Delhi Board 2014]**

(iii) Lyophilic

(iv) Lyophobic sol **[Delhi Board 2014]**

(v) Sol

(vi) Gel **[Delhi Board 2014]**

3. What are the dispersed phase and dispersion medium of the following colloidal systems:

(i) Smoke

(ii) Milk **[Delhi Board 2013]**

4. What are the dispersed phase and dispersion medium in milk? **[Outside Delhi 2014]**

5. What are lyophobic colloids? Give an example. **[Outside Delhi 2011]**

6. Give an example of shape-selective catalyst. **[Delhi Board 2010]**

7. What are emulsions? Give one example. **[Delhi Board 2010, Outside Delhi Comptt. 2009, Outside Delhi 2012, 2013, 2014]**

8. What are lyophilic and lyophobic sols? Give one examples of each type. Which one of these two types of sols is easily coagulated and why? **[Delhi Board 2008, 2013]**

9. What is an adsorption isotherm? Describe Freundlich adsorption isotherm. **[Outside Delhi Comptt. 2012]**

(A) The Solid State

1. (i) **Ferromagnetism:** When the magnetic dipoles are aligned in same direction so that the substance is strongly attracted by magnetic field, the phenomena is called ferromagnetism.

(ii) **Paramagnetism:** This type of magnetism arises due to presence of unpaired electrons in the metal of a substance due to which it is weakly attracted by magnetic field.

(iii) **Schottky defect:** It occurs when equal number of cations and anions are missing from the lattice sites. It decreases the density of the solid.

For example: NaCl, KCl.

(iv) **Interstitial defect:** When some constituent particles (atoms or molecules) occupy an interstitial site, the defect is called interstitial defect It increases the density of the solid.

For example: Non-ionic solids.

(v) **Doping :** Increasing conductivity of a semi-conductor (group 14 elements) by adding an impurity from group 13 or group 15 is called doping.

(vi) Frenkel defects is a combination of two basic types of point defects : Schottky and interstitial. It occurs when an ion leaves its position in the lattice and occupies an interstitial site leaving a gap in the crystal.

(vii) When there is an excess of metal ions in non-stoichiometric compounds, the crystal lattice has vacant anion sites. These sites are occupied by electrons. The anion sites occupied by electrons are called F-centres.

(viii) Ferrimagnetism is the phenomenon shown by substances in which the number of magnetic moments oriented in one direction out number those in the other direction.

Examples are Fe_3O_4 and ferrites of formula $M^{2+}Fe_3O_4$, where M = Mg, Cu and Zn.

2. (i) AgBr

(ii) Glass, rubber and plastics.

(iii) Ferroelectric solid — Barium titanate, $BaTiO_3$.

(iv) Anti-ferroelectric solid — Lead zirconate, ($PbZrO_3$).

(v) Ice (solid form of H_2O) is an example of hydrogen bonded crystal.

(vi) Crystal of sodium metal (melting point 98 °C).

3. A semiconductor is a substance in which the gap between valence band and conduction band is very small and the electron can jump from valence band to conduction band by supplying small amount of heat. Two types of semiconductor are following:

(i) **Intrinsic semiconductor:** Conduction is due to jumping of electron from valence band to conduction band on increasing temperature.

(ii) **Extrinsic semiconductor:** Conduction is due to addition of impurity i.e. doping. Extrinsic semiconductor is further divided into following two types:

(a) *n-Type semiconductor:* When element of group 15 impurity is added to element of group 14, conductivity increases due to movement of extra electrons.

(b) *p-Type semiconductor:* When element of group 13 impurity is added to element of group 14, conductivity increases due to movement of holes.

4. Frenkel defect

5. (i) Metal excess defect due to anionic vacancies.

(ii) Frenkel defect

6. (i) Anti-ferromagnetism

(ii) Frenkel defect

7. Substances like MnO in which the magnetic dipoles are equal and oppositely oriented exhibit antiferromagnetism.

8. The molecules of a polar solid are held together by dipole-dipole interactions.

9. Metal excess defect arises when a solid is heated.

10. (a) When Si is doped with B, *p*-type semiconductor is produced.

(b) Ferromagnetism is shown by the given alignment of magnetic moments.

(c) Impurity defect is produced when AgCl is doped with $CdCl_2$.

11. Ferromagnetic substances would make better permanent magnets because when a ferromagnetic substance is placed in a magnetic field, all domains get oriented in the direction of magnetic field and a strong magnetic effect is produced.

12. Interstitial defect increases the density of solid because besides being present at the interstitial sites, some species (atoms / molecules) are also present in interstitial sites.

13. Asymmetric crystals.

(B) Solutions

1. (i) **Mole fraction** (x) of a component in a solution is defined as the ratio between the number of moles of that component to the total number of moles of all the components of the solution.

i.e. mole fraction of a component A in solution is:

$$x_A = \frac{n_A}{n_A + n_B \ldots n_i}$$

(ii) **van't Hoff factor (*i*)** is a correlation factor for molecular mass as calculated using colligative properties and is given by:

$$i = \frac{\text{Observed value of colligative property}}{\text{Normal value of colligative property}}$$

(iii) **Molality** is defined as the number of moles of solute dissolved per kg of the solvent. It is denoted by m.

$$m = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$$

Its units are mol kg^{-1}

(iv) **Osmotic Pressure:** The pressure which must be applied on the solution side to prevent the flow of solvent into the solution through the semi-permeable membrane is called osmotic pressure.

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

(vi) **Reverse Osmosis:** The direction of osmosis can be reversed if a pressure greater than osmotic pressure is applied on solution side. As a result, the pure solvent now flows from solution side to solvent side through semi-permeable membrane and the process is called reverse osmosis.

(vii) **Ideal Solution:** An ideal solution is one which obey's the Raoult's law under all conditions of temperature and concentrations. For an ideal solution, $\Delta_{mix}H = 0$ and $\Delta_{mix}V = 0$.

At molecular level, for an ideal solution, *A-B* interactions are nearly the same as *A-A* and *B-B* interactions.

For example: *n*-hexane and *n*-heptane, benzene and toluene etc.

K M C

(viii) **Henry's law:** See Q.1 of section B.

(ix) **Boiling point elevation constant:**

$\Delta T_b = K_b m$

where, K_b is boiling point elevation constant and 'm' is the molality of the solution.

Thus, K_b is defined as the elevation in boiling point of a solution when the concentration of the solution is 1 molal.

(x) **Isotonic solutions:** Those which have the same osmotic pressure at a given temperature.

(xi) **Azeotropes:** A liquid mixture having a definite composition and boiling like a pure liquid is called an azeotropic mixture.

2. (i) Ethanol – water system.

(ii) $HNO_3 - H_2O$ system.

(iii) Aerated water.

(iv) Hydrated salts, i.e., contain water of crystallisation $CuSO_4.5H_2O$.

3. Raoult's law states that for a solution of volatile solute, the partial vapour pressure of each component in the solution is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of that component in the pure state.

4. **Henry's law:** According to this law, at constant temperature, the solubility of a gas (x) in a liquid is directly proportional to the pressure of the gas (P), i.e.

$P \propto x$

or, $P = K_H x$ K_H = Henry's constant

Important applications of Henry's law: It is used in

(i) production of carbonated beverages

(ii) deep sea diving

(iii) function of lungs

5. (i) Dispersion forces

(ii) Hydrogen bonding

6. The pressures required for reverse osmosis are quite high. Hence, membranes which can withstand high pressures are used.

Cellulose acetate is permeable to water, but impermeable to impurities and ions present in sea water.

7. Maximum boiling point azeotrope.

8. Liquids having similar structures and polarities.

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C. *Electrochemistry*

1. (i) Molar conductivity (Λ_m) of a solution is defined as the conductance of a solution which contains one mole of the electrolyte such that the entire solution is placed between the two electrodes kept 1 cm apart.

   i.e. $\Lambda_m = \frac{\kappa}{C}$

   (ii) According to this 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.

   (iii) **Limiting molar conductivity (Λ_m°):** It is that value of molar conductivity which is obtained when the concentration of the solution approaches zero, i.e. at infinite dilution.

   (iv) **Secondary batteries:** These are those cells which can be reused again by reversing the cell reaction. For example, lead storage battery, Ni-Cd battery etc.

2. Primary cells are those in which the redox reaction occurs only once. The cell becomes dead after sometime and cannot be reused again. For example: Leclanche cell, mercury cell.

3. **Kohlrausch law:** It states that the limiting molar conductivity of an electrolyte can be represented as the sum of the limiting conductivities of the cation and the anion individually.

   i.e. $\Lambda_m^\circ (A_xB_y) = x\,\lambda^\circ_{A^{y+}} + y\,\lambda^\circ_{B^{x-}}$

   The degree of dissociation (α) for a weak electrolyte like acetic acid is given by:

   $$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ}$$

   where Λ_m^C is molar conductivity and Λ_m° is limiting molar conductivity.

(D) *Chemical kinetics*

1. (i) Order of reaction is defined as the sum of the powers to which various concentration terms are raised in the rate law expression of the reaction.

(ii) **Rate of a reaction:** It is defined as the change in the concentration of reactant or product with time.

$$\text{Rate of a reaction} = \frac{\text{decrease in conc. of reactants}}{\text{time}}$$

or

$$= \frac{\text{increase in conc. of products}}{\text{time}}$$

Its units are mol L^{-1} $time^{-1}$.

(iii) **Activation energy:** The minimum extra amount of energy that must be supplied to reactant molecules so that their energy becomes equal to threshold value is called activation energy. It is denoted by E_a.

(iv) **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 the reaction.

(v) **Rate determing step of a reaction:** For a complex reaction, the overall rate of the reaction depends upon the slowest step of the reaction which is called the rate determining step of the reaction.

(vi) **Pseudo first order reaction:** In some cases, the concentration of one of the reactants remains practically constant during the reaction even after the completion of the reaction

For ex: For a reaction : $A + B \rightarrow$ Products.

if $[A]_0 = 0.01$ M and $[B]_0$ (solvent) = 55.5 M

then, after reaction, $[B] = 55.49$ M i.e. it does not change much.

For such reaction, rate = $K_0\,[A]$ where $K_0 = k\,[B]$

The reaction thus behaves as a first order reaction with respect to A. Such reactions are called pseudo first order reactions.

(vii) **Half-life of a reaction:** It is the time during which the initial concentration of the reactant is reduced to half.

(viii) It is a process (or a chemical reaction) in which a photosensitive substance is used to start a photochemical reaction.

2. (i) (a) $2NH_3 \xrightarrow{W} N_2 + 3H_2$ Rate = k $[NH_3]^0$ = k

(b) $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$ Rate = k $[H_2]^0\,[Cl_2]^0$ = k

(c) $2HI \xrightarrow{Au} H_2 + I_2$ Rate = k $[HI]^0$ = k

(ii) (a) $H_2 + Br_2 \longrightarrow 2HBr$ Rate = k $[H_2]^1 [Br_2]^{1/2}$

(b) $CH_3CHO \longrightarrow CH_4 + CO$ Rate = k $[CH_3 CHO]^{3/2}$

(c) $CO + Cl_2 \longrightarrow COCl_2$ Rate = k $[CO]^2 [Cl]^{1/2}$

(iii) Example are

(a) $2N_2O_5 \longrightarrow 4NO_2 + O_2$ Rate = k $[N_2O_5]$

(b) $2H_2O_2 \longrightarrow 2H_2O + O_2$ Rate = k $[H_2O_2]$

(c) $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$ Rate = k $[SO_2Cl_2]$

(d) $C_2H_5Cl \longrightarrow C_2H_4 + HCl$ Rate = k $[C_2 H_5 Cl]$

(iv) Dissociation of HI.

$2HI \longrightarrow H_2 + I_2$

Order of reaction = 2

Molecularity = 2.

3. Rate constant, $k = \dfrac{\text{Rate}}{(\text{Conc.})^n}$

Thus, rate constant (k) is defined as the rate of reaction when the concentration of reactants is taken to be unity.

As $k = \dfrac{\text{Rate}}{(\text{Conc.})^n} = \dfrac{\text{mol L}^{-1}\text{ s}^{-1}}{(\text{mol L}^{-1})^n}$

$\therefore$ Units of k for (i)zero order reaction: mol L^{-1} s^{-1}

(ii)first order reaction : s^{-1}

(E) Surface chemistry

1. (i) The movement of colloidal particles under an applied electric field is called electrophoresis.

(ii) When a beam of light is passed through a colloidal solution and viewed perpendicular to the path of incident light, the path of light becomes visible. This phenomena is called Tyndall effect.

(iii) The process of setting of colloidal particles is called coagulation.

(iv) The catalytic reaction which depends on the pore structure of the catalyst and the size of reactant and product molecules is called shape-selective catalysis. For example: reactions involving reactions involving zeolites.

(v) It is the process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane.

(vi) **Peptization:** It is a process of converting a freshly prepared precipitate into colloidal sol by shaking it with a dispersion medium in the presence of a small amount of electrolyte.

(vii) **Reversible sols:** The sols that can be made again by simply remixing with the dispersion medium and shaking are called reversible sols. Lyophilic sols are reversible sols.

(viii) When the forces of attraction existing between the adsorbate and adsorbent molecules are almost of the same strength as chemical bonds, the adsorption is called chemical adsorption or chemisorption.

(ix) **Micelles:** Some substances at low concentrations behave as strong electrolytes but at higher concentrations, they show colloidal behaviour due to formation of aggregated particles called micelles.

(x) **Aerosol:** It is a colloidal system in which dispersion medium is gas and dispersed phase is either solid or liquid. For example: smoke.

2. (i) Oil in water :Milk

(ii) Water in oil :Butter

(iii) Lyophilic sol:Starch sol

(iv) Lyophobic sol :Metal sulphide sol

(v) Sol:Muddy water

(vi) Gel :Cheese

3.

	Colloidal system	**Dispersed phase**	**Dispersion medium**
(i)	Smoke	Solid	Gas
(ii)	Milk	Liquid	Liquid

4. Refer sol. no. 3 (ii) of section E.

5. Lyophobic means liquid-hating. These colloids cannot be prepared by simply mixing the dispersed phase with the dispersion medium. They can be prepared by special methods only. They are irreversible. For example: colloids of metals, colloids of metal sulphides, etc.

6. Zeolite or ZSM-5

7. Emulsions are colloidal solutions in which both dispersed phase and dispersion medium are liquids.

Example: Milk, cream, etc.

8. **Lyophilic sols:** In lyophilic sols, the particles of dispersed phase have strong affinity for particles of dispersion medium. For example: starch, rubber, etc.

Lyophobic sols: In lyophobic sols, particles of dispersed phase have little or no affinity for particles of dispersion medium. For example: As_2S_3 sol.

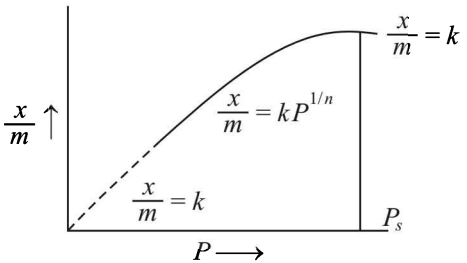
Lyophobic sols get easily coagulated on the addition of a small amount of electrolytes or by heating or even shaking as they are not stable.

9. A plot between the amount of gas adsorbed per gram of adsorbent $\left(\frac{x}{m}\right)$ and the pressure of the gas (adsorbate) at constant temperature is called adsorption isotherm.

Freundlich adsorption isotherm gives the relation:

$$\frac{x}{m} = k\,P^{1/n} \text{ where, } k \text{ and } n \text{ are constants}$$

The plot is:



This isotherm explains the behaviour of $\frac{x}{m}$ with pressure; $\frac{1}{n}$ can have any value between 0 and 1.

(i) When $\frac{1}{n} = 0, \frac{x}{m} = k$ which shows adsorption is independent of pressure.

(ii) When $\frac{1}{n} = 1, \frac{x}{m} = kP$, i.e. adsorption varies directly with pressure.

However, at high P, saturation reaches which cannot be explained by Freundlich isotherm.

CHAPTER 2

Why does this happen?

(A) The Solid State

1. Account for the following:

(i) Frenkel defects are not found in alkali metal halides.

(ii) Schottky defect lowers the density of related solids.

(iii) Impurity doped silicon is a semiconductor.

[DelhiBoard2008]

(iv) Fe_3O_4 is ferrimagnetic at room temperature but becomes paramagnetic at 850 K.

(v) Zinc oxide on heating becomes yellow.

(vi) Frenkel defect does not change the density of AgCl crystals.

[Outside Delhi Comptt. 2008]

(vii) Glass considered as a supercooled liquid

[Outside Delhi Comptt. 2008]

(viii) Stability of a crystal is related to the magnitude of its melting point. **[Outside Delhi Comptt. 2009]**

(ix) Crystalline solids are anisotropic in nature. **[DelhiBoard2011]**

(x) Some glass objects recovered from ancient monuments look milky instead of being transparent.

[Outside Delhi Comptt. 2012]

(xi) LiCl crystal become pink on heating with Li vapours.

[Outside Delhi Comptt. 2012, Outside Delhi 2014]

(xii) Ionic solids, which have anionic vacancies due to metal excess defect, develop colour.

(B) Solutions

1. Account for the following :

(i) The depression in freezing point of water observed for same concentration of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order as stated above.

[Delhi Board Comptt. 2008]

(ii) Osmotic pressure as compared to other colligative properties is preferred for the determination of molar masses of solutes in solution. **[Outside Delhi 2010]**

(iii) Molality is preferred over molarity as a unit of concentration. **[Outside Delhi Comptt. 2010]**

(iv) A solution of chloroform and acetone shows negative deviation from Raoult's law. **[Delhi Comptt. 2011]**

(v) Positive deviation from Raoult's law is shown by the mixture of ethanol and acetone. **[Outside Delhi 2014]**

(vi) Aquatic species are more comfortable in cold water rather than in warm water. **[Delhi Comptt. 2012]**

(vii) Gases become less soluble in liquids as temperature is raised? **[Outside Delhi Comptt. 2012]**

(viii) Cutting onions taken from the fridge is more comfortable than cutting onions lying at room temperature.

(ix) Liquid ammonia bottle is first cooled in ice before opening it.

(x) NaCl solution freezes at lower temperature than water but boils at higher temperature than water.

(xi) There is an increase in vapour pressure when HgI_2 is added to the aqueous solution of KI.

(C) Electrochemistry

1. Account for the following :

(i) Electrolysis of an aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode **[Outside Delhi Comptt. 2008, 2009]**

(ii) Increase in molar conductivity with dilution of a weak electrolyte is sharp but for strong electrolyte it is small. **[Delhi Board 2009]**

(iii) Conductivity of a solution decreases with dilution. **[Outside Delhi 2014]**

(iv) Conductivity of metals decreases with rise in temperature

(v) The electrochemical cells stop working after sometime.

(vi) Co^{3+} are salts unstable in aqueous solution.

(vii) Electrolysis of NaBr and NaI in aqueous solution liberate Br_2 and I_2 respectively while that of NaF liberates O_2 instead of F_2.

(viii) Rusting of iron is quicker in saline water than in ordinary water.

(ix) Iron does not rust even if zinc coating is broken in galvanised iron pipe.

2. Why corrosion is considered as an electrochemical process. Explain the reactions occurs during corrosion of iron kept in an open atmosphere. **[Delhi Board 2009, 2011, Delhi Comptt. 2012]**

(D) Chemical Kinetics

1. Account for the following :

(i) The rate of a reaction not remain constant throughout the reaction process.

[Delhi Comptt. 2009, Outside Delhi Comptt. 2009]

(ii) Hydrolysis of ethyl acetate with KOH is a second order reaction while with HCl, it is first order reaction.

(iii) Photosynthesis of sugar by plants from CO_2 and H_2O in the presence of chlorophyll and light classified as a fast reaction.

(iv) Instantaneous rate is preferred over average rate of a reaction.

(v) In some cases, it is found that a large number of colliding molecules have energy more than threshold value, yet the reaction is slow.

(vi) On the basis of enthalpy of formation, graphite is more stable than diamond, yet diamond does not change into graphite for years.

(vii) Equilibrium constant of a reaction does not change in the presence of a catalyst.

(viii) Coal does not burn by itself in air but once imitated by flame, it continues to burn.

(E) Surface Chemistry

1. Account for the following :

(i) Physiosorption decrease with the increase of temperature.

[Delhi Board Comptt. 2008]

(ii) In chemisorption, $\frac{x}{m}$ increases initially and then decreases with rise in temperature. **[Delhi Board Comptt. 2008]**

(iii) Adsorption is always exothermic?

[Outside Delhi Comptt. 2009]

(iv) A finely divided substance acts as a more effective adsorbent than its crystalline form.

[Delhi Comptt. 2010, Outside Delhi Comptt. 2011]

(v) Adsorption of a gas on the surface of a solid is generally accompanied by a decrease in entropy, still it is a spontaneous process.

(vi) Some substances can act both as colloids and crystalloids.

(vii) Deltas are formed when river and sea water meet.

(viii) Artificial rain is caused by spraying salt over clouds.

(ix) Physisorption is multilayered while chemisorption is mono-layered. **[Delhi Comptt. 2012]**

(x) True solutions not show Tyndall effect

[Outside Delhi Comptt. 2012]

2. Explain what is observed when:

(i) an electrolyte, KCl, is added to hydrated ferric oxide sol.

(ii) an electric current is passed through a colloidal sol.

(iii) a beam of strong light is passed through a colloidal solution.

[Delhi Board, 2008, 2012, Delhi Board Comptt. 2008, Outside Delhi, 2008, 2009]

3. What causes Brownian movement in a colloidal solution?

[Delhi Board 2008]

4. Out of NH_3 and CO_2, which gas will be adsorbed more readily on the surface of activated charcoal and why? **[Delhi Comptt. 2012]**

5. What will be the charge on AgI colloidal particles when it is prepared by adding small amount of $AgNO_3$ solution to KI solution? What is responsible for this charge? **[Delhi Comptt. 2012]**

(A) The Solid State

1. (i) In Frenkel defect, some of the ions (cations) are missing from their lattice sites and they occupy interstitial sites. This defect is not shown by alkali metal halides because alkali metal ions have large size which cannot fit into the interstitial sites.

(ii) In Schottky defect, equal number of cations and anions are missing from the lattice which decreases the density of the substance.

(iii) Intrinsic semiconductors like Si have low conductivity. In order to increase their conductivity, Si is doped with an impurity from either group 13 or group 15 elements. This increases the conductivity of silicon.

(iv) Ferrimagnetic materials have their magnetic dipoles oriented in opposite directions in unequal numbers. On heating, Fe_3O_4 loses this alignment of its dipoles and becomes paramagnetic.

(v) On heating, ZnO loses oxygen and turns yellow.

$$ZnO \xrightarrow{\text{heating}} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

(vi) In Frenkel defect, some cations leave the lattice sites and occupy interstitial sites. Since no ions are missing from the crystal as a whole, there is no change in density.

(vii) Glass is an amorphous solid. It has a tendency to flow very slowly. Thus, glass is a supercooled liquid.

(viii) The higher is the melting point of a crystal, more stable is the crystal and vice-versa.

(ix) Crystalline solids are anisotropic in nature. This means that some of their physical properties like resistance or refractive index show different values when measured along different directions.

(x) Glass is an amorphous solid and thus it tends to flow when left for a very long period of time. Thus, glass objects of ancient monuments look milky due to some crystallisation occurring after long exposure to atmosphere.

(xi) On heating with Li vapours, some of the Cl^- ions from LiCl crystal leaves the crystal and thus create a vacant site. This vacant site is occupied by an electron which imparts pink colour to the flame when heated. This vacant site is called F-center.

(xii) When the crystals of ionic solids say NaCl are heated in presence of sodium vapour, some chloride ions leave their lattice sites to combine with sodium to form NaCl. For this to happen, Na atoms lose electrons to form Na+ ions. The electrons thus released diffuse into the crystal to occupy the anion vacancies created by Cl– ions. The crystal now has excess of sodium. The site occupied by unpaired electrons are called F-centres. They impart yellow colour to the crystal because they absorb energy from the visible light and get excited.

(B) Solutions

1. (i) Fluorine, being the most electronegative, has the strongest –I effect. As a result, CF_3COOH is the strongest acid while CH_3COOH is the weakest acid due to absence of electron withdrawing substituents. Hence, CF_3COOH ionizes to the maximum extent while CH_3COOH ionizes to the minimum extent. Greater the ions produced, greater is the depression in freezing point. Thus, the order of depression in freezing point will be:

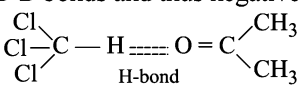
$$CF_3COOH > CCl_3COOH > CH_3COOH$$

(ii) The osmotic pressure method has the advantage over other methods as pressure measurement is done around room temperature and molarity is used instead of molality. As compared to other colligative properties, its magnitude is large even for very dilute solutions.

(iii) Molarity changes with temperature due to change in volume with temperature $\left(\because M = \frac{n_2}{V}\right)$. As a result, same solution will have different molarities at different temperatures.

(iv) Negative deviation from Raoult's law occurs when *A-B* interactions are stronger than *A-A* and *B-B* interactions.

When chloroform $(CHCl_3)$ *A* and acetone (CH_3COCH_3) *B* are mixed, H-bonding takes place which is much stronger than dipole-dipole interaction between two $CHCl_3$ or two CH_3COCH_3 molecules. As a result, *A-B* bond becomes stronger than *A-A* and *B-B* bonds and thus negative deviation occurs.



(v) A mixture of ethanol and acetone shows positive deviation from Raoult's law. This is because on mixing ethanol and acetone, acetone molecules enter between ethanol molecules thus breaking the H-bonding between two ethanol molecules, thereby weakening the attractive forces and showing positive deviation from Raoult's law.

(vi) This is explained by Henry's law i.e. $P = K_H x$ or $P \propto x$ where P is pressure, x is mole fraction of gas in solution. Also, $\boxed{x \propto \frac{1}{T}}$

i.e. as temperature increases, solubility of dissolved gases in water decreases. Hence, aquatic species find difficult to breath in warm water due to decreased availability of oxygen.

(vii) The dissolution of gas in a liquid is an exothermic process. Thus, as temperature increases, equilibrium gets disturbed and so in order to restore the equilibrium, reaction shifts in backward direction i.e. gas escapes out of solution, and hence solubility decreases.

(viii) This is because at lower temperature, the vapours pressure in low. Hence, lesser vapours of tear producing chemicals are produced.

(ix) At room temperature, the vapour pressure of liquid ammonia is very high. On cooling, vapour pressure decreases. Hence, the liquid ammonia will not splash out.

(x) When a solute is dissolved in a solvent the vapour pressure decreases. As a result, the solution boils at a higher temperature while solvent freezes at a lower temperature.

(xi) When HgI_2 is mixed with KI (aq), a complex $K_2Hg\ I_4$ is formed and thus the number of particles in the solution are decreased.

$$2\ KI + Hg\ I_2 \longrightarrow K_2\ [Hg\ I_4] \longrightarrow 2K^+ + [Hg\ I_4]^{2-}$$

Due to the decrease in number of particles, vapour pressure is increased.

(C) *Electrochemistry*

1. (i) Electrolysis of aqueous NaCl gives the following:

At cathode:

$$Na^+(aq) + e^- \longrightarrow Na(s),\ E° = -2.71\ V \quad ...(i)$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq),\ E° = -0.83\ V \quad ...(ii)$$

As E°_{red} of water is greater than E°_{red} for sodium, thus reaction (ii) occurs and **$H_2(g)$ is liberated at cathode**.

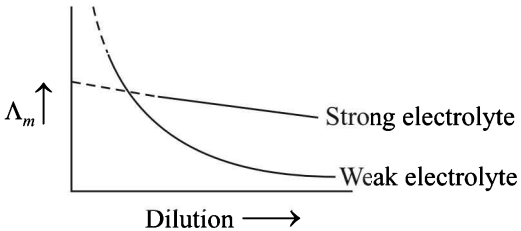
At anode:

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-, E^\circ = -1.36\ V \quad ...(iii)$$

$$H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-, E^\circ = -1.23\ V \quad ...(iv)$$

Reaction (iv) should occur but actually reaction (iii) occurs i.e. **$Cl_2(g)$ is liberated at anode**. This is because of over-voltage for oxidation of O_2 than that needed for oxidation of Cl^- to Cl_2.

(ii) The molar conductivity of both, strong and weak electrolyte increases with dilution, but the increase is small for strong electrolyte while it is sharp for weak electrolyte.



The small increase for strong electryte is due to decrease in the interionic interactions so that movement of ions becomes easier. On the other hand, for weak electrolyte, the extent of dissociation increases with dilution i.e. no. of ions increases and hence, there is a sharp increase in Λ_m for weak electrolytes.

(iii) Conductivity of a solution decreases with dilution because the number of ions carrying current per unit volume decrease on dilution.

(iv) This is because, with increase in temperature, vibration of positive kernels in atoms of a metal increases due to increase in kinetic charge. This increased vibration inteferes with the directed flow of electrons (electricity) through the metal. Thus, resistance increases and its conductivity decreases.

(v) We know that $E_{cell} = E_{cathode} - E_{anode}$. With passage of time $E_{cathode}$ decreases due to fall in concentration of ions which in turn is due to reduction. And similarly E_{anode} increases due to increase in concentration of ions due to oxidation so gradually E_{cell} reduces & eventually falls to zero.

(vi) Co^{3+} ion oxidises water and gets reduced to Co^{2+}.

(vii) The oxidation potentials of Br^- and I^- ions are higher than that of water, and thus these ions are more easily oxidised in comparison to water. But F^- ion have lower oxidation potential than that of water. Thus, in aqueous solution of NaF, water is more easily oxidised to O_2 gas.

(viii) The rate of corrosion (or rusting of iron) increases when other electrolytes (salts, etc.) are present in water in contact with metals or there are stains on metal surface (stains contain various salts). Saline water contains large number of ions (from dissolved salts like NaCl, $MgCl_2$, $MgSO_4$, etc.) then ordinary water and therefore, saline water makes the corrosion process quicker. These salts leads to increased conductivity of water larger in contact with metal surface, thereby, rusting (or corrosion) is speed up.

(ix) Zn is more reactive than iron, as it loses electrons more readily as compared to iron. In galvanised iron object, zinc act as anode and does not allow the iron to loose electron, *i.e.*, makes it a cathode. So long zinc is there on surface, it reduces the Fe_2+ (if any formed) to iron back.

2. At a particular spot of an object made of iron, oxidation takes place and that spot behaves as anode. Electrons released at anodic spot move through the metal and go to another spot of metal which behaves as cathode

The reactions are:

Anode: $2Fe(s) \longrightarrow 2Fe^{2+} + 4e^-$

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

Overall reaction: $2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$

(D) *Chemical Kinetics*

1. According to the following :

(i) This is because rate of reaction depends upon concentration of reactants which changes with time.

(ii) Hydrolysis of an ester (*i.e.*, ethyl acetate) by KOH depends upon the concentration of both the reactants, *i.e.*, concentration of ester as well as concentration of alkali and is expressed as,
Rate = k [Ester] [Alkali]
Hydrolysis of ester by HCl depends only on the concentration of ester. It is independent of H^+ ion concentration.

(iii) It takes place instantaneously (*i.e.*, within a few pico seconds), therefore, it is regarded as fast reaction.

(iv) The rate of a reaction at any time depends up on the concentration of the reactants at that time, which is not constant but goes on decreasing with time continuously. Therefore, instantaneous rate gives more correct information at that time as compared to average rate.

(v) This is because of improper orientation of the colliding molecules at the time of collision.

(vi) The activation energy for the reaction, C (diamond) $\longrightarrow$ C (graphite), is very high which is not available at room temperature.

(vii) The catalyst increases the speed of forward reaction as well as backward reaction to the same extent. Hence, equilibrium constant is not distributed but equilibrium is attained quickly.

(viii) Activation energy for the combustion reaction is very high and is not available at room temperature. On applying flame, a part of the coal and air in contact with the flame absorb heat which provides the necessary activation energy and combustion starts. The heat liberated further provides activation energy for the combustion to continue.

(E) *Surface Chemistry*

1. (i) Adsorption is an exothermic process. Thus, as temperature increases, the extent of adsorption decreases in accordance with the Le-Chatelier's principle.

(ii) In chemisorption, $\frac{x}{m}$ first increases and then decreases with temperature. The initial increase is due to the heat supplied which acts as activation energy required in chemisorption.

(iii) Adsorption is a surface phenomena and occurs due to attraction between adsorbate and adsorbent molecules. As a result, energy is released during adsorption and hence, adsorption is an exothermic process.

(iv) Powdered substances have greater surface area as compared to a substance in crystalline form. Greater the surface area, greater is the adsorption.

(v) For a spontaneous process,

$$\Delta G = \Delta H - T\Delta S$$

ΔG is negative

Now, for adsorption, $\Delta H = -$ ve, $\Delta S = -$ ve

$$\Rightarrow -T\Delta S = +\text{ve}$$

$\therefore$ ΔG will be negative only when

$$\Delta H > T\Delta S$$

as adsorption is spontaneous, $\therefore$ ΔH is highly – ve i.e. the process is highly exothermic.

(vi) Depending upon conditions, a given substance can act as a colloid as well as a crystalloid. For example: NaCl in water is a crystalloid while in benzene, it behaves as a colloid. Similarly, a dilute soap solution behaves as a crystalloid while a concentrated one behaves as a colloid. It is the size of particles which decides the state in which a substance exists.

(vii) The rivers carry sediments (gravel, sand, clay) into the sea and delta is formed.

(viii) Clouds possess charge, when salt is sprayed, clouds absorb oppositely charged particles and hence get neutralised. Consequently, they precipitate in the form of artificial rain.

(ix) In physisorption, the forces of attraction between the adsorbate and adsorbent are van der Waal's forces, therefore, this type of adsorption can be easily reversed by heating or decreasing pressure.

In chemisorption, the forces of attraction are very strong and are of chemical nature. Therefore, adsorption cannot be reversed easily.

(x) True solutions do not show Tyndall effect because of very small size of the particles so that no scattering of light is observed.

2. (i) When an electrolyte, KCl, is added to $Fe(OH)_3$ sol, the positively charged colloidal sol of $Fe(OH)_3$ gets coagulated by oppositely charged Cl^- ions provided by KCl.

(ii) On passing electric current, colloidal particles move towards oppositely charged electrodes where they lose their charge and get coagulated.

(iii) When a beam of light is passed through a colloidal solution, scattering of light by colloidal particles takes place and the path of light becomes visible. This phenomena is called Tyndall effect.

3. Brownian movement is the zig-zag movement of the colloidal particles. It arises due to continuous motion of particles of dispersed phase due to collision with the particles of dispersion medium.

4. $CO_2(T_C = -31.1°C)$ gets adsorbed more in comparison to NH_3 $(T_C = -33.3°C)$. Greater the critical temperature, easier will be the liquefication of the gas and more will be its extent of adsorption on a particular solid such as activated charcoal.

5. The AgI particles will carry negative charge due to adsorption of I^- ions from the solution by the colloidal particles.

♦♦♦

CHAPTER 3

What is the role/effect of ?

(A) The Solid State

1. What is the effect of mechanical stress on a piezoelectric crystal?
2. What is the effect on density of crystal due to schottky defect?

(B) Solutions

1. What is the effect of change in temperature of a solution on its molarity and molality? **[Delhi Board 2009]**
2. What is the effect of temperature on the solubility of a gas in a liquid?
3. What role does the molecular interaction play in solution of alcohol and water ?

(C) Electrochemistry

1. What is the effect of decreasing concentration on molar conductivity of a weak electrolyte?
2. CO_2 is always present in natural water. Explain its effect (increase, stops or no effect) on rusting of iron.
3. What is the role of platinised platinum in normal hydrogen electrode?
4. What is the function of the salt bridge in a voltaic cell?

(D) Chemical Kinetics

1. For a chemical reaction, what is the effect of a catalyst on the following?
   (i) Activation energy of reaction
   (ii) Rate constant of the reaction **[Outside Delhi Comptt. 2008]**
2. What is the effect of temperature on the rate constant of a reaction? How can it be expressed quantitatively?
   [Outside Delhi Comptt. 2009, Delhi Comptt. 2010]
3. What effect activation energy has on the rate of reaction if its value is
   (i) low, and
   (ii) high.

K M C

4. With the help of diagram, explain the role of activated complex in a reaction. **[Delhi Comptt. 2012]**

(E) Surface Chemistry

1. Discuss the effect of pressure and temperature on the adsorption of gases on solids.
2. What is the effect of addition of gelatine to freshly formed gold sol?
3. What is the effect of increase of temperature on the adsorption of a gas on a solid surface?
4. Explain how the phenomenon of adsorption finds application in the following processes.
   (i) Production of vacuum **[DelhiBoard2011]**
   (ii) Heterogeneous catalysis
   [Outside Delhi Comptt. 2008, Delhi Board 2011]
5. What is the role of adsorption in catalytic reactions?
6. What is the role of emulsifier in forming emulsions.

(A) The Solid State

1. A stress applied to piezoelectric crystal will change the state of polarisation of dipoles and a small electrical signal is thus produced.
2. This defect leads to decrease in density of crystal lattice.

(B) Solutions

1. Molarity = $\frac{n_2}{\text{Vol. of solution}}$; Molality = $\frac{n_2}{\text{Mass of solvent}}$

   As molarity depends on volume and volume of solution changes with temperature, thus molarity changes with temperature. On the other hand, mass of solvent does not change with temperature and hence, molality is unaffected by temperature .
2. The solubility of a gas in a liquid decreases with increase in temperature.
3. The alcohol molecules are able to form hydrogen bonds with water molecules. As a result, alcohol and water are miscible with each other in all proportions.

(C) Electrochemistry

1. Molar conductivity increases on decreasing the concentration of weak electrolytes. The degree of ionisation of weak electrolyte increases on dilution.
2. The presence of CO_2 in water increases rusting of iron. CO_2 present in water is in the form of H_2CO_3, which dissociates into H^+ and CO_3^- as shown below:

   $$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$
   $$H_2O \rightleftharpoons H^+ + OH^-$$
   $$2H^+ + 2e^- \longrightarrow H_2$$

   Hydroxyl ion or bicarbonate ions attack the iron surface to form anodic regions in which iron loses electrons and pass into ferrous state, which is further oxidized to ferric state by oxygen of the air.

K M C

The released electrons move towards the cathodic region where H^+ ions are converted into hydrogen gas.

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

$$O_2 + 2H_2O + 4e^-4 \longrightarrow OH^-$$

$$4Fe^{2+} + 3O_2 + 2xH_2O \longrightarrow 2Fe_2O_3 \,.\, xH_2O$$

Thus, CO_2 increases rusting because H_2CO_3 gives H^+ which gains electrons to form H_2 gas. The electrons are released by iron.

3. It provides an inert metal connection to H^+/H_2 system. It also allows adsorption of H_2 gas on its surface.

4. The salt bridge maintains the electrical neutrality of half cells and it completes the circuit.

(D) Chemical Kinetics

1. (i) A catalyst decreases the activation energy.

(ii) A catalyst generally increases the speed of a reaction without itself being consumed in the reaction. Thus, rate constant of the reaction increases.

2. Rate of a reaction becomes almost double for every 10° rise in temperature. This is because the fraction of molecules possessing the required amount of energy become double.

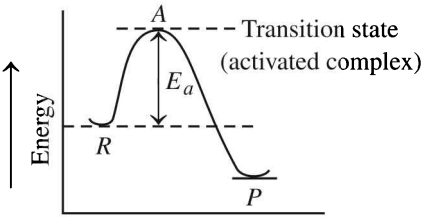
This is expressed as:

$$\text{Temperature coefficient} = \frac{\text{Rate constant at } (T + 10)°C}{\text{Rate constant at } T°C}$$

3. (i) If the activation energy (E_a) is low, the rate of reaction is fast.

(ii) If the activation energy (E_a) is high, the rate of reaction is slow.

4. A diagram showing the reaction profile of a reaction $R \rightarrow P$ is:



K M C

E_a is the activation energy which must be supplied to the reactants so that they form activated complex and hence the products. The peak at A represents activated complex after which products are formed.

(E) *Surface Chemistry*

1. (i) Adsorption decreases with an increase in temperature since it is an exothermic process and applying Le Chatelier's principle the reaction will proceed in backward direction with increase in temperature.

(ii) At a constant temperature, adsorption increases with pressure.

2. Gold sol gets stabilised as gelatine is a protective colloid.

3. In case of physical adsorption, the adsorption of the gas on the solid surface decreases with rise in temperature whereas in chemisorption it first increases and then decreases.

4. (i) **Production of vacuum:** Air can be adsorbed from liquid air which helps to create a high vacuum in a vessel. The process is used in high vacuum instruments for storage of liquid hydrogen. The remaining traces of air can be removed by adsorption on charcoal.

(ii) **Heterogeneous catalysis:** Heterogeneous catalysis involves the adsorption of reactant molecules on the surface of the catalyst, thus bringing them closer and hence increasing the rate of reaction.

5. Adsorption plays an important role in catalytic reactions. Adsorption is surface phenomenon in which the substance (reactant) gets concentrated only on the surfaces of solid adsorbent and do not penetrate into it. This increases concentration of reactant and there is a great probability of occurrance of reaction. The catalyst adsorbs reactants and forms an intermediate compound known as activated complex.

The various ways in which catalytic adsorption increases the rate of reaction are:

(a) The concentration of reactants on surface of solid adsorbent increases and it becomes easier for molecules to attack each other for effective collisions, and thus forming products.

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K M C

(b) A particular part of reactant molecules may come in contact with other molecules which otherwise is difficult.

(c) Some adsorbed molecules dissociated into atoms or free radicals which are very reactive and thus increase the reaction rate.

(d) Heat of adsorption released provides activation energy for formation of activated complex and then increase the rate of reaction.

6. Emulsifier (or emulsifying agent) stabilises the emulsions.

CHAPTER 4

How will you differentiate between ?

(A) *The Solid State*

1. How will you differentiate between the following:

(i) Tetrahedral and octahedral voids

(ii) Crystal lattice and unit cell **(Outside Delhi 2014)**

(iii) Cubic close packing and hexagonal close packing

(iv) A conductor and an insulator.

(v) A conductor and a semiconductor.

(vi) Ferromagnetism and paramagnetism

(vii) Schottky defects and frenkel defects

(viii) Amorphous silica and quartz

(ix) Hexagonal and monoclinic unit cells.

(x) Face-centred and end-centred unit cells.

2. What is the distinguishing feature of metallic solids?

[Outside Board 2010]

(B) *Solutions*

1. (*a*) Distinguish between ideal and non-ideal solution.

2. Distinguish between molality and molarity. Under what conditions are molarity and molality of a solution nearly the same?

[Outside Delhi Comptt. 2008, Delhi Board 2011]

3. Taking suitable examples, explain the meaning of positive and negative deviations from Raoult's law.

[Delhi Board 2008, 2010, Outside Delhi 2008, Outside Delhi Comptt. 2009]

(C) *Electrochemistry*

1. How do metallic and ionic substances differ in conducting electricity? **[Outside Delhi 2009, Delhi Board 2010, 2012]**

2. List points of difference between galvanic cell and electrolytic cell.

(D) *Chemical Kinetics*

1. How will you differentiate the following:

(i) Average and instantaneous rate of reaction.

[Outside Delhi Comptt. 2010]

(ii) Rate law and rate constant

[Delhi Board 2011, Outside Delhi 2011]

(iii) Photochemical reactions and thermochemical reactions.

2. Distinguish between order and molecularity of a reaction. When could order and molecularity of a reaction be the same?

[Delhi Comptt. 2008, 2011, Outside Delhi Comptt. 2010, Delhi Board 2014]

(E) *Surface Chemistry*

1. How will you differentiate between the following:

(i) Micelles and colloidal particles. **[Outside Delhi Comptt. 2008]**

(ii) Homogeneous and heterogeneous catalysis.

[Outside Delhi Comptt. 2008, Delhi Board 2012]

(iii) Absorption and adsorption **[Outside Delhi Comptt. 2010]**

(iv) Chemisorption and physisorption.

[Outside Delhi 2012, Delhi Board 2013]

(v) A sol and an emulsion **[Outside Delhi Comptt. 2012]**

(vi) A sol and a gel

(vii) Colloidal solution and emulsions.

(viii) Lyophilic and lyophobic sols.

2. Differentiate between multimolecular and macromolecular colloids. Give an example of each. How are these two types of colloids different from associated colloids?

[Outside Delhi 2008, Delhi Board 2009, 2010, Delhi Comptt. 2011]

3. How are the following colloids different from each other in respect of dispersion medium and dispersed phase? Give one example of each type.

(a) an aerosol (b) a hydrosol (c) an emulsion.

[Delhi Board 2009, Outside Delhi 2010]

4. How are two types of emulsions different from one other. Give examples. Give two applications of emulsions.

[Outside Delhi Comptt. 2012, Delhi Board 2013, Outside Delhi 2014]

5. What is an adsorption isotherm? Distinguish between Freundlich adsorption and Langmuir adsorption isotherm.

SOLUTION

A The Solid State

1. (i) **Tetrahedral voids :** A simple triangular void surrounded by four spheres is called tetrahedral void.

Octahedral voids : A double triangular void surrounded by six spheres is called octahedral void.

(ii) **Crystal lattice :** A regular arrangement of constituent particles in 3D space is called crystal lattice.

Unit cell : It is the smallest 3D portion of a complete space lattice which when repeated over and again in different directions produces the complete space lattice.

(iii) **Cubic close packing:** When the third layer is placed over the second layer in such a way that the spheres cover the octahedral voids, a layer different from first (A) and second (B) is produced. If we continue packing in this manner, then a packing is obtained where the spheres in every fourth layer will vertically aligned. This pattern of packing spheres is called ABCABC..... pattern or cubic close packing.

Hexagonal close packing: When a third layer is placed over the second layer in such a manner that the spheres cover the tetrahedral void, a three dimensional closet packing is obtained where the spheres in every third or alternate layers are vertically aligned. If we continue packing in this manner, then the packing obtained would be called ABAB..... pattern or hexagonal close packing.

(iv) In case of conductor, the energy gap between the valence band and the conduction band is very small or there is overlapping between valence and conduction band whereas in case of insulator the energy gap between the valence band and the conduction band is very large.

(v) In case of conductor, there is very small energy gap or there is overlapping between valence and conduction band but in a semiconductor there is always a small energy gap between valence and conduction band.

(vi) Due to the property of ferromagnetism, a substance remains magnetised even in absence of magnetic field. Such substances are used in making permanent magnets. Paramagnetism is the property due to which substances becomes magnetic in presence of magnetic field and it is due to presence of unpaired electrons in the substance.

(vii)

Schottky defect	Frenkel defect
(a) The positive and negative ions are missing completely from their lattice positions in the crystal.	(a) The cations occupies an interstial position rather than its correct lattice position.
(b) The presence of this defect lowers the density of crystal.	(b) The presence of this defect does not effect the density of crystal.
(c) Generally shown by ionic solids having high coordination number	(c) Generally shown by ionic solids having low coordination number and in which cations are smaller and fit in interstitials.

(viii) In amorphous silica, SiO_4 tetrahedra are randomly joined to each other. In quartz, SiO_4 tetrahedra are linked in a regular manner and thus, quartz is crystalline solid. Amorphous silica is obtained when molten silica is cooled rapidly and it lacks the long range order of repeating SiO_4 tetrahedra.

Quartz has high degree of crystallinity in its structure.

(ix) In hexagonal unit cell, $a = b \neq c$ and $\alpha = \beta = 90°$, $\gamma = 120°$.

In monoclinic unit cell, $a \neq b \neq c$, $\alpha = \gamma = 90°$, $\beta \neq 90°$.

(x) In face-centred unit cell, one constituent particle is present at centre of each face in addition to the particles present at the corners.

In end-centred unit cell, one constituent particle is present at the centre of any two opposite faces in addition to the particles present at the corners.

2. Metallic solids are malleable, ductile and good conductors of heat and electricity.

(B) *Solutions*

(*i*) Ideal solutions

(*i*) A – B interactions are very much similar to A – A and B – B interactions.

(*ii*) There is no change in volume in the formation of solution, *i.e.*, $\Delta V_{mix} = 0$.

(*iii*) No heat change takes place, *i.e.*, $\Delta H_{mix} = 0$.

(*iv*) They obey Raoult's Law at all temperature and concentrations.

1. **Non-ideal solutions**

(*i*) A – B interactions are very much different (either stronger or weaker) from A – A and B – B interactions

(*ii*) The volume of solution is either less or more than the total volume of components, *i.e.*, $\Delta V_{mix} \neq 0$.

(*iii*) Enthalpy change takes place, *i.e.*, $\Delta H_{mix} \neq 0$. Heat is evolved or absorbed in the process of solution formation.

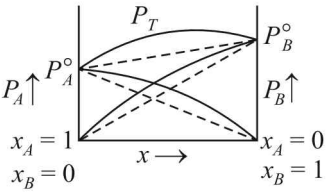
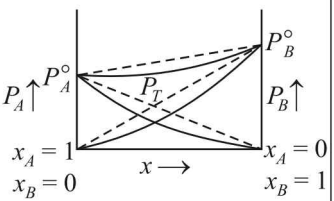
(*iv*) They do not obey Raoult's Law.

2.

Molality		Molarity
It is the number of moles of solute dissolved per Kg of the solvent. It is denoted by *m*.	1.	It is defined as the number of moles of solute dissolved per litre of solution. It is denoted by M.
$m = \frac{\text{no. of moles of solute}}{\text{mass of solvent in Kg}}$ $m = \frac{n_2}{w_1} = \frac{w_2}{M_2} \times \frac{1}{w_1}$ $= \frac{w_2}{M_2} \times \frac{1000}{w_1}$ (if w_1 is in g)		$M = \frac{\text{no. of moles of solute}}{\text{volume of solution (in litre)}}$ $M = \frac{n_2}{V} = \frac{w_2}{M_2} \times \frac{1}{V(L)}$ $= \frac{w_2}{M_2} \times \frac{1000}{V(mL)}$

The molarity and molality of a solution will be nearly same if the mass of the solvent is nearly equal to the volume of the solution.

3.

	Positive deviation		Negative deviation
•	When the A-B interactions are weaker than the A-A/B-B interactions such that the total vapour pressure of the solution becomes greater than the expected vapour pressure the solution is said to show positive deviation from Raoult's law.	•	When the A-B interactions are stronger than A-A/B-B interactions such that the total vapour pressure of the solution is lower than that expected from Raoult's law, the solution is said to show negative deviation from Raoult's law.
•	Graphically, it is shown as:	•	Graphically, it is shown as:
			
•	For example: A solution of ethanol and acetone.	•	For example: A solution of phenol and aniline.

(C) *Electrochemistry*

1. Conductivity of metals is due to free electrons while that of ionic substances is due to ions which move in solution.

2.

	Galvanic (Electrochemical) cell		Electrolytic cell
(a)	It is a device to convert chemical energy into electrical energy.	(a)	It is a device to convert electrical energy into chemical energy.
(b)	Anode is negatively charged (i.e., anode is rich in electrons and the electrons in external circuit.	(b)	Anode is positively charged as it is connected to the terminal of battery.
	Cathode is positively charged (i.e., electron deficient).		Cathode is negatively charged as it is connected to negative terminal of battery).

(c)	Useful work is obtained from cell, i.e., $\Delta G < 0$.	(c)	Work is done on cell by supplying electric energy, i.e., $\Delta G > 0$.
(d)	Two electrodes are in two separated half- cells connected by salt bridges.	(d)	Two electrodes are placed in same solution of cell in a vessel.
(e)	Examples : Dry cells, daniell cell, mercury cell, fuel cell, lead storage battery, Ni-Cd battery.	(e)	Examples: Water voltmeter, copper voltmeter, electrolysis of brine, or any other electrolyte in a vessel.

(D) Chemical Kinetics

1. (i)

	Average rate of reaction		**Instantaneous rate of reaction**
•	It is defined as the change in concentration of any one of the reactants or products with time.	•	It is defined at any instant of time and it is the change in concentration of any of the reactant or product at that particular instant of time.
•	avg. rate ($r_{av.}$) $= \dfrac{\text{change in concentration}}{\text{time interval}}$ $= \dfrac{-d[R]}{dt} = \dfrac{+d[P]}{dt}$	•	$r_{inst} = \dfrac{dx}{dt}$ $= \dfrac{-d[R]}{dt} = \dfrac{+d[P]}{dt}$

(ii)

	Rate law		**Rate constant**
1.	It is the change in concentration of reactant or product with time.	1.	It is a constant of proportionality in rate law equation and is equal to rate of reaction when molar concentration of each reactant is unity.
2.	Its units are mol L^{-1} $time^{-1}$	2.	Its units depend on the order of reaction

(iii)

	Photochemical reaction		Thermochemical reaction
(a)	The energy of activation of the reaction is provided by the absorption of quantum of light (or other radiations).	(a)	The energy of activation required for the reaction is provided by molecular collisions or heat.
(b)	The presence of light or radiation is an essential requirement of these reaction.	(b)	These may occur even is the dark.
(c)	The free energy change (DG) for photochemical reaction may not be negative. For example, ozonisation of oxygen and photosynthesis in plants occur with DG as positive.	(c)	All such reactions proceed with a decrease in free energy.
(d)	The rate of photochemical reaction does not depend much on temperature. The rate of reaction depends upon the intensity of radiation used.	(d)	Temperature has a significant effect on the rates of such reactions.

2.

	Order of a reaction		Molecularity of a reaction
1.	It is the sum of the powers of the concentration of reactants in the rate law expression.	1.	It is the number of reacting species taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction.
2.	It does not need to be a whole number. It can be fraction also.	2.	It is always a whole number.

- For an elementary reaction, the order of a reaction is equal to molecularity of reaction.

(E) Surface Chemistry

1. (i)

	Micelles		Colloidal particles
1.	When an electrolyte or soap or detergent molecules form aggregated particles which behave like colloidal particles, the aggregated particles are called micelles.	1.	Colloidal particles have their sizes between 1 nm to 100 nm and have large surface area per unit mass due to their small size.
2.	For example: Soap, detergent	2.	For example: Sulphur sol

(ii)

	Homogeneous catalysis		Heterogeneous catalysis
1.	In this, the reactants and the catalyst are in the same phase.	1.	In this the reactants and the catalyst are in different phases.
2.	For example: $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$	2.	For example: $2SO_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$

(iii) In **absorption**, the substance is uniformly distributed throughout the bulk of the solid, whereas in **adsorption**, the concentration of the substance increases on the surface and does not penetrate to the bulk.

(iv)

	Physisorption		Chemisorption
1.	The forces between adsorbate and adsorbent are van der Waal's forces.	1.	The forces between adsorbate and adsorbent are of nature of chemical bond.
2.	It is not specific in nature.	2.	It is highly specific in nature.
3.	It is reversible in nature.	3.	It is irreversible.

(v) Sol is a colloid of solid in a liquid whereas emulsion is a colloid of liquid in a liquid.

(vi) Sol is a colloidal system when solid is dispersed generally in liquid. Gel is also a colloidal system when liquid is dispersed in a solid.

(vii) Colloidal solution is generally referred to a system in which a solid is dispersed in a liquid.

For example, starch $\xrightarrow{K}$ solid starch (dispersed phase), water (dispersion medium);

$Fe(OH)_3 \longrightarrow$ solid $Fe(OH)_3$ (dispersed phase), water (dispersion medium).

Emulsions are generally referred to systems in which both the dispersed phase and the dispersion medium are liquids, *e.g.,* milk in which oil droplets are dispersed in water.

(viii)

	Lyophilic sols		Lyophobic sols
(a)	They are prepared easily by shaking or warming the substances with the solvent.	(a)	They are prepared by chemical methods.
(b)	They are quite stable and are not easily coagulated.	(b)	They are comparatively less stable and can be easily precipitated by the addition of a small amount of an electrolyte.
(c)	The particles are true molecules (molecular colloids) due to their large size	(c)	The particles consist of aggregate of molecules (associated collards)
(d)	Their particles are heavily hydrated, e.g., starch sol.	(d)	The particles are usually not hydrated, e.g., gold sol.
(e)	They are reversible, i.e., the coagulated particles can be redispersed.	(e)	They are irreversible.

2.

	Multimolecular colloids		Macromolecular colloids
1.	Their particles are aggregate of atoms or molecules with diameter less than 1 nm.	1.	These are particles of large molecules of colloidal dimension.
2.	For example: Sulphur sol.	2.	For example: Proteins, etc.
3.	They are held together with van der Waal's forces.	3.	They have H-bonds, dipole-dipole interactions, etc.

Associated colloids behave as normal strong electrolytes under low concentrations but at higher concentration (called critical micelle concentration), they start to show colloidal behaviour.

3.

	Colloids	Dispersion medium	Dispersed phase	Example
1.	Aerosol	Gas	Liquid	Fog
2.	Hydrosol	Water	Solid	Starch
3.	Emulsion	Liquid	Liquid	Milk

4. Emulsions are of two types: oil in water and water in oil.

	Oil in water		Water in oil
1.	Dispersed phase is oil. Dispersion medium is water.	1.	Dispersed phase is water. Dispersion medium is oil.
2.	For example: Milk	2.	For example: Butter

Applications:

1. Emulsions find use in daily consumable items like butter, milk, etc.
2. Phenyl, which is used as a disinfectant, is an emulsion of fat in water.

5. A relation or a graph between the magnitude of adsorption x/m and the pressure 'p' of the gas at constant temperature is called adsorption isotherm.

	Freundlich adsorption isotherm		Langmuir adsorption isotherm
(a)	It is given by equation $x/m = kp^{1/n}$.	(a)	It is represented by the relation $\frac{x}{m} = \frac{ap}{1 + bp}$
(b)	It fails at high pressure of the gas.	(b)	At high pressure x/m becomes constant and the change in pressure has no effect.

CHAPTER 5

Calculation based on formula

(A) *The Solid State*

1. Silver crystallises in a *fcc* lattice. The edge length of its unit cell is 4.077×10^{-8} cm and its density is 10.5 g cm^{-3}. Calculate the atomic mass of silver. ($N_A = 6.02 \times 10^{23}$ mol^{-1}).

[Outside Delhi 2008, 2010]

2. Iron has a body centered cubic unit cell with an edge length of 286.65 pm. The density of iron is 7.87 g cm^{-3}. Use this information to calculate Avogadro's number. (At. mass of Fe = 56 g mol^{-1})

[Delhi Board 2009, Outside Delhi 2009, 2012]

3. Silver crystallises with a face-centered cubic unit cell. Each side of unit cell has length of 409 pm. What is the radius of an atom of silver? **[Outside Delhi 2009, Delhi Board 2011]**

4. Copper crystallizes in a *fcc* lattice with an edge length of 3.61×10^{-8} cm. Calculate the density of copper.

[Given: Cu = 63.5 g mol^{-1}; Na = 6.022×10^{23} mol^{-1}]

[Delhi Comptt. 2009, Outside Delhi 2012]

5. A well known mineral fluorite is chemically calcium fluoride. It is known that in one unit cell of this mineral there are 4 Ca^{2+} ions and 8 F^- ions and that Ca^{2+} ions are arranged in a *fcc* lattice. The F^- ions fill all the tetrahedral holes in *fcc* lattice of Ca^{2+} ions. The edge of the unit cell is 5.46×10^{-8} cm in length. The density of the solid is 3.18 g cm^{-3}. Use this information to calculate Avogadro's number. (Molar mass of CaF_2 = 78.08 g mol^{-1}) **[Delhi Board 2010]**

6. Chromium metal crystallises in a body centred cubic lattice. The length of the unit cell edge is found to be 287 pm. Calculate the atomic radius of chromium. **[Delhi Comptt. 2010]**

7. The edge of a face-centred cubic unit cell of aluminium is 404 pm. Calculate the radius of aluminium atom. **[Delhi Comptt. 2010]**

8. Copper crystallises in face-centred cubic lattice and has a density of 8.930 g cm^{-3} at 293 K. Calculate the radius of copper atom. (Atomic mass of Cu = 63.5 u, $N_A = 6.02 \times 10^{23}$ mol^{-1})

[Outside Delhi Comptt. 2010]

9. The density of lead is 11.35 g cm^{-3} and it crystallizes with *fcc* unit cell. Estimate the radius of lead atom. (at mass of Pb = 207 g mol^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1}) **[Outside Delhi 2011]**

10. Calculate the packing efficiency of a metal crystal for a simple cubic unit cell. **[Outside Delhi 2011]**

11. Tungsten crystallises in a body centered cubic unit cell. If the edge length of the unit cell is 316.5 pm, what is the radius of tungsten atom? **[Delhi Board 2012]**

12. Iron(II) oxide has a cubic structure and each side of the unit cell is 5 Å. If the density of the oxide is 4 g cm^{-3}, calculate the number of Fe^{2+} and O^{2-} ions present in each unit cell.

(Atomic mass: Fe = 56 u, O = 16 u

$N_A = 6.023 \times 10^{23}$ mol^{-1})

[Outside Delhi Comptt. 2012]

13. An element X crystallises in *fcc* structure. 208 g of it has 4.2832×10^{24} atoms. Calculate the edge of the unit cell if density of X is 7.2 g cm^{-3}. **[Delhi Comptt. 2012]**

14. The unit cell an element of atomic mass 108 u and density 10.5 g cm^{-3} is a cube with edge length 409 pm. Find the type of unit cell of the crystal. **[Delhi Comptt. 2012]**

15. An element with density 11.2 g cm^{-3} forms a *fcc* lattice with edge length of 4×10^{-8} cm. Calculate the atomic mass of the element.

(Given: $N_A = 6.022 \times 10^{23}$ mol^{-1}) **[Delhi Board 2014]**

16. An element with density 2.8 g cm^{-3} forms a *fcc* unit cell with edge length 4×10^{-8} cm. Calculate the molar mass of the element.

(Given: $N_A = 6.022 \times 10^{23}$ mol^{-1}) **[Outside Delhi 2014]**

(B) Solutions

1. Calculate the temperature at which a solution containing 54 g of glucose ($C_6H_{12}O_6$) in 250 g of water will freeze.

(K_f for water = 1.86 K kg mol^{-1})

[Delhi Board 2008, Outside Delhi 2008]

2. A solution containing 8 g of a substance in 100 g of diethyl ether boils at 36.86 °C whereas pure ether boils at 35.60°C. Determine the molecular mass of the solute. (K_b for ether = 2.02 K kg mol^{-1})

[Outside Delhi 2008]

3. Calculate the depression in freezing point of water when 20 g of $CH_3CH_2CHClCOOH$ is added to 500 g of water.
(Given: $K_a = 1.4 \times 10^{-3}$, $K_b = 1.86$ K kg mol^{-1})
[Delhi Comptt. 2008]

4. 100 mg of a protein is dissolved in just enough water to make 10.0 mL of solution. If this solution has an osmotic pressure of 13.3 mm Hg at 25°C, what is the molar mass of the protein?
($R = 0.0821$ L atm K^{-1} mol^{-1} and 1 atm = 760 mm Hg)
[Delhi Board 2009, Outside Delhi 2009]

5. Calculate the freezing point of a solution containing 18 g glucose ($C_6H_{12}O_6$) and 68.4 g sucrose ($C_{12}H_{22}O_{11}$) in 200 g of water. The freezing point of pure water is 273 K and K_f for water is 1.86 K mol^{-1} kg. **[Outside Delhi Comptt. 2009]**

6. Calculate the amount of NaCl which must be added to 1 kg of water so that the freezing points of water is depressed by 3 K.
[Given: $K_f = 1.86$ K kg mol^{-1}; Na = 23.0; Cl = 35.5]
[Delhi Board Comptt. 2009]

7. A solution prepared by dissolving 1.25 g of oil of winter green (methyl salicylate) in 99.0 g of benzene has a boiling point of 80.31°C. Determine the molar mass of this compound.
(Given: B.Pt. of benzene = 80.10°C; K_b for benzene = 2.53°C kg mol^{-1}) **[Delhi Board 2010]**

8. What mass of NaCl (M = 58.5 g mol^{-1}) be dissolved in 65 g of water to lower the freezing point by 7.5°C? K_f for water = 1.86 K kg mol^{-1}. Assume i for NaCl to be 1.87.
[Outside Delhi 2010, 2011]

9. What mass of ethylene glycol (molar mass = 62.0 g mol^{-1}) must be added to 5.50 kg of water to lower the freezing point of water from 0°C to – 10°C. (K_f for water = 1.86 K kg mol^{-1})
[Outside Delhi 2010]

10. 15 g of an unknown molecular substance was dissolved in 450 g of water. The resulting solution freezes at – 0.34°C. What is the molar mass of the substance?
(K_f for water = 1.86 K kg mol^{-1}) **[Outside Delhi 2010]**

11. Calculate the mass of ascorbic acid ($C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5°C. (K_f for acetic acid = 3.9 K kg mol^{-1}) **[Delhi Comptt. 2010]**

12. Find the boiling point of a solution containing 0.520 g of glucose ($C_6H_{12}O_6$) dissolved in 80.2 g of water. (K_b = 0.52 K/m)

[Outside Delhi Comptt. 2010]

13. Calculate the freezing point of an aqueous solution containing 10.50 g of $MgBr_2$ in 200 g of water. (Molar mass of $MgBr_2$ = 184 g; K_f = 1.86 K kg mol^{-1}) **[Delhi Board 2011]**

14. A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 mL of water has an osmotic pressure of 0.335 torr at 25°C. Assuming that the gene fragment is non-electrolyte, calculate its molar mass. **[Outside Delhi 2011]**

15. 15.0 g of an unknown molecular material is dissolved in 450 g of water. The resulting solution freezes at – 0.34°C. What is the molar mass of the material? (K_f for water = 1.86 K kg mol^{-1})

[Outside Delhi 2012, Delhi Board 2012]

16. A solution of glycerol ($C_3H_8O_3$) in water was prepared by adding some glycerol in 500 g of water. This solution has a boiling point of 100.42°C while pure water boils at 100°C. What mass of glycerol was dissolved to make the solution?

[Delhi Board 2012, Outside Delhi 2012]

17. Calculate the amount of KCl which must be added to 1 kg of water so that the freezing point is depressed by 2 K. (K_f for water = 1.86 K kg mol^{-1}) **[Delhi Board 2012]**

18. A 1 molal solution of trichlorosacetic acid (CCl_3COOH) is heated to its boiling point. The solution has a boiling point of 100.18°C. Determine the Van't Hoff factor for CCl_3COOH.

(K_b = 0.512 K kg mol^{-1}) **[Delhi Board 2012]**

19. 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) **[Delhi Board 2013]**

20. Detrmine the osmotic pressure of a solution, prepared by dissolving 2.5×10^{-2} g of K_2SO_4 in 2L of water at 25°C, assuming that is completely dissociated.

(R = 0.082 L atm mol^{-1}, molar mass of K_2SO_4 = 174 g mol^{-1})

[Delhi Board 2013]

21. A solution of glucose ($C_6H_{12}O_6$) in water is labelled as 10% by weight. What would be the molality of the solution?

[Outside Delhi 2013, 2014]

22. Calculate the mass of a compound (molar mass = 256 g mol^{-1}) to be dissolved in 75 g of benzene to lower its freezing point by 0.48 K. (K_f = 5.12 K kg mol^{-1}) **[Delhi Board 2014]**

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

[Outside Delhi 2014]

(C) Electrochemistry

1. The conductivity of a 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1}. Calculate its molar conductivity.

[Delhi Board 2008]

2. Conductivity of 0.00241 M acetic acid solution is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity. If Λ_m° for acetic acid is 390.5 S cm^2 mol^{-1}, what would be its dissociation constant?

[Delhi Board 2008, Outside Delhi 2008]

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

[Delhi Board 2008, 2012, Outside Delhi 2008]

4. Calculate the standard cell potential of a galvanic cell in which the following reaction takes place:

$$2Cr(s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd(s)$$

Calculate $\Delta_r G^0$ and equilibrium constant for the above reaction at 25°C.

[Given $E^0_{Cr^{3+}|Cr} = -0.74$ V; $E^0_{Cd^{2+}|Cd} = -0.40$ V, F = 96500 C mol^{-1}]

[Delhi Board Comptt. 2008]

5. (i) Formulate the electrochemical cell representing the reaction:

$$2Cr(s) + 3Fe^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Fe(s)$$

(ii) Calculate E^0_{cell}

(iii) Calculate E_{cell} at 25°C if $[Cr^{3+}] = 0.1$ M and $[Fe^{2+}] = 0.01$ M

[Outside Delhi Comptt. 2008]

[Given: $E^0_{Cr^{3+}|Cr} = -0.74$ V; $E^0_{Fe^{2+}|Fe} = -0.44$ V]

6. A voltaic cell is set up at 25°C with following half-cells: Ag^+ (0.001 M) | Ag and Cu^{2+} (0.10 M) | Cu. What would be the voltage of this cell? (E^0_{cell} = 0.46 V) **[Delhi Board 2009, 2013]**

7. Calculate the equilibrium constant for the reaction:

$Fe(s) + Cd^{2+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cd(s)$

(Given: $E^{\circ}_{Cd^{2+}|Cd} = -0.40$ V; $E^{\circ}_{Fe^{2+}|Fe} = -0.44$ V)

[Delhi Board 2009]

8. Calculate the cell emf and $\Delta_r G^0$ for a cell at 25°C.

$Zn(s) | Zn^{2+}(0.1\ M) || Cd^{2+}(0.01\ M) | Cd(s)$

[Given $E^0_{Zn^{2+}|Zn} = -0.763$ V; $E^0_{Cd^{2+}|Cd} = -0.403$ V]

[Output Delhi Comptt. 2009]

9. Calculate the emf of the cell in which the following reaction takes place:

$Ni(s) + 2Ag^+(0.002\ M) \longrightarrow Ni^{2+}(0.160\ M) + 2Ag(s)$

Given that $E^0_{cell} = 1.05$ V **[Delhi Comptt. 2010]**

10. 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 the solution. **[Outside Delhi Comptt. 2010, Outside Delhi 2012]**

11. Determine the values of K_C and ΔG^0 for the reaction:

$Ni(s) + 2Ag^+(aq) \longrightarrow Ni^{2+}(aq) + 2Ag(s)$, $E^0 = 1.05$ V

[Delhi Board 2011]

12. Calculate the potential for the half-cell containing 0.10 M $K_2Cr_2O_7$ (aq), 0.20 M Cr^{3+} (aq) and 1×10^{-4} M H^+ (aq). The half cell reaction is:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7\,H_2O(l)$

and the standard electrode potential is given as $E^0 = 1.33$ V

[Outside Delhi 2011]

13. For the cell: $Zn(s) | Zn^{2+}(2\ M) || Cu^{2+}(0.5\ M) | Cu(s)$

(a) Write equation for each half-reaction

(b) Calculate cell potential at 25°C.

[Given: $E^0_{Zn^{2+}|Zn} = -0.76$ V; $E^0_{Cu^{2+}|Cu} = +0.34$ V]

[Outside Delhi Comptt. 2011, Outside Delhi 2013]

14. Calculate the equilibrium constant for the reaction:

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

(Given: $E^0_{Zn^{2+}|Zn} = -0.76$ V; $E^0_{Cu^{2+}|Cu} = +0.34$ V)

[Outside Delhi Comptt. 2011]

15. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is $5.55 \times 10^3\ \Omega$. Calculate its resistivity, conductivity and molar conductivity.

[Delhi Board 2012, Outside Delhi 2012]

K M C

16. In a button cell, widely used in watches, the following reaction takes place:

$$Zn(s) + Ag_2O(s) + H_2O(l) \longrightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$$

Determine E^0 and ΔG^0 for the reaction.

[Given: $E^0_{Ag^+|Ag} = +0.80$ V $E^0_{Zn^{2+}|Zn} = -0.76$ V)

[Delhi Board 2012]

17. The cell in which the following reaction occurs;

$$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$$

has $E^0_{cell} = 0.236$ V at 298 K. Calculate the standard Gibb's energy and equilibrium constant of the cell reaction.

[Outside Delhi Comptt. 2012]

18. (a) How many coulombs are required to reduce 1 mole $Cr_2O_7^{2-}$ to Cr^{3+}?

(b) The conductivity of 0.001 M acetic acid is 4×10^{-5} S/m. Calculate the dissociation constant of acetic acid if Λ°_m for acetic acid is 390 $S\,cm^2\,mol^{-1}$. **[Outside Delhi Comptt. 2012]**

19. Calculate the emf of the following cell at 298 K:

$$Fe(s) \mid Fe^{2+}(0.001\ M) \mid\mid H^+(1\ M) \mid H_2(g)\ (1\ bar), Pt(s)$$

(Given: $E^\circ_{cell} = +0.44$ V) **[Delhi Board 2013]**

20. Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is $1.29 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$.

[Delhi Board 2014]

21. Calculate $\Delta_r G^\circ$ for the reaction:

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

(Given: $E^0_{cell} = +2.71$ V; 1F = 96500 C mol^{-1})

[Outside Delhi 2014]

22. Calculate emf of the following cell at 298 K:

$$Mg(s) \mid Mg^{2+}(0.1\ M) \mid\mid Cu^{2+}(0.01\ M) \mid Cu(s)$$

(Given: $E^0_{cell} = +2.71$ V; 1F = 96500 C mol^{-1})

[Delhi Board 2014]

(D) Chemical Kinetics

1. A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate its $t_{1/2}$ value.

[Delhi Board 2008, Outside Delhi 2008]

2. The rate constants of a reaction at 500 K and 700 K are 0.02 S^{-1} and 0.07 S^{-1}. Calculate the values of E_a and A.

[Delhi Board 2008]

3. The decomposition of phosphine, $4PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$ has rate law, rate = k [PH_3]. The rate constant is 6.0×10^{-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}]

[Delhi Comptt. 2008]

4. A first order reaction has a rate constant of 0.0051 min^{-1}. If we begin with 0.10 M concentration of the reactant, what concentration of the reactant will remain after 3 hours?

[Delhi Board 2009, Outside Delhi, 2009]

5. For a decomposition reaction, the values of rate constant k at two different temperatures are given below:

$k_1 = 2.15 \times 10^{-8}$ L mol^{-1} S^{-1} at 650 K

$k_2 = 2.39 \times 10^{-7}$ L mol^{-1} S^{-1} at 700 K

Calculate the activation energy for this reaction.

[Outside Delhi 2009]

6. A first order reaction is 20% complete in 5 mins. calculate the time for the reaction to be 60% complete.

[Outside Delhi Comptt. 2009]

7. The half life for a first order reaction is 5×10^4 s. What percentage of the initial reactant will react in 2 hours?

[Outside Delhi Comptt. 2009]

8. Show that for a first order reaction, the half-life period is independent of initial concentration. **[Delhi Board Comptt. 2009]**

9. A reaction is first order in reactant A and second order in reactant B. How is the rate of this reaction affected when (i) concentration of B is increased to three times (ii) concentration of both A and B is doubled? **[Delhi Board 2010, 2013]**

10. The decomposition of phosphine proceeds according to the following equation:

$$4PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$$

The reaction follows following rate equation:

$$\text{Rate} = k\,[PH_3]$$

The half life of PH_3 is 37.9 S at 120°C.

(i) How much time is required for 3/4th of PH_3 to decompose?

(ii) What fraction of original sample remains after 1 min?

[Outside Delhi 2010]

K M C

11. The rate of a reaction increases four time when temperature changes from 300 K to 320 K. Calculate the energy of activation of the reaction, assuming that it does not change with temperature.
($R = 8.314$ J K^{-1} mol^{-1}) **[Outside Delhi 2010, 2013]**

12. The decomposition of a compound is found to follow first order rate law. If it takes 15 mins for 20% of the original material to react, calculate the rate constant. **[Delhi Comptt. 2010]**

13. The thermal decomposition of HCOOH is a first order reaction with a rate constant of 2.4×10^{-3} S^{-1} at a certain temperature. Calculate how long it will take for 3/4th of initial quantity of HCOOH to decompose. (log 0.25 = 0.6021) **[Outside Delhi 2011]**

14. The rate of most reactions become double when their temperature is increased from 298 K to 308 K. Calculate the activation energy. **[Delhi Comptt. 2011, 2012]**

15. A reaction has a half-life of 10 min.

(i) Calculate rate constant for the first order reaction.

(ii) What fraction of the reactant will be left after an hour of the reaction? **[Delhi Comptt. 2011]**

16. In a first order reaction, the concentration of the reactant is reduced from 0.6 mol L^{-1} to 0.2 mol L^{-1} in 5 mins. Calculate the rate constant of the reaction. **[Outside Delhi Comptt. 2011]**

17. A first order reaction is 15% complete in 20 mins. How long will it take to complete 60% of the reaction? **[Delhi Comptt. 2012]**

18. A first order reaction takes 40 minutes for 30% decomposition. Calculate $t_{1/2}$ for this reaction.
(Given log 1.428 = 0.1548) **[Delhi Board 2013]**

19. For a first order reaction, show that time required for 99% completion is twice the time required for 90% completion of reaction. **[Delhi Board 2013]**

20. (a) For a reaction, $A + B \longrightarrow P$, rate law is given by:

$$r = k\,[A]^{1/2}\,[B]^2$$

What is the order of this reaction?

(b) A first order reaction has a rate constant $k = 5.5 \times 10^{-14}$ S^{-1}. Find the half-life for this reaction. **[Outside Delhi 2013]**

 Approved: 0777 023 444

(A) The Solid State

1. **Given:** Edge length, $a = 4.077 \times 10^{-8}$ cm
Density, $d = 10.5$ g cm^{-3}
For *fcc* lattice, $z = 4$
Atomic mass, $M = ?$

Solution:
$$d = \frac{z \cdot M}{a^3 \cdot N_A}$$

$$\Rightarrow \quad M = \frac{d \times a^3 \times N_A}{z}$$

$$= \frac{10.5 \times (4.077 \times 10^{-8})^3 \times 6.02 \times 10^{23}}{4}$$

$$= 107.9 \text{ g mol}^{-1}$$
$$\simeq 108 \text{ g mol}^{-1}$$

2. **Given:** $a = 286.65\ pm = 286.65 \times 10^{-10}$ cm
$d = 7.87$ g cm^{-3}
$M = 56$
for *bcc*, $z = 2$

To find: $N_A = ?$

Solution: Using the formula,

$$\boxed{d = \frac{z \cdot M}{a^3 \cdot N_A}}$$

$$\Rightarrow \quad N_A = \frac{z \cdot M}{a^3 \cdot d}$$

$$\Rightarrow \quad N_A = \frac{2 \times 56}{(286.65 \times 10^{-10})^3 \times 7.87}$$

$$= \frac{112}{23.63 \times 7.87 \times 10^{-24}}$$

$$= 0.6022 \times 10^{24}$$

$$\boxed{N_A = 6.022 \times 10^{23}}$$

3. Edge length, $a = 409$ pm

$$\boxed{\text{Radius of } fcc \text{ unit cell, } r = \frac{a}{2\sqrt{2}} = 0.3535\, a}$$

$$r = 0.3534 \times 409 = 144.58 \text{ pm}$$

4. For *fcc*, $z = 4$

$M = 63.5 \text{ g mol}^{-1}$

$a = 3.61 \times 10^{-8}$ cm

$$\therefore \quad d = \frac{z \cdot M}{a^3 \cdot N_A}$$

$$= \frac{4 \times 63.5}{(3.61 \times 10^{-8})^3 \times 6.022 \times 10^{23}}$$

$$= \frac{254}{28.33} = 8.965 \text{ g cm}^{-3}$$

5. For *fcc*, $z = 4$

$M = 78.08 \text{ g mol}^{-1}$

$a = 5.46 \times 10^{-8}$ cm

$d = 3.18 \text{ g cm}^{-3}$

Using formula, $d = \dfrac{z \cdot M}{a^3 \cdot N_A}$

$$\Rightarrow \quad N_A = \frac{z \cdot M}{a^3 \cdot d}$$

$$= \frac{4 \times 78.08}{(5.46 \times 10^{-8})^3 \times 3.18}$$

$$= 6.022 \times 10^{23} \text{ mol}^{-1}$$

6. $a = 287$ pm, $r = ?$

For *bcc*, $\boxed{r = \dfrac{\sqrt{3}}{4} a}$

$$= \frac{\sqrt{3}}{4} \times 287 = \frac{1.73 \times 287}{4}$$

$$= 124.127 \text{ pm}$$

7. For *fcc*, $\boxed{r = \frac{a}{2\sqrt{2}}}$

$a = 404$ pm, $r = ?$

$\therefore \quad r = \frac{404}{2\sqrt{2}} = \frac{404}{2 \times 1.414}$

$r = 142.857$ pm

8. For *fcc*, $z = 4$

$d = 8.930$ g cm^{-3}

$M = 63.54$; $N_A = 6.02 \times 10^{23}$ mol^{-1}

Using formula, $\boxed{d = \frac{z \cdot M}{a^3 \cdot N_A}}$

$\Rightarrow \quad a^3 = \frac{z \cdot M}{d \cdot N_A}$

$= \frac{4 \times 63.6}{8.930 \times 6.0 \times 10^{23}}$

$= 47.2 \times 10^{-24}$

$\Rightarrow \quad \boxed{a = 3.614 \times 10^{-8}}$

For *fcc*, radius, $r = \frac{a}{2\sqrt{2}}$

$= \frac{3.606 \times 10^{-8}}{2 \times 1.414}$

$\boxed{r = 1.27 \times 10^{-8} \text{cm}}$

9. **Given:** $d = 11.35$ g cm^{-3}

$z = 4$ for *fcc*

$M = 207$ g mol^{-1}

$N_A = 6.02 \times 10^{23}$ mol^{-1}

To find: $r = ?$

Solution: $\boxed{d = \frac{z\,M}{a^3 N_A}}$

$$\Rightarrow \qquad a^3 = \frac{zM}{d \cdot N_A}$$

$$\simeq a^3 = 1.21 \times 10^{-22}$$

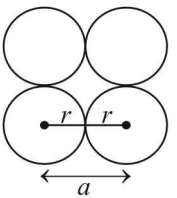
$$a = 4.95 \times 10^{-8}$$

$$\boxed{\text{For } fcc,\ r = \frac{a}{2\sqrt{2}}}$$

$$= \frac{4.95 \times 10^{-8}}{2 \times 1.414}$$

$$\Rightarrow \qquad r = 1.75 \times 10^{-8}$$

10. Let the edge length be 'a' and the radius of the sphere be 'r'.



$\therefore$ for simple unit cell, $a = 2r$

Now, number of spheres per unit cell $= \frac{1}{8} \times 8 = 1$

$$\boxed{\text{Volume of the sphere} = \frac{4}{3} \neq r^3}$$

Volume of cube $= a^3 = (2r)^3 = 8r^3$

$$\boxed{\text{Packing efficiency} = \frac{\text{Vol. of the sphere}}{\text{Vol. of the cube}}}$$

$$\therefore \text{ Packing efficiency} = \frac{\text{Vol. of the sphere}}{\text{Vol. of the cube}}$$

$$= \frac{\frac{4}{3} \neq r^3}{8r^3} = \frac{\neq}{6} = 0.524$$

$\therefore$ Packing efficiency = 52.4%

11. **Given:** *bcc* unit cell
$a = 316.5$ pm

To find: $r = ?$

Solution: For *fcc*, $r = \frac{\sqrt{3}}{4} a$

$$= \frac{1.732 \times 316.5}{4} = 137.04 \text{ pm}$$

12. $a = 5$ Å $= 5 \times 10^{-8}$ cm
$N_A = 6.023 \times 10^{23}$
M (FeO) = 72 g mol^{-1}
$d = 4$ g cm^{-3}

$$d = \frac{z \cdot M}{a^3 N_A} \quad \Rightarrow \quad z = \frac{d a^3 N_A}{M}$$

$$\Rightarrow \qquad z = \frac{4 \times (5 \times 10^{-8})^3 \times 6 \times 10^{23}}{72} = 4$$

$= Fe^{2+}$ ions $= 4$; O^{2-} ions $= 4$

13. For *fcc*, $z = 4$, $d = 7.2$ g cm^{-3}
Let 'a' be edge length

$$d = \frac{z M}{a^3 \times 10^{-30}}$$

$$\text{Mass per atom} = \frac{208}{4.2832 \times 10^{24}}$$

$$\therefore \qquad a^3 = \frac{z M}{d \times 10^{-30}}$$

$$a^3 = \frac{4 \times 208}{7.2 \times 4.2832 \times 10^{24}} = 27 \times 10^{-24}$$

$\therefore \qquad a = 3 \times 10^{-8}$ cm. $= 300$ pm

14. $M = 108$ u; $d = 10.5$ g cm^{-3}, $a = 409$ pm $= 409 \times 10^{-10}$ cm

To find: $z = ?$

Solution: $\boxed{d = \frac{z \cdot M}{a^3 \cdot N_A}}$

$$\Rightarrow \quad z = \frac{a^3 \cdot d \cdot N_A}{M}$$

$$= \frac{(409 \times 10^{-10})^3 \times 10.5 \times 6.023 \times 10^{23}}{108} = 4$$

$\therefore$ it is a face-centered cubic (*fcc*) unit cell.

15. **Given:** $d = 11.2$ g cm^{-3}

For *fcc*, $z = 4$

$a = 4 \times 10^{-8}$ cm

$N_A = 6.022 \times 10^{23}$ mol^{-1}

To find: Atomic mass, $M = ?$

Solution: Using formula,

$$\boxed{d = \frac{z \cdot M}{a^3 \cdot N_A}}$$

$$\Rightarrow \quad M = \frac{d \cdot a^3 \cdot N_A}{z}$$

$$= \frac{11.2 \times (4 \times 10^{-8})^3 \times 6.022 \times 10^{23}}{4} = 107.9 \text{ g}$$

$$\boxed{M \simeq 108 \text{ g}}$$

16. **Given:** $d = 2.8$ g cm^{-3}

For *fcc*, $z = 4$

$a = 4 \times 10^{-8}$ cm

To find: $M = ?$

Solution: Using formula,

$$d = \frac{z\,M}{a^3\,N_A}$$

$$\Rightarrow \quad M = \frac{d \cdot a^3 \cdot N_A}{z} = \frac{2.8 \times (4 \times 10^{-8})^3 \times 6.022 \times 10^{23}}{4}$$

$$= 269.78 \times 10^{-1} \text{ g mol}^{-1}$$

$$\boxed{M = 26.97 \text{ g mol}^{-1}}$$

(B) Solutions

1. **Given:** Mass of solvent, $w_1 = 250$ g

Mass of glucose, $w_2 = 54$ g

$K_f = 1.86$ K kg mol^{-1}

To find: $T_f = ?$

Solution: $\Delta T_f = K_f \times m = K_f \cdot \frac{w_2}{M_2} \times \frac{1000}{w_1}$

$$= 1.86 \times \frac{54}{180} \times \frac{1000}{250}$$

$$\left[\begin{array}{l}\text{molar mass of glucose} \\ M_2 = 180 \text{ g}\end{array}\right]$$

$$= 2.23$$

as $\Delta T_f = T_f^\circ - T_f \Rightarrow T_f = \Delta T_f^\circ - \Delta T_f$

$$= 0 - 2.23$$

$\boxed{T_f = -2.23°C}$ freezing point of solution

2. **Given:** Mass of solute, $w_2 = 8$ g

Mass of solvent, $w_1 = 100$ g

$T_b = 36.86°C$, $T_b^\circ = 35.6°C$

$K_b = 2.02$ K kg mol^{-1}

To find: $M_2 = ?$

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

$$T_b - T_b^\circ = \frac{K_b \times w_2 \times 1000}{M_2 \times w_1}$$

$$\Rightarrow \quad M_2 = \frac{K_b \times w_2 \times 1000}{(T_b - T_b^\circ) \times w_1} = \frac{2.02 \times 8 \times 1000}{(36.86 - 35.6) \times 100}$$

$$= 128.25 \text{ g mol}^{-1}$$

$\therefore$ molar mass of solute, $M_2 = 128.25$ g mol^{-1}

3. $\Delta T_f = i\,K_f m = i\,K_f \times \frac{w_2}{M_2} \times \frac{1000}{w_1}$

$$CH_3CH_2\underset{\underset{Cl}{|}}{C}HCOOH \rightleftharpoons CH_3CH_2\underset{\underset{Cl}{|}}{C}HCOO^- + H^+$$

initial conc.	C	0	0
at equi.	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$K_a = \frac{C\alpha^2}{1-\alpha} \simeq C\alpha^2$$

($\because$ The value of α is neglegible as compare to 1)

$\therefore$ $1 - \alpha \approx 1$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.4 \times 10^{-3}}{0.3264}}$$

here concentration (C in mol litre $^{-1}$) is

$$= \frac{20}{122.5} \times \frac{1000}{500} = 0.3265$$

$\alpha = 0.065$

Now, $i = 1 - \alpha + \alpha + \alpha = 1 + \alpha$

$i = 1 + 0.065 = 1.065$

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

$$= 1.065 \times 1.86 \times \frac{20}{122.5} \times \frac{1000}{500}$$

$= 0.65°C$

4. **Given:** $w_2 = 100$ mg $= 0.1$ g

$V = 10$ mL $= 0.01$ L

Osmotic pressure (π) = 13.3 mm Hg = $\frac{13.3}{760}$ atm

$T = 25°C = 298$ K

$R = 0.0821$ L atm K^{-1} mol^{-1}

To find: $M_2 = ?$

Solution: Using formula osmotic pressure,

$$(\pi) = CRT = \frac{n_2}{V} RT = \frac{w_2}{M_2 V} RT$$

$$\Rightarrow \quad M_2 = \frac{w_2 RT}{\neq V} = \frac{0.1 \times 0.0821 \times 298 \times 760}{13.3 \times 0.01}$$

$$M_2 = 13980.4 \text{ g, mol}^{-1}$$

5. Moles of solute = Moles of (glucose + sucrose)

$$= \frac{w_{glu}}{M_{glu}} + \frac{w_{suc}}{M_{suc}}$$

$$n_2 = \frac{18}{180} + \frac{68.4}{342} = 0.1 + 0.2 = 0.3$$

Now,

$$\Delta T_f = K_f m = K_f \times \frac{n_2}{w_1} \times 1000$$

$$= \frac{1.86 \times 0.3 \times 1000}{200} = 2.79 \text{ K}$$

$$\Delta T_f = T_f^0 - T_f = 273 - T_f$$

$$\Rightarrow \quad T_f = 273 - 2.79 \quad \Rightarrow \quad T_f = 270.21 \text{ K}$$

6. Using formula, $\Delta T_f = K_f m = K_f \times \frac{w_2}{M_2} \times \frac{1000}{w_1}$

$$\Rightarrow \quad w_2 = \frac{\Delta T_f \times M_2 \times w_1}{K_f \times 1000}$$

$$\Rightarrow \quad w_2 = \frac{3 \times 58.5 \times 1000}{1.86 \times 1000}$$

$$w_2 = 93.35 \text{ g}$$

7. **Given:** $w_2 = 1.25$ g
$w_1 = 99.0$ g
$T_b = 80.31°C$
$T_b^0 = 80.10°C$
$K_b = 2.53°C$

To find: $M_2 = ?$

Solution: Using formula,

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

$$T_b - T_b^0 = K_b \times \frac{w_2}{M_2} \times \frac{1000}{w_1}$$

$$\Rightarrow \quad M_2 = \frac{K_b \times w_2 \times 1000}{(T_b - T_b^0)\, w_1} = \frac{2.53 \times 1.25 \times 1000}{(8.31 - 80.10) \times 99}$$

$$= \frac{3162.5}{20.79} = 152.11$$

$$\simeq 152 \text{ g mol}^{-1}$$

8. **Given:** $\Delta T_f = 7.5°C$; $K_f = 1.86$ K kg mol^{-1};
$M_2 = 58.5$ g mol^{-1}, $w_1 = 65$ g

To find: $w_2 = ?$

Solution: $\boxed{\Delta T_f = iK_f m = i\, K_f \frac{w_2}{M_2} \times \frac{1000}{w_1}}$

$$\Rightarrow \quad w_2 = \frac{\Delta T_f \times M_2 \times w_1}{i \times K_f \times 1000} = \frac{7.5 \times 58.5 \times 65}{1.87 \times 1.86 \times 1000}$$

$$\boxed{w_2 = 8.19 \text{ g}}$$

9. **Given:** $M_2 = 62$ g mol^{-1}
$w_1 = 5.50$ kg $= 5500$ g
$K_f = 1.86$ K kg mol^{-1}
$\Delta T_f = T^0_f - T_f = 0 - (-10) = 10°C$ or 10 K

To find: $w_2 = ?$

Solution: Using formulae,

$$\Delta T_f = K_f m = K_f \times \frac{w_2}{M_2} \times \frac{1000}{w_1}$$

$$\Rightarrow \quad w_2 = \frac{\Delta T_f \times M_2 \times w_1}{K_f \times 1000}$$

$$= \frac{10 \times 62 \times 5500}{1.86 \times 1000} = 1833.33 \text{ g}$$

$w_2 = 1.83$ kg

10. **Given:** $w_2 = 15$ g; $w_1 = 450$ g; $K_f = 1.86$ K kg mol^{-1}
$T_f = -0.34°C$

To find: $M_2 = ?$

Solution: $\Delta T_f = T^0_f - T_f = 0° - (-0.34)°$
$= 0.34°C$ or 0.34 K

Using formula, $\boxed{\Delta T_f = K_f m = K_f \times \frac{w_2}{M_2} \times \frac{1000}{w_1}}$

$$0.34 = 1.86 \times \frac{15}{M_2} \times \frac{1000}{450}$$

$$\Rightarrow \quad M_2 = \frac{1.86 \times 15 \times 1000}{0.34 \times 450}$$

$$= 182.35 \text{ g mol}^{-1}$$

11. **Given:** $M_2 = 176$ g mol^{-1}
$\Delta T_f = 1.5°C$
$w_1 = 75$ g

To find: $w_2 = ?$

Solution: Using the formula,

$$\boxed{\Delta T_f = K_f m}$$

$$= K_f \times \frac{w_2}{M_2} \times \frac{1000}{w_1}$$

$$1.5 = 3.9 \times \frac{w_2}{176} \times \frac{1000}{75}$$

$$\Rightarrow \quad w_2 = \frac{1.5 \times 176 \times 75}{3.9 \times 1000}$$

$$\boxed{w_2 = 5.08 \text{ g}}$$

12. **Given:** $w_2 = 0.520$ g
$M_2 = 180$ g
$w_1 = 80.2$ g
$K_b = 0.52$ K kg mol^{-1}

To find: $T_b = ?$

Solution: Using formula,

$$\boxed{\begin{aligned}\Delta T_b &= K_b\, m \\ &= K_b \times \frac{w_2}{M_2} \times \frac{1000}{w_1}\end{aligned}} = \frac{0.52 \times 0.52 \times 1000}{180 \times 80.2}$$

$$= 0.018$$

Now, $\Delta T_b = T_b - T_b^0$

$\Rightarrow$ $T_b = \Delta T_b + T_b^0 = 0.018 + 100$

$\therefore$ $\boxed{T_b = 100.018°\text{C}}$

13. Using formula, $\boxed{\Delta T_f = i\, K_f m.}$

Here, $w_2 = 10.5$ g; $i = 3$; $w_1 = 200$ g

$$\therefore \quad \Delta T_f = 3 \times 1.86 \times \frac{w_2}{M_2} \times \frac{1000}{w_1}$$

$$= \frac{3 \times 1.86 \times 10.5 \times 1000}{184 \times 200}$$

$$= 3 \times 0.525 = 1.575$$

Now, $\Delta T_f = T_f^0 - T_f \Rightarrow T_f = 0 - 1.575$
$= -1.575°\text{C}$

14. **Given:** $T = 25°\text{C} = 298$ K
$w_2 = 8.95$ mg $= 0.00895$ g
$V = 35$ mL
$\pi = 0.335$

To find: $M_2 = ?$

Solution: Using formula,

$$\boxed{\pi = CRT}$$

$$= \frac{w_2}{M_2 \times V} RT$$

$$\Rightarrow \quad M_2 = \frac{w_2 RT}{\neq V} = \frac{8.95 \times 0.00821 \times 298 \times 760 \times 1000}{0.335 \times 35}$$

$$= 14193.294 \text{ g mol}^{-1}$$

15. **Given:** $w_2 = 15$ g
$w_1 = 450$ g
$\Delta T_f = 0 - (-0.34) = 0.34°C$

To find: $M_2 = ?$

Solution: Using formula,

$$\boxed{\begin{aligned}\Delta T_f &= K_f m \\ &= K_f \times \frac{w_2}{M_2} \times \frac{1000}{w_1}\end{aligned}}$$

$$M_2 = \frac{K_f \times w_2 \times 1000}{w_1 \times \Delta T_f}$$

$$= \frac{1.86 \times 15 \times 1000}{450 \times 0.34}$$

$$= 182.3 \text{ g mol}^{-1}$$

16. **Given:** $w_1 = 500$ g; $\Delta T_b = T_b - T_b^0$
$= 100.042 - 100 = 0.042°C$

To find: $w_2 = ?$

Solution:

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

$$0.042 = 0.512 \times \frac{w_2}{92} \times \frac{1000}{500}$$

$$\Rightarrow \quad w_2 = \frac{0.042 \times 92 \times 500}{0.512 \times 1000}$$

$$\boxed{w_2 = 3.77 \text{ g}}$$

17. **Given:** $\Delta T_f = 2$ K
$K_f = 1.86$ K kg mol^{-1}
$w_1 = 1$ kg

To find: $w_2 = ?$

Solution: $\boxed{\Delta T_f = i\,K_f\,m}$

$$= i\,K_f \times \frac{w_2}{M_2} \times \frac{1000}{w_1}$$

$$\Rightarrow \qquad w_2 = \frac{\Delta T_f \times M_2 \times w_1}{i \times K_f \times 1000} = \frac{2 \times 74.5 \times 1000}{2 \times 1.86 \times 1000}$$

($\because$ i = 2 for 100% dissocation)

$$\boxed{w_2 = 40.05 \text{ g}}$$

18. $m = 1 \text{ mol kg}^{-1}$

$\Delta T_b = T_b - T_b^0 = 100.18 - 100$

$= 0.18°\text{C}$

$K_b = 0.512 \text{ K kg mol}^{-1}$

Now, $\boxed{\Delta T_b = i\,K_b\,m}$

$0.18 = i \times 0.512 \times 1$

$$\Rightarrow \qquad i = \frac{0.18}{0.512} = 0.35156$$

19. **Given:** $w_1 = 1 \text{ kg}$

$w_2 = 18 \text{ g}$

$M_2 = 180 \text{ g mol}^{-1}$

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

Now, $\boxed{\Delta T_b = K_b\,m = K_b \cdot \frac{w_2}{M_2} \times \frac{1000}{w_1}}$

$$= 0.52 \times \frac{18}{180} \times \frac{1000}{1000} = 0.052 \text{ K}$$

$\therefore \qquad \Delta T_b = T_b - T_b^0 \Rightarrow$

$$\boxed{T_b = T_b^0 + \Delta T_b = 373.15 + 0.052 = 373.202 \text{ K}}$$

20. **Given:** $w_2 = 2.5 \times 10^{-2} \text{ g}$

$M_2 = 174 \text{ g mol}^{-1}$

$V = 2 \text{ L}$

$R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$

$T = 25°\text{C} = 298 \text{ K}$

$i = 3$

To find: $\pi = ?$

Solution: $\pi = iCRT = i\frac{n_2}{V}RT$

$$= 3 \times \frac{2.5 \times 10^{-2}}{174} \times \frac{0.0821}{2} \times 298\text{ K}$$

$$= \frac{3 \times 61.1645 \times 10^{-2}}{348}$$

$$= 5.28 \times 10^{-3}\text{ atm}$$

21. **Given:** $w_2 = 10$ g
$w_1 = 90$ g
$M_2 = 180$ g

To find: $m = ?$

Solution: $m = \frac{w_2}{M_2} \times \frac{1000}{w_1}$

$$= \frac{10}{180} \times \frac{1000}{90}$$

$$= \frac{100}{18 \times 9}$$

$$= 0.617\text{ mol kg}^{-1}$$

22. **Given:** $\Delta T_f = 0.48$ K
$M_2 = 256$ g mol^{-1}
$w_1 = 75$ g
$K_f = 5.12$ K kg mol^{-1}

To find: $w_2 = ?$

Solution: $\boxed{\Delta T_f = K_f m = K_f \frac{w_2}{M_2} \times \frac{1000}{w_1}}$

$$\Rightarrow \quad w_2 = \frac{\Delta T_f \times M_2 \times w_1}{K_f \times 1000}$$

$$= \frac{0.48 \times 256 \times 75}{5.12 \times 1000} = 1.8\text{ g}$$

23. Given:

Urea (1)	Glucose (2)
$w_1 = 15$ g	$w_2 = ?$
$M_1 = 60$ g mol^{-1}	$M_2 = 180$ g mol^{-1}
$V_1 = 1$L	$V_2 = 1$L

and, $\pi_1 = \pi_2$

To find: $w_2 = ?$

Solution: As $\pi_1 = \pi_2$

$\therefore C_1RT = C_2RT$

$$C_1 = C_2$$

$$\frac{n_1}{V} = \frac{n_2}{V}$$

$$\frac{w_1}{M_1} = \frac{w_2}{M_2}$$

$$\Rightarrow \quad w_2 = \frac{w_1}{M_1} \times M_2$$

$$= \frac{15}{60} \times 180$$

$\boxed{w_2 = 45\ g}$ mass of glucose

(C) Electrochemistry

1. Given: Conductivity, $\kappa = 0.0248$ S cm^{-1}

Molarity, $C = 0.20$ M

To find: Molar Conductivity, $\Lambda_m = ?$

Solution:

$$\Lambda_m = \frac{\kappa}{C} \times 1000$$

$$= \frac{0.0248 \times 1000}{0.20}$$

$$= 124 \text{ S cm}^2 \text{ mol}^{-1}$$

2. Given: $\kappa = (\text{conductivity}) = 7.896 \times 10^{-5}$ S cm^{-1}

$\Lambda_m^\circ = 390.5$ S cm^2 mol^{-1}

$C = 0.00241$ M

To find: $\Lambda_m = ?$

$K_a = ?$

Solution: $\Lambda_m = \dfrac{\kappa \times 1000}{C}$

$$= \frac{7.896 \times 10^{-5} \times 1000}{0.00241}$$

$$\boxed{\Lambda_m = 32.76 \text{ S cm}^2 \text{ mol}^{-1}}$$

Dissociation constant, $K_a = \dfrac{C\alpha^2}{1-\alpha}$

and, $\alpha = \dfrac{\Lambda_m}{\Lambda_m^\circ} = \dfrac{32.76}{390.5} = 8.4 \times 10^{-2}$

$\therefore$ $K_a = \dfrac{(0.00241)\,(8.4 \times 10^{-2})^2}{1 - 0.0084}$

$= 1.06 \times 10^{-5}$

3. **Given:** Conductivity (κ) = 0.146×10^{-3} S cm^{-1}

Resistance (R) = 1500 Ω

To find: Cell constant (G^*)

Solution: $G^* = \kappa \times R$

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

$= 0.219$ cm^{-1}

4. **Given:** $T = 25°C = 298$ K

$n = 6$

To find: $E^0_{cell} = ?$; $\Delta_r G° = ?$; $K_C = ?$

Solution: $E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$= -0.40 - (-0.74)$

$= 0.34$ V

$\Delta_r G° = -nFE^0_{cell}$

$= -6 \times 96500 \times 0.34$

$= -196860$ J mol^{-1}

$\Delta_r G° = -2.303\, RT \log K_C$

$-196860 = -2.303 \times 8.314 \times 298 \log K_C$

$\Rightarrow$ $\log K_C = 34.5014$

$\Rightarrow$ $K_C = \text{anti-log}\,(34.5014)$

$= 3.172 \times 10^{34}$

5. (i) The cell is represented as:

$Cr(s) \mid Cr^{3+}(aq) \mid\mid Fe^{2+}(aq) \mid Fe(s)$

(ii) $E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$= -0.44 - (-0.74)$

$= 0.30$ V

(iii) $$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[Cr^{3+}(aq)]^2}{[Fe^{2+}(aq)]^3}$$

$$= 0.30 - \frac{0.059}{6} \log \frac{(0.1)^2}{(0.01)^3}$$

$$= 0.30 - 0.009 \log \frac{0.01}{0.000001}$$

$$= 0.30 - 0.009 \log 10^4 = 0.30 - 0.036 = 0.264 \text{ V}$$

6. The cell reaction is:

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

$n = 2$

$E^0_{cell} = 0.46$ V

from Nernst equation,

$$\boxed{E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[Ag^+]^2}{[Cu^{2+}]}}$$

$$= 0.46 - \frac{0.059}{2} \log \frac{(0.001)^2}{0.10}$$

$$= 0.46 - \frac{0.059}{2} \log 10^{-5}$$

$$= 0.46 - \frac{0.059}{2} (-5 \log 10)$$

$$= 0.46 + \frac{0.059 \times 5}{2}$$

$= 0.46 + 0.146$

$= 0.606$ V

7. Cathode: $Cd^{2+}(aq) \longrightarrow Cd(s)$

Anode: $Fe(s) \longrightarrow Fe^{2+}(aq)$

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$
$$= -0.40 - (-0.44)$$
$$= 0.04 \text{ V}$$

as $\boxed{E^0_{cell} = \frac{0.059}{n} \log K_C}$

$$\therefore 0.04 = \frac{0.059}{2} \log K_C$$

$$\Rightarrow \log K_C = \frac{0.04 \times 2}{0.059} = 1.356$$

$$\Rightarrow \quad K_C = \text{anti-log } (1.356)$$
$$= 22.70$$

8. $E^0_{cell} = E^0_{cathode} - E^0_{anode}$
$$= -0.403 - (-0.763)$$
$$= 0.360 \text{ V}$$

from Nernest equation,

$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[Zn^{2+}]}{[Cd^{2+}]}$$

$$= 0.36 - \frac{0.059}{2} \log \frac{(0.1)}{(0.01)}$$

$$= 0.36 - \frac{0.059}{2} \log 10$$

$$= 0.33 \text{ V}$$

now, $\Delta_r G^0 = -nFE^0_{cell}$
$$= -2 \times 96500 \times 0.36$$
$$= -69480 \text{ J mol}^{-1}$$

9. $E^0_{cell} = 1.05$ V, $n = 2$

Using Nernst Eq. $\boxed{E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[P]}{[R]}}$

$$E_{cell} = 1.05 - \frac{0.059}{2} \log \frac{[Ni^{2+}]}{[Ag^{+}]^2}$$

$$= 1.05 - \frac{0.059}{2} \log \frac{[0.160]}{[0.002]^2}$$

$$= 1.05 - \frac{0.059}{2} \log 4 \times 10^4$$

$$= 1.05 - \frac{0.059}{2} (2 \log 2 + 4 \log 10)$$

$$= 1.05 - \frac{0.059}{2} (2 \times .3010 + 4) = 1.05 - 0.14$$

$$\boxed{E_{cell} = 0.91 \text{ V}}$$

10. **Given:** $\Lambda_m = 138.9 \text{ S cm}^2 \text{ mol}^{-1}$
$C = 1.5$ m

To find: $\kappa = ?$

Solution: $\boxed{\Lambda_m = \frac{\kappa \times 1000}{C}}$

$$\Rightarrow \quad \kappa = \frac{\Lambda_m \times C}{1000} = \frac{138.9 \times 1.5}{1000}$$

$$\boxed{\kappa = 0.208 \text{ S cm}^{-1}}$$

11. The cell reaction is:

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

$$\boxed{\Delta G^\circ = -nFE^0_{cell}}$$

$$= -2 \times 96500 \times 1.05$$

$$= -202650 \text{ J mol}^{-1}$$

Now, $\boxed{\Delta G^0 = -2303\, RT \log K_C}$

$$\Rightarrow \qquad \log K_C = \frac{\Delta G^0}{-2.303\,RT}$$

$$= \frac{-202650}{-2.303 \times 8.314 \times 298} = 35.516$$

$$\Rightarrow \qquad \boxed{K_C = 3.28 \times 10^{35}}$$

12. The eq. is; $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

from Nernst eq. we have

$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

$$= 1.33 - \frac{0.059}{6} \log \frac{(0.2)^2}{(0.1)(10^{-4})^{14}}$$

$$= 1.33 - \frac{0.059}{6} \log \frac{2 \times 2 \times 10^{55}}{1}$$

$$= 1.33 - \frac{0.059}{6} (2 \log 2 + 55)$$

$$= 1.33 - 0.546$$

$$\boxed{E_{cell} = 0.783\ V}$$

13. (a) $Zn \longrightarrow Zn^{++} + 2e^-$

$Cu^{++} + 2e^- \longrightarrow Cu$

(b) $E^\circ_{cell} = E_{cathode} - E_{anode}$

$= 0.34 - (-0.76)$

$= 0.34 + 0.76$

$= 1.10\ V$

from Nernst eq,

$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{cell} = 1.1 - \frac{0.059}{2} \log \frac{2}{0.5} = 1.1 - \frac{0.059}{2} (\log 20 - \log 5)$$

$$= 1.1 - \frac{0.059}{2} \times 0.6021 = 1.1 - 0.0177 = 1.09 \text{ V}$$

14. $\boxed{E^0_{cell} = \frac{0.059}{n} \log K_C}$

$$\Rightarrow \quad \log K_C = \frac{E^0_{cell} \times n}{0.059} \quad [E^0_{cell} = E_{cathode} - E_{anode}$$

$$= \frac{1.1 \times 2}{0.059} \quad = 0.34 - (-0.76)$$

$$= 1.10 \text{ V}]$$

$$\log K_C = 37.288$$

$$\Rightarrow \quad K_C = \text{anti-log } (37.288)$$

$$= 1.941 \times 10^{37}$$

15. **Given:** $d = 1$ cm $\Rightarrow$ $r = 0.5$ cm

$l = 50$ cm

$k = 5.55 \times 10^3\ \Omega$

$C = 0.05$ M

To find: $\kappa = ?$, $\rho = ?$, $\Lambda_m = ?$

Solution: $\boxed{R = \rho \frac{l}{a}}$ $\Rightarrow$ $\rho = \frac{R \cdot a}{l}$ $[a = \text{area} = \pi r^2]$

$$\Rightarrow \quad \rho = \frac{5.55 \times 10^3 \times 3.14 \times (0.5)^2}{50}$$

$$= 87.135\ \Omega \text{ cm}$$

Conductivity, $\boxed{\kappa = \frac{1}{\rho}}$

$$= \left(\frac{1}{87.135}\right) \text{S cm}^{-1}$$

$$= 0.001148 \text{ S cm}^{-1}$$

Molar conductivity, $\boxed{\Lambda_m = \frac{\kappa \times 1000}{C}}$

$$= \frac{0.01148 \times 1000}{0.05}$$

$$= 229.6 \text{ S cm}^2 \text{ mol}^{-1}$$

16. Zn is getting oxidised while Ag_2O is getting reduced

$\therefore$ anode: $Zn \longrightarrow Zn^{2+} + 2e^-$

cathode: $2Ag^+ + 2e^- \longrightarrow 2Ag$

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

$= +0.80 - (-0.76)$

$= 1.56$ V

and, $\Delta G^0 = -nFE^0_{cell}$

$= -2 \times 96500 \times 1.56$

$= 301080 \text{ J mol}^{-1}$

17. $2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$

$2I^- \longrightarrow I_2 + 2e^-$

$\therefore$ $n = 2$

Now, $\Delta G^0 = -nFE^0_{cell}$

$= -2 \times 96500 \times 0.236$

$= -45.55 \text{ kJ mol}^{-1}$

Also, $\Delta G^0 = -2.303\, RT \log K_C$

$\Rightarrow$ $\log K_C = \frac{-\Delta G^0}{2.303\, RT}$

$$= \frac{-(-45.55)}{2.303 \times 8.314 \times 10^{-3} \times 298}$$

$= 7.983$

$\Rightarrow$ $K_C = \text{antilog } (7.983)$

$= 9.616 \times 10^7$

18. (a) $Cr_2O_7^{2-} + 6e^- + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$

for 1 mole of $Cr_2O_7^{2-}$, charge required = 6 F

$= 6 \times 96500$

$= 579000$ C

(b) $\Lambda_m = \dfrac{\kappa \times 1000}{C}$

$$= \frac{4 \times 10^{-5} \times 1000}{0.001} = 40 \text{ Scm}^2\text{mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = 0.103$$

$$\therefore \quad K_C = \frac{C\alpha^2}{1-\alpha} = \frac{0.001 \times (0.103)^2}{1 - 0.103}$$

$$= 1.19 \times 10^{-5}$$

19. Anode: $Fe \longrightarrow Fe^{2+} + 2e^-$

Cathode: $2H^+ + 2e^- \longrightarrow H_2$

$\therefore \quad n = 2$

$E^0_{cell} = +0.44$ V

Applying Nernst eq, $E_{cell} = E^0_{cell} - \dfrac{0.059}{n} \log \dfrac{[Fe^{2+}]}{[H^+]^2}$

$$\therefore \quad E_{cell} = 0.44 - \frac{0.059}{2} \log \frac{0.001}{1^2} = 0.44 - \frac{0.059}{2} \log 10^{-3}$$

$$= 0.44 - \frac{0.059}{2}(-3) \qquad [\because \log 10 = 1]$$

$$= 0.44 + 0.08865$$

$$= 0.53 \text{ V}$$

20. **Given:**

Case I	**Case II**
$R = 100\ \Omega$	$R = 520\ \Omega$
$C = 0.1$ mol L^{-1}	$C = 0.02$ mol L^{-1}
$\kappa = 1.29 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$	$\kappa = ?$, $\Lambda_m = ?$

Case I: $G^* = R\kappa = 100 \times 1.29 \times 10^{-2}$

$= 1.29\ cm^{-1}$ ($G^* \rightarrow$ cell constant)

Case II: $\kappa = \dfrac{G^*}{R}$

$\therefore \quad \kappa\,(0.02\text{ M KCl}) = \dfrac{G^*}{R} = \dfrac{1.29}{520} = 2.48 \times 10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}$

and, $\quad \Lambda_m = \dfrac{\kappa \times 1000}{C} = \dfrac{1.29}{520} \times \dfrac{1000}{0.02} = 124.038\ \Omega^{-1}\ \text{cm}^{-1}$

21. $\Delta_r G^0 = -\,nFE^0_{cell}$

$n = 2$

$\therefore\ \Delta_r G^0 = -\,2 \times 96500 \times 2.71$

$= -\,523030\ \text{J mol}^{-1}$

22. **To find:** $E_{cell} = ?$

Solution: Using Nernst equation,

$$\boxed{E_{cell} = E^0_{cell} - \frac{0.059}{n}\log\frac{[P]}{[R]}}$$

The equation for the above cell is:

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

$\therefore\ E_{cell} = E^0_{cell} - \dfrac{0.059}{n}\log\dfrac{[Mg^{2+}]}{[Cu^{2+}]}$

$= 2.71 - \dfrac{0.059}{2}\log\dfrac{(0.1)}{(0.01)} = 2.71 - \dfrac{0.059}{2}\log 10$

$= 2.71 - \dfrac{0.059}{2} \times 1 \qquad (\because \log 10 = 1)$

$= 2.68\ \text{V}$

(D) Chemical Kinetics

1. **Given:** $t = 40$ mins

if $R_0 = 100$ (initial conc.)

$R = 100 - 30 = 70$ (amount left)

To find: $t_{1/2} = ?$

Solution: $t_{1/2} = \dfrac{0.693}{k}$ (for 1st order reaction)

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

$$= \frac{2.303}{40} \log \frac{100}{70}$$

$$= \frac{2.303}{40} (\log 10 - \log 7) = \frac{2.303}{40} (1 - 0.8451)$$

$$k = 0.0089 \text{ min}^{-1}$$

$\therefore$ $t_{1/2} = \dfrac{0.693}{0.0089} = 77.86$ min

$$\boxed{t_{1/2} = 77.86 \text{ min}}$$

2. **Given:** $k_1 = 0.02 \text{ S}^{-1}$, $T_1 = 500$ K
$k_2 = 0.07 \text{ S}^{-1}$, $T_2 = 700$ K

To find: E_a and A

Solution: $\log \dfrac{k_2}{k_1} = \dfrac{E_a}{2.303\,R} \left[\dfrac{1}{T_1} - \dfrac{1}{T_2} \right]$

$$\log \frac{0.07}{0.02} = \frac{E_a}{2.303 \times 8.314} \left[\frac{1}{500} - \frac{1}{700} \right]$$

$$0.5441 = \frac{E_a}{2.303 \times 8.314} \left[\frac{700 - 500}{700 \times 500} \right]$$

$$E_a = \frac{0.5441 \times 2.303 \times 8.314 \times 35\cancel{00}}{2\cancel{00}}$$

$$= 18{,}231.43 \text{ J} = 18.231 \text{ kJ}$$

Now, $k = A e^{-E_a/RT}$

$$\Rightarrow \qquad \log k = \log A - \frac{E_a}{2.303\,RT}$$

at $\qquad T = 500$ K,

$$\log 0.02 = \log A - \frac{18231.43}{2.303 \times 8.314 \times 500}$$

On solving, we have

$A = 1.60$

3. **Given:** $T_1 = 300$ K; $k_1 = 6.0 \times 10^{-4}$ S^{-1}

$T_2 = 310$ K; $E_a = 3.05 \times 105$ J mol^{-1}

To find: $k_2 = ?$

Solution: $\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$$\log k_2 - \log k_1 = \frac{3.05 \times 10^5}{2.303 \times 8.314}\left(\frac{1}{300} - \frac{1}{310}\right)$$

$$\log k_2 - \log (6 \times 10^{-4}) = \frac{3.05 \times 10^5}{2.303 \times 8.314}\left(\frac{310 - 300}{300 \times 310}\right)$$

$$\log k_2 = \log (6 \times 10^{-4}) + \frac{3.05 \times 10^5 \times 10}{19.147 \times 93000}$$

$= -3.22 + 1.71$

$= -1.51$

On taking anti-log

$k_2 = -3.1 \times 10^{-2}$ sec^{-1}

4. **Given:** $[R]_0 = 0.10$ M

$t = 3$ hours $= 3 \times 60 = 180$ min.

$k = 0.0051$ min^{-1}

To find: $[R] = ?$

Solution: Using formula,

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

$$0.0051 = \frac{2.303}{180} \log \frac{0.1}{[R]}$$

$$\Rightarrow \quad \frac{0.0051 \times 180}{2.303} = \log \frac{0.1}{[R]}$$

$$\Rightarrow \quad \frac{0.1}{[R]} = \text{anti-log } (0.3986)$$

$$\frac{0.1}{[R]} = 2.503$$

$$\Rightarrow \quad [R] = \frac{0.1}{2.503} = 0.039 \text{ M}$$

5. Using formula, $\boxed{\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$

$$\log \frac{2.39 \times 10^{-7}}{2.15 \times 10^{-8}} = \frac{E_a}{2.303 \times 8.31}\left(\frac{1}{650} - \frac{1}{700}\right)$$

$$\log 1.111 \times 10 = \frac{E_a}{19.147} \times \frac{50}{455000}$$

$$\Rightarrow \quad 1.0457 = \frac{E_a}{19.147} \times \frac{1}{9100}$$

$$\therefore \quad E_a = 1.0457 \times 19.147 \times 9100$$
$$= 182200.36 \text{ J}$$

6. For 1st order reaction

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

$$t_1 = 5 \text{ min} \quad k = \frac{2.303}{5} \log 100 \frac{[A]_0}{80\,[A]_0}$$

$$k = \frac{2.303}{5} \log \frac{10}{8}$$

$$t_2 = ? \qquad k = \frac{2.303}{t_2} \log \frac{100}{40}$$

Dividing the two,

$$\frac{5}{t_2} = \log \frac{10/8}{10/4}$$

$$\frac{5}{t_2} = \frac{\log 10 - \log 8}{\log 10 - \log 4} = \frac{0.969}{0.3979} = 0.2435$$

Solving $\boxed{t_{60\%} = 20.53 \text{ mins}}$

7. $t_{1/2} = 5 \times 10^4\, s$; $t = 2$ hours $= 7200\, s$.

Now, for first order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$\therefore \quad \frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$\frac{0.693}{5 \times 10^4} = \frac{2.303}{7200} \log \frac{[A]_0}{[A]}$$

$$\Rightarrow \quad \log \frac{[A]_0}{[A]} = \frac{0.693 \times 7200}{5 \times 10^4 \times 2.303}$$

$$= 0.0433$$

$$\frac{[A]_0}{[A]} = \text{anti-log } (0.0433) = 1.105$$

and $$\frac{[A]}{[A]_0} = \frac{1}{1.105} \times 100 = 90.49\%$$

8. For 1st order reaction, $k = \dfrac{2.303}{t} \log \dfrac{[R]_0}{[R]}$

When $t = t_{1/2}$, $[R] = [R]_0/2$

$$\therefore \quad t_{1/2} = \frac{2.303}{k} \log \frac{[R]_0}{[R]_0/2} = \frac{2.303}{k} \log 2 = \frac{2.303}{k} \times 0.3010$$

$$\Rightarrow \quad \boxed{t_{1/2} = \frac{0.693}{k}}$$ $\therefore$ $t_{1/2}$ is independent of 'R'.

9. According to question, rate $\propto [A]^1$

and, rate $\propto [B]^2$

$\therefore$ $\boxed{\text{rate} = k\,[A]\,[B]^2}$

(i) when $[B]^1 = 3B$, rate$^1 = k\,[A]\,[3B]^2 = 9\,k\,[A]\,[B]^2$

i.e. rate becomes 9 times = 9 rate

(ii) when $[A]^1 = 2A$; $[B]^1 = 2B$, rate$^1 = k\,[2A]\,[2B]^2$

$= 8\,k\,[A]\,[B]^2 = 8$ rate

i.e. rate becomes 8 times.

10. (i) It is a first order reaction.

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

$$t_{1/2} = 37.9 \text{ S}$$

$$\therefore \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{37.9}$$

$$\Rightarrow \quad \frac{0.693}{37.9} = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

when $[R] = \frac{1}{4}[R]_0$, we have

$$\frac{0.693}{37.9} = \frac{2.303}{t_{3/4}} \log \frac{[R]_0}{\frac{1}{4}[R]_0}$$

$$\Rightarrow \quad t_{3/4} = \frac{2.303 \times 37.9}{0.693} \log \frac{4}{1}$$

$$\Rightarrow \quad \boxed{t_{3/4} = 75.82 \text{ s}}$$

(ii) $t = 1$ min $= 60$ s; $[A]_0 / [A] = ?$

Now, $$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$\Rightarrow \quad \log \frac{[A]_0}{[A]} = \frac{0.693 \times t}{2.303 \times t_{1/2}}$$

$$= \frac{0.693 \times 60}{2.303 \times 37.9}$$

$$= \frac{41.58}{2.303 \times 37.9}$$

$$= 0.4763$$

$$\therefore \quad \frac{[A]_0}{[A]} = \text{anti-log } (0.4763)$$

$$= 2.994$$

11. **Given:** $k_1 = k, \quad T_1 = 300$ K

$k_2 = 4\,k, \quad T_2 = 320$ K

To find: $E_a = ?$

Solution: Using formula, $\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$$\log \frac{4k}{k} = \frac{E_a}{2.303 \times 8.314}\left(\frac{1}{300} - \frac{1}{320}\right)$$

$$\Rightarrow \quad \log 4 = \frac{E_a}{2.303 \times 8.314}\left(\frac{20}{300 \times 320}\right)$$

$$\Rightarrow \quad E_a = \frac{\log 4 \times 2.303 \times 8.314 \times 300 \times 320}{20}$$

$$\boxed{E_a = 55333.09 \text{ J mol}^{-1}}$$

12. For 1st order, $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

If $[R]_0 = 100\%$, then $[R] = 100 - 20 = 80\%$

$t = 15$ min

$$\therefore \quad k = \frac{2.303}{15} \log \frac{100}{80}$$

$$= \frac{2.303}{15} \log \frac{10}{8} = \frac{2.303}{15} (\log 10 - \log 8)$$

$$= \frac{2.303}{15} (\log 10 - 3 \log 2)$$

$$= \frac{2.303}{15} (1 - 3 \times .3010)$$

$$\boxed{k = 0.0148 \text{ min}^{-1}}$$

13. **Given:** $k = 2.4 \times 10^{-3}\ S^{-1}$

$[R]_0 = a$

$[R] = a - \frac{3}{4}a = \frac{1}{4}a$

Solution: Using formula,

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

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

$$= \frac{2.303}{2.4 \times 10^{-3}} \log \frac{a}{\frac{1}{4}a}$$

$$= \frac{2.303}{2.4 \times 10^{-3}} \log 4 = \frac{2.303}{2.4 \times 10^{-3}} \times 0.6020$$

$= 577.67$ s

14. **Given:** $k_1 = k, k_2 = 2k$

$T_1 = 298$ K, $T_2 = 308$ K

To find: $E_a = ?$

Solution: $$\boxed{\log \frac{k_2}{k_1} = \frac{E_a}{2.303\, k} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)}$$

$$\log \frac{2k}{k} = \frac{E_a}{2.303 \times 8.314}\left(\frac{1}{298} - \frac{1}{308}\right)$$

$$\Rightarrow \qquad E_a = \frac{\log 2 \times 2.303 \times 8.314 \times 298 \times 308}{10}$$

$$= 52897.78 \text{ J mol}^{-1}$$

15. $t_{1/2} = 10$ min

(i) $\boxed{k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10}}$

$k = 0.0693 \text{ min}^{-1}$

(ii) $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$

$$0.0693 = \frac{2.303}{10 \times 60} \log \frac{[A]_0}{[A]}$$

$$\Rightarrow \qquad \log \frac{[A]_0}{[A]} = \frac{0.0693 \times 60}{2.303}$$

$$\log \frac{[A]_0}{[A]} = 1.805$$

$$\therefore \qquad \frac{[A]_0}{[A]} = \text{anti-log } (1.805)$$

$$= 6.383 \times 10^1$$

16. $a = 0.6 \text{ mol L}^{-1}$; $a - x = 0.2 \text{ mol L}^{-1}$

$t = 5$ min

$$\boxed{k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} = \frac{2.303}{t} \log \frac{a}{a-x}}$$

$$= \frac{2.303}{5} \log \frac{0.6}{0.2} = \frac{2.303}{5} \log 3 = \frac{2.303}{5} \times 0.4771$$

$= 0.219 \text{ min}^{-1}$

17. For 1st order reaction,

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

$$k = \frac{2.303}{20} \log \frac{100}{85} = \frac{2.303 \times 0.0706}{20}$$

Now $$t_{60\%} = \frac{2.303}{k} \log \frac{100}{40}$$

$$= \frac{2.303 \times 20}{2.303 \times 0.0706} (\log 10 - \log 4)$$

$$= \frac{20}{0.0706} \times 0.3979 = 112.7 \text{ min}$$

18. **Given:** $t = 40$ mins

$[A]_0 = 100$

$[A] = 100 - 30 = 70$

To find: $t_{1/2} = ?$

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

and, $$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$\therefore \quad \frac{0.693}{t_{1/2}} = \frac{2.303}{40} \log \frac{100}{70}$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{4} \times 0.1549$$

$$\Rightarrow \quad t_{1/2} = \frac{0.693 \times 40}{2.303 \times 0.1549}$$

$$\therefore \quad \boxed{t_{1/2} = 77.78 \text{ min.}}$$

19. For 1st order reaction, $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$

For 99% completion, $= \frac{2.303}{t_{99\%}} \log \frac{100}{1}$

For 90% completion, $k = \frac{2.303}{t_{90\%}} \log \frac{100}{10}$

$\therefore$ $$t_{99\%} = \frac{2.303}{k} \log \frac{100}{1}$$

$$t_{90\%} = \frac{2.303}{k} \log \frac{100}{10}$$

$$\frac{t_{99\%}}{t_{90\%}} = \frac{\frac{2.303}{k} \log 100}{\frac{2.303}{k} \log 10}$$

$$= \frac{2 \log 10}{\log 10}$$

$$= 2 \qquad [\because \log 10 = 1]$$

$\therefore$ $$\boxed{t_{99\%} = 2\, t_{90\%}}$$

20. (a) Order of reaction $= \frac{1}{2} + 2 = \frac{1+4}{2}$

$$= \frac{5}{2}$$

(b) For 1st order reaction,

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

$$= \frac{0.693}{5.5 \times 10^{-14}\, S^{-1}}$$

$$= 1.26 \times 10^{13}\ S$$

CHAPTER 6 Numerical based on laws

(B) Solutions

1. What concentration of nitrogen should be present in a glass of water at room temperature? Assume the temperature to be 25°C, a total pressure of 1 atm and mole fraction of nitrogen in air of 0.78.
[K_H for nitrogen = 8.42×10^{-7} M/mm Hg] **[Outside Delhi 2009]**

2. If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1L of water? Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 K bar. **[Outside Delhi Comptt. 2012]**

3. The partial pressure of ethane over a saturated solution containing 6.56×10^{-2} g of ethane is 1 bar. If the solution contains 5.0×10^{-2} g of ethane, then what will be the partial pressure of the gas?
[Outside Delhi Comptt. 2012]

4. The partial pressure of ethane over a solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what shall be the partial pressure of the gas?

5. Henry's Law constant for the molality of methane is benzene at 298 K is 4.27×10^5 mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.

6. An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the boiling point of the solvent. What is the molecular mass of the solute?

7. Vapour pressure of water at 293 K is 17.535 mm Hg. Calculate the vapour pressure of water at 293 K when 25g of glucose is dissolved in 450g of water.

8. 100g of liquid A (molar mass 140 g mol^{-1}) was dissolved in 1000g of liquid B (molar mass 180g mol^{-1}). The vapour pressure of pure liquid B was found to be 500 torr. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475 torr.

9. At 25 °C, the vapour pressure of pure water is 23.76 mm Hg and that of an aqueous dilute solution of urea is 22.98 mm Hg. Calculate the molality of this solution.

(C) *Electrochemistry*

1. Calculate Λ_m° for acetic acid. Given that
Λ_m° (HCl) = 426 Scm^2mol^{-1}; Λ_m° (NaCl) = 126 Scm^2mol^{-1}
Λ_m° (CH_3COONa) = 91 S cm^2 mol^{-1}.
[Delhi Board 2010, Outside Delhi Comptt. 2011]

2. How much charge in terms of Faraday is required for the reduction of 1 mol of Cu^{2+} to Cu. **[Delhi Board 2014]**

3. How much charge is required for the following reaction:
(i) 1 mol of Al^{3+} to Al
(ii) 1 mol of Cu^{2+} to Cu
(iii) 1 mol of MnO^{4-} to Mn^{2+}

4. How much electricity in terms of faraday is required to produce
(i) 20.0g of Ca from molten $CaCl_2$,
(ii) 40.0 g of Al from molten Al_2O_3.

5. How many coulombs are required for the following oxidation reactions:
(i) 1 mol of H_2O to O_2
(ii) 1 mol of FeO to Fe_2O_3

6. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5.0 ampere for 20 minutes. What mass of nickel will be deposited at the cathode? (Atomic mass of Ni = 58.7).

7. Three electrolytic cells A, B, C containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

8. How much charge is required to reduce one mole of nitrobenzene to aniline?

9. Given a galvanic cell in which the over all reaction is:

$Zn(s) + Cl_2(g) \longrightarrow Zn^{2+} + 2Cl^-$

If the cell uses 6.5g of Zn in the reaction, how long could it deliver 0.20 A of current to outside in the external circuit? Atomic number of Zn = 65g per mole.

10. How many hours does it take to reduce 3 mol of Fe^{3+} to Fe^{2+} with 2.0 A current? (F = 96500 C).

11. Silver is electrodeposited on a metallic surface area of 800 cm^2 by passing a current of 0.2A for 3 hours. Calculate the thickness of silver deposited. Density of silver is 10.47 g cm^3 and atomic mass of Ag = 108.

12. Calculate the (NH_4OH) when corresponding values of NH_4Cl, NaOH and NaCl are 150, 248.1 and 126. 4 S cm^2 mol^{-1} respectively.

(B) Solutions

1. $P_{N_2} = 1$ atm

From Henry's law,

$$P_{N_2} = K_H \cdot x_{N_2}$$

or, $$x_{N_2} = P_{N_2} / K_H = 1 / 8.42 \times 10^{-7}$$

Also, $$x_{N_2} = \frac{n(N_2)}{n(N_2) + n(H_2O)} \simeq \frac{n(N_2)}{n(H_2O)}$$

$$[\because n(N_2) << n(H_2O)]$$

$\Rightarrow$ $$n(N_2) = x_{N_2} \times n(H_2O)$$

$$= \frac{1}{8.42 \times 10^{-7}} \times 55.5$$

$$\left\{\because n(H_2O) = \frac{1000}{18} = 55.5\right\}$$

$$n(N_2) = 6.59 \times 10^7 \text{ moles (concentration of } N_2 \text{ in water)}$$

2. The solubility of gas is related to its mole fraction in aqueous solution. The mole fraction of the gas in a solution is calculated by applying Henry's law.

Thus, from Henry's law

$$P_{(N_2)} = K_H x_{(N_2)}$$

$\therefore$ $$x(N_2) = \frac{P(N_2)}{K_H} = \frac{0.987 \text{ bar}}{76480 \text{ bar}}$$

$\therefore$ $$x(N_2) = 1.29 \times 10^{-5}$$

Now, 1L of water $= \frac{1000}{18}$ moles $= 55.5$ moles

and, $$x(N_2) = \frac{n(N_2)}{n(N_2) + n(H_2O)} \simeq \frac{n(N_2)}{n(H_2O)}$$

$$\left[n_{(N_2)} <<< n_{(H_2O)}\right]$$

$$1.29 \times 10^{-5} = \frac{n(N_2)}{55.5}$$

$\therefore$ $$n(N_2) = 1.29 \times 10^{-5} \times 55.5$$

$$= 0.716 \text{ millimoles}$$

3. From Henry's law,

$$P = K_H \times x$$

$\therefore$ $$1 \text{ bar} = K_H \times 6.56 \times 10^{-2}$$

$\Rightarrow$ $$K_H = \frac{1}{6.56 \times 10^{-2}}$$

$$= 15.24 \text{ bar g}^{-1}$$

Now, when $x = 5 \times 10^{-2}$ g,

$$P = K_H \times x$$

$$= \frac{1}{6.56 \times \cancel{10^{-2}}} \times 5 \times \cancel{10^{-2}}$$

$$\boxed{P = 0.762 \text{ bar}}$$

4. We know that, $m = K_H \times P$

$\therefore$ 6.56×10^{-2} g $= K_H \times 1$ bar ...(i)

$\therefore$ 5.00×10^{-2} g $= K_H \times P$ ...(ii)

$K_H = 6.56 \times 10^{-2}/1$ bar (from i)

$K_H = 5.00 \times 10^{-2}/$ p bar (from ii),

$\therefore$ $$\frac{6.56 \times 10^{-2}}{1} = \frac{5.00 \times 10^{-2}}{P}$$

$\therefore$ $$P = \frac{5{\cdot}00}{6{\cdot}56} = 0{\times}762 \text{ bar.}$$

5. Using relation, $P = K_H x$

$$\therefore \quad x = \frac{P}{K_H} = \frac{760 \text{ mm}}{4{\cdot}27 \times 10^5 \text{ mm}} = 1.78 \times 10^{-3}$$

i.e., mole fraction of methane in benzene

$= 1.78 \times 10^{-3}$.

6. Vapour pressure of pure water at the boiling point (P°) = 1.013 bar

Vapour pressure of solution (P_s) = 1.004 bar

Mass of solute (w_2) = 2g

Molar mass of solvent, water = 18g

Mass of solvent (w_1) = 98g

Mass of solution = 100g

Apply Raoult's Law for dilute solution,

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n_2}{n_1 + n_2} \simeq \frac{n_2}{n_1} \quad \{\text{Dilute solution being 2\%}\}$$

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n_2}{n_1} = \frac{W_2/M_2}{W_1/M_1}$$

$$\frac{(1{\cdot}013 - (1{\cdot}004)}{(1{\cdot}013)} = \frac{2 \times 18}{M_2 \times 98}$$

$$\therefore M_2 = \frac{2 \times 18}{98 \times 0{\cdot}009} \times 1{\cdot}013 = 41.35 \text{ g mol}^{-1}.$$

7. P° = 17.535 mm

Molar mass of glucose = 180 g mol^{-1}

Molar mass of water = 18 g mol^{-1}

According to Raoult's's Law,

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n_2}{n_1 + n_2} \simeq \frac{n_2}{n_1} = \frac{W_2/M_2}{W_1/M_1}$$

$$1 - \frac{P_s}{P_0} = \frac{25/180}{450/18} = \frac{25 \times 18}{180 \times 450}$$

$$1 - \frac{P_s}{P_0} = \frac{5}{90}; \quad 1 - \frac{5}{90} = \frac{P_s}{P_0}$$

$$\frac{90 - 5}{90} = \frac{P_s}{17{\cdot}535}$$

$$\frac{85}{90} = \frac{P_s}{17{\cdot}535}$$

$$\therefore \qquad P_s = \frac{85 \times 17{\cdot}535}{90} = 17.44 \text{ mm.}$$

8. No. of moles of solute, $n_2 = \frac{100}{140} = \frac{5}{7}$ mole

No. of moles of solvent, $n_1 = \frac{1000}{180} = \frac{50}{9}$ mole

Mole fraction of solute,

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{5/7}{5/7 + 50/9} = 0{\cdot}114$$

Mole fraction of solvent, $x_1 = (1 - x_2) = (1 - 0.114) = 0.886$

According to Raoult's law

$P_A = x_A \, P_A^\circ = 0.114 \times P_A^\circ$

$P_B = x_B \, P_B^\circ = 0.886 \times 500 = 443$ torr

$P_{Total} = P_A + P_B$

$475 = 0.114 + 443$

$$P_A^\circ = \frac{475 - 443}{0{\cdot}114} = 280.7 \text{ torr}$$

$\therefore P_A = 0.114 \times 280.7 = 32$ torr.

9. $P_A^o = 23.75\text{mm}$; $P_A = 22.98$ mm

Let x_B mole fraction of solute

According to Raoult's Law, $\dfrac{P_A^o - P_A}{P_A^o} = x_B$

$$\therefore x_B = \frac{23{\cdot}76 - 22{\cdot}98}{23{\cdot}76} = \frac{0{\cdot}78}{23{\cdot}76} = 0{\cdot}0328$$

For dilute solutions, $x_B = n_B/n_A$

or $\quad n_B = n_A x_B$

If we consider 1 kg of water, then n_B becomes number of moles of solute per kg of solvent and thus molality of solution,

$$\therefore \quad n_B = \frac{1000}{18} \times 0.0328 = 55.5 \times 0.0328$$

$= 1{\times}82$ mol/kg of solvent.

(C) Electrochemistry

1. Applying Kohlrausch law,

$\Lambda_m^\circ (CH_3COOH) = \lambda^\circ(CH_3COO^-) + \lambda^\circ(H^+) = ?$

$\Lambda_m^\circ (HCl) = \lambda^\circ(H^+) + \lambda^\circ(Cl^-) = 426 \text{ S cm}^2 \text{ mol}^{-1}$ ...(1)

$\Lambda_m^\circ (NaCl) = \lambda^\circ(Na^+) + \lambda^\circ(Cl^-) = 126 \text{ S cm}^2 \text{ mol}^{-1}$ ...(2)

$\Lambda_m^\circ (CH_3COONa) = \lambda^\circ(CH_3COO^-) + \lambda^\circ(Na^+) = 91 \text{ S cm}^2 \text{ mol}^{-1}$ ...(3)

To find the value of $\Lambda_m^\circ (CH_3COOH)$ add equations 1 & 3 and then subtract equation 2 from it.

$\Rightarrow$ '$(H^+) + \lambda^\circ(\cancel{Cl^-}) + \lambda^\circ(CH_3COO^-)$

$+ \lambda^\circ(\cancel{Na^+}) - \lambda^\circ(\cancel{Na^+}) + \lambda^\circ(\cancel{Cl}$

$426 + 91 - 126$

$\Rightarrow \lambda^\circ(H^+) + \lambda^\circ(CH_3COO^-) = 391 \text{ S cm}^2 \text{ mol}^{-1}$

2. Reduction of 1 mol of Cu^{2+} to Cu is given by:

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

as the charge required for 1 mole of $e^- = 1F$

$\therefore$ the charge required for 2 moles of $e^- = 2F$

3. (i) The electrode reaction is $Al^{3+} + 3e- \longrightarrow Al$

$\therefore$ Quantity of charge required for reduction of 1 mol of Al^{3+}

$= 3F = 3 \times 96500\ C = 289500\ C.$

(ii) The electrode reaction is

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

$\therefore$ Quantity of charge required for reduction of 1 mol of Cu^{2+}

$= 2F = 2 \times 96500 = 193000\ C.$

(iii) The electrode reaction is

$$MnO_4^- \longrightarrow Mn^{2+}.$$

i.e., $Mn^{7+} + 5e^- \longrightarrow Mn^{2+}.$

$\therefore$ Quantity of charge required $= 5F = 5 \times 96500\ C = 482500\ C.$

4. (i) $Ca^{2+} + 2e^- \longrightarrow Ca$

Thus, 1 mol of Ca, i.e., 40g of Ca require = 2F electricity

$\therefore$ 20 g of Ca require = 1F electricity

(ii) $Al^{3+} + 3e^- \longrightarrow Al$

Thus, 1 mole of Al, i.e., 27g of Al require = 3F electricity

$\therefore$ 40g of Al will require elecricity

$$= \frac{3}{27} \times 40 = 4.44\ F \text{ of electricity.}$$

5. (*i*) The electrode reaction for 1 mol of H_2O is

$$H_2O \longrightarrow H_2 + \frac{1}{2}O_2$$

i.e., $O_2^- \longrightarrow \frac{1}{2}O_2 + 2e^-$

∴ Quantity of electricity required

= 2F = 2 × 96500 C = 193000 C.

(*ii*) The electrode reaction for 1 mol of FeO is

$$FeO \rightarrow \frac{1}{2}Fe_2O_3$$

i.e., $Fe^{2+} \longrightarrow Fe^{3+} + e^-$

∴ Quantity of electricity required = 1F = 96500 C

6. Quantity of electricity passed

= (5A) × (20 × 60 sec.) = 6000C

$Ni^{2+} + 2e^- \longrightarrow Ni$

Thus, 2F, *i.e.*, 2 × 96500C of charge deposit

= 1 mole of Ni = 58.7 g

∴ 6000 C of charge will deposite

$$= \frac{58.7 \times 6000}{2 \times 96500} = 1.825\text{g of Ni.}$$

7. Given: I = 1.5 A, W = 1.45 g Ag, t = ?, E = 108, n = 1

Using Faraday's 1st law of electrolysis W = ZIt or, $W = \frac{E}{nF}$ It

or, $t = \frac{1.45 \times 96500}{1.5 \times 108}$ = 863.73 seconds.

Now for Cu, W_1 = 1.45 g Ag, E_1= 108, W_2 = ?, E_2 = 31.75

From Faraday's 2nd law of electrolysis $\frac{W_1}{W_2} = \frac{E_1}{E_2}$

$$\frac{1.45}{W_2} = \frac{108}{31.75} \therefore \quad W_2 = \frac{1.45 \times 31.75}{108}$$

= 0.426 g of Cu.

Similarly, for Zn, W_1 = 1.45 g Ag, E_1 = 108,

$W_2 = ?, E_2 = 32.65$

Using formula, $\frac{W_1}{W_2} = \frac{E_1}{E_2}$

$\therefore W_2 = \frac{1.45}{W_2} = \frac{108}{32.65} = 0.438$ of Zn.

8. The reduction of nitrobenzene takes place as

$C_6H_5NO_2 + 6H^+ + 6e^- \longrightarrow C_6H_5NH_2 + 2H_2O$

1 mole of nitrobenzene needs 6 mole of electrons

$\therefore$ Charge required, Q = 6F

$= 6 \times 96500 = 579000$ C.

9. $Zn(s) + Cl_2(g) \longrightarrow Zn^{2+} + 2Cl^-$

Here Zn is oxidised as zinc is anode.

Anode reaction : $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

1 mol = 65g $\qquad$ 2F = 2 × 96500C

As can be seen from above reaction, 65g of Zn produces = 2× 96500 C

$\therefore$ 6.5g of Zn will produces = $\frac{2\times96500}{65}\times6{\cdot}5$C

= 19300 C of charge

We know that, Q = I × t; $\quad 19300 = 0.2 \times t$

Time, $t = \frac{19300}{0{\cdot}2} = 96500$ sec.

Time for which it can deliver 0.2 A = 96500 sec.

$= \frac{19600}{60\times60}$ hours = 26.80 hours.

10. $Fe^{3+} + \underset{1mol}{e^-} \longrightarrow Fe^{2+}$

1 mol = 1 F

$\therefore$ 3 mol = 3 F

$\therefore$ Q = 3F = 3 × 96500 C $\qquad$ (*i*)

But, Q = I × t $\qquad$ (*ii*)

= 2.0 × t

Comparing equation (*i*) and equation (*ii*), we get

$2.0 \times t = 3 \times 96500$

$t = \frac{3\times96500}{2} = 144750$ sec

$t = \frac{144750}{60\times60}$ hours = 40.21 hours.

Thus, 3 moles of Fe^{3+} will require 40.21 hours for reduction to Fe^{2+} ion.

11. Amount of coulombs provided by 0.2A in 3 hours, *i.e.*, 3 × 3600 sec = 0.2 × 3 × 3600 = 2160 C.

Let the thickness of silver deposited by x cm.

∴ volume of silver deposited = 80 cm^2 × x cm = 80x cm^3

and mass of silver deposited = 80 x cm^3 × 10.47 g cm^{-3} = 837.6 xg (*i*)

Mass of Ag deposited in relation to quantity of electricity by following reaction is:

$$\underset{1\,mol}{Ag^+(aq)} + \underset{1\,mol}{e^-} \longrightarrow Ag(s) \quad = 96500\ C$$

∴ 96500 C deposits Ag = 108g

$$2160\ C \text{ deposits Ag} = \frac{108 \times 2160}{96500} = 2{\cdot}417\,g \quad (ii)$$

Comparing equation (*i*) and equation (*ii*), we get

837.6 x = 2.417

$$x = \frac{2{\cdot}417}{837{\cdot}6} = 0.002886\ cm = 2.886 \times 10^{-3}\ cm.$$

12. $\lambda_m^\infty(NH_4OH) = \lambda_m^\infty(NH_4^+) + \lambda_m^\infty(OH^-)$

Using Kohlrausch law of independent migration of ions,

$\lambda^\infty(NH_4OH)$

$$= \left[\lambda_m^\infty(NH_4^+) + \lambda_m^\infty(Cl^-)\right] + \left[\lambda_m^\infty(Na^+) + \lambda_m^\infty(OH^-)\right] - \left[\lambda_m^\infty(Na^+) + \lambda_m^\infty Cl^-\right]$$

$$= \lambda_m^\infty(NH_4Cl) + \lambda_m^\infty(NaOH) - \lambda_m^\infty NaCl$$

$$= 150 + 248.1 - 126.4$$

$$= 271.7\ S\ cm^2\ mol^{-1}.$$

CHAPTER 7

Numericals based on Application/Skill

(A) The Solid State

1. The composition of a sample of wustite is $Fe_{0.93}O_{1.00}$ what percentage of iron is present in the form of Fe(III)?

[Outside Delhi 2010]

2. A solid with cubic crystal is made of two elements *P* and *Q*. Atoms of *Q* are at corners and *P* at body centre. What is the formula of the compound? **(Outside Delhi 2013)**

(B) Solutions

1. The boiling point elevation of 0.30 g acetic acid in 100 g benzene is 0.0633 K. Calculate the molar mass of acetic acid from this data. What conclusion can you draw about the molecular state of the solute in the solution?

(Given K_b for benzene = 2.53 K kg mol^{-1})

(Outside Delhi Comptt. 2008)

2. A decimolar solution of $K_4[Fe(CN)_6]$ is 50% dissociated at 300 K. Calculate the value of Van't Hoff factor for $K_4[Fe(CN)_6]$.

[Delhi Comptt. 2010]

3. Phenol associates in benzene to a certain extent to form a dimer. A solution containing 20.0 g of phenol in 1.0 kg of benzene has its freezing point lowered by 0.69 K. Calculate the fraction of phenol that has dimerised. (K_f for benzene = 5.1 Km^{-1}) **[Delhi Comptt. 2011]**

4. An aqueous solution containing 12.48 g of $BaCl_2$ in 1.0 kg of water boils at 373.0832 K. Calculate the degree of dissociation of $BaCl_2$.

(K_b for H_2O = 0.52 Km^{-1}, molar mass of $BaCl_2$ = 208.34 $gmol^{-1}$)

[Delhi Comptt. 2011]

5. A solution containing 30 g of a non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further, 18 g of water is added to this solution and new vapour pressure becomes 2.9 kPa at 298 K. Calculate

(i) molar mass of solute

(ii) vapour pressure of water at 298 K **[Delhi Comptt. 2012]**

(C) Electrochemistry

1. Three electrolytic cells *A*, *B* and *C* containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$ are connected in series. A steady current of 1.5 ampere was passed through them. 1.45 g of Ag were deposited at the cathode of cell B. How long did the current flow? What mass of Cu and Zn were deposited in the concerned cells? (Atomic masses of Ag = 108, Zn = 65.4, Cu = 63.5)

[Delhi Board 2008, Outside Delhi 2008]

2. Formulate the galvanic cell in which the following reaction takes place:

$$Zn(s) + 2Ag^+ (aq) \longrightarrow Zn^{2+} (aq) + 2Ag(s)$$

(i) Which electrode is negatively charged?

(ii) The reaction taking place at each electrode.

(iii) The carriers of current in the cell. **[Delhi Board 2008]**

3. The resistance of a conductivity cell when filled with 0.05 M solution of an electrolyte *X* is 100 Ω at 40°C. The same conductivity cell filled with 0.01 M solution of electrolyte *Y* has a resistance of 50 Ω. The conductivity of 0.05 M solute of electrolyte *X* is 1.0×10^{-4} S cm^{-1}. Calculate

(i) Cell constant

(ii) Conductivity of 0.01 M *Y* solution

(iii) Molar conductivity of 0.01 M *Y* solution

[Outside Delhi Comptt. 2008]

4. One half-cell in a voltaic cell is constructed from a silver wire dipped in $AgNO_3$ solution of unknown concentration. Its other half-cell consists of zinc electrode dipping in 1.0 M solution of $Zn(NO_3)_2$. A voltage of 1.48 V is measured for this cell. Use this information to calculate the concentration of $AgNO_3$ solution.

(Given: $E^\circ_{Zn^{2+}|Zn} = -0.76$; $E^\circ_{Ag^+|Ag} = +0.80$ V)

[Delhi Board 2009]

5. Two half-cell reactions of an electrochemical cell are given below:

$$MnO_4^- (aq) + 8H^+ (aq) + 5e^- \longrightarrow Mn^{2+} (aq) + 4H_2O(l), \quad E^\circ = +1.51 \text{ V},$$

$$Sn^{2+} (aq) \longrightarrow Sn^{4+} (aq) + 2e^-; \quad E^\circ = +0.51 \text{ V}$$

Construct the redox equation for the two half cell reactions and predict if this reaction favours the formation of reactants or products shown in the equation. **[Outside Delhi Board 2009, 2010, 2011]**

6. A copper-silver cell is set up. The copper ion concentration in it is 0.10 M. The concentration of silver ion is not known. The cell potential is 0.422 V. Determine the concentration of silver ions in the cell.

(Given: $E^{\circ}_{Ag^+|Ag} = +0.80$ V; $E^{\circ}_{Cu^{2+}|Cu} = 0.34$ V)

[Outside Delhi 2009]

7. Calculate the strength of the current required to deposit 1.2 g of Mg from molten $MgCl_2$ in 1 hour.

[1F = 96500 C mol^{-1}; atomic mass of Mg = 24.0]

[Delhi Comptt. 2009]

8. How many grams of mercury will be produced by electrolysing 1.0 M $Hg(NO_3)_2$ solution with a current of 2.00 A for 3 hours?

[$Hg(NO_3)_2$] = 200.6 g mol^{-1}] **[Outside Delhi 2011]**

9. A voltaic cell is set up at 25°C with the half cells [Al^{3+}(0.001 M) | Al and Ni^{2+}(0.5 M) | Ni]. Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.

[Given: $E^0_{Ni^{2+}|Ni} = -0.25$ V; $E^0_{Al^{3+}|Al} = -1.66$ V]

[Delhi Board 2009, Outside Delhi 2011, 2012]

10. A zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at 298 K. Calculate the electrode potential.

($E^{\circ}_{Zn^{2+}|Zn} = -0.76$) **[Delhi Comptt. 2012]**

11. When a certain cell was filled with 0.1 M KCl, it has a resistance of 85 Ω at 25°C. When the same cell was filled with an aqueous solution of 0.052 M unknown electrolyte, the resistance was 96 Ω. Calculate the molar conductance of the electrolyte at this concentration.

(Specific conductance of 0.1 M KCl = $1.29 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$)

[Outside Delhi Comptt. 2012]

(D) Chemical Kinetics

1. (a) List the factors on which rate of a chemical reaction depends.

   (b) The half-life for decay of radioactive ^{14}C is 5730 years. An archaeological artefact containing wood had only 80% of ^{14}C found in living trees. Calculate the age of the artefact.

[Delhi Board 2008, Outside Delhi 2008]

2. The data given below is for the reaction:

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g) \text{ at } 298 \text{ K}$$

K M C

S. No.	$[N_2O_5]$ (mol L^{-1})	Rate of disappearance of N_2O_5 (mol L^{-1} min^{-1})
1.	1.13×10^{-2}	34×10^{-5}
2.	0.84×10^{-2}	25×10^{-5}
3.	0.62×10^{-2}	18×10^{-5}

Determine (i) order of reaction
(ii) rate constant
(iii) rate law **[Outside Delhi Comptt. 2008]**

3. A reaction is second order w.r.t. a reactant. How will the rate of reaction be affected if the concentration of the reactant is
(i) doubled
(ii) reduced to half **[Delhi Board 2009, Outside Delhi 2012]**

4. The following results have been obtained during the kinetic study of the reaction:

$$2A + B \rightarrow C + D$$

Expt. No.	[A]	[B]	Initial rate of formation of D
1	0.1 M	0.1 M	6.0×10^{-3} M min^{-1}
2	0.3 M	0.2 M	7.2×10^{-2} M min^{-1}
3	0.3 M	0.4 M	2.88×10^{-1} M min^{-1}
4	0.4 M	0.1 M	2.40×10^{-2} M min^{-1}

Determine the rate law and rate constant for the reaction.

[Delhi Comptt. 2010]

5. In a pseudo order hydrolysis of ester in water, following results are obtained:

t (in s)	0	30	60	90
[Ester] M	0.55	0.31	0.17	0.085

(i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.
(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester. **[Outside Delhi Comptt. 2010]**

6. For the reaction: $2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$, the following data were collected at 263 K:

Expt. No.	Initial [NO] (M)	Initial $[Cl_2]$ (M)	Initial rate of disappearance of Cl_2 (M/min)
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	2.40
4	0.25	0.25	?

(a) Write the expression for rate law.

(b) Calculate the value of rate constant and specify its units.

(c) What is the initial rate of disappearance of Cl_2 in experiment 4? **[Delhi 2012]**

7. Rate constant 'k' of a reaction varies with temperature 'T' according to the equation:

$$\log k = \log A - \frac{E_a}{2.303\,R}\left(\frac{1}{T}\right)$$

when a graph is plotted for $\log k$ vs. $\frac{1}{T}$, a straight line with a slope of – 4250 K is obtained. Calculate 'E_a' for the reaction.

($R = 8.314$ J K^{-1} mol^{-1}) **[Delhi Board 2013]**

8. The following data were obtained during first order thermal decomposition of SO_2Cl_2 at constant volume:

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Experiment	Time (s^{-1})	Total pressure (atm)
1	0	0.4
2	100	0.7

Calculate rate constant.

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

[Delhi 2014, Outside Delhi 2014]

(A) The Solid State

1. Let the number of Fe^{3+} ions = x

Then, the number of Fe^{2+} ions = $0.93 - x$

For electrical neutrality,

Total positive charge = Total negative charge

$$\therefore \quad 2(0.93 - x) + 3x = +2$$

$$1.86 - 2x + 3x = +2$$

$$1.86 + x = +2$$

$$x = 0.14$$

% of Fe^{3+} ions = $\frac{0.14}{0.93} \times 100 = 15.05\%$

2. Atoms of Q are at the corners,

$\therefore$ no. of atoms of $Q = \frac{1}{8} \times 8 = 1$

as, atoms of P are at body centre,

$\therefore$ no. of atoms of $P = 1$

Now, ratio of $P : Q = 1 : 1$

$\therefore$ formula of the compound = PQ

(B) Solutions

1. $w_1 = 100$ g; $w_2 = 0.30$ g

$\Delta T_b = 0.0633$ K

$K_b = 2.53$ K kg mol^{-1}

As $$\Delta T_b = K_b.m = K_b \times \frac{w_2}{M_2} \times \frac{1000}{w_1}$$

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

$$= \frac{2.53 \times 0.30 \times 1000}{0.0633 \times 100}$$

$$= 119.90$$

actual molar mass of solute (CH_3COOH)

$= 12 + 3 + 12 + 16 + 16 + 1$

$= 60$

we find that actual and calculated molar masses are different.

$$\therefore \quad i = \frac{\text{normal molar mass}}{\text{abnormal molar mass}}$$

$$= \frac{60}{119.90} = 0.5$$

As $i < 1$, $\therefore$ solute undergoes association in water.

2. Here, $\alpha = 50\% = 0.50$

Now, $i = 1 + 2\alpha = 1 + 2 \times 0.50$

$= 1 + 1 = 2$

3.

	$2C_6H_5OH$	$\rightleftharpoons$	$(C_6H_5OH)_2$
initial	1		0
after association	$1 - \alpha$		$\alpha / 2$

$$\therefore \quad i = 1 - \alpha + \alpha / 2 = 1 - \frac{\alpha}{2}$$

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

$$= i K_f \frac{w_2}{M_2} \times \frac{1}{w_1 (\text{in kg})}$$

$$0.69 = \left(1 - \frac{\alpha}{2}\right) \times 5.1 \times \frac{20}{94 \times 1}$$

$$\Rightarrow \quad 1 - \frac{\alpha}{2} = \frac{0.69 \times 94}{5.1 \times 20}$$

$$\Rightarrow \quad 1 - \frac{\alpha}{2} = 0.63$$

$$\text{or,} \quad 1 - 0.63 = \frac{\alpha}{2}$$

$$\Rightarrow \quad \alpha = 2(1 - 0.63)$$

$$\boxed{\alpha = 0.74}$$

4. **Given:** $M_2 = 208.34\ \text{gmol}^{-1}$

$K_b = 0.52\ \text{Km}^{-1}$

$T_b = 373.0832\ \text{K}$

$w_2 = 12.48\ \text{g}$

$w_1 = 1\ \text{kg} = 1000\ \text{g}$

To find: $\alpha = ?$

Solution: $\Delta T_b = T_b - T_b^o = 373.0832 - 373$

$= 0.0832$ K

Now, $\Delta T_b = i\,K_b\,m$

$$= i K_b \times \frac{w_2}{M_2} \times \frac{1000}{w_1}$$

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

$$= \frac{0.0832 \times 208.34 \times \cancel{1000}}{0.52 \times 12.48 \times \cancel{1000}}$$

$i = 2.67$

Now,	$BaCl_2$	$\longrightarrow$	Ba^{2+}	+	$2Cl^-$
initial	1		0		0
after diss	$1-\alpha$		α		2α

$\therefore \quad i = 1-\alpha+\alpha+2\alpha = 1 + 2\alpha \Rightarrow \alpha = (i-1)/2$

$$\Rightarrow \boxed{\alpha = (2.67 - 1)/2 = 0.835}$$

5. **Given:** $w_2 = 30$ g $\qquad w_2^1 = 30$ g

$w_1 = 90$ g $\qquad w_1^1 = 90 + 18 = 108$ g

$P_1 = 2.8$ kPa $\qquad P_2 = 2.9$ kPa

To find: (i) $M_2 = ?$

(ii) $P^0_{H_2O} = ?$

Solution: From relative lowering of vapour pressure,

$$\frac{P^0 - P_s}{P^0} = x_2 \simeq \frac{n_2}{n_1 + n_2}$$

Case 1: $$\frac{P^0 - 2.8}{P^0} = \frac{30/M_2}{90/18 + 30/M_2}$$

$$\frac{P^0 - 2.8}{P^0} = \frac{30/M_2}{5 + 30/M_2}$$

Solving, $$\frac{P^0}{2.8} = 1 + \frac{6}{M_2} \qquad (1)$$

Case 2: $$\frac{P^0 - 2.9}{P^0} = \frac{30/M_2}{108/18 + 30/M_2} = \frac{30/M_2}{6 + 30/M_2}$$

Solving, $$\frac{P^0}{2.9} = 1 + \frac{5}{M_2} \qquad (2)$$

Dividing (2) by (1),

$$\frac{2.9}{2.8} = \frac{1 + (6/M_2)}{1 + (5/M_2)}$$

$$2.9\left(1 + \frac{5}{M_2}\right) = 2.8\left(1 + \frac{6}{M_2}\right)$$

Solving, $$\frac{2.3}{M_2} = 0.1$$

or, $$\boxed{M_2 = 23 \text{ g mol}^{-1}}$$

Now, $$\frac{P^0}{2.8} = 1 + \frac{6}{M_2} = 1 + \frac{6}{23}$$

$$\frac{P^0}{2.8} = \frac{29}{23} \quad \Rightarrow \quad P^0 = \frac{29}{23} \times 2.8$$

$$\boxed{P^0_{H_2O} = 3.53 \text{ kPa}}$$

(C) Electrochemistry

1. $Ag^+ + e^- \longrightarrow Ag$

For 108 g of Ag, charge required = 1F = 96500 C

$\therefore$ For 1.45 of Ag, charge required = $\frac{96500}{108} \times 1.45$

= 1295.6 C

as $$Q = It \quad \Rightarrow \quad t = \frac{Q}{I} = \frac{1295.6}{1.5} = 863.75 \text{ s}$$

Now, $Cu^{2+} + 2e^- \longrightarrow Cu$

From Faraday's 2nd law,

$$\frac{m_{Ag}}{m_{Cu}} = \frac{Z_{Ag}}{Z_{Cu}}$$

$$\Rightarrow \quad \frac{1.45}{m_{Cu}} = \frac{108}{63.5/2} \quad \Rightarrow \quad m_{Cu} = \frac{1.45 \times 63.5}{108 \times 2}$$

$$\boxed{m_{Cu} = 0.426 \text{ g}}$$

Similarly, $\frac{m_{Ag}}{m_{Zn}} = \frac{Z_{Ag}}{Z_{Zn}}$

$$\frac{1.45}{m_{Zn}} = \frac{108}{65.4/2} \qquad [\because Zn^{2+} + 2e^- \rightarrow Zn]$$

$$m_{Zn} = \frac{1.45 \times 65.4}{2 \times 108} = 0.439 \text{ g}$$

2. The cell representation is:

$Zn(s) \mid Zn^{2+}(aq) \mid\mid Ag^+(aq) \mid Ag(s)$

(i) Zinc electrode i.e. anode is negatively charged.

(ii) At anode : $Zn(s) \longrightarrow Zn^{2+} + 2e^-$ (oxidation)

At cathode: $Ag^+ + e^- \longrightarrow Ag$ (reduction)

(iii) The current flow will be from silver to zinc in the external circuit.

3.

Electrolyte X	**Electrolyte Y**
$M = 0.05$ M	$M = 0.01$ M
$R = 100\ \Omega$	$R = 50\ \Omega$
$\kappa = 1.0 \times 10^{-4}$ S cm^{-1}	$\kappa = ?$

(i) Cell constant $(G^*) = \kappa \times R$

$= 1.0 \times 10^{-4} \times 100$

$= 10^{-2}$ cm^{-1}

(ii) κ for solution Y

$$\kappa = \frac{G^*}{R} = \frac{10^{-2}}{50} = 0.02 \times 10^{-2}$$

$= 2 \times 10^{-4}$ S cm^{-1}

(iii) Molar conductivity (Λ_m) of solution Y

$$\Lambda_m = \frac{K}{C} \times 1000 = \frac{2 \times 10^{-4} \times 1000}{0.01}$$

$= 20$ S cm^2 mol^{-1}

4. The half cell reactions will be:

Anode: $Zn \longrightarrow Zn^{2+} + 2e^-$

Cathode: $Ag^+ + e^- \longrightarrow Ag$

$\therefore$ The cell representation is:

$$Zn \mid Zn^{2+} \mid\mid Ag^+ \mid Ag$$

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

$= 0.80 - (-0.76)$

$= 1.56$ V

From Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \frac{[Zn^{2+}]}{[Ag^+]^2}$$

$$1.48 = 1.56 - \frac{0.059}{2} \log \frac{1}{[Ag^+]^2}$$

$$\Rightarrow \quad \frac{0.059}{2} (\log 1 - \log [Ag^+]^2) = 1.56 - 1.48$$

$$\Rightarrow \quad -2 \log [Ag^+] = \frac{0.08 \times 2}{0.059}$$

$$\Rightarrow \quad \log [Ag^+] = -1.356 \qquad \text{(on taking the antilog)}$$

$$\boxed{[Ag^+] = 4.406 \times 10^{-2} \text{ M}}$$

5. Anode: $Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2e^-$; $E^\circ = 0.51$ V

Cathode: $MnO_4^-(aq) + 8H^+ + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$

$E^\circ = +1.51$ V

On balancing and then adding both the equations.

Overall reaction: $5Sn^{2+}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \longrightarrow$

$5Sn^{4+}(aq) + 2Mn^{2+}(aq) + 8H_2O(l)$

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

$= 1.51 - 0.51$

$= 1.00$ V

Since the value of E°_{cell} is positive, the reaction is spontaneous and favours the product formation.

6. Cathode: $2Ag^+ (aq) + 2e^- \xrightarrow{K\ M\ C} 2Ag(s)$

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

The cell reaction is:

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

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

$$= 0.80 - 0.34$$

$$= 0.46 \text{ V}$$

From Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$0.422 = 0.46 - \frac{0.059}{2} \log \frac{(0.1)}{[Ag^+]^2}$$

$$0.422 - 0.46 = -\frac{0.059}{2} [\log 0.1 - \log [Ag^+]^2]$$

$$-0.038 = -\frac{0.059}{2} [-1 - \log [Ag^+]^2]$$

$$\Rightarrow \quad \frac{0.038 \times 2}{0.059} + 1 = -2 \log [Ag^+]^2$$

$$\Rightarrow \quad -2 \log [Ag^+]^2 = \frac{0.038 \times 2}{0.059} + 1$$

On solving $[Ag^+] = 0.023$ M

7. $Mg^{2+} (aq) + 2e^- \longrightarrow Mg(s)$

$n = 2$

$t = 1$ hour $= 3600$ s

$m = 1.2$ g

If the current is I ampere, then quantity of electricity passed $= It$

$= I \times 3600 = I \times 3600$ C

Now to deposit 24.0 g of Mg, charge required $= 2$ F

$= 2 \times 96500$ C

$\therefore$ to deposit 1.2 g of Mg, charge $= \frac{2 \times 96500}{24} \times 1.2$

$$\therefore \quad \frac{2 \times 96500}{24} \times 1.2 = 3600 \text{ I}$$

$$\Rightarrow \quad \boxed{I = 2.68 \text{ A}}$$

8. $t = 3$ hours $= 3 \times 60 \times 60$

$= 10800$ s

$I = 2$ A

$Q = It = 2 \times 10800$

$= 21600$ C

According to the reaction,

$$Hg(NO_3)_2 \longrightarrow Hg^{2+} + 2NO_3^-$$

$$Hg^{2+} + 2e^- \longrightarrow Hg$$

$\because$ for 1 mol (63g of Hg), charge = 2F = 2×96500 C

or, 2×96500 C $\longrightarrow$ 63 g

$\therefore$ $21600 \text{ C} \longrightarrow \dfrac{63}{2 \times 96500} \times 21600$

$\therefore$ mass of Hg deposited = 7.05 g

9. As $E^0_{Ni^{2+}|Ni} = -0.25$ V and $E^0_{Al^{3+}|Al} = -1.66$ V

i.e. Ni has greater tendency to get reduced.

$\therefore$ Ni form cathode and Al forms anode.

$\therefore$ cell reactions are:

Anode: $Al \longrightarrow Al^{3+} + 3e^-$] $\times 2$

Cathode: $Ni^{2+} + 2e^- \longrightarrow Ni$] $\times 3$

Now, $E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$= -0.25 - (-1.66)$

$= 1.41$ V

$\therefore$ from Nernst equation,

$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[Al^{3+}]^2}{[Ni^{2+}]^3}$$

$$= 1.41 - \frac{0.059}{6} \log \frac{(0.001)^2}{(0.5)^3}$$

$$= 1.41 - \frac{0.059}{6} \log \frac{10^{-6}}{5^3 \times 10^{-3}} = 1.41 - \frac{0.059}{6} \log \frac{10^{-3}}{5^3}$$

$$= 1.41 - \frac{0.059}{6} (-3 \log 10 - 3 \log 5)$$

$$= 1.46 \text{ V}$$

10. The electrode reaction is:

$$Zn^{2+} + 2e^- \longrightarrow Zn$$

$\therefore \quad n = 2$

Applying Nernst eq,

$$E_{Zn^{2+}|Zn} = E^0_{Zn^{2+}|Zn} - \frac{0.059}{2}\log\frac{[Zn\,(s)]}{[Zn^{2+}]}$$

$$= -0.76 - \frac{0.059}{2}\log\frac{1}{[Zn^{2+}]}$$

Now according to question, 0.1 M $ZnSO_4$ solution is 95% dissociated

$\therefore \quad [Zn^{2+}] = 95\%$ of 0.1

$= 0.095$ M

$$\therefore \quad E_{Zn^{2+}|Zn} = -0.76 - \frac{0.059}{2}\log\frac{1}{0.095}$$

$$= -0.76 - 0.0295\,(\log 1000 - \log 95)$$

$$= -0.76 - 0.295\,(3 - 1.977)$$

$$\boxed{E_{Zn^{2+}|Zn} = -0.79021\text{ V}}$$

11. **Given:** $\kappa = 1.29 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$

To find: Λ_m = (unknown) = ?

Solution: R (KCl) = 85 Ω

κ (KCl) = $1.29 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$

Now, $\quad \kappa = \dfrac{G^*}{R} \qquad$ (G^* = cell constant)

$$G^* = \kappa \times R$$

$$= 1.29 \times 85$$

$$= 109.65\ cm^{-1}$$

Now, $\quad \kappa\,(\text{unknown}) = \dfrac{G^*}{R\,(\text{unknown})}$

$$= \frac{109.65}{96}$$

$$= 1.142\ S\ cm^{-1}$$

K M C

$$\therefore \quad \Lambda_m \text{ (unknown)} = \frac{\kappa \times 1000}{C}$$

$$= \frac{1.142 \times 1000}{0.052}$$

$$= 2.19 \times 10^4 \text{ S cm}^2 \text{ mol}^{-1}$$

(D) Chemical Kinetics

1. (a) The rate of a chemical reaction depends on:

1. nature of reacting species
2. concentration of reacting species
3. temperature
4. surface area
5. presence of catalyst

(b) Radioactive decay follows first order kinetics.

initial conc., $[R]_0 = 100$

conc. after time t, $[R] = 80$

as $\quad t_{1/2} = 5730$ years

$$\therefore \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730}$$

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

$$t = \frac{2.303}{k} \log \frac{100}{80} = \frac{2.303}{\frac{0.693}{5730}} \log \frac{100}{80}$$

Solving, $t = 1845$ years

2. Rate = $k\,[N_2O_5]^a$

From (1) and (2),

$$34 \times 10^{-5} = k\,(1.13 \times 10^{-2})^a$$

$$25 \times 10^{-5} = k\,(0.84 \times 10^{-2})^a$$

Dividing,

$$\frac{34 \times 10^{-5}}{25 \times 10^{-5}} = \frac{k\,(1.13 \times 10^{-2})^a}{k\,(0.84 \times 10^{-2})^a}$$

$$\frac{34}{25} = \left(\frac{1.13 \times 10^{-2}}{0.84 \times 10^{-2}}\right)^a$$

$\Rightarrow$ $1.36 = (1.34)^a$

$\therefore$ $a = 1$

(i) order of reaction = 1

(ii) as rate = $k\,[N_2O_5]^a$ $(\because a = 1)$

$\therefore$ rate = $k\,[N_2O_5]$

$$k = \frac{\text{rate}}{[N_2O_5]} = \frac{34 \times 10^{-5}}{1.13 \times 10^{-2}}$$

$k = 0.03\ \text{min}^{-1}$

(iii) rate law = $0.03\,[N_2O_5]$

3. As rate = $k\,[A]^2$

Let $[A] = a$, then rate = ka^2

(i) When $[A] = 2a$

rate = $k\,(2a)^2 = 4\,ka^2$

i.e. the rate becomes 4 times

(ii) When $[A] = \dfrac{a}{2}$

$$\text{rate} = k\left(\frac{a}{2}\right)^2 = \frac{1}{4}ka^2$$

i.e. rate becomes $\dfrac{1}{4}$ times

4. Let the order w.r.t. A be α and B be β.

Then, rate $= k\,[A]^{\alpha}\,[B]^{\beta}$

$\therefore$ we have for the experiments,

$$\text{Rate}_1 = k\,[0.1]^{\alpha}\,[0.1]^{\beta} \quad (1)$$

$$\text{Rate}_2 = k\,[0.3]^{\alpha}\,[0.2]^{\beta} \quad (2)$$

$$\text{Rate}_3 = k\,[0.3]^{\alpha}\,[0.4]^{\beta} \quad (3)$$

$$\text{Rate}_4 = k\,[0.4]^{\alpha}\,[0.1]^{\beta} \quad (4)$$

From (1) and (4),

$$\frac{\text{Rate}_1}{\text{Rate}_4} = \frac{k[0.1]^{\alpha}[0.1]^{\beta}}{k[0.4]^{\alpha}[0.1]^{\beta}}$$

$$\frac{6.0\times10^{-3}}{2.40\times10^{-2}} = \left(\frac{0.1}{0.4}\right)^{\alpha} = \left(\frac{1}{4}\right)^{\alpha}$$

$$\frac{1}{4} = \left(\frac{1}{4}\right)^{\alpha} \Rightarrow \boxed{\alpha = 1}$$

From (2) and (3),

$$\frac{\text{Rate}_2}{\text{Rate}_3} = \frac{k[0.3]^{\alpha}[0.2]^{\beta}}{k[0.3]^{\alpha}[0.4]^{\beta}}$$

$$\frac{7.2\times10^{-2}}{2.88\times10^{-1}} = \left(\frac{0.2}{2\times0.2}\right)^{\beta} = \left(\frac{1}{2}\right)^{\beta}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^{\beta} \Rightarrow \boxed{\beta = 2}$$

$\therefore$ Order w.r.t. $A = 1$

Order w.r.t. $B = 2$

Thus, rate law expression is:

rate $= k\,[A]\,[B]^2$

Now, from (1)

$$6\times10^{-3} = k\,(0.1)\,(0.1)^2$$

$$k = \frac{6\times10^{-3}\times10^{3}}{1\times1\times1}$$

$\Rightarrow$ rate constant $\boxed{k = 6.0\ \text{min}^{-1}}$

5. (i) The average rate of reaction between the time interval of 30 to 60 seconds is:

$$r_{av} = \frac{-(0.17 - 0.31)}{60 - 30} = \frac{0.14}{30}$$

$$= 4.67 \times 10^{-3}\ s^{-1}$$

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

at $t = 30$ s, $k = \frac{2.303}{30} \log \frac{0.55}{0.31} = 1.91 \times 10^{-2}\ s^{-1}$

at t = 60 s, $k = \frac{2.303}{60} \log \frac{0.55}{0.17} = 1.96 \times 10^{-2}\ s^{-1}$

at t = 90 s, $k = \frac{2.303}{90} \log \frac{0.55}{0.085} = 2.07 \times 10^{-2}\ s^{-1}$

$\therefore$ average value of $k = \frac{1.91 \times 10^{-2} + 1.96 \times 10^{-2} + 2.07 \times 10^{-2}}{3}$

$$= 1.98 \times 10^{-2}\ s^{-1}$$

6. (a) From expt. 1 and 2, when [NO] is constant and that of $[Cl_2]$ is doubled, rate also become double

$\therefore$ rate $\propto [Cl_2]^1$

From expt. 1 and 3, when $[Cl_2]$ is constant and that of [NO] is doubled, rate becomes 4 times

$\therefore$ rate $\propto [NO]^2$

$\therefore$ the rate law expression is:

$$\boxed{\text{rate} \propto k\,[NO]^2\,[Cl_2]^1}$$

(b) From expt. 1,

$$\text{rate} = k\,[NO]^2\,[Cl_2]$$

$$k = \frac{\text{rate}}{[NO]^2\,[Cl_2]} = \frac{0.6}{(0.15)^2\,(0.15)}$$

$$k = \frac{0.6}{(0.15)^3} = 177.75$$

$$\therefore\ k = 1.77 \times 10^2\ M^{-2}\ min^{-1}$$

(c) From expt. 4,

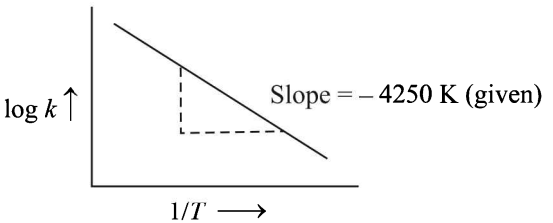
$$\text{rate} = k\,[NO]^2\,[Cl_2]$$

$$= 177.75 \times (0.25)^2\,(0.25)$$

$$= 2.78\ M\ min^{-1}$$

7. **Given:** $\log k = \log A - \dfrac{E_a}{2.303\,R}\left(\dfrac{1}{T}\right)$

a graph between $\log k$ and $1/T$ is given below:



from the above equation, slope = $\dfrac{-E_a}{2.303\,R}$

$$\therefore \quad \frac{-E_a}{2.303\,R} = -4250\ K$$

$$\Rightarrow \quad E_a = 4250 \times 2.303 \times 8.314$$

$$= 31{,}375.35\ J\ mol^{-1}$$

$$\boxed{E_a = 81.3753\ kJ\ mol^{-1}}$$

8.

$$SO_2Cl_2(g) \xrightarrow{K} SO_2(g) + Cl_2(g)$$

	$SO_2Cl_2(g)$	$SO_2(g)$	$Cl_2(g)$
initial	P_o	0	0
after time t	$P_o - P$	P	P

Total pressure after time t, $P_t = P_o - P + P + P$

$$= P_o + P$$

or, $P = P_t - P_o$

Now, $a = P_o$ and $a - x = P_o - P = P_o - (P_t - P_o)$

$\therefore$ $a - x = 2P_o - P_t$

For 1st order reaction,

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$= \frac{2.303}{t} \log \frac{P_o}{2P_o - P_t}$$

$$= \frac{2.303}{100} \log \frac{0.4}{2 \times 0.4 - 0.7}$$

$$= \frac{2.303}{100} \log \frac{0.4}{0.8 - 0.7}$$

$$= \frac{2.303}{100} \log \frac{4}{1}$$

$$= \frac{2.303}{100} \log 4$$

$$= \frac{2.303 \times 0.6021}{100}$$

$$\boxed{k = 1.38 \times 10^{-2}\ s^{-1}}$$

CHAPTER 8 Miscellaneous

(A) Solid State

1. What is the total number of atoms per unit cell in a face-centred cubic (*fcc*) structure?

[Delhi Board 2008, 2013, Outside Delhi 2008, 2009]

2. What is the coordination number of each type of ions in a rock salt type crystal structure?

[Delhi Board 2008, Outside Delhi 2008]

3. Which point defect decreases the density of a solid?

[Outside Delhi 2009]

4. How can the conductivity of an intrinsic semi-conductor be increased? **[Outside Delhi, 2012]**

5. Examine the given defective crystal:

A^+	B^-	A^+	B^-	A^+
B^-	O	B^-	A^+	B^-
A^+	B	A^+	O	A^+
B^-	A^+	B^-	A^+	B^-

Answer the following questions:

(i) What type of stoichiometric defect is shown by the crystal?

(ii) How is the density of the crystal affected by this defect?

(iii) What type of ionic substances shows such defect.

[Delhi Board 2014]

(B) Solutions

1. What is the similarity between Raoult's law and Henry's law?

[Delhi Board 2014]

2. What is the expected value of vant Hoff factor for $K_3Fe(CN)_6$?

3. CCl_4 and H_2O are immiscible whereas C_2H_5OH and H_2O are miscible in all proportions. Correlate this behaviour with the molecular structures of the three compounds.

4. At the same temperature, hydrogen is more soluble in water than

helium. Which of them will have a higher value of K_H and Why ? (K_H = Henry's constant).

5. Two liquids A and B on mixing produce a warm solution which type of deviation from Raoult's Law does it show?

(C) Electrochemistry

1. State the relationship between cell constant of the cell, resistance of solution and conductivity of solution.

[Delhi Board 2009, Outside Delhi 2010, 2012]

2. Express the relation between conductivity and molar conductivity of a solution.

[Delhi Board 2008, 2009, 2011, Outside Delhi, 2008, 2010]

3. What type of a cell is lead storage battery? Write the anodic and cathodic reactions and the overall reaction occurring in a lead storage battery while operating.

[Outside Delhi 2009, Delhi Board 2009, 2010, 2011, 2012, Outside Delhi Comptt. 2012]

4. Given that the standard electrode potentials (E°) of metals are:

$K^+ | K = -2.93$ V; $Ag^+ | Ag = 0.80$ V; $Cu^{2+} | Cu = 0.34$ V;

$Mg^{2+} | Mg = -2.37$ V; $Cr^{3+} | Cr = -0.74$ V; $Fe^{2+} | Fe = -0.44$ V

Arrange these metals in increasing order of their reducing power.

[Outside Delhi 2010]

5. Mention the reactions occurring at (i) anode (ii) cathode during working of a mercury cell. Why does the voltage of a mercury cell remain constant during its operation? **[Delhi Comptt. 2011]**

6. Give an example of fuel cell and write the cathode and anode reactions for it. **[Outside Delhi Comptt. 2011]**

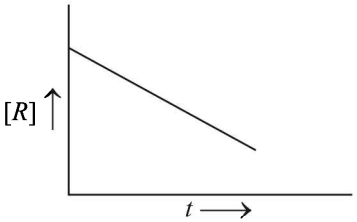
(D) Chemical kinetic

1. What is the order of the reaction if the units of rate constant are:

(i) L^{-1} mol s^{-1} (ii) L mol^{-1} s^{-1} **[Outside Delhi 2011]**

2. For a chemical reaction, $R \rightarrow P$, the variation in concentration

(R) vs. time (t) plot is given as:



(i) Predict the order of reaction.

(ii) What is the slope of the curve? **[Outside Delhi 2014]**

(E) Surface chemistry

1. What are the signs of ΔH and ΔS when a gas is adsorbed on the surface of an adsorbent? **[Delhi Comptt. 2009]**

2. Name any one method by which coagulation of a lyophobic sol can be carried out. **[Outside Delhi 2010]**

3. (a) In a reference to Freundlich adsorption isotherm, write the expression for adsorption of gases on solids in form of an equation.

(b) Write an important characteristic of lyophilic sols.

(c) Based on type of particles of dispersed phase, give one example each of associated colloid and multimolecular colloid.

[Delhi Board 2014]

4. Which has higher enthalpy of adsorption-physiosorption or chemisorption? **[Delhi Board 2008]**

5. Explain how the phenomenon of adsorption finds application in the following processes:

(i) Production of vacuum

(ii) Heterogeneous catalysis **[Delhi Board 2011]**

(F) Value Based Question

K M C

1. Two friends Ajit and Rohit while working on an unknown salt detected that given salt is AgBr. Density of AgBr is less than theoritically expected value. Ajit predicted it is due to Frenkel defect but Rohit said that Frenkel and Schottky defect both are present.
   (a) Whom would you support and why?
   (b) Write atleast two values each Ajit and Rohit do possess.

2. In a class, a teacher was explaining about the properties of solid. She gave a description of solid as insulator in solid as well as in molten state, very hard and brittle, very high melting point. After explaining the topic she asked students to identify the type of solid. Rohit said it would be an ionic solid but Reena said it would be covalent solid.
   (a) Whom do you favour and why?
   (b) What values are shown by one giving correct answer?

3. A school xyz went for a trip but when they were coming back suddenly snow fall started and the road get blocked. One group of students advised sprinkling of salt and another group advised use of calcium chloride. The first suggestion was taken to clear the snow.
   (a) Why was the first suggestion adopted?
   (b) What are the values shown by group giving correct advice?

4. There are many types of water purifiers available in the market now-a-days. For example : R.O. purifiers is based on desalination of water; zero B is based on disinfecting properties of iodine, etc.
   (a) What values are shown by people using water purifiers?
   (b) What is the full form of R.O. purifier?
   (c) On what principle the R.O. purifier works?
   (d) What is the function of semi-permeable membrane?
   (e) What type of semi-permeable membrances are used?

5. Manu went on to buy a new watch for himself along with his father. He chose a digital watch and enquired about the cells with the salesman. The salesman told him that these were mercury cells, commonly called button cells and asked him not to throw away the cells after use, but to give them for reprocessing.
   Now, answer the following question:

 Approved: 0777 023 444

K M C

(a) What type of a cell is mercury cell?

(b) Write the reaction involved.

(c) Why the used cell should not be thrown away? What values were shown by the salesman?

6. Akshay wanted to fix a photoframe on the wall. He searched for a box of iron nails. On locating the box, he found that most of the nails were rusted. He remembered that his teacher had tought him about rusting of iron and its disadvantages. Keeping that in mind he went to market and bought some new iron nails.

(a) What is rust chemically? Is it an electrochemical process?

(b) Give some other examples of corrosion.

(c) How can we prevent rusting of iron to reduce national wastage of money?

(d) What are the values shown by Akshay?

7. Mr. Sharma gifted a diamond ring to his wife as an anniversary gift. Their son Jay got curious to know about the ring. His mother told him that its a diamond ring. Jay told his parents that he had learnt in class that graphite and diamond both are allotropes of a carbon and graphite is thermodynamically more stable than diamond. He argued if it so than diamond will ultimately change into graphite which has no value. His mother who is a chemistry professor explained him that this would never happen.

(a) Why conversion of diamond to graphite is not possible though it is thermodynamically favourable process?

(b) Is it possible for a chemical reaction to have zero activation energy?

(c) What values are shown by Jay?

8. During 'Road safety week', the Delhi Traffic Police organized an awareness programme to prevent road accidents. They showed a presentation on two vehicles colliding with one another. This was followed by certain points like

(i) Multi vehicle collisions are rare.

(ii) Vehicles moving at high speed and colliding head on suffer maximum damage.

This was followed by certain do's and dont's while driving compare this situation with collision theory and answer the following questions.

(a) Why molecularity greater than three is rare?

 Approved: 0777 023 444

K M C

(b) What type of collisions are effective and lead to products?

(c) What is collision frequency?

(d) What values are shown by people who follow driving rules.

9. A factory was situated very close to the residential area. The factory worked round the clock and the smoke coming out of the chimneys was causing a lot of health problems to people living in the area. President and other members of welfare society decided to meet the top officials of the factory and give them the idea of installing the Cottrell's Smoke Precipitator.

(a) What is the purpose of having the Cottrell's Precipitator installed ?

(b) Mention the values shown by society members.

10. While playing basket ball match in the playground of school a student of opposite team player pushed kushagra. He fell down and had a bad cut in his knee and it started bleeding. Shishir immediately brought a bottle of ferric chloride while Sharad brought a bottle of potassium chloride from chemistry lab. After debating for a few seconds, a small amount of ferric chloride was applied to the wound and the bleeding was stopped.

(a) Why is ferric chloride preferred over potassium chloride in case of a cut leading to bleeding?

(b) What values do you attribute to shishir's and sharad's concern?

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(A) Solid State

1. Total number of atoms per unit cell in a *fcc* structure = 4.

$$\left[\underset{\text{corners}}{\frac{1}{8} \times 8} + \underset{\text{faces}}{6 \times \frac{1}{2}} = 4\right]$$

2. Rock salt type structure has 6 : 6 coordination number of each type of ion.

3. Schottky defect decreases the density of a solid because equal number of cations and anions are missing from the crystalattice.

4. The conductivity of an intrinsic semi-conductor can be increased by doping i.e. adding an impurity from outside i.e. either from group 13 or group 15.

5. (i) The given crystal shows Schottky defect.
   (ii) The density of the crystal decreases.
   (iii) Schottky defect is shown by those ionic substances in which cation and anion are of almost similar sizes. For example: NaCl, KCl, AgBr.

B. Solutions

1. Henry's law: $P = K_H x$ (for solubility of gases in liquids)
   Raoult's law: $P = P^o x$ (for a liquid-liquid solution)
   Thus, from both $P \propto x$
   i.e. K_H in Henry's law is replaced by P^o in Raoult's law.

2. Four, $K_3 [Fe (CN)_6] \rightarrow 3K^+ + [Fe(CN)_6]^-$.

3. CCl_4 is a non-polar compound, whereas H_2O is a polar compound having hydrogen bonding. When CCl_4 is mixed with H_2O, CCl_4 is not able to break the hydrogen bonding of H_2O and hence remains immiscible.

However, both C_2H_5OH and H_2O are polar compounds and form hydrogen bonding. When C_2H_5OH is mixed with H_2O, the hydrogen bonding between the two takes place and thus mixing occurs.

4. As H_2 is more soluble than helium, H_2 will have lower value of K_H than that of helium.

5. Warming up of a solution means that the process of mixing is exothermic, i.e., ΔH_{mixing} = negative.

   This implies that the solution shows a negative deviation.

(C) Electrochemistry

1. The cell constant (G^*) of a cell, resistance (R) of the solution and conductivity (κ) are related by the expression:

$$\kappa = \frac{G^*}{R}$$

2. If conductivity is κ, molar conductivity Λ_m and concentration C, then

$$\Lambda_m = \frac{\kappa}{C}$$

3. The lead storage battery is an example of secondary cell i.e. it can be reused again.

The cell reactions are:

Anode : $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

Cathode : $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$

Overall reaction : $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

4. More positive is the value of standard electrode potential, more is its tendency to get reduced. Thus, the increasing order of reducing power of the metals is:

$Ag^+ | Ag < Cu^{2+} | Cu < Fe^{2+} | Fe < Mg^{2+} | Mg < K^+ | K$

or, $Ag < Cu < Fe < Hg < K$

5. Mercury cell is a miniature cell which finds frequent use in watches, hearing aids, etc. In this cell, anode is zinc-mercury amalgam and cathode is a paste of mercury oxide and carbon. The electrolyte is a moist paste of KOH-ZnO.

The operating voltage for this cell is approximately 1.35 V and the cell reactions are:

Anode : $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O(l) + 2e^-$

Cathode : $HgO(s) + H_2O(l) + 2e^- \longrightarrow Hg(l) + 2OH^-$

Overall reaction : $Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$

6. Fuel cells convert chemical energy of fuels like H_2, CO, CH_4 etc. directly into electrical energy.

For example: H_2–O_2 fuel cell.

The cell reactions are:

Anode : $H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-$

Cathode : $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Overall reaction : $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

(D) Chemical kinetic

1. $$k = \frac{[\text{Rate}]}{[R]^n} = \frac{\text{mol L}^{-1}\,\text{s}^{-1}}{(\text{mol L}^{-1})^n} = (\text{mol L}^{-1})^{1-n}\,\text{s}^{-1}$$

(i) When $n = 0$, $k \rightarrow \text{mol L}^{-1}\,\text{s}^{-1}$, $\therefore$ order = 0

(ii) When $n = 2$, $k \rightarrow \text{L mol}^{-1}\,\text{s}^{-1}$, $\therefore$ order = 2

2. (i) The order of the reaction is zero.

(ii) For zero order reaction

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

$$\Rightarrow \quad kt = [R]_0 - [R]$$

$$\Rightarrow \quad [R] = [R]_0 - kt$$

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

This is of the form $y = mx + C$ where m is the slope

Here, $m = -k$

$\therefore$ Slope of the curve $= -\boldsymbol{k}$

(E) Surface chemistry

1. $\Delta H = -$ ve and $\Delta S = -$ ve for adsorption.

2. The coagulation of a lyophobic sol can be brought about by adding excess amount of an electrolyte.

3. (a) According to Freundlich adsorption isotherm, the quantity of gas adsorbed by unit mass of solid adsorbent and pressure of a gas (adsorbate) at a particular temperature is given by:

$$\frac{x}{m} = kP^{1/n} \quad (n > 1)$$

x = mass of gas adsorbed on mass m of adsorbent at pressure P

k and n = constants.

(b) Lyophilic sols are liquid-loving. An important characteristic of these sols is that if dispersion medium is separated from dispersed phase, the sol can be reconstituted by simply mixing the dispersion medium.

(c) An example of:

(i) Multimolecular colloid: gold sol, sulphur sol

(ii) Associated colloid: soap, synthetic detergent

4. Enthalpy of chemisorption is high as it involves chemical bond formation.

5. (i) **Production of Vacuum:** Air can be adsorbed from liquid air which helps to create a high vacuum in a vessel. The process is used in high vacuum instruments for storage of liquid hydrogen. The remaining traces of air can be removed by adsorption on charcoal.

   (ii) **Heterogeneous Catalysis:** Heterogeneous catalysis involves the adsorption of reactant molecules on the surface of the catalyst, thus bringing them closer and hence increasing the rate of reaction.

(F) Value Based Question

1. (a) Rohit's statement is correct because AgBr shows both Frenkel and Schottky defect.
   (b) Decision making ability, expresses ideas and opinion freely.
2. (a) Reena, because ionic solids are insulators only in solid state, but they conduct electricity in molten state or in solution.
3. (a) Sodium chloride or salt is the most commonly available and inexpensive de-icing material. When salt is applied to the road, it lowers the freezing/melting point of water. Whereas Calcium Chloride is an expensive de-icing chemical.
   (b) Choose the best alternative, knows their way of dealing with the situation, critical thinking etc.
4. (a) Health consious, awareness etc. are some values shown by people using water purifiers.
   (b) R.O. purifier stands for Reverse Osmosis purifier.
   (c) It works on the principle of Reverse Osmosis i.e, when pressure greater than osmotic pressure is applied on the solution side, solvent particles from solution side begin to move towards the pure solvent side.
   (d) The semi-permeable membrane allows only the solvent particles to pass through while stopping the flow of solid particles.
   (e) Examples of semi-permeable membranes are animal membrane, parchment paper.

5. (a) Mercury cell is an example of primary cell, i.e. the redox reaction occurs only once. After some time, the cell becomes dead and cannot be used again

(b) At anode :

$$Zn(s) + 2OH^- \rightarrow ZnO(s) + H_2O(l) + 2e^-$$

At Cathode :

$$HgO(s) + H_2O(l) + 2e^- \rightarrow Hg(l) + 2OH^-$$

Overall reaction : $Zn(s) + HgO(s) \rightarrow ZnO(s) + Hg(l)$

(c) The used cells should be reprocessed for mercury recovery or treated to prevent mercury and mercury compounds from entering atmosphere and causing pollution. Concern about the environment and society, awareness etc. are the values shown by salesman.

6. (a) Chemically, rust is hydrated ferric oxide, $Fe_2O_3 . xH_2O$. Yes, it is an electrochemical process.

(b) Some other examples include tarnishing of silver, development of green coating on copper and bronze etc.

(c) Ways to prevent corrosion are (i) painting, oiling, greasing i.e. barrier protection, and (ii) sacrificial protection like galvanization.

(d) Knowledgable, awareness and good memorising ability etc. are some values shown by Akshay.

7. (a) This is because the activation energy for the conversion of C (diamond) to C (graphite) is very high which is not available at room temperature.

(b) No, according to Arrhenius equation $k = Ae^{-E_a/RT}$ if activation energy is zero then k = A. i.e. rate constant will be equal to collision frequency due to which all reacting species will give product which does not happen.

(c) Curiosity, observational skill, good memory are some of the values shown by Jay.

8. (a) The probability that more than three molecule come together at one time and collide is rare. Hence, molecularity greater than three is rare.

(b) The collisions with desired amount of threshold energy are effective and lead to products.

(c) The number of collisions per second per unit volume of the reaction mixture is called collision frequency (Z).

(d) Such people are concerned for their own life as well as the life of other people on the roads. Awareness, infelligence are some other values displayed by people who follow driving rules properly.

9. (a) Cottrell's precipitator helps in precipitating smoke before it come out of the chimney which contains solid particles such as carbon, arsenic compounds, dust etc.

(b) Sensitive and supportive towards others health, takes initiatives in planning activities for betterment of environment, responsibility etc. are some values shown by society members.

10. (a) Ferric chloride results in faster coagulation of blood around the wound , stopping further bleeding. Coagulating power of an electrolyte is proportional to its valency. since valency of Fe+3 is higher compared to K+, hence Fe3+ will be more effective in coagulation.

(b) Recognizes and analyzes a problem, sensitive and careful towards others, helping, maintains balance in a difficult situation etc.

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PART B

Inorganic Chemistry

CHAPTER 1

What are the structures of the following compounds/ions?

Draw the structures of the following compounds/ions?

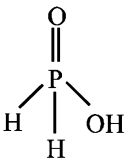
1. H_3PO_2 **(Delhi 2012, AI 2009, 2012)**
2. H_3PO_3 **(Foreign 2011, 2012, Delhi 2010C)**
3. N_2O_5 **(AI 2009, 2012)**
4. NF_3 **(Foreign 2011)**
5. $H_4P_2O_7$ **(Delhi 2010)**
6. $PCl_5\,(s)$ **(AI 2008, 2009)**
7. $H_2S_2O_8$ **(Delhi 2012, 2013, AI 2009, 2009C, Foreign 2012)**
8. SO_3^{2-} **(Delhi 2012, AI 2009)**
9. $H_2S_2O_7$ **(Delhi 2007, 2012, AI 2009, Foreign 2009)**
10. O_3 **(Delhi 2010, Foreign 2010)**
11. S_8 **(AI 2008, Foreign 2010)**
12. SF_4 **(Delhi 2008, Foreign 2007)**
13. SO_2 **(AI 2008C)**
14. H_2SO_5 **(Delhi 2007)**
15. SF_6 **(Foreign 2007)**
16. H_2SO_3 **(Delhi 2007)**
17. H_2SO_4 **(Delhi 2007)**
18. BrF_3 **(Delhi 2009, 2011, 2013, AI 2009, 2011, Foreign 2009, 2010, 2012)**
19. ClF_3 **(Delhi 2012, AI 2008, 2012)**
20. $HClO_4$ **(Delhi 2011C, AI 2009, 2012, Foreign 2010)**
21. $HOClO_2$ **(AI 2009, 2011C)**

K M C

22. HOClO (hypochlorous acid) **(Delhi 2007)**
23. HOCl (chlorous acid) **(Delhi 2007)**
24. XeF_2 **(Delhi 2011, 2012, 2013, AI 2013, Foreign 2010, 2012)**
25. XeF_4 **(AI 2008, 2010, 2011C, 2013, AI 2009C, 2010, Foreign 2009)**
26. XeF_6 **(Delhi 2012, AI 2013)**
27. $XeOF_4$ **(AI 2012, 2013, Delhi 2012)**
28. XeO_3 **(Delhi 2007C)**
29. MnO_4^- (manganate ion)
30. $Ni(CO)_4$ **(AI 2007)**
31. $[Ni(CN)_4]^{2-}$ **(AI 2011, 2012)**
32. $Fe(CO)_5$ **(AI 2007)**
33. $[CoCl_2(en)_2]^+$ **(Foreign 2011, 2012, AI 2012)**
34. $[Pt(NH_3)_2Cl(NO_2)]$ **(Foreign 2011)**
35. $[Cr(NH_3)_4Cl_2]^+$ **(Foreign 2011, AI 2011, 2012)**
36. $[Co(en)_3]^{3+}$ **(Foreign 2011, AI 2011)**
37. $[Fe(NH_3)_2(CN)_4]^-$ **(Delhi 2006C)**
38. $[Co(NH_3)_4Cl_2]^+$
39. $[Cr(C_2O_4)_3]^{3-}$ **(AI 2012, Foreign 2012)**
40. $[Pt(NH_3)_2Cl_2]$ **(Foreign 2012)**
41. $[Co(NH_3)_3Cl_3]$ **(AI 2011, 2012)**
42. $[Fe(NH_3)_4Cl_2]^+$ **(AI 2011)**
43. $[Fe(CN)_6]^{4-}$ **(AI 2012)**
44. $[Co(NH_3)_4(H_2O)_2]^{3+}$ **(Delhi 2007)**
45 $[Pt(NH_3)_4][NiCl_4]$ **(Delhi 2007)**
46 *cis*-Dichloridotetracyanochromate (III)
47 Pentaaminenitrito – N – cobalt (III)
48 Hexamethyl dialuminium

SOLUTIONS

1.



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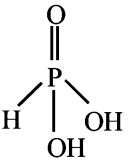

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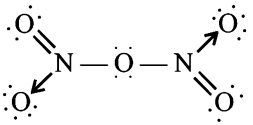

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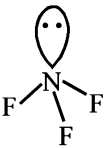

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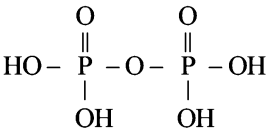

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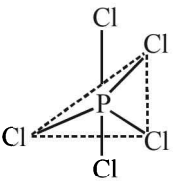

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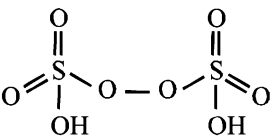

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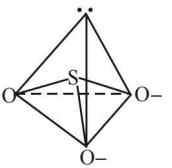

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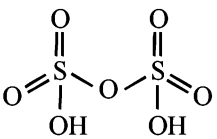

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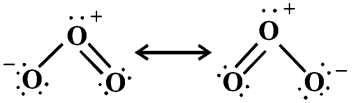

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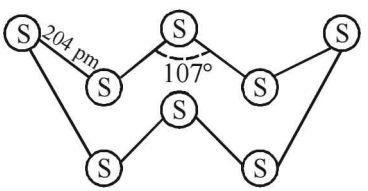

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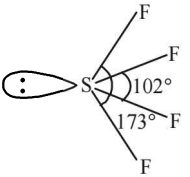

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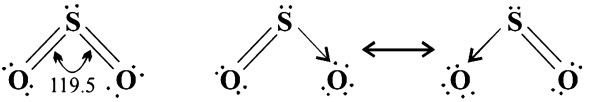

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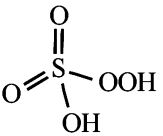

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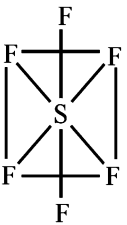

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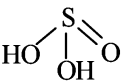

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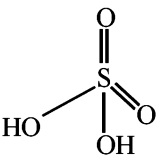

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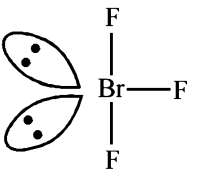

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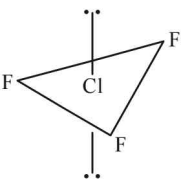

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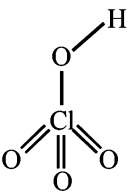

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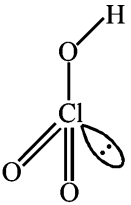

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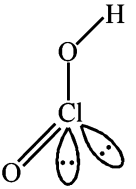

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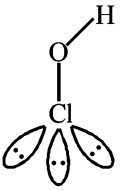

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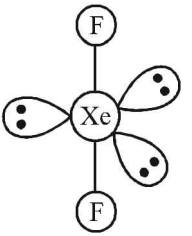

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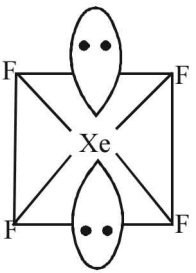

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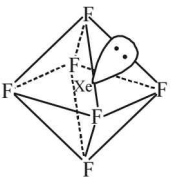

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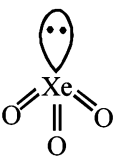

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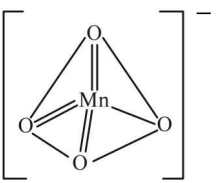

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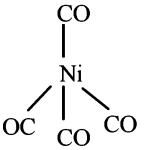

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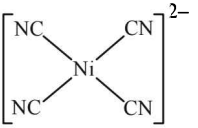

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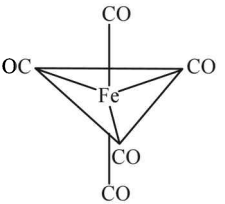

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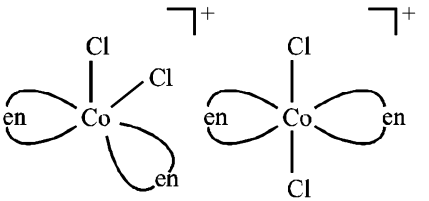

Cis *Trans*

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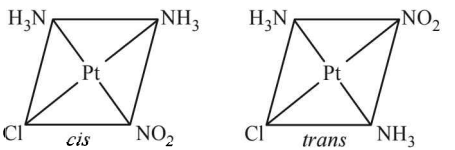

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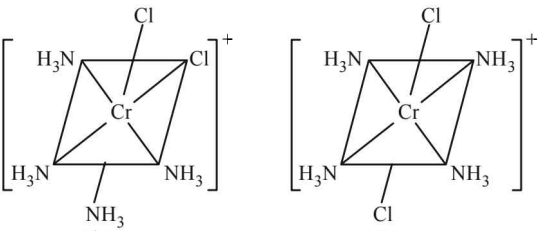

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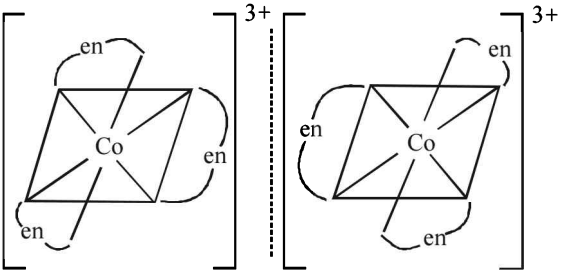

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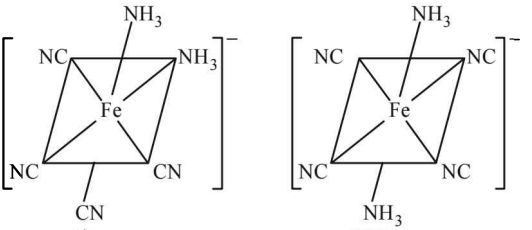

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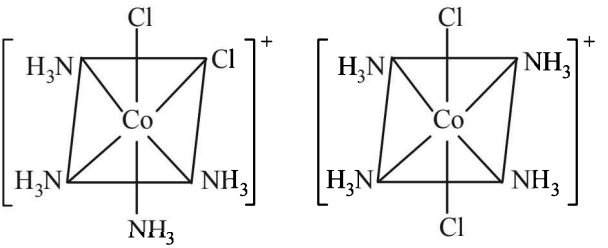

cis-form trans-form

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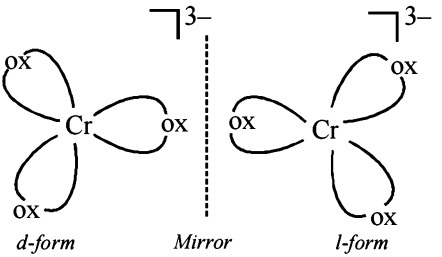

d-form *Mirror* *l-form*

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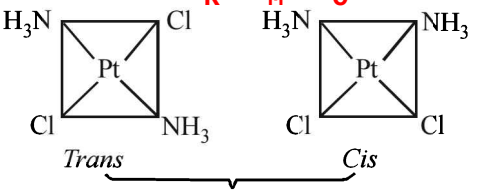

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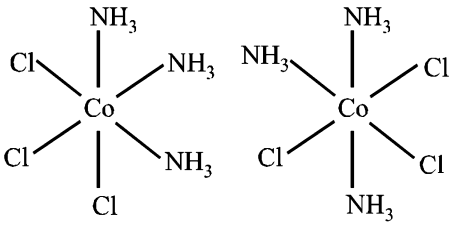

Geometrical isomers

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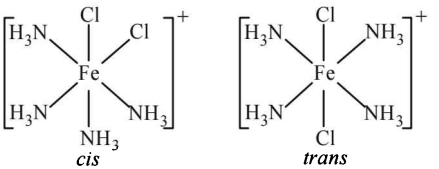

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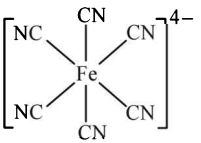

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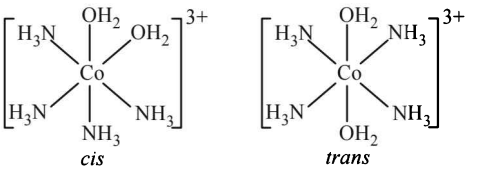

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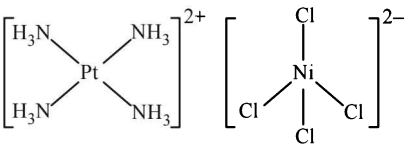

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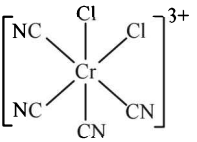
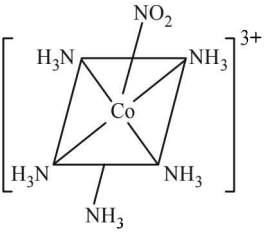
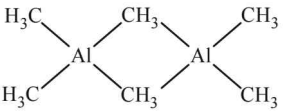

Cl
NC
Cl
3+
Cr
NC
CN
CN

cis

47.


NO2
H3N
NH3
3+
Co
H3N
NH3
NH3

48.


H3C
CH3
CH3
Al
Al
H3C
CH3
CH3

CHAPTER 2

What is the role of the following?

(A) *Metallurgy*

Explain the role of the following

1. Collectors in froth-floatation process ? **(AI 2012)**
2. Depressant in froth-floatation process for the concentration of a sulphide ore ? **(Foreign 2012)**
3. Stabiliser in froth-floatation process.
4. Graphite in the electrometallurgy of aluminium ? **(Delhi 2012)**
5. Cryolite in electrometallurgy of aluminium? **(Delhi 2012, AI 2010)**
6. Carbon monoxide in the refining of crude nickel ? **(Delhi 2011, 2012)**
7. SiO_2 in the extraction of copper ? **(AI 2011, 2012)**
8. SiO_2 in the extraction of copper from copper matte. **(Delhi 2010)**
9. Iodine in the refining of zirconium. **(Delhi 2010, AI 2010)**
10. NaCN in the extraction of silver ? **(AI 2010, 2012)**
11. Zinc in the extraction of silver. **(Delhi 2011)**
12. NaCN in the extraction of gold from gold ore. **(Delhi 2010)**

(A) *Metallurgy*

1. Collectors like pine oil, fatty acids, xanthates, etc. enhance non-wettability of mineral particles.

2. A depressant helps in the separation of two sulphide ores by preventing one type of sulphide ore particles from forming froth with air bubbles e.g., NaCN (a depressant) helps in the separation of ZnS and PbS present in a ore, it prevents ZnS from coming into froth but allows PbS to come with froth.

3. Stabilisers are those substances which stabilize the froth, examples are cresol and aniline.

4. Graphite acts as an anode. During electrolysis, Al is liberated at the cathode, while CO and CO_2 are liberated at the anode.

5. Cryolite reduces melting point of Al_2O_3 and increases electrical conductivity of the melt.

6. Carbon monoxide reacts with crude Ni to form nickel tetracarbonyl which on heating gives pure Ni.

$$\underset{\text{Crude}}{Ni} + 4CO \xrightarrow{330-350K} Ni(CO)_4 \xrightarrow[450-470K]{heat} \underset{\text{Pure}}{Ni} + 4CO\uparrow$$

7. SiO_2 acts as an acidic flux. Copper ore is heated with silica in a reverberatory furnance when FeO is removed as $FeSiO_3$ (slag) and copper is produced in the form of copper matte.

8. Copper matte consists mainly of Cu_2S along with some unchanged FeS. When a blast of air is passed through molten matte in a silica lined convertor, FeS present in matte is oxidised to FeO which combines with silica to form $FeSiO_3$(slag).

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \longrightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

Thus the role of silica lined crucible is to remove FeS in the matte as $FeSiO_3$. Due to evolution of SO_2, Cu is obtained as copper blister.

9. Pure zirconium can be obtained from impure Zr by van Arkel method. Impure Zr is heated in an evacuated vessel with iodine to form ZrI_4 which is electrically heated on a tungsten filament to about 1800°K to form Zr and I_2.

$$Zr + 2I_2 \longrightarrow ZrI_4 \xrightarrow{1800K} Zr + 2I_2$$

10. NaCN reacts with silver to form complex compound which on reduction with Zn gives silver metal.

$$4Ag + 8KCN + 2H_2O + O_2 \longrightarrow 4K[Ag(CN)_2] + 4KOH$$

$$2K[Ag(CN)_2] + Zn \longrightarrow K_2[Zn(CN)_4] + 2Ag$$

11. Same as Q. 10.

12. Gold is leached with a solution of NaCN in presence of air; the complex formed is reduced with zinc to give gold.

$$4Au + 8KCN + 2H_2O + O_2 \longrightarrow 4K[Au(CN)_2] + 4KOH$$

$$2K[Au(CN)_2] + Zn \longrightarrow K_2[Zn(CN)_4] + 2Au$$

■■■

CHAPTER 3

What or which principle is involved in the following processes?

(A) *Metallurgy*

Write the principle involved in the following

1. Column chromatography for purification of rare elements : **(Delhi 2012, AI 2008C, 2011C)**
2. Mond's process for refining of nickel. **(Delhi 2012, AI 2012)**
3. Vapour phase refining of metals. **(AI 2010, 2013, Foreign 2009)**
4. Vapour phase refining of titanium metal. **(Delhi 2008, 2011, AI 2011, Foreign 2011)**
5. Purification of germanium. **(AI 2012)**
6. Zone refining of metals. **(Delhi 2008, AI 2010, 2011, 2011C, 2013, Foreign 2008, 2009)**
7. Froth floatation method of concentration of sulphide ore. **(Delhi 2008, AI 2010, 2011, Foreign 2008)**
8. Electrolytic refining of metals. **(Delhi 2008, 2011, AI 2008, 2010, 2011, Foreign 2011)**
9. Preparation of cast iron from pig iron. **(AI 2011)**
10. Preparation of pure alumina, Al_2O_3 from bauxite. **(AI 2011)**
11. Recovery of silver after silver ore was leached with NaCN. **(Delhi 2011, Foreign 2011)**
12. Liquation method. **(Delhi 2008, AI 2011C, Foreign 2008)**
13. On choosing a reducing agent for metal oxides (Al_2O_3 and Fe_2O_3) to respective metal. **(AI 2008)**
14. Extraction of Sn from SnO_2.
15. Extraction of Zn from ZnO.
16. Extraction of Cr from Cr_2O_3.

(A) *Metallurgy*

1. **Column chromatography** is based on the principle that different components of a mixture are differently adsorbed on an adsorbent packed in column. Adsorbed components, known as **adsorbates** are removed by using suitable solvent, known as **eluant**, and the process is known as **elution**. This method is used for the purification of substances which are available in minute quantities and the impurities have neary similar chemical properties from the element to be purified.

2. **Mond's process** for refining (**vapour phase refining**) of nickel is based on the fact that nickel when heated in a stream of carbon monoxide forms volatile nickel tetracarbonyl which decomposes to pure nickel on strong heating.

$$\underset{\text{Impure}}{Ni} + 4CO \xrightarrow{330-350K} \underset{\text{Nickel tetracarbonyl}}{Ni(CO)_4} \xrightarrow{450-470K} \underset{\text{Pure}}{Ni} + 4CO\uparrow$$

3. **Vapour phase refining** of metals is based on the principle that certain metals (e.g. Ni and Ti) forms volatile compounds on heating with some reagents (e.g. CO in Ni and I_2 in Ti). The volatile compound on further heating decomposes back into the constituent compounds.

$$Ti + 2I_2 \xrightarrow{870K} TiT_4 \xrightarrow{1800K} Ti + 2I_2$$

4. Vapour phase refining of Ti (consult 3) is called **van Arkel process** of refining.

5. Germanium is purified by **zone refining** which is based on the fact that the impurities are more soluble in the melt than in the solid state of the metal. In the process, one end of the impure metal rod is heated by means of a movable heater. The molten zone carrying impurities moves forward. In this way impurities are concentrated at the other end of the rod which is cut off. The process is repeated several times to obtain ultrapure metals (Ge, Si, Ga and In) used as semiconductors.

6. Consult Q.5.

7. **Froth floatation process** is based on the fact that sulphide ores are preferentially wetted by pine oils, whereas the gangue particles are wetted by water. A rotating paddle agitates the mixture and draws air in it. As a result, a froth carrying the mineral particles is formed. The froth, being light, comes upwards and skimmed off. It is then dried for recovering the ore particles.

8. **Electrolytic refining of metals**. In this method, the impure metal is made to act as anode and a strip of the same metal in pure form is made as cathode. The electrodes are immersed in a suitable electrolytic solution of soluble salt of the same metal. On passing an electric current, following reactions take place.

Anode : $M \longrightarrow M^{n+} + ne^-$

Cathode : $M^{n+} + ne^- \longrightarrow M$

Thus, in electrolysis, a metal is transferred in **pure form** from anode to cathode.

9. **Preparation of cast iron from pig iron**. Iron obtained from blast furnance is called **pig iron** and contains about 4% carbon. Cast iron contains about 3% carbon and obtained by melting pig iron with scrap iron and coke using hot air blast. It is extremely hard and brittle.

10. **Preparation of pure alumina from bauxite ore** is based on the fact that alumina present in bauxite disolves in conc. NaOH solution, while impurities (like iron oxide, TiO_2) present in bauxite remain insoluble. Thus the powdered bauxite ore is digested with conc. NaOH solution at 473–532 K and 35–36 bar pressure to form sodium aluminate

$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow \underset{\text{Sod. aluminate}}{2Na[Al(OH)_4]}$$

which is neutralized with CO_2 gas to get hydrated alumina

$$2Na[Al(OH)_4] + CO_2 \longrightarrow Al_2O_3.xH_2O + 2NaHCO_3$$

$$Al_2O_3.xH_2O \longrightarrow Al_2O_3 + xH_2O \uparrow$$

11. **Recovery of silver after the ore was leached with NaCN**. This is based on the principle of oxidation and reduction. The soluble silver complex (obtained by treating the ore with NaCN solution) is reduced with zinc

$$4Ag + 8CN^- + 2H_2O + O_2 \longrightarrow 4[Ag(CN)_2]^- + 4OH^-$$

$$2[Ag(CN)_2]^- + Zn \longrightarrow [Zn(CN)_4]^{2-} + 2Ag \downarrow$$

12. **Liquation method**. A low melting metal like tin can be made to flow on a sloping furnace and thus separated from higher melting impurities like Fe. Magnesium can also be separated by this method.

13. **Choosing a reducing agent :** Thermodynamic factor helps in choosing a suitable reducing agent for the reduction of a metal oxide to metal. From Ellingham diagram, it is evident that metals which have more negative $\Delta_f G^0$ of their oxides can reduce those metal oxides for which $\Delta_f G^0$ is less negative. Since the free energy change for the formation of Fe_2O_3 is less negative than CO, CO is a good reducing agent for it.

$$Fe_2O_3 + CO \longrightarrow 2Fe + 3CO_2, \quad \Delta G = -ve$$

$[\Delta_f G^0\ Fe_2O_3$ is less negative than $\Delta_f G^0$ CO$]$

The free energy change for the formation of Al_2O_3 is highly negative (about – 1000 to – 1100), thus no reducing agent is suitable for its reduction. Hence Al_2O_3 is reduced by electrolysis of its oxide.

14. $SnO_2 + 2C \xrightarrow{heat} Sn + 2CO$

15. $ZnO + C \xrightarrow{heat} Zn + CO$

16. $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$

■■■

CHAPTER 4

Why do the following happens?

Explain the following:

(A) *Metallurgy*

1. Copper and silver are below hydrogen in electrochemical series, yet they are found in the combined state as sulphides in nature.
2. Elements with higher atomic numbers are rare.
3. Iron is an abundant element on earth.
4. Copper, but not zinc, can be extracted by hydrometallurgy.
5. Alumina is dissolved in cryolite for electrolysis instead of being electrolysed directly. **(Delhi 2010C)**
6. Zinc oxide can be reduced to the metal of heating with carbon, but not with Cr_2O_3. **(Delhi 2010C)**
7. Extraction of copper directly from sulphide ores is less favourable than that from its oxide ore through reduction. **(Delhi 2010C)**

(B) *Group 15*

1. Nitrogen is much less reactive than phosphorus. **(Delhi 2012, AI 2012, Foreign 2012)**
2. Phosphorus has greater tendency for catenation than nitrogen. **(AI 2012)**
3. Stability of +5 oxidation state decreases down the group. **(Delhi 2010, 2011, 2012)**
4. Tendency to form pentahalides decreases down the group in group 15 of the periodic table. **(Delhi 2011)**
5. The N–O bond in NO_2^- is shorter than the N–O bond in NO_3^- **(Delhi 2011, AI 2011)**
6. The bond angles (O – N – O) are not of the same value in NO_2^- and NO_2^+. **(Delhi 2012)**
7. Nitric oxide becomes brown when released in air.
8. NO_2 dimerises. **(Delhi 2010)**

9. NO_2 is coloured but its dimer N_2O_4 is colourless.

10. The molecules NH_3 and NF_3 have dipole moments in opposite directions. **(Delhi 2012)**

11. NF_3 is an exothermic compound, while NCl_3 is not. **(AI 2010, 2012, Delhi 2010, 2011)**

12. Concentrated HNO_3 turns yellow on expossure to sunlight.

13. All the bonds in PCl_5 molecule are not equivalent. **(Delhi 2011, 2012)**

14. Solid phosphorus pentachloride behaves as an ionic compound. **(AI 2007, Delhi 2010)**

15. PCl_4^+ exists but PCl_4^- not. **(Delhi 2012)**

16. SbF_5 is much more stable than BiF_5.

17. Bismuth is a strong oxidising agent in pentavalent state.

18. Bi(V) is a stronger oxidising agent than Sb(V).

19. Bismuth oxide is not acidic in any of its reactions.

20. The acidic strength of compounds increases in the order :
$PH_3 < H_2S < HCl$ **(AI 2011)**

21. In group 15, the bond angle H–M–H decreases in the order : NH_3(107.8°), PH_3(93.6°) and AsH_3 (91.8°).

22. Nitrogen is a gas, while phosphorus is a solid.

23. Acidity of oxyacids of nitrogen increases with increase in oxidation state.

24. Basic character of the hydrides of group 15 elements decreases with increasing atomic numbers.

25. White phosphorus is more reactive than red phosphorus. **(Delhi 2010)**

26. The bond angle in PH_3 molecule is less than in NH_3. **(AI 2008)**

27. Oxides of nitrogen have open chain structure, while those of phosphorus have closed chain or cage structure.

28. Nitrogen does not form pentahalides, why phosphorus does so.

29. Ammonia is a good complexing agent (ligand) **(AI 2008)**

30. PH_3 is a weaker base than NH_3.

31. Phosphoric acid is syrupy.

32. Nitrogen exists as gas whereas phosphorus exists as a solid.

33. H_3PO_3 is diprotic acid.
34. Phosphinic acid behaves as a monoprotic acid.
35. On being slowly passed through water, PH_3 forms bubbles but NH_3 dissolves.
36. The maximum number of covalent bonds formed by N is 4.
37. Phosphorus (Z = 15) and vanadium (Z = 23) exhibit variable oxidation states for different reasons.

(C) Group 16

1. Group 16 elements are called chalcogens.
2. Oxygen is gas but sulphur is solid. **(AI 2012)**
3. Sulphur has greater tendency for catenation than oxygen. **(AI 2012, Delhi 2011)**
4. Sulphur in vapour state exhibits paramagnetism. **(Delhi 2012)**
5. The value of electron gain enthalpy with negative sign for sulphur is higher than that for oxygen. **(Delhi 2010)**
6. Tendency to show –2 oxidation state diminishes from S to Po in group 16 elements.
7. Oxygen does not show oxidation state of +4 and +6, while S does so.
8. Compound OF_6 is not known.
9. Oxygen-oxygen bond length in ozone is same.
10. H_2S is more acidic than water. **(AI 2012, Foreign 2012, AI 2011)**
11. Thermal stability of H_2O is much higher than that of H_2S.
12. H_2S is more acidic than PH_3. **(Delhi 2012)**
13. Although H_2S has greater molecular mass than H_2O, former is gas while latter is liquid at room temperature.
14. The bond angle in H_2O is larger than in H_2S.
15. O_2 and F_2 both stabilize higher oxidation states of metals, but O_2 exceeds F_2 in doing so. **(Delhi 2012)**
16. Despite having greater polarity, hydrogen fluoride boils at a lower temperature than water. **(AI 2012)**
17. Although the H-bonding in HF is much stronger than in water, yet water has a much higher b.p. than HF. **(Foreign 2012)**
18. All the bonds in SF_4 are not equivalent. **(AI 2012)**
19. SF_6 is not easily hydrolysed.
20. SF_6 is kinetically inert. **(Foreign 2012, Delhi 2011, AI 2011)**

K M C

21. SF_6 is known, while SCl_6 is not known.
22. SF_6 exists but SH_6 does not.
23. SF_6 is much less reactive than SF_4.
24. SF_6 used as a gaseous electrical insulator.
25. The highest oxidation state of a metal is exhibited in its oxide or fluoride.

(D) Group 17

1. F, Cl, Br and I are called halogens.
2. Halogens are coloured ? **(AI 2012)**
3. Halogens are strong oxidising agents. **(Delhi 2010)**
4. Fluorine always exhibits an oxidation state of –1 only.
5. Fluorine is better oxidising agent than chlorine, although it has less electron affinity than chlorine.
6. Fluorine is most reactive of all the four common halogens **(Delhi 2011)**
7. Fluorine does not exhibit any positive oxidation state **(AI 2010, 2012, Foreign 2012)**
8. Despite lower value of its electron gain enthalpy with negative sign, fluorine (F_2) is a stronger oxidising agent than Cl_2. **(AI 2010, 2012)**
9. Bond dissociation energy of fluorine molecule is less than that of chlorine molecule.
10. Among halogenes, fluorine provides the largest variety of inter-halogen compounds.
11. Interelectronic repulsion between valence electrons of F atoms is more than those between Cl atoms.
12. Fluorine and oxygen compounds are called oxygen fluorides, but not fluorine oxides.
13. HF is a weaker acid than HCl in aqueous solution **(Foreign 2012)**
14. HF is the weakest acid among hydrohalo acids ($HF < HCl < HBr < HI$).
15. HF is much less volatile than hydrogen chloride.
16. ICl is more reactive than I_2. **(AI 2012)**
17. ClF_3 exists but FCl_3 does not.
18. Metal fluorides are more ionic than metal chlorides.

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19. In interhalogen compounds of the type AB_5 and AB_7, B is invariably fluorine.
20. ClF_3 molecule has a T-shaped structure and not a trigonal planar. **(Delhi 2010)**
21. Iodine (I_2) is more soluble in KI than in water.
22. Addition of Cl_2 to KI solution gives it a brown colour, but excess of Cl_2 turns it to colourless.
23. Interhalogen compounds are strong oxidising agents.
24. Perchloric acid is a stronger acid than sulphuric acid.
25. Bleaching of flowers by Cl_2 is permanent, while that by SO_2 is temporary.
26. Special methods are used to prepare HBr and HI.
27. Fluorine does not form polyhalides.
28. The pK_a value of four oxyacids of chlorine follows the order $HClO > HClO_2 > HClO_3 > HClO_4$
29. The oxidising power of the four oxyacids follows the order : $HClO > HClO_2 > HClO_3 > HClO_4$

(E) Group 18

1. Noble gases exist as monoatomic.
2. Noble gases have low boiling points. **(AI 2011)**
3. Helium forms no real chemical compound. **(AI 2012, Foreign 2012)**
4. Neon is not known to form compounds.
5. Among noble gases only xenon forms chemical compounds.
6. Noble gases form compounds only with fluorine and oxygen.
7. Xenon readily forms compounds, but Kr does not form compounds easily.
8. Only higher members of group 18 of the periodic table are expected to form compounds.
9. Helium is used for inflating aeroplane tyres.
10. Deep sea divers use a mixture of He (80%) and O_2 (20%) instead of air for breathing.
11. Structures of xenon fluorides cannot be explained by VB approach. **(Delhi 2012)**

12. XeF_2 is a linear molecule without a bend. **(AI 2010)**
13. Xenon does not form fluorides such as XeF_3 and XeF_5.

(F) **d- *and* f-block *Elements***

1. There is a general increase in density from Ti (Z = 22) to Cu (Z = 29) **(AI 2012)**
2. There is hardly any increase in atomic size with increasing atomic numbers, in a series of transition metals. **(AI 2012)**
3. Most of the transition metal ions exhibit characteristic colours in aqueous solution. **(Delhi 2012, Foreign 2012, Delhi 2011)**
4. Many of the transition elements are known to form interstitial compounds. **(Delhi 2012, AI 2012)**
5. Transition elements and their compounds are known to act as catalysts. **(Foreign 2012)**
6. The enthalpies of atomisation of transition metals are high.
7. Transition elements tend to be unreactive with increasing atomic number in the series.
8. Transition metals and their compounds generally exhibit a paramagnetic behaviour.
9. Only transition metals form complex compounds with ligands like CO.
10. The π-complexes are known for transition elements only **(AI 2009, 2010, Foreign 2012)**
11. Transition elements show variable oxidation states.
12. Transition elements have high value of hydration enthalpy.
13. The atomic radii do not change very much in a transition series with an increase in atomic number.
14. Zn, Cd and Hg are generally not regarded as transition elements.
15. The higher oxidation states are usually exhibited by the members in the middle of a series of transition elements. **(Foreign 2012)**
16. Among lanthanoids, Ln (III) compounds are predominant. However, occasionally in solutions or in solid compounds, +2 and +4 ions are also obtained. **(AI 2012)**
17. Unlike Cr^{3+}, Mn^{2+}, Fe^{3+} and the subsequent other M^{2+} ions of the 3*d* series of elements, the 4*d* and the 5*d* series metals generally do not form stable cationic species.
18. The M–M bonding is more frequently found with the second (4*d*) and third (5*d*) series of transition elements.
19. The metallic radii of the third (5*d*) series of transition metals are

virtually the same as those of the corresponding members of the second (4*d*) series.

20. $La(OH)_3$ is more basic than $Lu(OH)_3$.

21. Ce^{4+} is a good oxidising agent in aqueous solution.

22. Colour of solution of $K_2Cr_2O_7$ changes from orange to yellow on adding NaOH.

23. In volumetric estimation, $K_2Cr_2O_7$ is preferred over $Na_2Cr_2O_7$ solution.

24. During estimation of Fe^{2+} or $C_2O_4^{2-}$, $KMnO_4$ is not acidified by HCl.

25. V_2O_5 is used as a catalyst.

26. Cr^{3+} is more stable than Cr^{2+} in aqueous solution.

27. Cu^{2+} has d^9 electronic configuration, while Co^{2+} has d^7, yet it is less paramagnetic than Co^{2+}.

28. Copper (Z = 29) has d^{10} electrons, yet it is considered as transition element.

29. K_2PtCl_6 is well known compound, while corresponding compound of Ni is not known.

30. Radius of Fe^{2+} is less than that of Mn^{2+}.

31. All bonds in MnO_4^- are covalent.

32. Fe^{3+} is more stable than Fe^{2+}.

33. Cu^{2+} is more stable than Cu^+.

34. $KMnO_4$ is kept in dark bottles.

35. Zinc salts are white while Cu^{2+} salts are coloured.

36. All scandium salts are white.

37. First ionisation energies of the 5*d* transition elements are higher than those of the 3*d* and 4*d* transition elements in respective groups.

38. It is difficult to separate lanthanoids in pure state.

39. Zirconium and hafnium exhibit similar properties.

40. $KMnO_4$ is dissolved in dil. H_2SO_4, but never in conc. H_2SO_4.

41. Co^{2+} is easily oxidized to Co^{3+} in presence of a strong ligand.
(AI 2010, Delhi 2012)

42. Cr^{2+} is a stronger oxidising agent than Fe^{2+}.

43. Cu(I) is not stable in aqueous solution.
(Foreign 2012, Delhi 2010, 2011)

44. Manganese exhibits the highest oxidation state of +7 among the 3*d* series of transition elements. **(Delhi 2011)**

45. With the same *d*-orbital configuration (d^4), Cr^{2+} is a reducing agent while Mn^{3+} is an oxidising agent. **(Delhi 2012m AI 2012)**

46. La^{3+} (Z = 57) and Lu^{3+} (Z = 71) do not show any colour in solution.

47. The oxidising power of oxoanions are in the order :
$VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$.

48. The third ionization enthalpy of Mn (Z = 25) is exceptionally high.

49. The E^0 value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+} couple.

50. Among the divalent cations in the first series of transition elements, Mn exhibits maximum paramagnetism.

51 Lanthanoids form primarily +3 ions, while the actinoids usually have higher oxidation states in their compounds, +4 or even +6 being typical. **(Delhi 2012)**

52 The actinoids exhibit a large number of oxidation states than the corresponding members in the lanthanoid series.
(Delhi 2012, AI 2012, Delhi 2011)

53. Chemistry of actinoids is much more complicated than that of the lanthanoids.

(G) Coordination compounds

1. Formation of complex is exothermic process.

2. Stability of complex decreases with increase in temperature.

3. A chelating complex is more stable than an unchelated complex.

4. $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1 : 1 molar ratio gives the test of Fe^{2+} ion, but $CuSO_4$ solution mixed with aqueous ammonia in 1 : 4 molar ratio does not give the test of Cu^{2+} ions.

5. CO is a strong ligand than Cl^-. **(Foreign 2011)**

6. CO is a stronger complexing reagent than NH_3. **(Delhi 2012)**

7. CO is a stronger ligand than NH_3 for many metals. **(AI 2009)**

8. Nickel does not form low spin octahedral complexes. **(AI 2009, 2010)**

9. $[NiCl_4]^{2-}$ is paramagnetic, while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral.

10. Although $[Ni(CN)_4]^{2-}$ and $Ni(CO)_4$ have different structures, both are diamagnetic.

11. $[Ni(CN)_4]^{2-}$ and $[Ni(Cl_4)]^{2-}$ have different structures and also possess different magnetic properties.

12. $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic, while $[Fe(CN)_6]^{3-}$ is weakly paramagnetic.

13. $[Fe(CN)_6]^{3-}$ is weakly paramagnetic, while $[Fe(CN)_6]^{4-}$ is diamagnetic.

14. $[Cr(NH_3)_6]^{3+}$ is paramagnetic, while $[Ni(CN)_4]^{2-}$ is diamagnetic.

15. Aqueous solution of copper sulphate gives green precipitate with aqueous KF solution, while it gives bright green solution with aqueous KCl solution.

16. A solution of $[Ni(H_2O)_6]^{2+}$ is green, while solution of $[Ni(CN)_4]^{2-}$ is colourless.

17. Dilute solutions of $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ have different colours. **(Foreign 2012)**

18. $[Co(NH_3)_6]^{3+}$ is an inner orbital complex, while $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

19. Square planar complexes with a coordination number 4 exhibit geometrical isomerism, while tetrahedral complexes do not exhibit geometrical isomerism.

(A) *Metallurgy*

1. Copper and silver can react with sulphur at high temperature inside the earth crust to form their sulphides.

2. Elements with higher atomic numbers are rare because they are unstable due to low nuclear binding energy.

3. Iron is most abundant due to its very high nuclear binding energy.

4. The E^0 of zinc ($Zn^{2+}/Zn = -0.76$ V) is lower than that of copper ($Cu^{2+}/Cu = +0.34$ V), hence Zn can displace Cu from solutions of Cu^{2+} salts. Since iron ($Fe^{2+}/Fe = -0.44$ V) in much cheaper than zinc, iron scrap is chiefly used in hydrometallurgy and Cu.

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

For displacing Zn from solution of Zn^{2+} ions, a metal more reactive than Zn should be used. However, metals like Al, Mg, Ca and K, although have lower reduction potential than zinc,

$$Al\left(E^0_{Al^{3+}/Al} = -1.66\,V\right), Mg\left(E^0_{Mg^{2+}/Mg} = -2.37\,V\right),$$

$$Ca\left(E^0_{Ca^{2+}/Ca} = -2.87\,V\right), K\left(E^0_{K^+/K} = -2.93\,V\right)$$

These cannot be used to displace Zn from solution of Zn^{2+} ions, because they react with water ($2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$, $E^0 = -0.83V$) forming corresponding ions along with the evolution of H_2 gas. Thus **copper can be extracted by hydrometallurgy but not zinc.**

5. The role of cryolite are:

   (*a*) It makes alumina a good conductor of electricity.

   (*b*) It lowers the fusion or melting temperature of the bath from 2323 K to about 1140 K.

6. The reaction in both the cases may be written as

$$ZnO(s) + C(s) \longrightarrow Zn(s) + CO(g)$$

$$ZnO(s) + Cr_2O_3(s) \longrightarrow Zn(s) + 2CrO_2(s)$$

In the first case, there is increase in entropy while no change occurs in the second case. Thus, the change is thermodynamically feasible or spontaneous in the first case only.

7. The chemical reactions in the two cases may be expressed as :

$$2CuS(s) + C(s) \longrightarrow CS_2(l) + 2Cu(s)$$

$$CuO + C(s) \longrightarrow CO(g) + Cu(s)$$

In the first case, carbon disulphide formed in the reaction is a liquid whereas carbon monoxide is in the gaseous state in the second case. Consequently, the reduction reaction is more thermodynamically feasible in the second case than in the first case.

(B) Group 15

1. Due to formation of triple bond ($N \equiv N$), N_2 molecules are smaller and held by weak van der Waal's forces. Thus N_2 exists as gas and boils at lower temperature. On the other hand, phosphorus molecules are bigger (P_4) due to presence of P–P single bond, hence exists as solid.

2. Nitrogen molecules have triple bond ($N \equiv N$) which has high bond dissociation energy, while P_4 molecules have P–P single bond which has low bond dissociation energy.

3. Lone pair-lone pair repulsions in between two adjacent smaller N atoms, N_2 molecule does not show catenation, while there is no such repulsion in phosphorus molecules having larger P atoms.

$$-\overset{..}{N} \leftrightarrow -\overset{..}{N} \leftrightarrow -\overset{..}{N}$$

4. The configuration of group 15 elements in the outermost orbit is ns^2np^3. The ns^2 electrons become inert and do not participate in bonding (**inert pair effect**) as we move downwards.

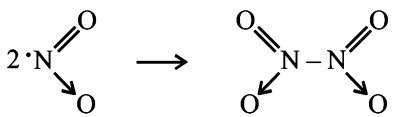
- Same as above (7)

5. Oxidation state of N in NO_2^- is +3, while it is +5 in NO_3^-. Due to this difference, N–O bond in NO_2^- is shorter than that in NO_3^-.

6. Nitrogen in NO_2^- is sp^2 hybridised, while it is sp hybridised in NO_2^+; hence the bond angles in the two will be different.

7. Nitric oxide reacts with O_2 of air to form NO_2 which is brown in colour ($2NO + O_2 \longrightarrow 2NO_2$).

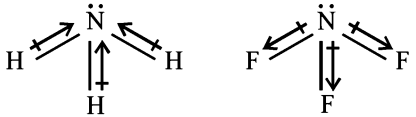
8. NO_2 contains one unpaired electron, it is unstable, hence it easily dimerises to form stable dimer, N_2O_4.



NO_2 (brown) Dimer, N_2O_4 (colourless)

9. As shown above, NO_2 has an unpaired electron, it absorbs light from visible region and radiates colour, while N_2O_4 does not have any unpaired electron, it does not absorb light from visible region, hence it is colourless.

10. In NH_3, N is more electronagative than H, while in NF_3, F is more electronegative than N.



11. Fluorine is stronger oxidising agent than chlorine, hence NF_3 is exothermic while NCl_3 is endothermic. Alternatively, during NF_3 formation strong N – F bond is formed due to small size of F and large electronegativity difference between two atoms, while formation of NCl_3 leads to comparatively weaker N – Cl bond due to large size of Cl and nearly same electronegativity of the two atoms. Hence NF_3 is exothermic, while NCl_3 is endothermic.

12. Nitric acid decomposes to NO_2 in presence of sunlight. The brown colour of NO_2 makes HNO_3 yellow.

13. The five P – Cl bonds are not in same plane. The two axial P – Cl bonds are longer and weaker than the other three equatorial P – Cl bonds due to more repulsion.

14. In solid state, PCl_5 exists as an ionic compound, $[PCl_4]^+ [PCl_6]^-$.

15. In PCl_4^-, octet of P is not complete, thus it is unstable.

16. As we move down the group, stability of +5 oxidation state decreases due to inert pair effect, thus SbF_5 is more stable than BiF_5.

17. Due to inert pair effect, Bi^{3+} is more stable than Bi^{5+}, hence Bi^{5+} easily gains two electrons to form stable Bi^{3+} and thus acts as oxidising agent.

18. Due to inert pair effect, Bi^{3+} is more stable than Bi^{5+} (as compared to stability between Sb^{3+} and Sb^{5+}) because Bi lies at the bottom of the group, i.e., inert pair effect is more prominent in Bi than in Sb.

19. As we move down a group in *p*-block, metallic character increases. Bismuth, being the last number in group 15, is distinctly metallic and metallic oxides are basic in nature.

20. Acidic strength of a hydrogen compound depends upon the electronegativity difference between hydrogen and the second element. Greater the electronegativity of atom other than H,

greater will be the acidic strength. Since electronegativity of P, S and Cl are 2.1, 2.44 and 3.2 respectively, acidic strength will be $PH_3 < H_2S < HCl$.

21. Due to increase in size of group 15 elements, bond length increases and thus the bond pair – bond pair repulsion decreases leading to increase in the H–M–H bond angle from NH_3 to AsH_3 through PH_3.

22. Non-metallic character of N increases with increase in oxidation state, therefore acidic character of oxyacids increases, e.g., $\overset{+5}{HNO_3}$ is more acidic than $\overset{+3}{HNO_2}$.

23. Due to increase in atomic size, density of electron decreases down the group. Hence the basic character decreases.

24. NH_3, PH_3, AsH_3, SbH_3 and BiH_3 behaves as Lewis bases due to the presence of lone pair of electrons on the central atom. As we more from N to Bi, size of atom increases. Electron density on central atom decreases and hence the basic strength decreases from NH_3 to BiH_3. Thus basic strength order is

$$BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$$

25. White phosphorus exists as P_4 while red phosphorus is polymeric.

26. Low value of bond angle in PH_3 is due to smaller bond pair – bond pair repulsion.

27. Nitrogen forms multiple ($p\pi$-$p\pi$) bonds, while phosphorus does not form $p\pi$-$p\pi$ bonds, hence oxides of N are open chain while that of P are closed chain.

28. Nitrogen does not have *d*-orbital.

29. NH_3 can donate lone pair of electrons to other species forming complex compounds.

30. Although both PH_3 and NH_3 have lone pair of electrons on P and N respectively, P being bigger in size, electron density on P is smaller than on N, hence PH_3 is a weaker base than NH_3.

31. Phosphoric acid is syrupy because of intermolecular H-bonding.

32. Nitrogen is a small diatomic molecule (N_2) which has weak van der Waal's forces of attraction whereas phosphorous is tetra atomic molecule (P_4) which has significant force of attraction.

33. H_3PO_3 is diprotic (dibasic) because it gives two H^+ ions in aqueous solution, i.e., it has only two replacable hydrogens (–OH), the third hydrogen is directly linked to P and thus not replacable.

34. Phosphinic acid (H_3PO_2) has only one replacable hydrogen (– OH).

35. NH_3 dissolves in water due to H-bonding; phosphine being less soluble gives bubbles and escapes out.

36. The valence shell of N ($1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$) has three unpaired electrons which form three covalent bonds. The lone pair present in valence shell ($2s^2$) can also form coordinate covalent bond by donating electron pair to a good acceptor (e.g. H^+) as in NH_4^+.

37. Phosphorus shows +3 and +5 oxidation states due to presence of unpaired electrons in excited state. Vanadium loses different number of electrons to show different oxidation states, viz. +2, +3, +4 and +5.

(C) Group 16

1. Ore forming elements are called **chalcogens** and most of the ores are oxides and sulphides.

2. Oxygen is diatomic (O_2), therefore it has less van der Waal's forces of attraction, while sulphur is octa-atomic (S_8) and has more van der Waal's forces of attraction.

3. Oxygen has double bond, while sulphur forms single bond. Moreover, S–S bond is stronger than the O – O bond because there is more repulsion between valence electrons (*lp-lp* repulsion) in oxygen as it is smaller than sulphur. Since S forms only single bond, it satisfies its valency by catenation with other S atoms forming S_8 molecule.

4. Sulphur in vapour state exists as S_2 where sulphur has two unpaired electrons.

5. Oxygen is smaller than sulphur, a smaller atom offers greater repulsion to the added electron.

6. Due to increase in atomic size and decrease in electronegativity from S to Po.

7. Oxygen does not have *d*-orbitals.

8. Same as Q. 7.

9. This is due to resonance.

10. The H–S bond is longer and hence low bond dissociation energy. (weaker) than the H–O bond.

11. Same as above.

12. Sulphur is more electronegative than phosphorus, hence H–S bond is more polar (weaker) than the H–P bond.
13. H_2O molecules have intermolecular H-bonding, while H_2S has no H-bonding.
14. Due to smaller size of O atom, there will be greater *bp-bp* repulsion in H_2O than in H_2S.
15. Oxides have higher lattice energy than fluorides, because oxide ion is dinegative whereas fluoride ion is mononegative.
16. Extent of H-bonding in water is more than in HF.
17. Same as above
18. In SF_4, bonds are in different planes.
19. SF_6 molecule has no vacant *d*-orbital to accommodate lone pair of electrons of water molecules.
20. SF_6 has octahedral structure which is symmetrical and hence quite stable. It does not decompose or react easily (kinetically inert).
21. Fluorine is smaller in size, hence six fluorine atoms can be surrounded around one S atom. On the other hand, Cl is larger in size hence it is not possible for S to accommodate six Cl atoms.
22. SF_6 exists because F_2 is a strong oxidising agent, while SH_6 does not exist because H_2 is not an oxidising agent.
23. SF_6 is symmetrical molecule and hence stable. On the other hand, SF_4 is unstable due to presence of one lone pair of electrons and sea-saw geometry. Also all the bond angles in SF_4 are not equal.
24. SF_6 molecule does not have any unpaired electron, hence it acts as a gaseous electrical insulator.
25. Fluorine and oxygen are most electronegative elements and have minimum –1 and –2 oxidation states respectively

(D) Group 17

1. **Halogens mean salt producers** and a large number of salts contain one of these (F, Cl, Br or I) elements.
2. Halogen molecules absorb light from visible region leading to excitation of valence electrons to higher energy level. When the excited molecules come back to lower energy level, they radiate complementary colours.
3. Halogens are strong oxidising agents due to strong electronegative nature moreover, they have high standard reduction potential.
4. Fluorine is the most electronegative element and can accept only one electron as it does not have *d*-orbitals.

5. Reduction potential of F_2 is higher than that of chlorine. It is mainly due to low bond dissociation energy and high hydration energy of F^- ion as compared to Cl^- ion.

6. Fluorine is most reactive because of its highest electronegative character, lowest bond dissociation energy and formation of strong bonds with other elements.

7. Fluorine is the most electronegative element.

8. Refer Q. 5.

9. It is due to repulsion between valence electrons of two fluorine atoms which in turn is due to smaller size of fluorine.

10. Among halogens, fluorine is smallest in size, most electronegative and strongest oxidizing agent.

11. Enthalpy of dissociation of F_2 is much less than that for Cl_2. This is also due to smaller size fluorine atoms.

12. Fluorine is more electronegative than oxygen.

13. In aqueous solution, HCl is a stronger acid because it has lower bond dissociation energy due to longer bond length than HF.

14. The acid strength of the four halogen acids (H–X) follows the given order because of decrease in bond dissociation energy (from H–I to H–Cl) due to increase in bond length (from H–F to H–I) which in turn is due to increase in size of the halogen atom (from F to I).

15. Due to intermolecular H-bond in HF, it is less volatile than HCl.

16. ICl is more polar due to electronegativity difference between the two (I and Cl) atoms and has less effective overlapping than I_2.

17. Cl has vacant *d*-orbitals, while F does not have *d*-orbitals.

18. Fluorine is more electronegative than chlorine. Greater the electronegativity difference between the elements in a compound, higher will be the ionic character.

19. Being the strongest oxidising agent, F(B) can form compounds in +5 and +7 oxidation states. Further, being smallest in size, large number of F can be accommodated around A causing minimum steric hindrance.

20. Chlorine has 7 electrons in the valence shell. Three of these seven electrons form bonds with fluorine atoms leaving two lone pair of electrons on chlorine. The two lone pairs occupy the equatorial positions to minimise *lp-lp* and *bp-lp* repulsions which are greater than *bp-bp* repulsions. This leads to a shape similar to a bent T.

21. Due to formation of potassium tri-iodide which is fairly soluble in water.

$$KI + I_2 \longrightarrow KI_3$$

22. $$2KI + Cl_2 \longrightarrow 2KCl + \underset{\text{(brown)}}{I_2}$$

$$I_2 + 3Cl_2(excess) \longrightarrow \underset{\text{(colourless)}}{2ICl_3}$$

23. Interhalogen compounds have low bond dissociation energy than halogens because of less effective overlapping.

24. Greater the electronegativity and higher the oxidation state of the central atom, greater is the acid strength. Thus, $HClO_4$ having more electronegative Cl (+7 oxidation state) than S (oxidation state of +6) in H_2SO_4 is more acidic than H_2SO_4.

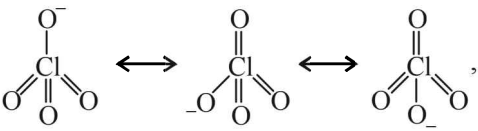
25. Bleaching action by chlorine involves oxidation, hence bleaching is permanent. Bleaching action by SO_2 involves reduction which may regain its colour on exposure to O_2 (oxidation) hence bleaching is temporary.

26. HBr and HI are comparatively unstable and get decomposed easily by oxidising agents.

27. Fluorine does not have *d*-orbitals.

28. The stability order of the conjugate bases of the four oxyacids of chlorine follows the orders : $ClO_4^- > ClO_3^- > ClO_2^- > ClO^-$.

This is due to resonance which is maximum in ClO_4^- and minimum in ClO^-.



, etc.

Thus $HClO_4$ will be most acidic (most unstable), i.e. it has maximum K_a or minimum pK_a value. Relative acidity (K_a or pK_a value) can also be explained on the basis of oxidation state of chlorine. Higher the oxidation state, more will be acidic character or K_a value and less will be the pK_a value. Thus

$$\overset{+7}{HClO_4}\quad \overset{+5}{HClO_3}\quad \overset{+3}{HClO_2}\quad \overset{+1}{HClO}$$

$$\xrightarrow[\text{or increasing } pK_a \text{ values}]{\text{decreasing } K_a \text{ values}}$$

K M C

29. As the stability of the anions increases, oxidising power decreases. Thus the oxidising power of the four acids or their anions is

$$HClO > HClO_2 > HClO_3 > HClO_4$$

(E) Group 18

1. Noble gases have stable electronic configuration, thus they have no tendency to form bonds with other elements under ordinary conditions.

2. The attractive forces between the atoms of noble gases are weak van der Waal's forces. Moreover, these gases are monoatomic and therefore have small surface area which further reduces the forces of attraction. Thus they have very low boiling points.

3. Due to small size and fully filled valence shell, helium has highest ionisation enthalpy.

4. Same as Q. 3.

5. Xenon has largest atomic size and smallest ionisation enthalpy of all the noble gases.

6. Fluorine and oxygen are the most electronegative elements in the periodic table.

7. Xenon has lower ionisation enthalpy than Kr.

8. Higher members of group 18 have low IE because being larger in size, their valence electrons experience smaller attraction by the nucleus.

9. Helium is light and non-inflammable.

10. Helium is least soluble in blood even under high pressure (difference from N_2 present in air). Thus it does not create any problem.

11. Xenon has lone pair of electrons in *d*-orbitals which are large enough for effective overlapping with *p*-orbitals of fluorine.

12. XeF_2 is a trigonal bipyramidal molecule, three equatorial positions are occupied by lone pair of electrons and two axial positions are occupied by fluorine atoms to give XeF_2 a linear shape. This is to reduce the repulsions between the lone pairs and bond pairs.

13. Under excited conditions Xe has unpaired electrons in even numbers and not in odd numbers. Therefore it shows +2, +4 and +6 oxidation states and not +1, +3 and +5.

 Approved: 0777 023 444

(F) *d- and f-block Elements*

1. Due to decrease in atomic size and increase in atomic mass, density increases from Ti to Cu.
2. It is because effective nuclear charge does not increase appreciably as pairing of electrons in *d*-orbitals takes place which causes repulsion after Mn (Z = 25).
3. Most of the transition metal ions have unpaired electrons, which undergo $d - d$ transition by absorbing visible light and then radiate complementary colour.
4. Transition elements have voids of suitable size in which small atoms like H, C, B, etc. can fit into forming interstitial compounds.
5. It is because they show variable oxidation states and can form unstable intermediates.
6. High enthalpies of atomisation of transition elements are attributed to the involvement of $(n-1)d$ electrons in addition to *ns* electrons in the M–M bonding.
7. Reactivity decreases with increase in atomic number due to decrease in size and increase in I.E.
8. Most of the transition metals contain a certain number of unpaired electrons in *d*-orbitals.
9. Transition elements are smaller in size and have vacant *d* orbitals of suitable energy which can accept lone pair of electrons from CO.
10. Transition metals / ions have empty *d*-orbitals which can easily accept electron pair donated by ligands containing π electrons, viz. $CH_2 = CH_2$, C_6H_6 etc.
11. *ns* and $(n-1)d$ orbitals have nearly similar energy.
12. Transition elements have smaller size and higher charge causing high hydration enthalpy.
13. This is because electrons are added to inner *d*-orbitals and effective nuclear charge does not change appreciably.
14. Neither these elements nor their ions have incomplete *d*-orbitals.
15. A middle member of transition series has maximum (d^5) number of unpaired *d* electrons.
16. Lanthanoids show +3 oxidation state mostly as 2 electrons from outer 6*s* orbital and 1 electron from 5*d* orbital take part in bond formation. However, +2 and +4 oxidation states are also sometimes observed due to half filled and completely filled 4*f* orbitals.

17. 4*d* and 5*d* series transition metals have greater enthalpis of atomisation, hence there are strong M–M interaction between them, and thus they do not form stable cationic species.

18. Same as above.

19. This is due to intervention of 4*f* orbitals which are filled before filling of 5*d* orbitals begins. This results in a regular decrease in atomic size (**lanthanoid contraction**), and compensates for the expected increase in atomic size with increasing atomic number. The net result is that the second and third *d* series exhibit similar atomic radii.

20. La is larger in size than Lu.

21. Ce^{4+} readily gains one electron and changed to more stable Ce^{+3} ion.

22. $$\underset{\text{(orange)}}{Cr_2O_7^{2-}} + 2OH^- \longrightarrow \underset{\text{(yellow)}}{2CrO_4^{2-}} + H_2O$$

23. $Na_2Cr_2O_7$ absorbs moisture from the atmosphere.

24. $KMnO_4$ oxidises HCl to chlorine.

25. It forms unstable intermediates with the reactants which readily change to stable products.

26. Cr^{3+} is smaller in size and has higher charge than Cr^{2+} which leads to greater hydration enthalpy.

27. Number of unpaired electrons in Cu^{2+} (d^9) is 1, while Co^{2+} (d^7) has 3 unpaired electrons, thus Cu^{2+} will be less paramagnetic.

28. Cu^{2+} ion has incomplete *d*-orbital (d^9).

29. Pt^{4+} is more stable than Ni^{4+}. Energy required to remove 4 electrons in Pt is less than that in Ni.

30. Effective nuclear charge in Fe^{2+} is more than that of Mn^{2+}.

31. Oxidation state of Mn in MnO_4^- is +7 and energetically it is not possible to lose 7 electrons to give ionic species. Hence Mn^{7+} forms covalent bonds by sharing of electrons.

32. Fe^{3+} has stable half-filled (d^5) *d*-orbital and high hydration energy.

33. Due to small size and higher charge, Cu^{2+} ion has higher hydration enthalpy than Cu^+ ion.

34. $KMnO_4$ decomposes in presence of light to K_2MnO_4.

$$2KMnO_4 \xrightarrow{\text{Light}} K_2MnO_4 + MnO_2 + O_2$$

35. Zn^{2+} does not have unpaired electrons, hence *d-d* transition is not possible, whereas Cu^{2+} has unpaired electrons which can undergo *d-d* transition on absorption of visible light.

36. In scandium salts, scandium has +3 oxidation state and Sc^{3+} does not have any unpaired *d*-electron (*d*-orbitals are empty).

37. Due to poor shielding effect of 5*d* and 4*f* electrons, effective nuclear charge increases, hence IE of 5*d* transition elements is more than that of 3*d* and 4*d* transition elements in respective groups.

38 Lanthanoids have similar properties due to their similar ionic size.

39. Due to lanthanoid contraction, Zr and Hf have similar ionic size.

40. Reaction of $KMnO_4$ with conc. H_2SO_4 leads to formation of Mn_2O_7 which is an explosive compound.

41. Co^{2+} has three unpaired electrons in *d*-orbital, thus in presence of strong ligands which cause pairing only two electrons get paired, leaving one unpaired. Co^{3+} ion has 4 unpaired electrons all of which can undergo pairing in presence of strong ligand leaving no unpaired electron in Co^{3+}, thus Co^{2+} is less stable than Co^{3+}.

	3*d*					4*s*
Co atom	↿⇂	↿⇂	↑	↑	↑	↿⇂
Co^{2+}	↿⇂	↿⇂	↑	↑	↑	
Co^{3+}	↿⇂	↑	↑	↑	↑	

42. Cr^{2+}(d^4-configuration) after losing one electron changes to Cr^{3+}(d^3) and d^3 configuration is more stable than d^4 because the three electrons are accommodated in lower t_{2g} orbitals. On the other hand, Fe^{2+}(d^6) on losing one electron changes to Fe^{3+}(d^5) which although half-filled, is comparatively less stable than the d^3 of Cr^{3+}.

43. Cu (I) ion does not have a sufficient negative value of enthalpy of hydration and the ions disproportionate in aqueous solution.

$$2Cu^+ \longrightarrow Cu^{2+} + Cu$$

44. The outer electronic configuration, $3d^5 4s^2$ of Mn allows it to exhibit oxidation states from +2 to +7.

45. The *d*-orbital configuration of Cr^{2+} is $3d^4$ and easily attains more stable $3d^3$ (half-filled t_{2g} orbitals) configuration by donating an

electron to form Cr^{3+}. Thus Cr^{2+} is a reducing agent. On the other hand, Mn^{3+} having $3d^4$ configuration attains the more stable $3d^5$ (half-filled *d*-orbitals) configuration by gaining one electron. Thus it acts as an oxidising agent.

46. La^{3+} and Lu^{3+} do not have *f*-electrons, hence there is no possibility of *f*-*f* transition.

47. The given relative oxidising power of the oxoanions is due to increasing stability of the respective species formed on reduction.

48. The IE_3 value of Mn is high due to high stability of $Mn^{2+}(3d^5)$.

49. More positive E^0 value for Mn^{3+}/Mn^{2+} is due to stability of Mn^{2+}(d^5-half filled configuration) than Mn^{3+}. Low value for Fe^{3+}/Fe^{2+} is due to more stability of $Fe^{3+}(d^5)$ and lower stability of Fe^{2+}. Similarly, E^0 value for Cr^{3+}/Cr^{2+} is lower because of lower stability of $Cr^{2+}(d^4)$ than $Cr^{3+}(d^3)$.

50. This is due to maximum number of unpaired electrons (5) in $Mn^{2+}(3d^5)$.

51. In actinoids *5f*, *6d* and *7s* orbitals have comparable energies and electrons from these orbitals can take part to exhibit higher oxidation states.

52. Same as above

53. Actinoids show a large number of oxidation states because energies of *5f*, *6d*, and *7s* orbitals are nearly same while lanthanoids show mainly +3 oxidation state.

(G) Coordination compounds

1. Heat is evolved when a bond is formed between central metal ion and ligands,

2. Formation of complex is exothermic process, so increase in temperature will decrease the stability of the complex (Le Chatelier principle). Further, on heating coordinate bond between central metal ion and ligand breaks up.

3. In a chelated complex, ligand is attached to the metal ion from many points.

4. $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution forms a double salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$ which ionises in the solution to give Fe^{2+} ions. On the other hand, $CuSO_4$ solution when mixed with aqueous ammonia forms a complex salt of the formula, $[Cu(NH_3)_4]SO_4$. Here copper is present in the complex ion, $[Cu(NH_3)_4]^{2+}$, hence does not ionize in solution to give Cu^{2+} ions.

5. CO has π bond, therefore it is stronger ligand than Cl^-.

6. CO can form σ as well as π bond, whereas NH_3 has lone pair of electrons and can form σ bond only, hence CO is a better complexing agent than NH_3.

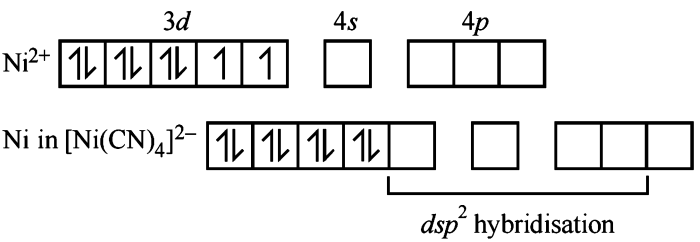
7. CO is a stronger ligand than NH_3 because of its small size and π bonding. However, both are unidentate ligand.

8. For octahedral complexes, coordination number should be 6. Since Ni has [Ar] $3d^8 4s^2$ configuration, i.e., only one d orbital is empty, so it can form only high spin octahedral complexes.

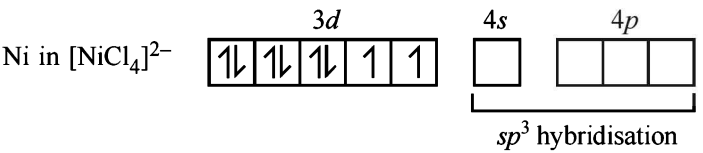
9. In $[NiCl_4]^{2-}$, Ni ($3d^8 4s^2$) is in +2 oxidation state with the configuration $3d^8 4s^0$; and Cl^-, being weak ligand cannot pair up the electrons in $3d$ orbitals. Hence it has 2 unpaired electrons and thus paramagnetic. In $[Ni(CO)_4]$, Ni is in zero oxidation state with the configuration $3d^8 4s^2$. However, CO being a strong ligand causes shifting of $4s^2$ electrons to $3d$ orbitals where they pair up. Thus there is no unpaired electron and the complex is diamagnetic.

10. In $[Ni(CN)_4]^{2-}$, Ni is present as $Ni^{2+}(3d^8)$; CN^- causes pairing of electrons leaving one of the $3d$ orbitals vacant, thus dsp^2 hybridisation takes place leading to square planar (diamagnetic complex). In $Ni(CO)_4$, Ni is present as $Ni^0(3d^8 4s^2)$, CO causes shifting of electrons from $4s$ to $3d$ and then pairing. Thus all the five $3d$ orbitals are completely filled. This leads to sp^3 hybridisation forming tetrahedral (diamagnetic) complex.

11. $[Ni(CN)_4]^{2-}$, Ni is dsp^2 hybridised with no unpaired electron.

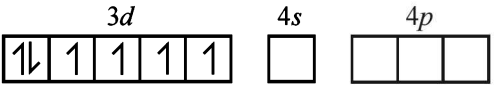


In $[NiCl_4]^{2-}$, Ni is sp^3 hybridised with two unpaired electrons (Cl is a weak ligand.)

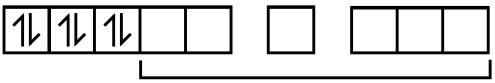


12. In both compounds, Fe is in +3 oxidation state with the configuration $3d^5$. In presence of CN^- (a strong ligand) four of the $3d^5$ electrons pair up leaving one unpaired electron and thus the complex is weakly paramagnetic. The hybridisation is d^2sp^3 forming inner orbital complex. However, in presence of H_2O (a weak ligand), $3d^5$ electrons do not pair up and the complex having 5 unpaired electrons is strongly paramagnetic. Here the hybridisation is sp^3d^2 forming outer orbital complex.

13. Fe^{2+}



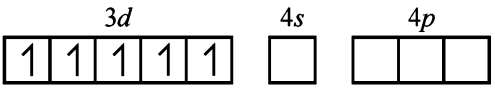
Fe in $[Fe(CN)_6]^{4-}$



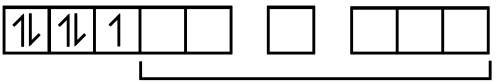
d^2sp^3 hybridisation

Thus $[Fe(CN)_6]^{4-}$ has no unpaired electrons, hence **diamagnetic**.

Fe^{3+}



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

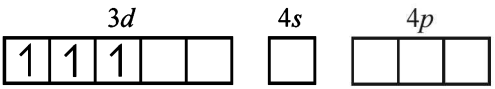


d^2sp^3 hybridisation

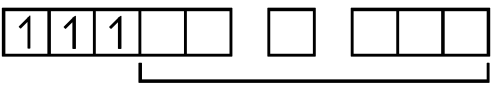
Thus $[Fe(CN)_6]^{3-}$ has one unpaired electron, hence **weakly paramagnetic**.

14. In $[Cr(NH_3)_6]^{3+}$, Cr is present as Cr^{3+}.

Cr^{3+}



NH_3 is a weak ligand pairing of electrons does not occur leading to

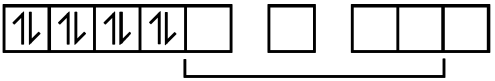


d^2sp^3 hybridisation

d^2sp^3 hybridisation with +3 unpaired electrons (paramagnetic). In case of $[Ni(CN)_4]^{2-}$, Ni^{2+} has 2 unpaired electrons which are

paired in presence of CN^- (a strong ligand). This leads to dsp^2 hybridisation with no unpaired electron (diamagnetic)

Ni^{2+} in presence of CN^-



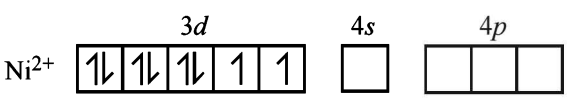
dsp^2 hybridisation

15. Aqueous $CuSO_4$ solution exists as $[Cu(H_2O)_4]SO_4$ which has blue colour. When KF (or KCl) is added to it, H_2O (weak ligands) molecules are replaced by F^-(or Cl^-) ligands forming corresponding complex.

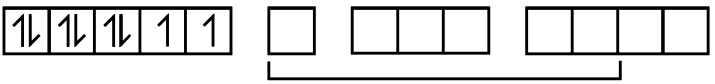
$$\underset{\text{(blule colour)}}{[Cu(H_2O)_4]^{2+}} + 4F^- \longrightarrow \underset{\text{(green ppt.)}}{[CuF_4]^{2-}} + 4H_2O$$

$$[Cu(H_2O)_4]^{2+} + 4Cl^- \longrightarrow \underset{\text{(bright green solution)}}{[CuCl_4]^{2-}} + 4H_2O$$

16. Formation of $[Ni(H_2O)_6]^{2+}$



Ni^{2+} in $[Ni(H_2O)_6]^{2+}$



sp^3d^2 hybridisation

H_2O is a weak ligand pairing of 3*d* electrons does not occur and thus $[Ni(H_2O)_6]^{2+}$ has two unpaired electrons. Thus due to *d-d* transition, complex absorbs red light and emit complementary light (green). $[Ni(CN)_4]^{2-}$ does not have any unpaired electron (See Q.16) Hence the complex is colourless.

17. $[Fe(CN)_6]^{4-}$ does not have unpaired electron, white $[Fe(H_2O)_6]^{2+}$ has two unpaired electrons. Thus only the later will absorb, light from visible region and radiate complementary colour.

18. In $[Co(NH_3)_6]^{3+}$, Co is in +3 oxidation state with the configuration $3d^6$. In presence of NH_3 (a strong ligand), $3d^6$ electrons pair up in three $3d$ orbitals leaving two $3d$ orbitals empty for forming bond with NH_3. Hence the hybridisation is d^2sp^3 forming an inner orbital complex. In $[Ni(NH_3)_6]^{2+}$, Ni is in +2 oxidation state with the configuration $3d^8$. Although ligand is same, the $3d^8$ electrons do not pair up leaving 2 unpaired electrons in two $3d$ orbitals. Thus none of the $3d$ orbital is empty and the hybridisation of the complex will sp^3d^2 forming outer orbital complex.

19. In tetrahedral complexes of the type Ma_2b_2, the relative positions of the atoms or ligands with respect to each other is same while in square complexes of the type Ma_2b_2, similar ligands may occupy positions adjacent to each other (*cis*-isomer) or opposite to each other (*trans*-isomer).

■■■

CHAPTER 5

How you will prepare the following?

Which reaction(s) or process is/are involved in the following?

(A) Metallurgy

1. Leaching of bauxite ore to pure alumina. **(Foreign 2010, 2011)**
2. Extraction of Al from bauxite ore. **(Delhi 2008C)**
3. Refining of zirconium by van Arkel method. **(Foreign 2011)**
4. Recovery of gold after gold ore has been leached with NaCN solution. **(Foreign 2011)**
5. Extraction of silver after the silver ore has been leached with NaCN solution. **(Foreign 2012)**
6. Impure copper into pure copper. **(Foreign 2010)**
7. Conversion of pig iron into steel. **(Delhi 2010, Foreign 2010)**
8. Zinc oxide into metallic zinc. **(Delhi 2010)**
9. Impure titanium into pure titanium. **(Delhi 2010)**
10. Extraction of iron from its ore. **(Delhi 2007)**
11. Extraction of Cu from sulphide ore. **(Delhi 2006C)**

(B) Group 15

1. Preparation of H_3PO_3. **(AI 2006)**
2. Ostwald's process for the manufacture of HNO_3. **(Delhi 2006C)**
3. Industrial manufacture of NH_3 by Haber's process. **(AI 2008, Foreign 2011)**

(C) Group 16

1. Describe the conditions and steps involved in the manufacture of sulphuric acid by the contact process. Write the necessary reactions. (No diagram is required) **(Delhi Board Comptt 2012)**
2. Preparation of SO_2 in laboratory. **(Delhi 2007, 2012C)**
3. Preparation of SO_2 in industry. **(Delhi 2007)**

(D) Group 17

1. Preparation of interhalogen compounds. **(AI 2013)**
2. Prepare Cl_2 from HCl and HCl from Cl_2. Write reactions only.

(F) d- and f-block Elements

1. Preparation of $K_2Cr_2O_7$ from Na_2CrO_4. **(Delhi 2007, AI 2008C, Foreign 2010)**
2. Preparation of $KMnO_4$ from K_2MnO_4. **(Delhi 2007, Foreign 2012)**
3. Manufacture of $KMnO_4$ from pyrolusite. **(Delhi 2006, 2008C, 2010)**
4. Preparation of $K_2Cr_2O_7$ from chromite ore. **(AI 2009, 2011)**
5. Preparation of Na_2CrO_4 from chromite ore. **(Delhi 2008)**
6. Preparation of K_2MnO_4 from pyrolusite ore. **(Delhi 2008)**

(A) *Metallurgy*

1. Leaching of bauxite ore to pure Al.

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O \xrightarrow[35-36\ bar]{473-523K} \underset{Soluble}{2Na[Al(OH)_4]}$$

$$\underset{(Filtrate)}{2Na[Al(OH)_4]} + 2CO_2(g) \longrightarrow Al_2O_3.xH_2O(s) + 2\,NaHCO_3$$

$$Al_2O_3.xH_2O(s) \xrightarrow{1470K} Al_2O_3(s) + xH_2O\uparrow$$

2. Aluminium from bauxite ore.

$$2Al_2O_3 + 3C \xrightarrow[reduction]{electrolytic} 4Al + 3CO_2$$

Or

At cathode : $Al^{3+}(melt) + 3e^- \longrightarrow Al(l)$

At anode : **(i)** $C(s) + O^{2-}(melt) \longrightarrow CO(g) + 2e^-$

(ii) $C(s) + 2O^{2-}(melt) \longrightarrow CO_2(g) + 4e^-$

3. Refining of Zr by van Arkel method.

$$\underset{Impure}{Zr} + 2I_2 \xrightarrow{870K} \underset{Volatile}{ZrI_4} \xrightarrow{1800K} \underset{Pure}{Zr} + 2I_2\uparrow$$

4. Recovery of gold.

$$4Au + 8CN^-(aq) + 2H_2O + O_2 \longrightarrow \underset{Soluble}{4[Au(CN)_2]^-} + 4OH^-$$

$$2[Au(CN)_2]^- + Zn(s) \xrightarrow{reduction} [Zn(CN)_4]^{2-} + 2Au$$

5. **Extraction of silver.**

$$Ag_2S + 4NaCN \longrightarrow 2Na[Ag(CN)_2] + Na_2S$$

$$2[Ag(CN)_2]^- + Zn \longrightarrow [Zn(CN)_4]^{2-} + 2Ag$$

6. **Impure copper to pure copper.**

Acidified aqueous solution of copper sulphate is electrolysed using impure sample of copper as anode and pure strips of copper as cathode.

Anode : $Cu \longrightarrow Cu^{2+} + 2e^-$

Cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$

Impurities consisting of Sb, Se, Te, Ag, Au, etc are deposited as anode mud below anode.

7. **Pig iron to wrought iron.**

$$\underset{\text{(2.5–4\% C, traces of S, P, Si and Mn)}}{\text{Pig iron}} + O_2\text{(excess)} \xrightarrow[\text{converter}]{\text{Bessemer}} \underset{\text{(0.12–0.25\% C)}}{\text{Wrought iron}}$$

+ Impurities are removed as oxides

8. **Zinc oxide to zinc.**

$$ZnO + \text{Coke} \xrightarrow{1673K} Zn + CO\uparrow$$

9. **Impure titanium to pure titanium.**

$$\underset{\text{(Impure Ti)}}{Ti} + 2I_2 \xrightarrow{700-800K} \underset{\text{(Volatile)}}{TiI_4} \xrightarrow{1800-2000K} \underset{\text{(Pure)}}{Ti} + 2I_2\uparrow$$

10. **Iron from haematite.**

$$\text{Concentrated haematite} + \text{Lime stone} + \text{Coke} \xrightarrow[\text{blast furnace}]{\text{heated in}} \text{Iron}$$

Reactions in blast furnace

(a) At lower temperature range (500-800K)

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2;$$

$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$$

$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$

(b) At higher temperature range (900 –1500K)

$$C + O_2 \longrightarrow CO_2$$

$$C + CO_2 \longrightarrow 2CO$$

$$FeO + CO \longrightarrow Fe + CO_2$$

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$CaO + SiO_2 \longrightarrow \underset{\text{Slag}}{CaSiO_3}$$

11. Extraction of copper from sulphide ore.

The finely powered and concentrated ore is roasted in presence of air. The roasted ore is mixed with sand (flux) and coke and then heated in smelter. Slag (ferrous silicate) and molten mass (Cu_2S and FeS) are removed from separate holes. Molten matte is heated in Bessemer converter where FeS is removed as slag and molten metallic copper is poured off into sand moulds. On cooling, metal gives up dissolved SO_2 which forms blister on the surface of the metal. Blister copper containing 98% Cu, is purified by electrolysis, where acidified $CuSO_4$ solution is electrolyte, impure copper (blister copper) acts as anode and pure strip of copper as cathode. Pure copper is diposited on cathode, impurities like Au and Ag settle down below the anode as **anode mud**, other impurities like Fe, Zn, Ni, Co etc. dissolve in solution as sulphates.

(B) Group 15

1. $P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$.

2. Ostwald's process to manufacture HNO_3.

$$4NH_3 + 5O_2 \xrightarrow[500K,\ 9\ bar]{\text{Pt catalyst}} 4NO + 6H_2O \uparrow$$

$$\underset{\text{Nitric oxide}}{2NO} + O_2 \longrightarrow \underset{\text{Nitrogen dioxide}}{2NO_2}$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

3. Haber's process for the manufacture of ammonia.

$$N_2 + 3H_2 \xrightarrow[\text{(ii) } 200\times10^5\ Pa]{\text{(i) } \sim 700K,\ Fe_3O_4,\ Al_2O_3} 2NH_3$$

(C) Group 16

1. Sulphuric acid is manufactured by the contact process by the following steps:

   (i) Burning of sulphur or sulphide ores in air to produce SO_2.

   (ii) Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst.

   $$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$$

   $$2SO_2(g) + O_2(g) \xrightarrow[400-500°C]{Pt,\ V_2O_5} 2SO_3(g)$$

   (iii) Absorption of SO_3 in H_2SO_4 to give oleum ($H_2S_2O_7$)

   Dilution of oleum with water gives H_2SO_4 of desired concentration.

   The sulphuric acid obtained by the contact process is 96-98% pure.

   $$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

2. **Laboratory preparation of sulphur dioxide.**

   $$\underset{\text{Sulphite}}{SO_3^{2-}} + 2H^+ \longrightarrow SO_2 + H_2O$$

3. **Industrial preparation of sulphur dioxide.**

   $$\underset{\text{Iron pyrites}}{4FeS_2} + 11O_2 \xrightarrow{\text{roasting}} 2Fe_2O_3 + \underset{\text{(as by-product)}}{8SO_2 \uparrow}$$

(D) Group 17

1. **Preparation of interhalogen compounds.**

   (i) $$Cl_2 + F_2 \xrightarrow{473K} 2ClF(g)$$

   $$ClF + F_2 \xrightarrow{473-575K} ClF_3(g)$$

   or $$Cl_2 + 3F_2(\text{excess}) \longrightarrow 2ClF_3$$

   (ii) $$Br_2 + \underset{\text{diluted with } N_2}{3F_2} \longrightarrow 2BrF_3$$

   $$Br_2 + 5F_2(\text{excess}) \longrightarrow 2BrF_5$$

(iii) $I_2(g) + F_2 \longrightarrow 2IF$

$I_2(g) + 5F_2 \longrightarrow 2IF_5$

$I_2(g) + 7F_2 \longrightarrow 2IF_7$

2. $\underset{\text{Oxidising agent}}{MnO_2} + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

We can also use $KMnO_4$, $K_2Cr_2O_7$, etc., in place of MnO_2.

$H_2 + Cl_2 \xrightarrow{\text{Diffused sunlight}} 2HCl$

(F)* d- *and* f-block *Elements

1. Potassium dichromate from sodium chromate.

$2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

2. Potassium permanganate from potassium manganate

$3MnO_4^{2-} + 4H^+ \xrightarrow{\text{disproportionation}} 2MnO_4^- + MnO_2 + 2H_2O$

or $MnO_4^{2-} \xrightarrow[\text{in alkaline medium}]{\text{electrolytic reduction}} MnO_4^-$

3. Potassium permanganate from pyrolusite.

$2MnO_2 + 4KOH + O_2 \longrightarrow \underset{\text{Pot. manganate}}{2K_2MnO_4} + 2H_2O$

$3K_2MnO_4 + 4HCl \longrightarrow 2KMnO_4 + MnO_2 + 2H_2O + 4KCl$

4. Potassium dichromate from chromite ore.

$\underset{\text{Chromite ore}}{FeCr_2O_4} + 8Na_2CO_3 + 7O_2 \longrightarrow \underset{\substack{\text{Sod. chromate}\\ \text{(yellow solution)}}}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$

$2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

$Na_2Cr_2O_7 + 2KCl \longrightarrow \underset{\substack{\text{Pot. dichromate}\\ \text{(orange crystal)}}}{K_2Cr_2O_7} + 2NaCl$

Note : Remember that chromates and dichromates are intercovertible in aqueous solution depending upon the pH of the solution.

$$\underset{\substack{\text{Chromate}\\\text{(yellow)}}}{2CrO_4^{2-}} + 2H^+ \longrightarrow \underset{\substack{\text{Dichromate}\\\text{(orange)}}}{Cr_2O_7^{2-}} + H_2O$$

$$Cr_2O_7^{2-} + 2OH^- \xrightarrow[\text{in pH}]{\text{increase}} 2CrO_4^{2-} + H_2O$$

5. Sodium chromate from chromite ore. Refer. 22.

6. Potassium manganate from pyrolusite ore. Refer. 21.

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CHAPTER 6

What happens when...

What happens when :

(B) Group 15

(i) sodium azide in thermally decomposed. **(Delhi 2007)**

(ii) ammonia is dissolved in water **(Delhi 2007)**

(iii) ammonia reacts with a solution of Cu^{2+} **(AI 2007)**

(iv) ammonia solution is added to silver chloride

(v) nitric acid reacts with (*a*) I_2, (*b*) C, (*c*) S_8, (*d*) P_4 **(Delhi 2006C)**

(vi) white phosphorus is heated with conc. NaOH solution in an inert gas atmosphere.

(vii) H_3PO_3 (orthophosphorous acid) is heated **(Delhi 2008, 2013, AI 2011C)**

(viii) PCl_5 is heated **(Delhi 2007, 2013)**

(ix) PCl_5 is treated with heavy water

(C) Group 16

(i) sulphur is boiled with sodium sulphite.

(ii) lead sulphide is heated in air

(iii) sulphide ore of mercury is roasted.

(iv) silver sulphide (argentite is treated with a dilute solution of NaCN)

(v) sulphur dioxide is passed through water. **(Delhi 2007)**

(vi) excess of SO_2 reacts with NaOH solution **(Delhi 2009, 2010C)**

(vii) sulphur dioxide reacts with hydrogen sulphide.

(viii) sulphur dioxide gas is passed through an aqueous solution of a Fe (III) salt. **(AI 2011)**

(ix) sulphur dioxide reacts with sodium chlorate in strongly acidic solution.

(D) Group 17

(i) sodium chloride is heated with sulphuric acid in presence of MnO_2.

(ii) chlorine gas is passed into a solution of NaI in water.

(iii) chlorine gas is passed through a hot conc. solution of NaOH. **(Delhi 2008C, 2010C, AI 2011, Foreign 2012)**

(iv) chlorine is passed through a hot conc. solution of $Ba(OH)_2$.

(v) fluorine and chlorine are treated separately with water.

(vi) fluorine is passed through alkaline solution of bromate ion.

(vii) sodium iodate ($NaIO_3$) is reduced with sod. hydrogen sulphite.

(E) Group 18

(i) PtF_6 and xenon are mixed together **(Delhi 2008)**

(ii) XeF_6 is hydrolysed **(Delhi 2009C, 2010)**

(iii) XeF_4 is hydrolysed **(Delhi 2006C)**

(iv) A xenon fluoride is treated with fluoride ion acceptor.

(v) A xenon fluoride is treated with fluoride ion donor.

(F) d- and f-Block Elements

(i) pyrolusite is fused with KOH in presence of air.

(ii) potassium permanganate is electrochemically oxidised.

(iii) excess of aqueous KCN solution is added to an aqueous solution of copper sulphate.

(iv) silver sulphide is treated with potassium cyanide and the product formed is treated with zinc.

(v) $S_2O_3^{2-}$ is oxidised by MnO_4^- in neutral aqueous medium. **(AI 2008)**

(vi) Fe^{2+} is oxidised by $Cr_2O_7^{2-}$ in acidic medium. **(AI 2008)**

(vii) *pH* of a solution of dichromate ions is raised.

(viii) an iodide ion is treated with an acidified dichromate ion in solution.

(ix) acidified potassium permanganate solution is treated with (*a*) iron (II) ions, (*b*) oxalic acid, (*c*) SO_2 **(AI 2010C)**

(B) Group 15

(i) $2NaN_3 \xrightarrow{heat} 2Na + 3N_2$

(ii) $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

(iii) $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons \underset{\text{Deep blue complex}}{[Cu(NH_3)_4]^{2+}}$

(iv) $AgCl + 2NH_3(aq) \longrightarrow \underset{\text{Soluble complex}}{[Ag(NH_3)_2]Cl}$

(v) (*a*) $I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

(*b*) $C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$

(*c*) $S_8 + 48HNO_3(conc.) \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$

(*d*) $P_4 + 20HNO_3(conc.) \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

(vi) $\underset{\text{White phosphorus}}{P_4} + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + \underset{\text{Phosphine}}{PH_3}$

(vii) $4H_3PO_3 \xrightarrow[\text{(disproportionation)}]{heat} \underset{\text{Orthophosphoric acid}}{3H_3PO_4} + \underset{\text{Phosphine}}{PH_3}$

(viii) $\underset{\text{Phosphorus pentachloride}}{PCl_5} \xrightarrow{heat} \underset{\text{Phosphorus trichloride}}{PCl_3} + Cl_2$

(ix)

$$PCl_5 + D_2O \longrightarrow POCl_3 + 2DCl$$

$$POCl_3 + 3D_2O \longrightarrow D_3PO_4 + 3DCl$$

On adding, $PCl_5 + 4D_2O \longrightarrow D_3PO_4 + 5DCl$

(C) Group 16

(i) $S + Na_2SO_3 \xrightarrow{\text{boil}} \underset{\text{Sod. thiosulphate}}{Na_2S_2O_3}$

(ii) $2PbS + 3O_2 \xrightarrow{\text{heat}} 2PbO + 2SO_2$

(iii) $HgS + O_2 \xrightarrow{\text{heat}} Hg(l) + SO_2$

(iv) $Ag_2S + 4NaCN \longrightarrow \underset{\text{Soluble complex}}{2Na[Ag(CN)_2]} + Na_2S$

(v) $SO_2 + H_2O \rightleftharpoons \underset{\text{Sulphurous acid}}{H_2SO_3}$

(vi) $2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$

$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3$

(vii) $SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$

(viii)

$$SO_2 + 2H_2O \longrightarrow SO_4^{2-} + 4H^+ + 2e^-$$

$$2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$$

On adding, $2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$

(ix) $2NaClO_3 + SO_2 \xrightarrow{\text{acid}} Na_2SO_4 + 2ClO_2$

(D) Group 17

(i)

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl] \times 4$$

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

On adding, $MnO_2 + 4NaCl + 4H_2SO_4 \longrightarrow$

$$MnCl_2 + 4NaHSO_4 + Cl_2 + 2H_2O$$

(ii) $2NaI + Cl_2(g) \longrightarrow 2NaCl + I_2(s)$

(iii) $3Cl_2 + 6NaOH \xrightarrow[\text{conc.}]{\text{hot}} 5NaCl + NaClO_3 + 3H_2O$

(iv) $6Cl_2 + 6Ba(OH)_2 \longrightarrow 5BaCl_2 + Ba(ClO_3)_2 + 6H_2O$

(v) (*a*) Fluorine, being a strong oxidising agent, oxidises H_2O to O_2 or O_3.

$$2F_2 + 2H_2O \longrightarrow 4H^+ + 4F^- + O_2$$

$$2F_2 + 3H_2O \longrightarrow 6H^+ + 6F^- + O_3$$

(*b*) On the other hand, Cl_2 reacts with water to form HCl and hypochlorous acid.

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

(vi) $\underset{\text{Bromate ion}}{BrO_3^-} + F_2 + 2OH^- \longrightarrow \underset{\text{Perbromate ion}}{BrO_4^-} + 2F^- + H_2O$

(vii) $NaIO_3 + 3NaHSO_3 \longrightarrow 3NaHSO_4 + NaI$

(E) Group 18

(i) $Xe + PtF_6 \longrightarrow \underset{\text{(red colour)}}{Xe^+PtF_6^-}$

(ii) $XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$

or $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

(iii) $6XeF_4 + 12H_2O \longrightarrow 2XeO_3 + 4Xe + 24HF + 3O_2$

(iv) $XeF_2 + PF_5 \longrightarrow [XeF]^+[PF_6]^-$

(v) $XeF_6 + NaF \longrightarrow Na^+[XeF_7]^-$

(F) d- and f-Block Elements

(i) $\underset{\text{Pyrolusite}}{2MnO_2} + 4KOH + O_2 \xrightarrow{\text{heat}} \underset{\text{Pot. manganate}}{2K_2MnO_4} + 2H_2O$

(ii) $\underset{\text{Permanganate}}{MnO_4^{2-}} \xrightarrow{\text{electrolysis}} \underset{\text{Manganate (purple)}}{MnO_4^-} + e^-$

(iii)

$$CuSO_4 + 2KCN \longrightarrow Cu(CN)_2 + K_2SO_4] \times 2$$

$$2Cu(CN)_2 \longrightarrow Cu_2(CN)_2 + (CN)_2$$

$$Cu_2(CN)_2 + 6KCN \longrightarrow 2K_3[Cu(CN)_4]$$

On adding, $2CuSO_4 + 10KCN \longrightarrow$

$$2K_3[Cu(CN)_4] + 2K_2SO_4 + (CN)_2$$

(iv) $Ag_2S + 4KCN \longrightarrow 2K[Ag(CN)_2] + K_2S$

$2K[Ag(CN)_2] + Zn \longrightarrow K_2[Zn(CN)_4] + 2Ag$

(v) $8MnO_4^- + 3S_2O_3^{2-} + 2H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

(vi) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

(vii) $\underset{\text{orange}}{Cr_2O_7^{2-}} + \underset{\text{higher pH}}{2OH^-} \rightleftharpoons \underset{\text{yellow}}{2CrO_4^{2-}} + H_2O$

(viii)

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$2I^- \longrightarrow I_2 + 2e^-] \times 3$$

On adding, $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

(ix) (*a*) $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(*b*) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

(*c*) $2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$

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CHAPTER 7

Complete the following

Complete the following:

(B) Group 15

(i) $Li + N_2 \longrightarrow$ **(Delhi 2009, 2010, 2011, Foreign 2009, 2012)**

(ii) $P_4(s) + NaOH(aq) + H_2O(l) \longrightarrow$ **(Delhi 2009, 2010, 2011, Foreign 2009-2012)**

(iii) $P_4 + SO_2Cl_2 \longrightarrow$ **(Delhi 2010, 2011, 2012 Foreign 2010, 2011)**

(iv) $HgCl_2 + PH_3 \longrightarrow$ **(AI 2010, 2011, Foreign 2012)**

(v) $Sn + PCl_5 \xrightarrow{heat}$ **(Foreign 2012)**

(vi) $PCl_5 + H_2O(excess) \longrightarrow$ **(Foreign 2009)**

(vii) $Ca_3P_2(s) + H_2O(l) \longrightarrow$ **(Delhi 2008)**

(viii) $Ca_3(PO_4)_2 + SiO_2 + C \longrightarrow$

(ix) $AgCl(s) + NH_3(aq) \longrightarrow$ **(Foreign 2010)**

(x) $Cu^{2+}(aq) + NH_3(aq) \longrightarrow$ **(Delhi 2008)**

(xi) $NH_3 + NaOCl \longrightarrow$ **(AI 2009)**

(xii) $NH_4Cl(aq) + NaNO_2(aq) \longrightarrow$ **(Foreign 2012)**

(xiii) $Cu + HNO_3(dil.) \longrightarrow$ **(Foreign 2009, AI 2012)**

(xiv) $I_2 + HNO_3(conc.) \longrightarrow$ **(AI 2010, Delhi 2011)**

(xv) $P_4O_{10} + HNO_3 \longrightarrow$

(C) Group 16

(i) $SO_3 + H_2SO_4(conc.) \longrightarrow$ **(AI 2011)**

(ii) $Fe^{3+} + SO_2 + H_2O \longrightarrow$ **(Delhi 2011C, Foreign 2011, 2012)**

(iii) $C + H_2SO_4(conc.) \longrightarrow$ **(Delhi 2011, Foreign 2011)**

(iv) $O_2^- + H_2O \longrightarrow$

(v) $O_3(g) + I^-(aq) + H_2O(l) \longrightarrow$ **(Delhi 2009, Foreign 2008, 2009)**

(D) Group 17

(i) $Cl_2 + NaOH(hot\ and\ conc.) \longrightarrow$ **(Delhi 2010, Foreign 2009, 2012)**

(ii) $Cl_2 + F_2(excess) \longrightarrow$ **(Foreign 2011, Delhi 2011, 2012)**

(iii) $Br_2 + F_2(excess) \longrightarrow$ **(Foreign 2011)**

(iv) $F_2(g) + H_2O(l) \longrightarrow$ **(Delhi 2008, Foreign 2009)**

(v) $Br_2 + NaI \longrightarrow$

(vi) $BrO_3^- + F_2 + OH^- \longrightarrow$

(vii) $I_2 + H_2O + Cl_2 \longrightarrow$ **(AI 2011C)**

(viii) $I_2 + S_2O_3^{2-} \longrightarrow$

(ix) $I_2 + NaClO_3 \longrightarrow$ **(AI 2009C)**

(x) $SiO_2(g) + HF(g) \longrightarrow$ **(Foreign 2010)**

(xi) $Ca(OCl)_2 + HCl \longrightarrow$

(xii) $IO_3^- + I^- + H^+ \longrightarrow$

(E) Group 18

(i) $Xe + F_2 \xrightarrow[7\ bar]{873K}$

(ii) $Xe(excess) + F_2(g) \longrightarrow$ **(Foreign 2012)**

(iii) $Xe + PtF_6 \longrightarrow$

(iv) $XeF_2 + H_2O(l) \longrightarrow$ **(Delhi 2011, Foreign 2012)**

(v) $XeF_4 + H_2O(excess) \longrightarrow$ **(Delhi 2010, 2011C, AI 2011C)**

(vi) $XeF_6 + H_2O \longrightarrow$ **(Delhi 2010, 2012, AI 2009C, Foreign 2011)**

(vii) $XeF_2 + PF_5 \longrightarrow$

(viii) $XeF_4 + PF_5 \longrightarrow$

(ix) $XeF_4 + SbF_5 \longrightarrow$ **(Delhi 2012, AI 2009, 2011, Foreign 2009)**

(x) $XeF_6 + KF \longrightarrow$ **(AI 2009C)**

(xi) $XeF_4 + O_2F_2 \xrightarrow{143K}$ **(Delhi 2012, AI 2009C, 2012, Foreign 2012)**

(F) d- and f-Block Elements

(i) $KMnO_4 \xrightarrow{heat}$ **(Delhi 2011, AI 2013)**

(ii) $MnO_2(s) + KOH(aq) + O_2 \longrightarrow$ **(Delhi 2009)**

(iii) $TiCl_4 + H_2O \longrightarrow$

(iv) $Cu^{2+}(aq) + I^-(aq) \longrightarrow$ **(AI 2010)**

(v) $Fe^{3+} + I^- \longrightarrow$ **(Foreign 2011)**

(vi) $CrO_4^{2-} + H^+ \longrightarrow$ **(Foreign 2011, Delhi 2013, AI 2013)**

(vii) $MnO_4^- + SO_2 + H_2O \longrightarrow$ **(Foreign 2009)**

(viii) $MnO_4^- + SO_3^{2-} + H^+ \longrightarrow$ **(Foreign 2012)**

(ix) $MnO_4^- + S_2O_3^{2-} + H_2O \longrightarrow$ **(AI 2010, 2011)**

(x) $MnO_4^- + NO_2^- + H^+ \longrightarrow$ **(Delhi 2012, AI 2012)**

(xi) $MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow$ **(Delhi 2009, 2011, 2013, AI 2009, Foreign 2011)**

(xii) $MnO_4^- + Fe^{2+} + H^+ \longrightarrow$ **(Delhi 2009, Foreign 2009)**

(xiii) $MnO_4^- + 2H_2O + 3e^- \xrightarrow[\text{medium}]{\text{alkaline}}$ .....$+ 4OH^-$

(xiv) $Cr_2O_7^{2-} + H^+ + I^- \longrightarrow$ **(Delhi 2009, 2012, AI 2012, Foreign 2012)**

(xv) $Cr_2O_7^{2-} + Fe^{2+} + H^+ \longrightarrow$ **(AI 2009, 2010, 2011, Delhi 2009, 2013)**

(xvi) $Cr_2O_7^{2-} + H_2S + H^+ \longrightarrow$ **(Delhi 2009, 2011, AI 2010, Foreign 2011)**

(xvii) $Cr_2O_7^{2-} + C_2O_4^{2-} + H^+ \longrightarrow$ **(Foreign 2009)**

(xviii) $Cr_2O_7^{2-} + Sn^{2+} + H^+ \longrightarrow$

(B) Group 15

(i) $6Li + N_2 \longrightarrow 2Li_3N$

(ii) $P_4(s) + 3NaOH(aq) + 3H_2O(l) \longrightarrow \underset{\text{Sod. hypophosphite}}{3NaH_2PO_2} + \underset{\text{Phosphine}}{PH_3}$

(iii) $P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$

(iv) $3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$

(v) $Sn + 2PCl_5 \xrightarrow{heat} SnCl_4 + 2PCl_3$

(vi) $PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$

$POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$

(vii) $Ca_3P_2(s) + 6H_2O(l) \longrightarrow 3Ca(OH)_2 + \underset{\text{Phosphine}}{2PH_3(g)}$

(viii) $2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow P_4 + 6CaSiO_3 + 10CO$

(ix) $AgCl(s) + 2NH_3(aq) \longrightarrow [Ag(NH_3)_2]Cl$

(x) $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons \underset{\text{Deep blue complex}}{[Cu(NH_3)_4]^{2+}}$

(xi) $NH_3 + NaOCl \longrightarrow NaNH_2 + HClO$

(xii) $NH_4Cl(aq) + NaNO_2(aq) \longrightarrow NH_4NO_2(aq) + NaCl(aq)$

(xiii) $3Cu + 8HNO_3(dil.) \longrightarrow 3Cu(NO_3)_2 + 2NO(g) + 4H_2O(l)$

(xiv) $I_2 + 10HNO_3(conc.) \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$

(xv) $P_4O_{10} + 4HNO_3 \longrightarrow 4HPO_3 + 2N_2O_5$

(C) Group 16

(i) $SO_3 + H_2SO_4(conc.) \longrightarrow H_2S_2O_7$

(ii) $2Fe^{3+} + SO_2 + H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$

(iii) $C + 2H_2SO_4(conc.) \longrightarrow CO_2 + 2SO_2 + 2H_2O$

(iv) $4O_2^- + 2H_2O \longrightarrow 4OH^- + 3O_2$

(v) $O_3 + 2I^- + H_2O \longrightarrow 2OH^- + I_2 + O_2(g)$

(D) Group 17

(i) $Cl_2 + 6NaOH(hot\ and\ conc.) \longrightarrow NaClO_3 + 5NaCl + 3H_2O$

(ii) $Cl_2 + 5F_2(excess) \longrightarrow 2ClF_5$

or $Cl_2 + 3F_2(excess) \longrightarrow 2ClF_3$

(iii) $Br_2 + 5F_2(excess) \longrightarrow 2BrF_5$

(iv) $2F_2(g) + 2H_2O(l) \longrightarrow 4HF + O_2$

(v) $Br_2 + 2NaI \longrightarrow 2NaBr + I_2$

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

(vii) $I_2 + 6H_2O + 5Cl_2 \longrightarrow \underset{\text{Iodic acid}}{2HIO_3} + 10HCl$

(viii) $I_2 + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2I^-$

(ix) $I_2 + 2NaClO_3 \longrightarrow 2NaI + 2ClO_2 + O_2$

or $I_2 + 2NaClO_3 \longrightarrow 2NaIO_3 + Cl_2$

(x) $SiO_2(g) + 4HF(g) \longrightarrow SiF_4 + 2H_2O$

or $SiF_4 + 2HF(g) \longrightarrow \underset{\text{Hydrofluorosilicic acid}}{H_2SiF_6}$

(xi) $Ca(OCl)_2 + 4HCl \longrightarrow CaCl_2 + 2Cl_2 + 2H_2O$

(xii) $IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$

(E) Group 18

(i) $Xe + 2F_2 \xrightarrow[7\text{ bar}]{873K} XeF_4$

(ii) $Xe(excess) + F_2 \xrightarrow[1\text{ bar}]{673K} XeF_2$

(iii) $Xe + PtF_6 \longrightarrow \underset{\text{(red colour)}}{Xe^+[PtF_6]^-}$

(iv) $XeF_2 + H_2O \longrightarrow Xe(g) + 2HF + \frac{1}{2}O_2$

(v) $6XeF_4 + 12H_2O(excess) \longrightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

(vi) $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

(vii) $XeF_2 + PF_5 \longrightarrow [XeF]^+[PF_6]^-$

(viii) $XeF_4 + PF_5 \longrightarrow [XeF_3]^+[PF_6]^-$

(ix) $XeF_4 + SbF_5 \longrightarrow [XeF_3]^+[SbF_6]^-$

(x) $XeF_6 + KF \longrightarrow K^+[XeF_7]^-$

(xi) $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$

(F) *d- and f-Block Elements*

(i) $\underset{\text{(dark pink)}}{2KMnO_4} \xrightarrow{\text{heat}} \underset{\text{(green)}}{K_2MnO_4} + MnO_2 + O_2$

(ii) $\underset{\text{(Pyrolusite)}}{2MnO_2} + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$

(iii) $TiCl_4 + 2H_2O \longrightarrow TiO_2 + 4HCl$

(iv) $2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow Cu_2I_2(s) + I_2(s)$

(v) $2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$

(vi) $2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$

(vii) $2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$

(viii)

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$

$$H_2O + SO_3^{2-} \longrightarrow SO_4^{2-} + 2H^+ + 2e^-] \times 5$$

On adding, $2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$

(ix) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

(x)

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$

$$H_2O + NO_2^- \longrightarrow NO_3^- + 2H^+ + 2e^-] \times 5$$

On adding, $2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$

(xi) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

(xii) $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(xiii) $MnO_4^- + 2H_2O + 3e^- \xrightarrow[\text{medium}]{\text{alkaline}} MnO_2 + 4OH^-$

(xiv)

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$2I^- \longrightarrow I_2 + 2e^-] \times 3$$

On adding, $Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

(xv) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

(xvi) $Cr_2O_7^{2-} + 3H_2S + 14H^+ \longrightarrow 2Cr^{3+} + 3S + 6H^+ + 7H_2O$

(xvii) $Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 6CO_2 + 7H_2O$

(xviii) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$

CHAPTER 8

What is the correct Increasing/decreasing order?

Arrange each of the following sets in correct order as per the mentioned property.

(i) PH_3, NH_3, SbH_3, AsH_3, BiH_3 – increasing basic strength **(Delhi 2009C, 2010)**

(ii) $HClO$, $HClO_2$, $HClO_3$, $HClO_4$ – increasing oxidising power **(Delhi 2008C, 2010C Foreign 2011)**

(iii) $HClO$, $HClO_2$, $HClO_3$, $HClO_4$ – decreasing acidic character

(iv) F_2, Cl_2, Br_2, I_2 – increasing bond dissociation enthalpy **(Delhi 2011C)**

(v) PH_3, H_2S, HCl – increasing acidic character **(Foreign 2011, Delhi 2011, AI 2011)**

(vi) HCl, HBr, HI, HF – increasing acidic strength **(Delhi 2009C, 2010C)**

(vii) VO_2^+, $Cr_2O_7^{2-}$, MnO_4^- – increasing oxidising power. **(AI 2010)**

(viii) Describe the following about halogens (Group 17 elements):

(a) Relative oxidising power of halogens.

(b) Relative acidic strength of the hydrogen halides.

(c) Formation of oxoacids of halogens and the structures of oxoacids of chlorine only. **(Delhi Board Comptt 2010)**

(i) Increasing basic strength of NH_3, PH_3, SbH_3, AsH_3 and BiH_3 :

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

(N is smallest in size) (Bi is largest in size)

The lone pair of electrons on N is concentrated over a small space, hence easily available, while in case of Bi, the lone pair of elecrons is diffused over a large volume space and hence comparatively less available for protonation.

(ii) Increasing oxidising power of HClO, $HClO_2$, $HClO_3$ and $HClO_4$:

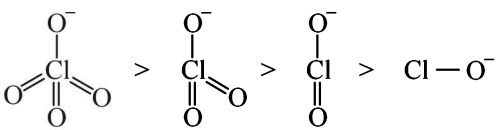
The oxidising power of an oxoacid of a halogen decreases with increase in oxidation number of the halogen. Thus,

$$\overset{+7}{HClO_4} < \overset{+5}{HClO_3} < \overset{+3}{HClO_2} < \overset{+1}{HClO}$$

Thus HClO is least stable and $HClO_4$ is the most stable.

(iii) Decreasing acidic strength of HClO, $HClO_2$, $HClO_3$ and $HClO_4$:

Higher the oxidation state of the halogen, more will be its acidic character, thus $HClO_4$ is most acidic and HClO is least acidic. Also, greater the stability of the conjugate base of the acid, more will be acidic character of the parent acid.



Most stable (Max. delocalisation of –ve charge) Least stable (Least delocalisation)

Thus acidic character of the four acids will be

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

(iv) Increasing bond dissociation enthalpy of F_2, Cl_2, Br_2 and I_2 :

Although the bond length in the four halogen molecules follows the order : F – F < Cl – Cl < Br – Br < I – I, so the bond energy is expected to follow the order : F – F > Cl – Cl > Br – Br > I – I

But in practice it is found to be

F – F < Cl – Cl > Br – Br > I – I

The low value of F – F bond enthalpy is due to larger inter-electronic (electron-electron) repulsion between the non-bonding electrons present on the two F atoms due to its smaller size.

(v) Increasing order of acidic strength : $PH_3 < H_2S < HCl$

Greater the difference in electronegativity of the two atoms of a molecule, higher will be the acidic character.

(vi) Increasing acidic strength of HCl, HBr, HI and HF :

HF < HCl < HBr < HI

(vii) Increasing oxidising power of VO_2^+, $Cr_2O_7^{2-}$ and MnO_4^- :

$VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$

Vanadium in its lower oxidation state is less stable than Cr which in turn is less stable than Mn. Thus, MnO_4^- has great tendency to get reduced and hence behaves as a good oxidising agent. Similarly, VO_2^+ has the least oxidising power.

(viii) (a) A halogen oxidises halide ions of higher atomic number. Thus the oxidising ability of the halogens in aqueous solution decreases down the group, i.e. from fluorine to iodine.

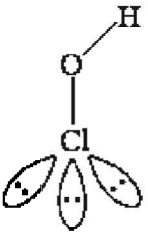
(b) The acidic strength of halogen acids varies in the order : HF<HCl<HBr<HI. The stability of these halides decreases down the group due to decrease in bond strength of H-X bond.

(c) Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as fluoric (I) acid. The other halogens form several oxoacids. Most of them cannot be isolated in pure state. They are stable only in aqueous solutions or in the form of their salts.

Structures of oxoacids of chlorine are as following:

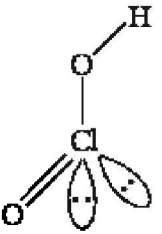
Hypochlorous acid

(HOCl)



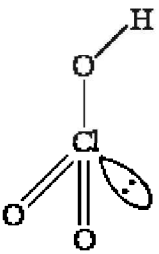
Chlorous acid

($HClO_2$)



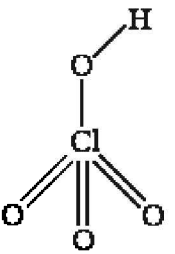
Chloric acid

($HClO_3$)



Perchloric acid

($HClO_4$)



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CHAPTER 9

Miscellaneous

(A) *Metallurgy*

1. Name one chief ore each of copper and aluminium. Name the method used for the concentration of these two ores. **(Foreign 2012)**

   What is composition of copper matte ? **(Delhi 2013)**

2. What is meant by the term pyrometallurgy ? **(AI 2009)**

3. Name two metals which occur in nature as oxides. **(Foreign 2009)**

4. Which of the two scraps, zinc or iron, would be preferred for the recovery of copper from the leached copper ore and why? **(AI 2009C)**

5. Which solution is used for the leaching of silver metal in the presence of air in the metallurgy of silver ? **(Delhi 2013)**

6. Out of C and CO, which is a better reducing agent in the lower temperature range in the blast furnace to extract iron from the oxide ore ? **(Delhi 2013)**

7. Give an example of zone refining of metals. **(Delhi 2013)**

8. Which of the following ores can be concentrated by froth floatation process and why ? Fe_2O_3, ZnS, Al_2O_3. **(Delhi 2013)**

9. Name the method used for removing gangue from sulphide ores. **(AI 2013)**

10. Name the principle ore of Al. Explain the significance of leaching in the extraction of Al. **(AI 2007, 2013)**

11. Name a metal each of which is obtained by

    (i) electrolytic reduction, (ii) chemical reduction. **(AI 2010C)**

12. What is the chief ore of Fe ? Write chemical reactions taking place in the extraction of Fe from its ore. **(Delhi 2007)**

13. Write the names of ores of Cu. Which method is commonly used to extract Cu? **(Delhi 2006)**

14. Write the names of any two principle ores of Zn. What are uses of Zn ? **(Delhi 2006)**

(B) Group 15

1. What is the covalency of nitrogen in N_2O_5 ? **(AI 2010C, Delhi 2013)**
2. What is the basicity of H_3PO_3 and why ? **(AI 2011, 2013. Delhi 2006C)**
3. Which one of PCl_4^+ and PCl_4^- is not likely to exist and why ? **(Delhi 2012)**
4. What is the oxidation number of phosphorus in H_3PO_2 molecule? **(Delhi 2010)**
5. In the structure of HNO_3 molecule, the N–O bond (121 pm) is shorter than the N–OH bond (140 pm). **(Delhi 2009, AI 2009)**
6. Give any two uses of nitric acid. **(Delhi 2006C)**

(C) Group 16

1. Of PH_3 and H_2S which is more acidic and why ? **(Delhi 2012)**
2. In solution of H_2SO_4 in water, the second dissociation constant, K_{a_2} is less than the first dissociation constant, K_{a_1}. Explain. **(Foreign 2009)**
3. Write any two uses of SO_2. **(Delhi 2007)**
4. O_2 and F_2 both stabilize higher oxidation states of metals but O_2 exceeds F_2 in doing so. **(Delhi 2012)**

(D) Group 17

1. ICl is more reactive than I_2. **(AI 2009, 2010C, 2011C, 2012C)**
2. Why fluorine does not play the role of a central atom in interhalogen compounds ? **(AI 2011)**
3. Which is stronger acid in aqueous solution, HCl or HF and why? **(AI 2009, Foreign 2010)**
4. Iron dissolves in HCl to form $FeCl_2$ but not $FeCl_3$. **(AI 2008C, Foreign 2009)**
5. Which neutral molecule would be isoelectronic with ClO^- ? **(AI 2008, 2008C)**
6. Give one use of ClF_3. **(Delhi 2008C)**
7. How are interhalogen compounds formulated and how are they prepared ? **(AI 2008C)**

8. Give reason. The pK_a value of HOCl is higher than that of HOClO. **(Foreign 2007)**

9. Write the formula and the structures of noble gas species (one each) which are isostructural with (i) ICl_4^- (ii) BrO_3^-. **(Delhi 2009C, 2010C)**

10. Name two poisonous gases which can be prepared from chlorine gas. **(AI 2013)**

(E) *Group 18*

1. Helium is used in diving equipment. **(Foreign 2009, Delhi 2013)**

2. Structures of xenon fluorides cannot be explained by valence bond approach. Explain. **(Delhi 2013)**

3. What inspired N. Bartlett for carrying out reaction between Xe and PtF_6 ? **(Delhi 2013)**

4. Helium forms no real chemical compound. Explain. **(AI 2009, 2012, Foreign 2009)**

5. Why do noble gases have very low boiling points ? **(AI 2011)**

6. XeF_2 has a straight linear structure and not a bent angular structure. Explain. **(Delhi 2010, AI 2010)**

7. State two important uses of noble gases. **(AI 2006)**

8. Does the hydrolysis of XeF_6 lead to a redox reaction ? **(Delhi 2006)**

(F) d- *and* f-*Block Elements*

1. Explain the metallic character of transition elements. **(AI 2006)**

2. What is meant by disproportionation ? Give two examples of disproportionation reactions in aqueous solution. **(AI 2011C, 2009C)**

3. Explain the variable oxidation states of transition elements. **(Delhi 2006)**

4. Calculate the number of unpaired electrons in the following gaseous state ions : Mn^{3+}, Cr^{3+}, V^{3+} and Fe^{2+}.

   Which one of these is most stable in aqueous solutions ?

   At. Nos. V = 23, Cr = 24, Mn = 25, Fe = 26. **(Foreign 2012)**

5. What may be possible oxidation states of the transition metals with the following *d*-electronic configurations if the ground state of their atoms have $3d^3 4s^2$, $3d^5 4s^2$ and $3d^6 4s^2$ configurations. Indicate relative stability of oxidation states in each case. **(Delhi 2008)**

6. Describe the following characteristics of the first series of the transition metals and their trends in the series (Sc to Zn). (a) Atomic radii (b) Oxidation states (c) Ionisation enthalpies. **(AI 2009C)**

7. What is meant by lanthanoid contraction ? **(AI 2011)**

   What is its effect on the chemistry of the elements which follow the lanthanoids ?

8. What is lanthanoid contraction ? List any two consequences of lanthanoid contraction. **(AI 2008C, 2009C)**

9. What is meant by lanthanoid contraction ?

   State one use each of lanthanoid metals and their oxides. **(Delhi 2006)**

10. Write the electronic configuration of Ce^{3+} ion and calculate the magnetic moment on the basis of spin only formula. [At. No. of Ce = 58] **(AI 2008C, 2010C)**

11. Name an important alloy which contains some of the lanthanoid metals. Mention its two uses. **(Delhi 2008C)**

12. Which element in the first series of transition elements does not exhibit variable oxidation states and why ? **(Delhi 2009)**

13. Compare the chemistry of the actinoids with that of lanthanoids with reference to (i) electronic configuration (ii) oxidation states (iii) chemical reactivity. **(Delhi 2010C, 2011C)**

(G) Coordination compounds

1. What do you understand by dentacity of a ligand ? **(Foreign 2011)**

2. What is an ambidentate ligand ? Give an example. **(Foreign 2010)**

3. Explain the following terms giving a suitable example in each case.

   (a) Ambidentate ligand

   (b) Denticity of ligand

   (c) Crystal field splitting in an octahedral field. **(AI 2011)**

4. Write the IUPAC name of

(i) $K_3[CrF_6]$ **(Foreign 2011)**

(ii) $[PtCl(NH_2CH_3)(NH_3)_2]Cl$ **(Delhi 2011C)**

(iii) $[Pt(NH_3)_4Cl_2]Cl_2$ **(AI 2011C)**

(iv) $[Cr(NH_3)_6][Co(CN)_6]$ **(AI 2011C)**

(v) $[Pt(NH_3)_3(NO)Cl_2]Br_2$ **(Delhi 2011C)**

(vi) $[Co(CN)_2(NH_3)_4]Cl$ **(Delhi 2011C)**

(vii) $[Cr(NH_3)_5(NCS)][ZnCl_4]$ **(AI 2011C)**

(viii) $[Co(NH_3)_5Cl]Cl_2$ **(Delhi 2010C)**

(ix) $[CoCl(NO_2)(NH_3)_4]Cl$ **(Delhi 2008C)**

(x) $[Co(NH_3)_4(H_2O)Cl]Cl_2$ **(Delhi 2010)**

(xi) $[CrCl_2(en)_2]Cl$ **(Delhi 2010)**

(xii) $[Cr(NH_3)_3Cl_3]$ **(Delhi 2013)**

(xiii) $K_3[Fe(CN)_6]$ **(Delhi 2013)**

(xiv) $[CoBr_2(en)_2]^+$ **(Delhi 2013)**

(xv) $[Co(NH_3)_4Cl(ONO)]Cl$ **(Delhi 2008C)**

(xvi) $[Co(H_2NCH_2CH_2NH_2)_3]_2[SO_4]_3$ **(Delhi 2006)**

(xvii) $[Cr(NH_3)_3(H_2O)_3]Cl_3$ **(Delhi 2006)**

(xviii) $[Ag(NH_3)_2][Ag(CN)_2]$ **(Delhi 2006)**

5. What is meant by chelate effect ? **(AI 2009C)**

6. Give an example of linkage isomerism. **(Delhi 2010)**

7. Give an example of ionisation isomerism. **(Delhi 2010)**

8. Give an example of coordination isomerism. **(Delhi 2010)**

9. Write the types of isomerism exhibited by the following complexes.

(i) $[Co(NH_3)_5Cl]SO_4$

(ii) $[Co(en)_3]^{3+}$

(iii) $[Co(NH_3)_6][Cr(CN)_6]$ **(Delhi 2013)**

10. For the complex, $[NiCl_4]^{2-}$, write

(a) the IUPAC name

(b) the hybridization type

(c) the shape of the complex. [At. No. of Ni = 28] **(AI 2013)**

K M C

11. For the complex, $[Fe(en)_2Cl_2]Cl$, identify the

(a) oxidation number of iron

(b) hybrid orbitals and shape of the complex

(c) magnetic behaviour of the complex

(d) number of its geometrical isomers

(e) whether there may be optical isomer also

(f) name of the complex **(Delhi 2009, 2011)**

12. Giving a suitable example for each, explain.

(a) ambidentate ligand **(AI 2009, 2011)**

(b) linkage isomerism **(AI 2009, Delhi 2010, Foreign 2009)**

(c) crystal field splitting **(AI 2009)**

(d) coordination isomerism **(Foreign 2010)**

(e) spectrochemical series **(Foreign 2010)**

13. Using the valence bond theory, predict the geometry and magnetic behaviour of

(a) $[CoF_6]^{3-}$ [At. No. of Co = 27] **(Delhi 2010C, AI 2009)**

(b) $[Co(NH_3)_6]^{3+}$ [At. No. of Co = 27]

(c) $[Ni(CO)_4]$ [At. No. of Ni = 28] **(AI 2006, 2009, Delhi 2009. 2012)**

14. Describe the limitations of valence bond theory. **(Foreign 2008)**

15. Describe the state of hybridization, shape and magnetic behaviour of the following complexes.

(a) $[Ni(CN)_4]^{2-}$ **(Delhi 2010, 2011, AI 2009, 2010, 2011)**

(b) $[Cr(H_2O)_2(C_2O_4)_2]^-$ [At. No. of Cr = 24] **(Foreign 2010, AI 2010, Delhi 2009)**

(c) $[Co(NH_3)_2(en)_2]^{3+}$ [At. No. of Co = 27] **(Foreign 2010)**

(d) $[Cr(NH_3)_4Cl_2]Cl$ **(AI 2011, Delhi 2009C, 2012)**

(e) $[Co(en)_3]Cl_3$ **(AI 2011)**

(f) $[Cr(NH_3)_6]^{3+}$ **(AI 2009, Foreign 2009)**

(g) $[Co(NH_3)_6]^{3+}$ **(AI 2007, 2009)**

(h) $[CoCl_4]^{2-}$ **(AI 2010)**

(i) $[K_4[Mn(CN)_6]$ [At. No. of Mn = 25]

(AI 2010C, Delhi 2011)

(j) $[CoF_4]^{2-}$ **(Delhi 2009)**

(k) $[NiCl_4]^{2-}$ **(AI 2007, 2009, Foreign 2009)**

(l) $[Fe(CN)_6]^{4-}$ [At. No. of Fe = 26] **(Foreign 2009)**

(m) $[Fe(H_2O)_6]^{2+}$ **(AI 2007)**

(n) $[Pt(NH_3)_2Cl(NO_2)]$ **(Delhi 2012)**

(o) $[Co(NH_3)_5Cl]Cl_2$ **(AI 2011)**

(p) $[Co(en)_2Cl(ONO)]^+$ **(AI 2009C)**

16. 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 ethylenediamine (en) molecules. **(Foreign 2012)**

(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. [At. No. of Co = 27, Ni = 28]

(Delhi 2012, Foreign 2012)

17. Describe with an example of each,the role of coordination compounds in:

(i) Biological systems

(ii) Analytical chemistry

(iii) Medicinal chemistry **(Outside Delhi Comptt 2009)**

18. What is meant by the term, 'Chromatography'? What criterion is followed for the selection of the stationary phase in chromatography?

(Delhi Board Comptt 2010)

19. What do you understand by stepwise stability constant and overall stability constant of a coordination compound?How are these two constants related? **(Outside Delhi Comptt 2011,2012)**

(H) *Value Based Question* K M C

1. The people of a village nearby metallurgical Zn plant were complaining about SO_2 air pollution effects like throat and eye irritation problem in breathing etc. An environmental agency collected and investigated air sample of metallurgical plant exhaust. Agency strictly ordered the industry authorities to connect metallurgical plant with sulphuric acid plant.
   (a) What values are displayed by environmental agency?
   (b) Which process of metallurgical operations is responsible for SO_2 pollution?
   (c) Why above process is necessary inspite of the fact that it leads to SO_2 pollution?
   (d) Why environmental agency ordered to connect metallurgical plant with sulphuric acid manufacturing plant.
2. Mr. Mittal an owner of aluminium plant found that in nearby area clay ($Al_2O_3.xH_2O$) is available in plenty. Thus he instructed his employees to use clay for extraction of aluminium. Mr. Mittal noticed that use of clay increases total cost of extraction process. Then Naveen senior engineer of company went to Mr. Mittal and adviced him to use bauxite ($Al_2O_3.xH_2O$) again for extraction of aluminium with suitable reasons.
   (a) What values are displayed by Naveen?
   (b) What is difference between ore and mineral?
   (c) Give two important ores of Ag?
3. Sohail and Dimple went to a confectionery to buy a pack of potato chips. On opening the pack, Dimple noticed change in shape of the packet she asked Sohail about this, Sohail answered that the packet was filled by N_2 gas. They discussed about the use of N_2 gas in potato chips packet but even after a long discussion they did not come to any conclusion. So, next day in school they discussed with their teacher about N_2 gas and its uses.
   (a) Why N_2 gas is filled in potato chips pack?
   (b) Why is N_2 inert at room temperature?
   (c) Mention the values shown by Sohail and Dimple.

K M. C

4. While working in school chemistry laboratory one of the students added water into sulphuric acid for diluting sulphuric acid. As he did this a sudden explosion occurred on the site and student got seriously injured. His friend soham immediately reported to class teacher and asked him to call a doctor.

(a) What process should have been followed by that student for diluting sulphuric acid and why?

(b) Mention the values shown by Soham.

5. Riya's mother had put some bleaching agent in a bucket of water and went inside. Riya thought it was plain water and dipped her orange coloured cotton dupatta in it. After some time, she found that her dupatta had become white.

(a) What happened to the dupatta?

(b) Which compound is present in bleaching agent?

(c) What is the reason for the bleaching action of this compound?

(d) What values are displayed by Riya's mother?

6. Due to scarcity of water, the residents of a colony decided to reuse their well which was not used for past six months. The secretary decided to clean the well by adding small amount of potassium permanganate in the well.

(a) Why do you think he added potassium permanganate in the well?

(b) What are the values involved in this process?

7. The head of the ordinance factories visited the gun carriage factory at Jabalpur and found that there is no incoming material check on raw materials for bullets, shells and lighter flint. Keeping in mind recently happened tragic incident of Mayapuri he ordered the supervisor to make chemical reports for the incoming raw materials.

(a) Name the alloy used to make bullets and shells.

(b) What is its composition?

(c) What are the other uses of lanthanoids?

(d) Recently, shells were located in Mayapuri which created a lot of concern. What values are shown by factories manufacturing these shells?

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8. Reena's neighbour Mr. Satish is suffering from cancer. After knowing this many people of her society started avoiding him. She went to the president of society and asks him to serve notice to all the members that

"*Cancer is not a communicable disease. We should shake hand; eat together with people suffering from cancer. These activities boost up the confidence in cancer patients for living.*"

(a) Write the name of coordination compound used as a chemotherapeutic agent for treatment of cancer.

(b) If you agree with Reena then by showing such attitude to cancer patients, mention the values reflected by us.

9. A student was preparing chemistry project on the topic 'Nickel content in different chocolates'. He first discussed the topic with his classmates but still was not satiesfied. Therefore he approached his teacher for some information on this and asked her certain questions.

(a) How will nickel be precipitated out?

(b) To which block of the periodic table does nickel belong? What is its atomic number?

(c) On the basis of valence bond theory, explain the geometry and hybridization of $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$.

(d) What are the values shown by that student?

(A) *Metallurgy*

1. **Chief ore of copper** is copper pyrites ($CuFeS_2$). It is concentrated by froth floatation process. **Chief ore of aluminium** is bauxite ($Al_2O_3.2H_2O$). It is concentrated by leaching (chemical method).

   Copper matte is composed of Cu_2S and FeS.

2. **Pyrometallurgy** is the process of extraction of a metal by heating the metal oxide with a suitable reducing agent.

3. Oxide ores of iron and copper are haematite (Fe_2O_3) and cuprite (Cu_2O) respectively.

4. **Zinc** is present above iron in the electrochemical series, hence it is more reactive than iron. However, it is costlier than iron, hence use of iron scraps is advised.

5. **Leaching of silver** is done by solution of sodium cyanide in presence of air.

$$4Ag + 8CN^- + 2H_2O + O_2 \longrightarrow 4[Ag(CN)_2]^+ + 4OH^-$$

6. At lower temperature (< 1073 K), ΔG^0 for the formation of CO from C is less negative than ΔG^0 for the formation of Fe_2O_3, thus $\Delta_r G^0$ for the reduction of Fe_2O_3 with carbon will be possitive and hence the reaction is not feasible. However, ΔG^0 for the formation of CO_2 from CO is more negative than ΔG^0 for the formation of Fe_2O_3. Thus $\Delta_r G^0$ for the reduction of Fe_2O_3 with CO will be negative which makes the reaction feasible. Thus **CO is a better reducing agent than C** at lower temperature for reducing Fe_2O_3.

7. **Zone refining** is used for the production of ultrapure metals (i.e., Si, Ge, Ga, In and B) used as semiconductors.

8. **Froth floatation method** is used to concentrate sulphide ores (e.g. ZnS) because of their preferential wettability by pine oil.

9. Gangue is removed from sulphide ores by froth floatation process because ore particles are preferentialy wetted by pine oil as compared to gangue.

10. **Principle ore of aluminium is bauxite**. It is concentrated by leaching with NaOH solution which removes the impurities like SiO_2, Fe_2O_3, TiO_2 etc. from the bauxite ore.

K M C

11. **Electrolytic reduction** is used for the extraction of sodium from fused NaCl, while **chemical reduction** is used for the extraction of iron.

12. **Haematite (Fe_2O_3)** is the **main ore of iron.**

Reactions at lower temperature (500-800K) in blast furnace.

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$$

$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$$

$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$

Reactions at higher temperature (900-1500K) in blast furnace.

$$FeO + CO \longrightarrow Fe + CO_2$$

$$CaCO_3 \longrightarrow CaO + CO_2$$

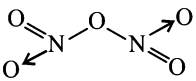
$$CaO + SiO_2 \longrightarrow \underset{\text{slag}}{CaSiO_3}$$

13. Main ores of copper are : copper pyrites ($CuFeS_2$), malachite [$CuCO_3.Cu(OH)_2$] and cuprite (Cu_2O). Copper is extracted from its ore by roasting followed by reduction.

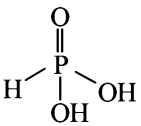
14. Principle ores of zinc are zinc blende (ZnS), calamine ($ZnCO_3$) and zincite (ZnO). Zinc is used (a) for galvanising iron, (b) as zinc dust as a reducing agent, (c) in the manufacture of dyestuffs, paints etc.

(B) Group 15

1. Covalency of nitrogen in N_2O_5 is four as is evident from its structure.



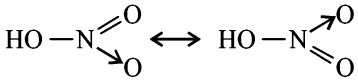
2. H_3PO_3 is dibasic because it has only two replacable hydrogen.



3. PCl_4^- does not exist because here the oxidation state of P is +3, which is less stable.

4. **Oxidation number** of P in $\overset{+1}{H_3}\overset{x}{P}\overset{-2}{O_2}$, $1 \times 3 + x - 4 = 0$, $x = +1$

5. HNO_3 molecule shows resonance, hence N–O bond is shorter



(121 pm) than the expected N–OH bond value of 140 pm. (note that the –OH of N–OH is not involved in resonance)

6. **Nitric acid is used** in the manufacture of ammonium nitrate (a fertilizer), trinitrotoluene (TNT), nitroglycerine (both are used as explosives), and other nitro compounds.

(C) Group 16

1. **More acidic character of H_2S** than PH_3 is due to more electronegativity of S than P.

2. K_{a_2} of H_2SO_4 is very less as compared to its K_{a_1}.

$$H_2SO_4 \longrightarrow H^+ + HSO_4^- \quad K_{a_1}$$

$$HSO_4^- \longrightarrow H^+ + SO_4^{2-} \quad K_{a_2}$$

$K_{a_1} > K_{a_2}$ because removal of H^+ from negative ion is difficult in comparison to removal of H^+ from a neutral molecule due to electrostatic forces of attraction.

3. Sulphur dioxide is used (i) in refining of sugar and petroleum, (ii) bleaching of wool and silk, (iii) in the manufacture of H_2SO_4 and other sulphur compounds, (iv) as an antichlor, disinfectant and preservative.

4. Oxygen stabilizes higher oxidation states of metals than fluorine because it can form multiple bonds with metals.

(D) Group 17

1. **I–Cl is more reactive** than I–I because former is polar due to difference in electronegativity of I and Cl.

2. Fluorine is not present as central atom in interhalogen compounds because of (i) low enthalpy of dissociation of F–F bond, and (ii) high hydration enthalpy of F^- ion.

3. H–I is more acidic than H–Cl because of its greater bond length than that of H–Cl which makes the molecule weaker.

4. $Fe + 2HCl \longrightarrow FeCl_2 + H_2$

The evolved hydrogen, being reducing in nature, reduces $FeCl_3$

as soon as it is formed to $FeCl_2$ and HCl.

5. Number of electrons in ClO^- are 17 + 8 + 1 = 26. Neutral molecule having 26 electrons is OF_2 (8 + 18 = 26).

6. ClF_3 is used for the production of UF_6, used in nuclear reactions.

$$U + 3ClF_3 \longrightarrow UF_6 + 3ClF$$

7. Interhalogen compounds are formulated as XX', XX'_3, XX'_5, etc. For preparation of interhalogen compounds, consult Ch. 'How will you prepare' Q. 18.

8. $HClO_2$ is stronger acid (i.e., its pK_a value is low) than HClO because its conjugate base is stabilised due to resonance.

$$HO-Cl=O \longrightarrow [^-O-Cl=O \leftrightarrow O=Cl-O^-]$$

Resonance is not possible in ClO^-.

9. $XeOF_4$ is isostructural with ICl_4^-; while XeO_3 is isostructural with BrO_3^-.

10. Phosgene ($COCl_2$), tear gas (Cl_3CNO_2) and mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$) are prepared from chlorine gas.

(E) Group 18

1. Helium is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

2. According to valence bond approach, covalent bonds are formed by the overlapping of half-filled atomic orbitals. But xenon has fully filled electronic configuration. Hence the structure of xenon fluorides cannot be explained by VBT.

3. Bartlett found that the IE_1 of molecular oxygen is almost similar with that of xenon. Thus after preparing $O_2^+(PtF_6)^-$, he got inspired and carried out reaction between Xe and PtF_6 for preparing $Xe^+[PtF_6]^-$.

4. Helium is chemically unreactive because of its small size and high IE.

5. Weak van der Waal's forces of attraction are present between atoms of noble gases.

6. XeF_2 is linear in shape because its two Xe–F bonds are present in axial positions, and three lone pairs are present in equitorial positions to minimise *lp-lp* and *lp-bp* repulsions.

7. Helium is used in filling balloons for meterological observations. Neon is used in discharge tubes and fluorescent bulbs for

advertisement display purposes.

8. Hydrolysis of XeF_6 gives $XeOF_4$ and XeO_2F_2; oxidation state of Xe in XeF_6, $XeOF_4$ and XeO_2F_2 is same, hence hydrolysis of XeF_6 is not a redox reaction.

(F) d- and f-Block Elements

1. Transition metals display metallic properties like high m.p., high b.p. high tensile, strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre.

2. Disproportionation reactions are those in which one molecule of the same substance is oxidised and other molecule is reduced. For exmple,

$$3\overset{+6}{Mn}O_4^{2-} + 4H^+ \longrightarrow 2\overset{+7}{Mn}O_4^- + \overset{+4}{Mn}O_2 + H_2O$$

$$2Cu^+ \longrightarrow Cu^{2+} + Cu$$

$$2HCHO \longrightarrow HCOOH + CH_3OH$$

3. The variation in oxidation states of the transition metals is due to incomplete filling of *d*-orbitals and nearly similar energy of the *d*-orbital and the next higher *s*-orbital. Manganese shows oxidation states from +2 to +7. In case of non-transition elements, variability of oxidation states is due to inert pair effect; here the oxidation state normally differs by a unit of two, e.g. Pb shows +2 and +4 oxidation states.

4. **Mn** = $3d^5 4s^2$; $Mn^{3+} = 3d^4$

Thus number of unpaired electrons = 4

Cr = $3d^4 4s^2$; $Cr^{3+} = 3d^3$

Thus number of unpaired electrons = 3

V = $3d^3 4s^2$; $V^{3+} = 3d^2$

Thus number of unpaired electrons = 2

Fe = $3d^6 4s^2$; $Fe^{2+} = 3d^6$

Thus number of unpaired electrons = 4

Among the four ions, Mn^{3+} is smallest in size and has maximum hydration energy, thus it will be most stable in aqueous solution.

5. Possible oxidation states of the transition metals with the following configurations.

(i) $3d^3 4s^2$ = +2 , +3, +4 and +5

+5 is more stable.

(ii) $3d^5 4s^2$ = +2, +3, +4, +5, +6 and +7

+2 and +7 are more stable.

(iii) $3d^6 4s^2$ = +2, +3, +4, and +6

+2 is stable, +3 is most stable.

6. (a) **Atomic radii :** Atomic radii decreases gradually from Sc to Cr due to increased nuclear charge but from Cr to Cu, it remains nearly constant.

(b) **Oxidation states :** Scandium shows only +3 oxidations state, while other members can show oxidation states equal to sum of electrons in *ns* and $(n-1)d$ orbials. Elements present in or near the middle of the series show greatest number of oxidation states, e.g. Mn shows all oxidation states from +2 to +7.

(c) **Ionisation enthalpies :** Ionisation energy increases from left to right in each series because of increase in nuclear charge. The irregular trend in the first series is due to irregular variation in atomic size.

7. The decrease in atomic and ionic radii with increase in atomic number along lanthanoids (from La to Lu) is called **lanhanide contraction**. It is due to imperfect shielding of one electron by another in the same subshell. The decreases in ionic radii (M^{3+}) is more regular than the decrease in atomic radii.

The cumulative effect of the contraction of the lanthanoid series causes the radii of the members of third transition series to be very similar to those of corresponding members of second series. Thus Zr (160 pm) and Hf (159 pm) have identical radii. Due to their similar radii, they have same physical and chemical properties.

8. **Consequences of lanthanoid contraction.**

(i) Lanthanoids have similar physical and chemical properties.

(ii) Zirconium (160 pm) and hafnium (159 pm) have similar physical and chemical properties.

9. **Uses of lanthanoid metals and oxides.**

Lanthanoids are used in preparing Mischmetal, a well known alloy used in bullets, shell and lighter flint. Mixed oxides of lanthanoids are used as catalysts in petroleum cracking.

10. $_{58}Ce = [Xe]\ 4f^1\ 5d^1\ 6s^2$

$Ce^{3+} = [Xe]\ 4f^1$

$\mu = \sqrt{n(n+2)} = \sqrt{1(3)} = 1.73$ BM

11. Consult Q.51.

12. Zinc does not show variable oxidation state because it has completely filled *d*-orbital.

13. (i) Electronic configuration

Lanthanoids = $[Xe]4f^{0-14}\ 5d^{0-1}\ 6s^2$

Actinoids = $[Rn]5f^{0-14}\ 6d^{0-1}\ 7s^2$

(ii) **Oxidation states.**

Lanthanides exhibit mainly +3 oxidation state, although +2 and +4 oxidation states are also found. Actinides exhibit a greater range of oxidation states (from +2 to +7) because 5*f* 6*d* and 7*s* orbitals are of comparable energy, although here also +3 is the main oxidation state.

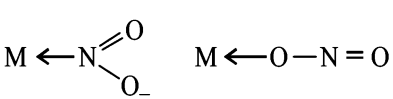
(iii) **Chemical reactivity.**

Lanthanoids, particularly higher members, are less reactive than actinoids. For example, lanthanoids react with dil. acids and liberate hydrogen gas, while actinides react even with boiling water and give a mixture of oxide and hydride.

(G) Coordination compounds

1. The number of ligating atoms present in a ligand is called **dentacity**, e.g., dentacity of oxalate ion is 2.

2. Ligands which can ligate through its two different atoms are known as **ambidentate ligands**, e.g., NO_2^-, CNO^- (they can form bonds with metal through their N as well as O), CNS^-, SCN^-, etc.

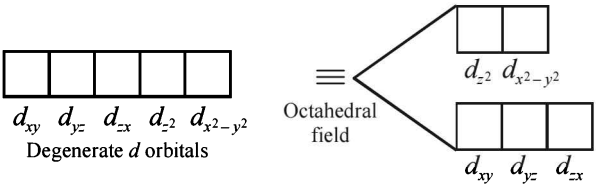


3. (a) Ambidentate ligand : Consult Q. 2.

(b) Dentacity of ligand : Consult Q. 1.

(c) Crystal field splitting in an octahedral field : The splitting of degenerate orbitals due to the presence of ligands in

octahedral geometry is known as crystal field splitting in an octahedral field, e.g.



4. (i) $K_3[CrF_6]$

Pot. hexafluorochromate (III).

(ii) $[PtCl(H_2NCH_3)(NH_3)_2]Cl$

Diamminechlorido (methyl amine) platinum (II) chloride.

(iii) $[Pt(NH_3)_4Cl_2]Cl_2$

Tetraammine dichlorido platinum (IV) chloride.

(iv) $[Cr(NH_3)_6][Co(CN)_6]$

Hexammine chromium (III) hexacyanocobaltate (III)

(v) $[Pt(NH_3)_3(NO)Cl_2]Br$

Triammine dichloridonitrosyl platinum (IV) bromide

(vi) $[Co(CN)_2(NH_3)_4]Cl$

Tetraammine dicyano cobalt (III) chloride.

(vii) $[Cr(NH_3)_5(NCS)][ZnCl_4]$

Pentaamminetriocyanato–N–chromium (III) tetrachlorozincate (II)

(viii) $[Co(NH_3)_5Cl]Cl_2$

Pentaammine chlorido cobalt (III) chloride.

(ix) $[CoCl(NO_2)(NH_3)_4]Cl$

Tetraammine chloridonitrocobalt (III) chloride.

(x) $[Co(NH_3)_4(H_2O)Cl]Cl_2$

Tetraammine aquachloridocobalt (III) chloride.

(xi) $[CrCl_2(en)_2]Cl$

Dichloridobis-(ethane-1, 2-diamine) chromium (III) chloride

(xii) $[Cr(NH_3)_3Cl_3]$

Triamminetrichloridochromium (III)

(xiii) $K_3[Fe(CN)_6]$

Potassium hexacyanoferrate (III)

(xiv) $[CoBr_2(en)_2]^+$

Dibromidobis-(ethane-1, 2-diamine) cobalt (III) ion

(xv) $[Co(NH_3)_4Cl(ONO)]Cl$

Tetraamminechloridonitrite–N–cobalt (III) chloride

(xvi) $[Co(H_2N.CH_2CH_2NH_2)_3]_2[SO_4]_3$

Tris-(ethane-1, 2-diamine) cobalt (III) sulphate

(xvii) $[Cr(NH_3)_3(H_2O)_3]Cl_3$

Triamminetriaquachromium (III) chloride

(xviii) $[Ag(NH_3)_2][Ag(CN)_2]$

Diammine silver (I) dicyanoargentate (I)

5. Chelating ligands form more stable complexes due to formation of chelate (ring) than the unchelating (monodentate) ligands. This is called chelating effect.

6. Example of linkage isomers.

$[Co(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5(ONO)]Cl_2$

7. Example of ionisation isomers.

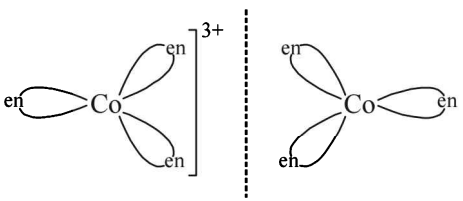
$[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5(SO_4)]Cl$

8. Example of coordination isomers.

$[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

9. (i) $[Co(NH_3)_5Cl]SO_4$ exhibits ionisation isomerism with $[Co(NH_3)_5SO_4]Cl$

(ii) $[Co(en)_3]^{3+}$ exhibits optical isomerism



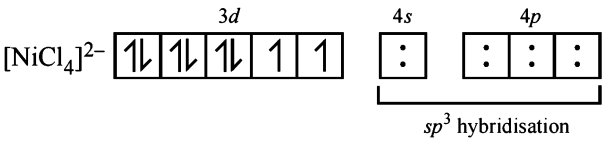
Enantiomers

(iii) $[Co(NH_3)_6][Cr(CN)_6]$ exhibits coordination isomerism with $[Cr(NH_3)_6][Co(CN)_6]$

10. (a) $[NiCl_4]^{2-}$ is tetrachloronickelate (II)

(b) Type of hybridization is sp^3.

$Ni^{2+} = 3d^8 4s^0$

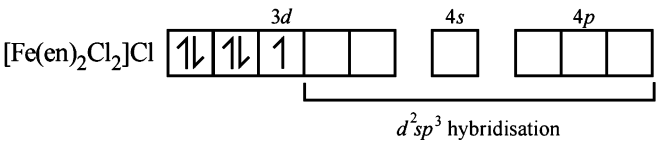


(c) sp^3 hybridisation leads to tetrahedral geometry.

11. For the complex, $[Fe(en)_2Cl_2]Cl$

(a) oxidation number of iron : $x + (2 \times 0) + (-2) = +1$; $x = +3$

(b) Fe^{3+} has $3d^5$ configuration, but in presence of ethylenediamine (a strong field ligand), pairing occurs and thus d^2sp^3 hybridisation occurs leading to octahedral geometry.



(c) Since the complex has one unpaired electron, it is paramagnetic.

(d) It has two geometrical isomers.

(e) Yes, the complex also shows optical isomerism due to the presence of polydentate ligand.

(f) Its IUPAC name is dichloridobis (ethane-1, 2-diamine) iron (III) chloride.

12. (a) **Ambidentate ligands** are NO_2, CNO^-, SCN, CN^- etc.

(b) **Linkage isomerism** exists in coordination compounds containing ambidentate ligand, e.g., $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$.

(c) **Crystal field splitting :** Consult Q. 58 (c).

(d) **Coordination isomerism** exists in complexes in which both cationic and anionic parts are present as complex, the metallic species in the cationic and anionic parts of one isomer are interchanged in other isomer. Example,

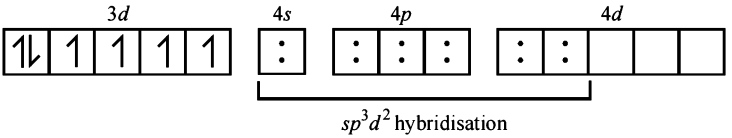
$[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

(e) **Spectrochemical series :** The arrangement of ligands in a series in the order of increasing field strength is known as spectrochemical series.

$$Br^- < Cl^- < F^- < H_2O < NH_3 < en < CO$$

13. Geometry and magnetic moment of

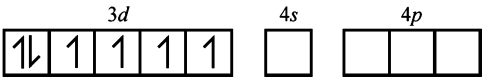
(a) $[CoF_6]^{3-}$. Here Co is present as Co^{3+} whose electronic configuration is $3d^6 4s^0$. Thus six fluoride ions will occupy one $4s$, three $4p$ and two $4d$, i.e., the complex is sp^3d^2 hybridised giving octahedral geometry.



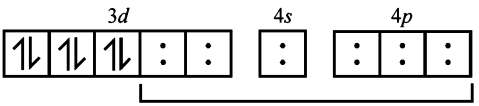
Since the complex has four unpaired electrons, it will be **paramagnetic**.

(b) $[Co(NH_3)_6]^{3+}$. Here Co is present as Co^{3+}.

Electronic configuration of Co^{3+} : [Ar] $3d^6 4s^0$



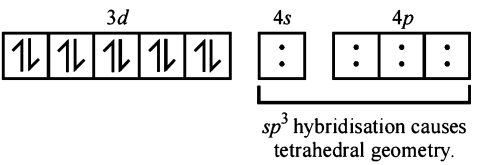
NH_3, being a strong field ligand, causes pairing of electrons.



Since the complex has no unpaired electron, it is **diamagnetic**.

(c) $[Ni(CO)_4]$. Here Ni is present as Ni^0 whose electronic configuration is [Ar] $3d^2 4s^2$.

CO, being strong field ligand, causes pairing of electrons thus the configuration of $Ni(CO)_4$ will be



The complex is **diamagnetic** since all electrons are paired.

14. Limitations of valence bond theory. K M C

(a) It is based on number of assumptions.

(b) It does not explain the colour exhibited by coordination compounds.

(c) It does not make exact prediction regarding the tetrahedral and square planar structures of four coordinate complexes.

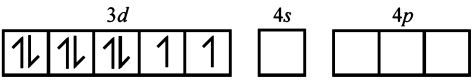
(d) It does not distinguish between strong and weak field ligands.

(e) It does not give quantitative interpretation of (i) magnetic data, (ii) thermodynamic or kinetic stabilities of complex compounds.

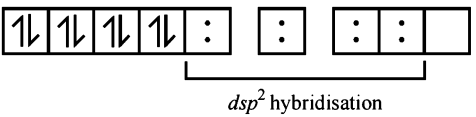
15. Hybridization, shape and magnetic behaviour of

(a) $[Ni(CN)_4]^{2-}$: Ni^{2+} = [Ar] $3d^8 4s^0$

Configuration of Ni^{2+}



Configuration of Ni^{2+} in presence of CN^- (a strong field ligand)

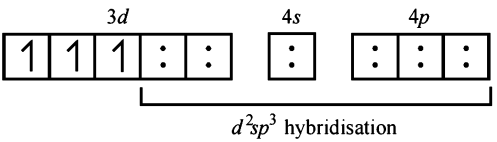


dsp^2 Hybridisation leads to square planar shape.

Since the complex has no unpaired electron, it is **diamagnetic**.

(b) $[Cr(H_2O)_2(C_2O_4)_2]^-$. Here Cr is present as Cr^{3+} = [Ar] $3d^3$.

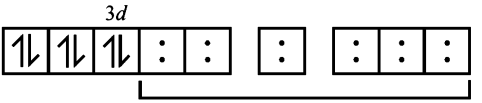
Electronic configuration of the above complex. Note that the oxalate ligand is bidentate, hence it occupies two orbitals.



Shape is octahedral and complex is **paramagnetic**.

(c) $[Co(NH_3)_2(en)_2]^{3+}$. Here Co is present as Co^{3+} = [Ar] $3d^6 4s^0$

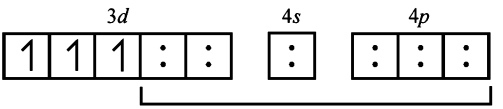
Electronic configuration in presence of en and NH_3, both are strong field ligands.



d^2sp^3 – Octahedral, diamagnetic

(d) $[Cr(NH_3)_4Cl_2]Cl$. Here Cr is present as Cr^{3+} = $3d^3 4s^0$

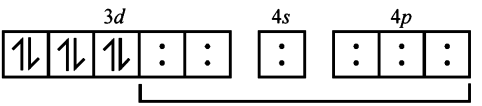
Electronic configuration of the complex



d^2sp^3 – Octahedral, paramagnetic

(e) $[Co(en)_3]Cl_3$. Here Co is present as Co^{3+} = $3d^6 4s^0$

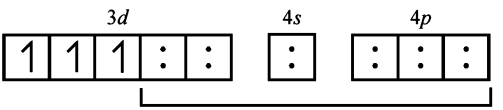
Co in presence of *en*, strong field ligand.



d^2sp^3 – Octahedral, diamagnetic

(f) $[Cr(NH_3)_6]^{3+}$Cr as Cr^{3+} = [Ar] $3d^3 4s^0$

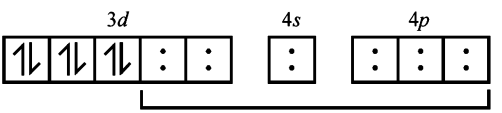
Cr^{3+} in presence of NH_3



d^2sp^3 – Octahedral, paramagnetic

(g) $[Co(NH_3)_6]^{3+}$. Co as Co^{3+} = [Ar] $3d^6 4s^0$

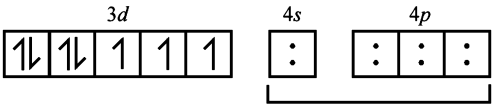
Co^{3+} in presence of NH_3, a strong field ligand



d^2sp^3 – Octahedral, diamagnetic

(h) $[CoCl_4]^{2-}$. Co as Co^{2+} = [Ar] $3d^7 4s^0$

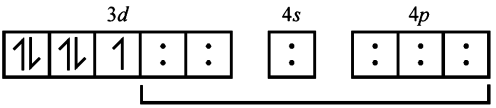
Co^{2+} in presence of Cl^- ions



sp^3-Tetrahedral, paramagnetic

(i) $[K_4[Mn(CN)_6]$. Mn as Mn^{2+} = [Ar] $3d^5$

Mn^{2+} in presence of CN^- (strong field ligand)

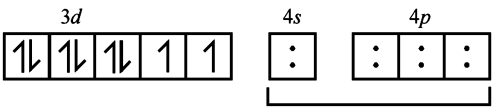


d^2sp^3 – Octahedral, paramagnetic

(j) $[CoF_4]^{2-}$. Same as $[CoCl_4]^{2-}$ discussed in **(h)**

(k) $[NiCl_4]^{2-}$. Here Ni as Ni^{2+} = [Ar] $3d^8 4s^0$

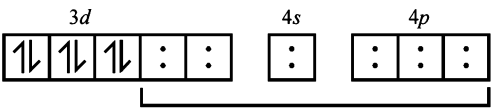
Ni^{2+} in presence of Cl^-



sp^3-Tetrahedral, paramagnetic

(l) $[Fe(CN)_6]^{4-}$. Here Fe is present as Fe^{2+} = [Ar] $3d^6 4s^0$

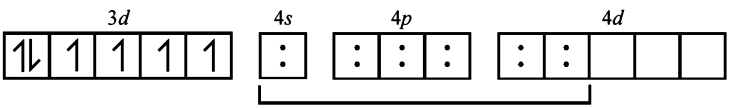
Fe^{2+} in presence of CN^-, strong field ligand



d^2sp^3 – Octahedral, diamagnetic

(m) $[Fe(H_2O)_6]^{2+}$. Fe is present as Fe^{2+} = [Ar] $3d^6 4s^0$

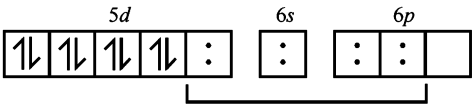
Fe^{2+} in presence of H_2O, a weak field ligand



sp^3d^2 - Octahedral, paramagnetic

(n) $[Pt(NH_3)_2Cl(NO_2)]$.

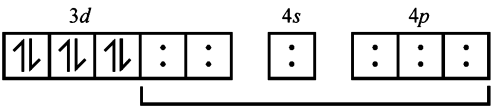
Electronic configuration of $[Pt(NH_3)_2Cl(NO_2)]$



dsp^2 - Square planar, diamagnetic

(o) $[Co(NH_3)_5Cl]Cl_2$. Here Co is present as Co^{3+} = [Ar] $3d^6 4s^0$

Configuration of Co^{3+} in presence of NH_3, a strong field ligand



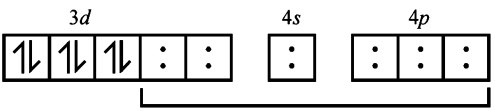
d^2sp^3 – Octahedral, diamagnetic

(p) $[Co(en)_2Cl(ONO)]^+$. Here Co is present as Co^{3+} = [Ar] $3d^6 4s^0$; the strong field *en* causes pairing, hence d^2sp^3 hybridisation occurs as in (**o**) leading to octahedral shape and diamagnetic complex.

16. (i) $[CoCl(NH_3)(en)_2]^{2+}$

Amminebis (ethane-1, 2-diamine) chloridocobalt (III) ion

Co^{3+} in presence of *en*, a strong field ligand.



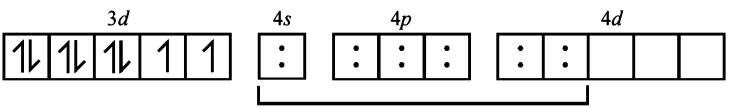
d^2sp^3 – Diamagnetic

(ii) $[Ni(H_2O)_2(C_2O_4)_2]^{2-}$

Diaquadioxalatonickelate (II) ion

Ni^{2+} = [Ar] $3d^8 4s^0$

Ni^{2+} in presence of oxalate ions



sp^3d^2 - Paramagnetic

17. (i) Biological systems: Many biologically important natural compounds exist as coordinated complexes. For example: chlorophyll, haemoglobin, etc.

(ii) Analytical chemistry: Coordination compounds find use in many qualitative and quantitative chemical analysis. For example: the familiar colour reactions given by metal ions with ligands like EDTA and DMG (dimethylglyoxime)

(iii) Medicinal chemistry: Certain complexing agents are used for the removal of metal poisoning. For example: *cis*-platin, a complex of platinum with the formula $[Pt(NH_3)_2Cl_2]$, is used for the treatment of cancer.

18. Chromatography : It is a technique for the separation and purification based on the differences in the adsorbing tendencies of the element and its impurities on a suitable adsorbent. It is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. Following are the criterion followed for the selection of the stationary phase in chromatography.

(i) It should have high and selective adsorption power.

(ii) It should be finely powdered to offer larger surface area for adsorption.

(iii) It should not react chemically with either of the sample components.

(iv) It should be pure.

19. This is explained with the help of the following example:

$$Cu^{2+} + NH_3 = [Cu(NH_3)]^{2+},\ K_1 = \frac{[Cu(NH_3)]^{2+}}{[Cu]^{2+}[NH_3]}$$

$$[Cu(NH_3)]^{2+} + NH_3 = [Cu(NH_3)_2]^{2+},\ K_2 = \frac{[Cu(NH_3)_2]^{2+}}{[Cu(NH_3)]^{2+}[NH_3]}$$

Here, K_1 and K_2 are the stepwise stability constants. The overall stability constant for this reaction is given by:

K M C

$$Cu^{2+} + 2NH_3 = [Cu(NH_3)_2]^{2+}$$

$$\beta = \frac{[Cu(NH_3)_2]^{2+}}{[Cu^{2+}][NH_3]^2}$$

Here, β is called the overall stability constant.

The relation between stepwise and overall stability constant is:

$\beta_2 = K_1 \times K_2$

In general, $\beta_n = K_1 \times K_2 \times K_3 \times ___ \times K_n$

(H) Value Based Question

1. (a) Deep concern for environment and well-being of villagers, courage to give adequate and right advice, problem solving approach, capable of making people aware about effects of harmful gases etc. are some values displayed by environmental agency.

(b) Roasting of sulphide ore of zinc results into formation of SO_2.

(c) Roasting of sulphide ore is necessary to remove organic matter and non-metals as their oxides. Sulphides of the metals are converted into their oxides.

(d) As roasting is very important process of metallurgical operation of extraction of Zn. Roasting results into discharge of SO_2 in atmosphere in significant amount on connecting with H_2SO_4 plant. SO_2 emitted gets utilised in manufacture of H_2SO_4 according to following reaction.

$$H_2O + SO_2 + \frac{1}{2}O_2 \longrightarrow H_2SO_4$$

2. (a) Loyality, intelligence, courage to give adequate and right advice, awareness etc. are some values displayed by Naveen.

(b) **Minerals:** The natural substance in which the metals or their compounds occur in the earth is called minerals.

Ores: The minerals from which the metals can be conveniently

and economically extracted are called ores.

(c) Two important ores of Ag are silver glance (Ag_2S) and horn silver (AgCl).

3. (a) N_2 gas is filled in potato chips pack to flush out O_2 which would otherwise cause oxidation of the chips.

(b) N_2 is inert at room temperature due to high bond enthalpy of $N \equiv N$ bond.

(c) Ability to solve problem by discussion, keen observation, curiousity etc. are some values shown by them.

4. (a) Sulphuric acid should be added to water for its dilution because sulfuric acid (H_2SO_4) reacts very vigorously with water, in a highly exothermic reaction. If you add water to concentrated sulfuric acid, it can boil and spit and you may get nasty acid burns. Water is less dense than sulfuric acid, so if you pour water on the acid, the reaction occurs on top of the liquid. Thus any vigrous or violent reaction does not occur.

(b) Sensitivity and care towards others, presence of mind etc. are some values shown by Soham.

5. (a) The dupatta got bleached.

(b) Cl_2 is present in the bleaching agent

(c) Bleaching action of Cl_2 is due to oxidation.

$Cl_2 + H_2O \rightarrow 2HCl + O$

Coloured substance + O $\rightarrow$ colourless substance.

Bleaching effect of Cl_2 is permanent.

(d) Carelessness, laziness etc. are some values displayed by Riya' mother.

6. (a) This is due to potassium permanganate's strong oxidant and disinfectant properties that are used to clean drinking water, water reservoirs and pipes. It helps to reduce levels of iron and manganese in drinking water. When it is added to water, its ions convert themselves to hydroxides and iron and

manganese sinks to the bottom of the water holder. It also helps to reduce the chlorination disinfection by-products in water. It is used for treating musty odours and sulfur smells from drinking water.

(b) Awareness towards the enviornment, knowledgable etc.

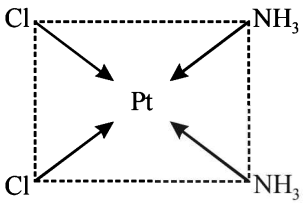
7. (a) Hg-based alloy containing misch metal.

(b) Misch metal consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al.

(c) Individual lanthanoid oxides are used as phosphors in television screens and similar fluorescing surfaces.

(d) Carelessness, unawareness about the harm that these shell would have caused to the lives of many people.

8. (a) Cis-platin is used as a chemotherapeutic agent for treatment of cancer.



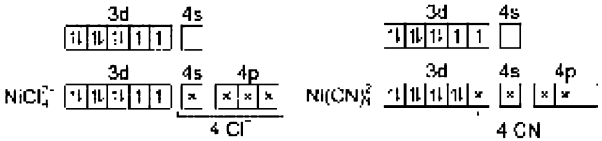
(b) Shows decency and courtesy towards others, demonstrate positive attitude, helpful to others etc.

9. (a) Nickel is precipitated in the form of an insoluble complex of nickel dimethylglyoxime, which gives a red ppt in group IV of qualitative analysis.

(b) Ni belongs to d-block of the periodic table. Its atomic number is 28.

(c) $\underline{[NiCl_4]^{2-}}$ $\underline{[Ni(CN)_4]^{2-}}$

	K	M	C
Ni(28)	$3d^8\ 4s^2$	$3d^8\ 4s^2$	
Ni^{2+}	$3d^8\ 4s^0$	$3d^8\ 4s^0$	



Hybridization sp^3 dsp^2 Geometry Tetrahedral Square planar

(d) Dedication towards his work, ability to solve the problems by discussion etc.

■■■

Sample Papers

SAMPLE PAPER-1

SECTION - A

1. How is xenon fluoride XeF_6 obtained?
2. Why are haloalkanes insoluble in water but soluble in benzene?
3. In the reaction $A + 2B \longrightarrow 3C + 2D$, the rate of disappearance of B is 1×10^{-2} mol L^{-1} s^{-1}. What will be the rate of change in concentration of A and C?
4. Give the IUPAC name of $[(CH_3)_2CH]_3COH$.
5. Out of NH_3 and N_2, which gas will be adsorbed more readily on the surface of charcoal and why?

SECTION - B

6. Why can not anhydrous calcium chloride be used for drying ethyl alcohol?
7. A compound is formed by two elements M and N. The element N forms ccp and atoms of M occupy 1/3rd of tetrahedral voids. What is the formula of the compound?
8. (a) SF_6 is used as a gaseous electrical insulator. Why?

   (b) H_3PO_2 and H_3PO_3 act as good reducing agents while H_3PO_4 does not. Discuss

   OR

   (a) How is XeO_3 prepared? Write chemical equation.

   (b) Molecular nitrogen N_2 is not particularly reactive. Explain.
9. Consider a cell composed of two half-cells:

   (*i*) $Cu(s) | Cu^{2+}(aq)$, and

   (*ii*) $Ag(s) | Ag^{+}(aq)$.

   Calculate

   (a) the standard cell potential, and

   (b) the cell potential when concentration of Cu^{2+} is 2M and concentration of Ag^{+} is 0·05 M, at 298 K.

   Given: $E^{\circ}_{Cu^{2+}/Cu} = +0.34V$, $E^{\circ}_{Ag^{+}/Ag} = 0{\cdot}80$ V, $R = 8{\cdot}314$ JK^{-1} mol^{-1}, $F = 96500$ C mol^{-1}

10. Assign the formula to complex formed by Fe^{2+} with following ligands:

(*a*) three cyanide ion and three ammonia molecules.

(*b*) one hydroxy ion and two ammonia molecules and three chloride ions.

SECTION - C

11. (a) Cesium chloride is more stable than sodium chloride. Assign reason.

(b) Addition of $CdCl_2$ to the crystals of AgCl will produce schottky defects but the same is not produced when NaCl crystals are added. Discuss.

12. Explain the following observation:

(a) Lyophilic colloid is more stable than lyophobic colloid.

(b) Coagulation takes place when sodium chloride solution is added to a colloidal solution of ferric hydroxide.

(c) Sky appears blue in colour.

OR

Account for the following :

(a) Ferric hydroxide sol is positively charged.

(b) The extent of physical adsorption decreases with rise in temperature.

(c) A delta is formed at the point where river enters the sea.

13. Answer the following questions in brief:

(*i*) What would happen if no salt bridge (or porous pot) were used in a galvanic cell like Daniell cell?

(*ii*) Which of two: HCl or NaOH (of same molar concentration) is expected to have higher value of λ_m^∞?

(*iii*) How are molar conductivity and equivalent conductivity related in case of $Al_2(SO_4)_3$?

14. (i) Among $Ag(NH_3)_2Cl$, $[Ni(CN)_4]^{2-}$ and $[CuCl_4]^{2-}$, which

(a) has square planar geometry?

(b) remains colourless in aqueous solution and why?

[Ag (Z = 47), Ni (Z = 28), Cu (Z = 29)].

(ii) Write the IUPAC name of $[Co(en)_2Cl_2]Cl$.

15. (a) In some reactions, the energy possessed by colliding molecules is more than the *threshold energy*, yet the reaction is slow. Why?

(b) State one condition in which a bimolecular reaction may be kinetically of the first order.

16. (a) What is the decreasing order of reactivity of the following in S_N2 reaction?

1-Bromo-2-methylbutane, 1-Bromo-2, 2-dimethylpropane, 1-Bromopentane.

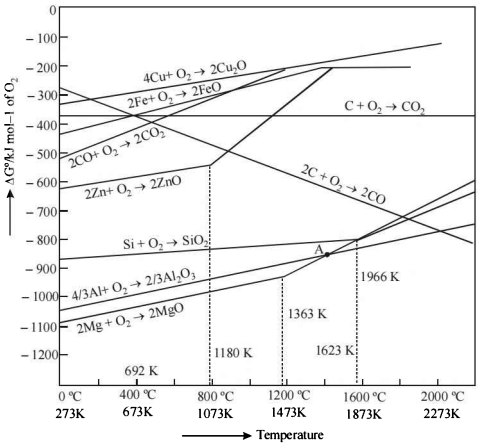
(b) Arrange the compounds CH_3F, CH_3I, CH_3Br, CH_3Cl in order of increasing reactivity in bimolecular nucleophilic substitution (S_N2) reactions.

17. Using the Ellingham diagram given below, predict the following:

(a) At what temperature can silicon reduce MgO.

(b) At what temperature can aluminium reduce MgO.

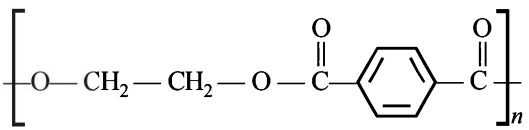
(c) At what temperature can carbon reduce MgO.



18. D – (+) – Glucose gives most of the characteristics of the aldehydic (–CHO) group but it does not react with sodium bisulphite, ammonia and also does not restore the pink colour of Schiff's reagent. Explain.

19. (i) What is the role of sulphur in the vulcanization of rubber ?

(ii) Identify the monomers in the following polymer :



(iii) Arrange the following polymers in the increasing order of their intermolecular forces : Terylene, Polythene, Neoprene

20. (a) Distinguish between thermosetting and thermoplastic polymers?

(b) What is phenol-formaldehyde polymer popularly known as?

21. Explain the following observations:

(a) ClF_3 exists but FCl_3 does not.

(b) Among the hydrides of elements of Group 16, water shows unusual physical properties.

(c) Justifying the order of your choice, arrange the following in decreasing order of property indicated:

$HClO_4$, $HClO_3$, $HClO_2$, $HClO$ oxidising power.

22. Aniline is reacted with bromine water and the resulting product is treated with an aqueous solution of sodium nitrite in presence of dilute hydrochloric acid. The compound so formed is converted into a tetrafluoroborate which is subsequently heated dry. Which final product is formed explain by giving reactions involved ?

SECTION - D

23. Raveena is preparing modak for Ganesh utsav but her grandmother is a diabetic patient, so for her she went to a nearby supermarket to buy artificial sweeteners to make sweets. There she found two brands of sweeteners, one containing aspartame and the other containing sucralose. Raveena chose the brand having sucralose.

(a) Why did Raveena prefer sucralose over aspartame?

(b) Give the structural formula of aspartame.

(c) Describe the values that Raveena brings out through her action.

SECTION - E

24. (a) (i) Which oxidation state of Mn is most stable and why?

(ii) Which transition element show highest oxidation state and in which compound?

(iii) Which is the densest transition element?

(b) Write balanced ionic equation for what happens when:

(i) Acidified potassium permanganate solution is treated with an oxalate ion in solution.

(ii) An iodide ion is treated with an acidified dichromate ion in solution.

OR

(a) Give reasons for each of the following :

(i) Size of trivalent lanthanoid cations decreases with increase in the atomic number.

(ii) Transition metal fluorides are ionic is nature, whereas bromides and chlorides are usually covalent in nature.

(b) Gas (A) and gas (B) both turn $K_2Cr_2O_7/H^+$ green. Gas (A) also turns lead acetate paper black. When gas (A) is passed into gas (B) in an aqueous solution, yellowish white turbidity appears. Identify gas (A) and (B) and explain the reactions.

25. (a) The degree of dissociation of $Ca(NO_3)_2$ in dilute aqueous solution containing 7.0 g of the solute per 100g of water at 100°C is 70 percent. If the vapour pressure of water at 100°C is 760 mm, calculate the vapour pressure of the solution.

(b) What is the van't Hoff factor (i) of the compound Na_2SO_4 if it is 100% dissociated.

(c) If glycerine $[C_3H_5 (OH)_3]$ and ethylene glycol $(C_2H_6O_2)$ are sold at same price per kg, which would be cheaper for preparing an antifreeze solution for the radiator of an automobile?

OR

(a) A solution containing 0.5126 g of naphthalene (molar mass = 128g mol^{-1}) in 50.0 g of carbon tetrachloride gave a boiling point elevation of 0.402 K while a solution of 0.6216 g unknown solute in the same mass of carbon tetrachloride gave a boiling point of elevation of 0.647 K. Find the molar mass of the unknown solute.

(b) Explain why is measurement of osmotic pressure more widely used for determining the molar mass of macro-molecules than the rise in boiling point or fall in freezing point temperature of their solutions.

(c) What will happen to the elevation in boiling point of a solution if the weight of the solute dissolved is doubled but the weight of solvent taken is halved ?

26. (a) An organic compound 'A' (molecular formula C_3H_6O) is resistant to oxidation but forms a compound 'B' (C_3H_8O) on reduction with $LiAlH_4$. 'B' reacts with HBr to form a bromide which on treatment with alcoholic KOH forms an alkene 'C' (C_3H_6). Deduce the structures of A, B and C.

K M C

(b) State chemical tests to distinguish between the following pairs of compounds:

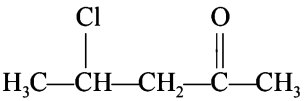
(i) Propanal and propanone.

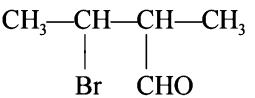
(ii) Phenol and benzoic acid.

OR

(a) An organic compound 'A', having characteristic odour, on treatment with NaOH forms two compounds 'B' and 'C'. Compound 'B' has the molecular formula C_7H_8O which on oxidation gives back compound 'A'. Compound 'C' is the sodium salt of an acid which when heated with soda lime yields an aromatic hydrocarbon 'D'. Deduce the structures of A, B, C and D.

(b) (i) Write the IUPAC name of the following compound :



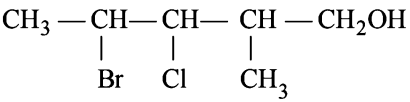
(ii) Write IUPAC name of 

$$CH_3-\underset{\text{Propene 'C'}}{CH}=CH_2 + KBr + H_2O$$

SAMPLE PAPER-2

SECTION - A

1. Chloroform ($CHCl_3$) is a compound of chlorine but it does not give white precipitate with $AgNO_3$. Why?
2. Write the rate equation for the reaction $2A + B \longrightarrow C$ if the order of the reaction is zero.
3. Give equations for the following :
   (a) $XeF_2 + H_2O \longrightarrow$ (b) $XeF_6 + H_2O \longrightarrow$
4. Gold numbers of gelatin and haemoglobins are 0.005 and 0.03 respectively. Which of them is a better protecting colloid?
5. Give IUPAC name of



SECTION - B

6. Give reasons for the following:
   (a) Concentrated nitric acid turns yellow on exposure to sunlight.
   (b) Bismuth oxide is not acidic in any of its reactions.
7. Write equations when
   (a) thionyl chloride acts upon 1-propanol.
   (b) cumene hydroperoxide is treated with dil H_2SO_4.
8. Explain why the lead storage battery needs no salt bridge.

OR

Given a galvanic cell in which the overall reaction is:

$$Zn(s) + Cl_2(g) \longrightarrow Zn^{2+} + 2Cl^-$$

If the cell uses 6·5g of Zn in the reaction, how long could it deliver 0·20 A of current to outside in the external circuit? Atomic number of Zn = 65g per mole.

9. Aluminium metal forms a cubic face centred close packed crystal structure. Its atomic radius is 125×10^{-12} m.
   (a) Calculate the length of the side of the unit cell.
   (b) How many unit cell are there in 1.0 m^3 of aluminium ?
10. (a) Write the chemical formula for pentaamminechloroplatinum (IV) chloride.
    (b) Name the type of isomerism exhibited by the following isomers:
    $[Pt(NH_3)_4][PtCl_6]$ and $[Pt(NH_3)_4Cl_2][PtCl_4]$

SECTION - C

11. (a) Assign the formula to complex formed by Fe^{2+} with following ligands

(i) three cyanide ion and three ammonia molecules.

(ii) one hydroxy ion, two ammonia molecules and three chloride ions.

(b) Write all isomers of $[Pt(NH_3)_3(SCN)](SCN)$

12. Give suitable explanations for the following :

(a) NF_3 is not hydrolysed while NCl_3 can be readily hydrolysed.

(b) H_3PO_3 a diprotic acid.

(c) Sulphur vapours exhibit some paramagnetic behaviour.

OR

Give suitable explanations for the following :

(a) SF_6 is used as a gaseous electrical insulator.

(b) NO becomes brown when released in air.

(c) NO is paramagnetic in the gaseous state but diamagnetic in the liquid and solid states.

13. In each of the following pairs, which will provide greater conduction of electricity and why?

(*i*) Copper wire at 30 °C or same copper wire at 100 °C.

(*ii*) KCl solution at 25 °C or same KCl solution at 50 °C.

(*iii*) 0·1 M NH_4OH at 25 °C or 2M NH_4OH at 25 °C.

14. (a) Cesium chloride is more stable than sodium chloride. Assign reason.

(b) Addition of $CdCl_2$ to the crystals of AgCl will produce schottky defects but the same is not produced when NaCl crystals are added. Discuss.

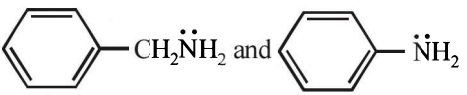
15. (a) Name two metals each of which can be obtained

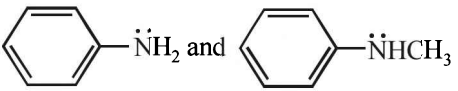
(i) by thermite process (ii) by electrolytic reduction

(iii) refined by liquation, and (iv) refined by electrolysis.

(b) Name the reducing agent which reduces the iron ore in the blast furnace.

16. Which is more basic in the following pairs? Give suitable explanation.

(i) 

(ii) 

K M C

17. An organic compound A (C_3H_5N) on boiling with alkali gives NH_3 and sodium salt of an acid B ($C_3H_6O_2$). The compound A on reduction gives C (C_3H_9N) which on treatment with nitrons acid gives an alcohol D (C_3H_8O). Identify A, B, C and D.

18. (i) Why do drugs designed to cure ailments in one body organ not affect other body parts?

(ii) Which macromolecules are chosen as drug targets?

19. (a) In reference to Freundlich adsorption isotherm write the expression for adsorption of gases on solids in the form of an equation.

(b) Write an important characteristic of lyophilic sols.

(c) Based on the type of particles of dispersed phase, give one example each of associated colloid and multimolecular colloid.

20. Give structures of monomers of the following polymers:

(i) PVC (ii) Teflon (iii) PMMA

21. (a) Explain why allyl chloride is hydrolysed more readily than *n*-propyl chloride.

(b) Vinyl chloride is hydrolysed more slowly than ethyl chloride. Explain why.

22. Consider the following data for the reaction :

$$A + B \longrightarrow \text{Products}$$

Run	Initial concentration [A]	Initial concentration [B]	Initial rate (mol $L^{-1}s^{-1}$)
1	0.10 M	1.0 M	2.1×10^{-3}
2	0.20 M	1.0 M	8.4×10^{-3}
3	0.20 M	2.0 M	8.4×10^{-3}

Determine the order of reaction with respect to A and with respect to B and the overall order of the reaction.

SECTION - D

23. Ramendra is working in a coal mine and from few days he is complaining about pain in his bones especially in his legs and arms. His supervisor asked to him to take leave for some days and go to sunny place for some days.

(a) Which vitamin deficiency may be there in Ramendra?

(b) Why his supervisor suggested him to go to a sunny place?

(c) What are the values associated with Ramendra's supervisor?

[Value Based]

SECTION - E

24. An organic compound [A] with molecular formula $C_9H_{10}O$ forms an orange-red precipitate [B] with 2, 4-DNP reagent. Compound [A] gives yellow precipitate [C] on heating with iodine in presence of sodium hydroxide along with a colourless compound [D]. The compound [A] neither reduces Tollen's reagent and Fehling's solution nor decolourises bromine water and Baeyer's reagent. On drastic oxidation with chromic acid, compound [A] gives a carboxylic acid [E] having molecular formula $C_7H_6O_2$. Deduce structures of the organic compounds [A] to [E].

OR

(a) You are provided with four reagents:

Fehling solution, I_2/NaOH, $NaHSO_3$ and Schiff's reagent. Write which reagent can be used to distinguish between the compounds in each of the following pairs:

(i) CH_3CHO and CH_3COCH_3 (ii) CH_3CHO and C_6H_5CHO

(iii) $C_6H_5COCH_3$ and $C_6H_5COC_6H_5$

(b) How will you convert?

(i) Formaldehyde to acetaldehyde

(ii) Acetaldehyde to formaldehyde

25. Explain the following:

(a) Why are Zn, Cd and Hg not considered transition metals?

(b) Why are the compounds of transition metals generally coloured?

(c) Why do Zr and Hf exhibit almost similar properties?

(d) What is the basic difference in electronic configuration of lanthanides and those of actinides?

(e) The first ionisation energies of elements of first transition series do not vary much with increasing atomic number.

OR

(a) Write the steps involved in the preparation of:

(i) $K_2Cr_2O_7$ from Na_2CrO_4

(ii) $KMnO_4$ from K_2MnO_4

(b) What is meant by lanthanoid contraction? What effect does it have on the chemistry of the elements which follow lanthanoids?

K M C

26. (*a*) Distinguish between ideal and non-ideal solution.

(*b*) Show that for a binary solution of two volatile components A and B, the total vapour pressure of solution may be expressed as:

$$P = P_A^o + (P_B^o + P_A^o) X_B$$

(*c*) Calculate the molarity of pure water.

(Density of water = 1 g/mol).

OR

(*a*) In a solution of three components A, B and C, mole fraction of A is 0·5 and that of C is 0·2. What is mole fraction of B?

(*b*) Under what condition, molality and molarity of a solution are equal?

(*c*) Calculate the osmotic pressure of mixture of 100 mL of 6% urea solution and 100 mL of 18% glucose solution at 27°C. [R = 0·0821 L atm mol^{-1} K^{-1}].

SAMPLE PAPER-3

SECTION - A

1. What causes Brownian movement in colloidal solution?
2. An alkyl halide having molecular formula C_4H_9Cl is optically active. What is its structure?
3. Arrange the following compounds in increasing order of their acid strengths.

   $(CH_3)_2CHCOOH$, $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$
4. Do vitamins provide energy to the body?
5. Give the structure of mesityl oxide.

SECTION - B

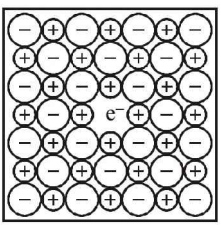
6. Arrange the following reducing agent in order of increasing reducing strength under standard state conditions. Also specify which out of following is strongest and which is weakest reducing agent?

   Al(s), Na(s), Zn(s), Ag(s)

   Given: $E^\circ_{Al^{3+}/Al} = -1{\cdot}66$ V, $E^\circ_{Na^+/Na} = -2{\cdot}71$ V, $E^\circ_{Zn^{2+}/Zn} = -0{\cdot}76$ V and $E^\circ_{Ag^+/Ag} = +0{\cdot}8$ V.
7. The following figure refers to the creation of F-centre.

   (a) What type of solids show this type of defect?

   (b) How are F-centres formed?



8. Density of Li is 0.53 g cm^{-3}. The edge length of Li is 3.5 Å. Find the number of Li atoms in a unit cell ($N_0 = 6.023 \times 10^{23}$, M = 6.94)

OR

Calculate the value of Avogadro's number from the following data : Density of NaCl = 2.165 g cm^{-3}, Distance between Na^+ and Cl^- ions in NaCl crystal = 281 pm.

9. The following values for the first order rate constant were obtained in a reaction: $T_1 = 298$ K, $k_1 = 3{\cdot}5 \times 10^5\ s^{-1}$, $T_2 = 308$ K, $k_2 = 14{\cdot}0 \times 10^{-5}\ s^{-1}$. What is E_a of reaction.

10. Complete the following chemical equations :

(a) $P_4(s) + NaOH\,(aq) + H_2O\,(l) \longrightarrow$

(b) $I^-\,(aq) + H_2O\,(l) + O_3\,(g) \longrightarrow$

SECTION - C

11. Resistance of a conductivity cell filled with 0.1 M KCl is 100 ohm. If the resistance of the same cell when filled with 0.02 M KCl solution is 520 ohms, calculate the conductivity and molar conductivity of 0.02 M KCl solution. Conductivity of 0.1 KCl solution is $1.29 \times 10^{-2}\ ohm^{-1}\ cm^{1}$.

12. Give reasons for the following :

(a) CN^- ion is known but CP^- ion is not known

(b) NO_2 dimerises to form N_2O_4

(c) ICl is more reactive than I_2.

OR

(a) Write the balanced equation for the following reaction :

$Ca_3P_2 + H_2O \longrightarrow$

(b) Discuss two similar and two dissimilar properties from the chemistry of nitrogen and that of phosphorus.

13. (a) Show graphically, how the amount of a gas adsorbed on a solid in physical adsorption varies with

(i) pressure, and (ii) temperature.

(b) Name a substance which can adsorb polluting gases present in air.

14. (a) At a site, low grade copper ores are available and zinc and iron scraps are also available. Which of the two scraps will be more suitable for reducing the leached copper ore and why?

(b) Why are metal carbonates and sulphides first converted into corresponding oxides for finally obtaining the corresponding metals?

15. (i) Give suitable reasons for following statements:

(a) HF is not stored in glass bottles but is kept in wax bottles.

(b) Interhalogen compounds are more reactive than halogens.

(ii) Complete the following reaction : $H_3PO_3 \xrightarrow{Heat}$

16. (a) Following reaction takes place in one step:

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

How will the rate of the above reaction change if the volume of the reaction vessel is diminished to one-third of its original volume? Will there be any change in the order of the reaction with reduced volume?

(b) The reaction $N_2O_5(aq) \rightarrow 2NO_2(aq) + \frac{1}{2}O_2(g)$ is found to be of first order with respect to N_2O_5. Given that k is $6.2 \times 10^{-4}\ s^{-1}$, what is the rate of reaction when molar conc. of N_2O_5 is 1.25 mol L^{-1}?

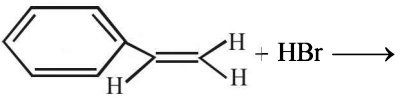
17. (i) Give suitable reasons for following statements:

(a) Two complexes of nickel $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$ have different structures but do not differ in magnetic behaviour.

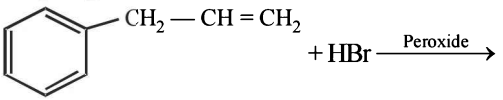
(b) Square planar complexes of MX_2L_2 type with co-ordination number of 4 exhibit geometrical isomerism while tetrahedral complexes with similar composition do not.

(ii) Among the octahedral and tetrahedral crystal fields, in which case the magnitude of crystal field splitting is larger ?

18. Write the products of the following reactions:

(a) 

(b) $CH_3CH_2CH=CH_2 + HCl$

(c) 

19. (a) An organic compound A (C_3H_5N) on boiling with alkali gives NH_3 and sodium salt of an acid B ($C_3H_6O_2$). The compound A on reduction gives C (C_3H_9N) which on treatment with nitrous acid gives an alcohol D (C_3H_8O). Identify A, B, C and D.

(b) Aniline is a weaker base than cyclohexylamine. Explain.

20. (a) Deficiency of which vitamin causes beriberi and pain in joints?

(b) Write down the structures and names of the products obtained when D–glucose is treated with

(i) acetic anhydride, (ii) hydrocyanic acid,

21. Write the information asked for the following polymers:

(a) Bakelite – Materials used for preparation.

(b) PVC – Monomer unit

(c) Synthetic rubber – Materials required for preparation.

22. Account for the following :

(a) Aspirin drug helps in the prevention of heart attack.

(b) Diabetic patients are advised to take artificial sweetners instead of natural sweetners.

(c) Detergents are non-biodegradable while soaps are biodegradable.

SECTION - D

23. Manish was driving a car with his friends. They were stopped by a policeman for driving rashly and Manish was asked to give the breath analyzer test for alcohol. He was asked to blow air into the device which contained a orange coloured solution. The solution faded in colour.

(a) What is the orange coloured solution? Why does it fade?

(b) Why are such tests conducted on drivers?

(c) Describe the values involved in the action of policeman?

SECTION - E

24. (a) Calculate the osmotic pressure of a solution obtained by mixing 100 cm^3 of 0.25 M solution of urea and 100 cm^3 of 0.1 M solution of cane sugar at 293 K. [$R = 0.082$ L atm mol^{-1} K^{-1}]

(b) What is meant by abnormal molecular mass of solute ? Discuss the factors which bring abnormality in the experimentally determined molecular masses of solutes using colligative properties.

OR

(a) Vapour pressure of pure water at 35°C is 31.82 mm Hg. When 27.0 g of solute is dissolved in 100 g of water (at the same temperature) vapour pressure of the solution, thus formed is 30.95 mm Hg. Calculate the molecular mass of solute.

(b) (i) What are non-ideal solutions ?

(ii) What role does the molecular interaction play in deciding the vapour pressure of solutions (1) alcohol and acetone (2) chloroform and acetone ?

25. (a) Write chemical equation for the conversion of:

(i) Chromite ore to sodium chromate

(ii) Pyrolusite to potassium manganate

(iii) Potassium permanganate to manganese dioxide

(b) Explain why

(i) E° for Mn^{3+}/Mn^{2+} couple is more positive than that for Fe^{3+}/Fe^{2+}. [Atomic numbers of Mn = 25, Fe = 26]

(ii) Ce^{3+} can be easily oxidised to Ce^{4+}.

[Atomic number of Ce = 58]

OR

(a) Complete the following :

(i) $Cr_2O_7^{2-}(aq) + H_2S(g) + H^+(aq) \rightarrow$

(ii) $Cu^{2+}(aq) + I^-(aq) \rightarrow$

(iii) $MnO_4^-(aq) + S_2O_3^{2-}(aq) + H_2O(l) \rightarrow$

(b) Explain why

(i) *d*-block elements have greater tendency to form complexes than *f*-block elements?

(ii) As compared to other transition elements Zn, Cd and Hg have very low melting point.

26. (a) Explain why

(i) During the preparation of ammonia derivatives from aldehydes or ketones, pH of the reaction is carefully controlled.

(ii) Carboxylic acids do not form oximes

K M C

(b) Write chemical equations to illustrate each of the following reactions

(i) Gatterman – Koch reaction

(ii) Cannizzaro reaction

OR

(a) Formic acid reduces Tollen's reagent while other carboxylic acids donot. Justify.

(b) Why are boiling points of aldehydes and ketones lower than those of the corresponding acids?

(c) Why is benzoic acid a stronger acid than acetic acid?

(d) Give IUPAC names of the following:

(*i*) $CH_3CH(CH_3)CH_2COCl$

(*ii*) $(CH_3CO)(CH_3CH_2CO)O$

543 Approved: 0777 023 444

HINTS & SOLUTIONS

Sample Paper 1

SECTION-A

1. XeF_6 is obtained by direct reaction between Xe and F_2 as follows:

$$\underset{\text{(1n 1:20 ratio)}}{Xe\,(g) + 3F_2\,(g)} \xrightarrow{573\text{ K, }60-70\text{ bar}} XeF_6\,(s)$$ **(1 mark)**

2. Haloalkanes do not dissolve in water due to the lack of hydrogen bonding among the molecules of solute and solvent. However, they dissolve in benzene (organic solvent) as the solubility is based on the principle that 'like dissolve like'.

3. Given reaction is $A + 2B \longrightarrow 3C + 2D$, thus rate of this reaction

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = \frac{1}{2}\frac{d[D]}{dt}$$

$$\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt} = \frac{1}{2}\times(1\times10^{-2}) = 0.5\times10^{-2}\text{ mol L}^{-1}\text{s}^{-1}$$ **(½ mark)**

$$\frac{d[C]}{dt} = \frac{3}{2}\frac{d[B]}{dt} = \frac{3}{2}\times(1\times10^{-2}) = 1.5\times10^{-2}\text{ mol L}^{-1}\text{s}^{-1}$$ **(½ mark)**

4. 2, 4-Dimethyl-3-(methylethyl) pentan-3-ol. **(1 mark)**

5. NH_3 is adsorbed more readily as it is more easily liquefiable compared to N_2. Moreover, NH_3 molecule has greater molecular size. **(1 mark)**

SECTION-B

6. Anhydrous calcium chloride cannot be used for drying ethyl alcohol because it forms an addition compound with the alcohol. **(1 mark)**

$4C_2H_5OH + CaCl_2\text{ (anhydrous)} \longrightarrow CaCl_2.4C_2H_5OH$ **(1 mark)**

7. Let the number of atoms of element N present in ccp $= x$

$\therefore$ The number of tetrahedral voids $= 2x$ **(½ mark)**

As 1/3rd of the tetrahedral voids are occupied by atoms of element M, therefore, number

of atoms of element M present $= \frac{1}{3}\times 2x = \frac{2x}{3}$ **(½ mark)**

$\therefore$ $N : M = x : \frac{2x}{3} = 3x : 2x = 3 : 2$

$\therefore$ The formula of the compound is N_3M_2 or M_2N_3. **(1 mark)**

8. (a) SF_6 is colourless, odourless and non-toxic gas at room temperature. It is thermally stable and chemically inert. Because of its inertness and high tendency to suppress internal discharges, it is used as a gaseous electrical insulator in high voltage generators and switch gears. **(1 mark)**

(b) Both $\overset{+1}{H_3PO_2}$ and $\overset{+3}{H_3PO_3}$ can increase the oxidation state of phosphorus upto + 5. They therefore, act as good reducing agents. However, in H_3PO_4, oxidation state of phosphorus is already + 5 (maximum possible oxidation state). It can act as an oxidising agent and not as a reducing agent. **(1 mark)**

OR

(a) XeO_3 is prepared by hydrolysis of XeF_6 or XeF_4.

$$XeF_6 + 3H_2O \xrightarrow{\text{Hydrolysis}} XeO_3 + 6HF$$

$$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$ **(1 mark)**

(b) N_2 is not reactive, particularly at ordinary conditions of temperature because there is triple covalent bond (N ≡ N) between two N-atoms. To break this bond to form N-atoms, a large amount of energy is required which is hardly available from enthalpies of reactions under ordinary conditions. **(1 mark)**

9. In this cell, Cu/Cu^{2+} electrode acts as anode, and Ag^+/Ag electrode acts as cathode. **(¼ + ¼ = ½ mark)**

(a) Standard electrode potential,

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{Anode} = 0{\cdot}80\,V - 0{\cdot}34\,V = 0{\cdot}46\,V.$$ **(½ mark)**

(b) The net cell reaction is

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

Here $n = 2$.

By Nernst equation, cell potential

$$E_{cell} = E^\circ_{cell} - \frac{2{\cdot}303\,RT}{nF}\log\frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$\therefore E_{cell} = 0{\cdot}46\,V - \frac{2{\cdot}303 \times 8{\cdot}314 \times 298}{2 \times 96500}\log\frac{2}{(0{\cdot}05)^2}$$ **(1 mark)**

$$= 0{\cdot}46 - \frac{0{\cdot}0591}{2}\log\frac{2\times10^4}{25} = 0{\cdot}46 - 0{\cdot}086 = 0{\cdot}37\,V.$$

10. (*a*) $[Fe(CN)_3(NH_3)_3]^-$ (*b*) $[Fe(OH)(NH_3)_2Cl_3]^{2-}$ **(1 + 1 = 2 marks)**

SECTION - C

11. (a) It may be remembered that higher the value of the C.N., more will be forces of attraction in the closely packed cations and anions and, thus, greater will be the stability of the crystal lattice. Ceasium chloride has higher C.N. (8 : 8) than sodium chloride (6 : 6) and is therefore, more stable in nature. **(1½ mark)**

(b) When $CdCl_2$ is added to the crystals of AgCl, the replacement of one Ag^+ ion with Cd^{2+} ion necessitates the removal of second Ag^+ ion from the lattice to maintain the electrical neutrality of the crystal. However, the same does not take place in case of NaCl because both Ag^+ and Na^+ ions are monovalent. Thus, Schottky defects are caused by the addition of $CdCl_2$ and not by NaCl. **(1½ mark)**

12. (a) The stability of the lyophobic colloid is only on account of charge while the stability of lyophilic colloid is on account of charge as well as solvation of colloidal particles. **(1 mark)**

(b) $Fe(OH)_3$ sol is positively charged which is coagulated by negatively charged Cl^- ion present in sodium chloride solution. **(1 mark)**

(c) Sky appears blue in colour due to scattering of light by colloidal particles like dust, mist etc. **(1 mark)**

OR

(a) Ferric hydroxide sol which is obtained by hydrolysis of $FeCl_3$ is positively charged because of preferential adsorption of ferric ions (Fe^{3+}) by colloidal particles from the solution. **(1 mark)**

(b) Adsorption is an exothermic process. According to Le Chatelier's principle, the magnitude of adsorption should decrease with rise in temperature and this is actually so. **(1 mark)**

(c) River water contains colloidal particles of clay, mud, etc., which are charged. Sea water contains large quantity of number of dissolved salts and acts as a sort of electrolyte. When river water comes in contact with sea water, coagulation of colloidal particles occurs. These coagulated clay, sand particles, etc., settle down at the point of contact resulting in the rise of river bed. This leads river water of adopt different course and a delta is formed in due course of time. **(1 mark)**

13. (*i*) The current stops flowing due to accumulation of charges in two half-cells, if no salt bridge (or porous pot) were used in galvanic cell. At anode, the charge gets accumulated due to formation of Zn^{2+} ions while at cathode negative charge gets accumulated due to discharge of Cu^{2+} ions (*i.e,* excess of SO_4^{2-} ions). Also, the inner circuit is not complete. **(1 mark)**

(*ii*) HCl will have higher value of λ_m^∞. This is due to the fact that H^+ being small in size has greater ionic mobility as compared to Na^+. **(1 mark)**

(*iii*) Equivalent weight of $Al_2(SO_4)_3 = \dfrac{\text{Molecular weight}}{6}$ **(1 mark)**

$\Rightarrow$ 1 mole = 6 equivalents

$\therefore \lambda_m = 6 \times \lambda_{eq}$

14. (i) (a) $[Ni(CN)_4]^{2-}$ has square planar geometry on account of dsp^2 hybridisation. **(1 mark)**

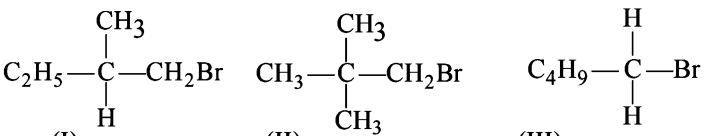
(b) $[Ag(NH_3)_2]^+ Cl^-$ remains colourless in aqueous solution. The complex does not have unpaired electron in central cation, Ag^+ and thus d-d transition is not possible. Ag in + 1 oxidation state which has electronic configuration : $[Kr]_{36}\, 4d^{10}\, 5s^0$. **(1 mark)**

(ii) The IUPAC name is Dichlorobis (ethylene-diammine) cobalt (III) chloride. **(1 mark)**

15. (a) Though the energy possessed by molecules is more than the threshold energy and the reaction should proceed at a reasonable rate yet in some cases the reaction is slow. It is due to the fact that in such cases the reacting molecules are **not** properly oriented. Due to this the number of effective collision decreases and so the reaction is slower than expected rate. **(1 + 1 = 2 marks)**

(b) By taking one of the reactants in large excess so that it may not contribute towards the order. **(1 mark)**

16. (a) All are primary alkyl halides and their structural formulae are:



(I) (II) (III)

The order of reactivity is : (III) > (I) > (II)

(½ mark)

Explanation : The S_N2 reactions are sensitive to steric hindrance. Greater the steric hindrance (near –Br) to the attacking nucleophile, lesser will be the reactivity. In the light of this, the reactivity order is justified. **(1 mark)**

(b) $CH_3F < CH_3Cl < CH_3Br < CH_3I$ **(½ mark)**

In these nucleophilic substitution reactions, the nucleophile is to displace the halide ion (X^-). Greater the bond dissociation enthalpy of the C—X bond, difficult is its cleavage and lesser will be the reactivity. The order of bond dissociation enthalpy of different C—X bond is

C — F > C — Cl > C — Br > C — I

The order of reactivity towards S_N2 reactions is the reverse. **(1 mark)**

17. (a) Silicon can reduce MgO above 1966 K. **(1 mark)**

(b) Aluminium can reduce MgO above 1623 K. **(1 mark)**

(c) Carbon cannot reduce MgO at any temperature. **(1 mark)**

18. To explain the above, it has been suggested that glucose does not have an open chain structure rather it has a *cyclic structure* in which the aldehydic (–CHO) group is a part of the six membered oxide ring (δ-oxide ring). **(1½ marks)**

Sodium bisulphite, ammonia etc. fail to cleave the ring but Tollen's reagent and Fehlings solutions etc. are strong enough to cleave the ring and then –CHO group is free to give its characteristic reactions. **(1½ marks)**

19. (i) Role of sulphur in the vulcanisation of rubber

Natural rubber becomes soft at high temperatures (> 335K) and brittle at low temperatures (< 283K).

Moreover, it is soluble in non-polar solvents and is non-resistant to the attacks by oxidising agents.

Sulphur is therefore added during its manufacturing to overcome these limitations. Sulphur forms cross linkages at reactive sites of double bonds and thus, the rubber gets stiffened. **(1 mark)**

(ii) Name of the polymer : Glyptal

Monomers:

(a) Ethylene glycol (b) Phthalic acid **(1 mark)**

(iii) Fibres have the strongest intermolecular forces, elastomers while have the least. Thermoplastics have the intermolecular forces intermediate between elastomers and fibres.

Thus, the increasing order of the intermolecular forces of the given polymers is as follows :

Neoprene < Polythene < Terylene **(1 mark)**

20. (a)

Thermosetting polymer	Thermoplastic polymer
(i) Cannot be reshaped on heating.	(i) Can be heated and then moulded in a desired shape.
(ii) Has extensive cross-linking.	(ii) No cross linking between the chains.
(iii) Examples are bakelite and melamine.	(iii) Examples are polythene and polystyrene. **(2 marks)**

(b) Bakelite. **(1 mark)**

21. (a) It is because Cl has vacant *d*-orbitals. F does not have *d*-orbitals so, it cannot show higher oxidation state. **(1 mark)**

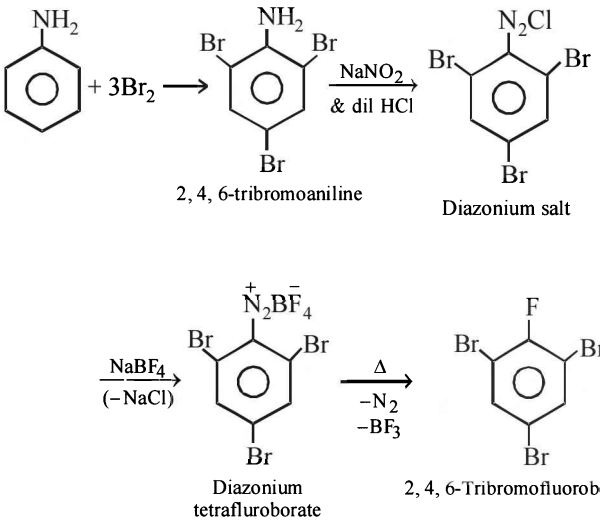
(b) (i) Water is liquid, others are gases (ii) Water is thermally most stable among hydrides of group 16 elements. This is due to intermolecular hydrogen bonding.

(½ + ½ = 1 mark)

(c) $HClO > HClO_2 > HClO_3 > HClO_4$.

HClO is unstable, breaks down to HCl and [O] due to which it is strong oxidising agent whereas others give oxygen less easily. Greater the oxidation state of Cl in the acid, lower the oxidising power. **(1 mark)**

22. Final product obtained is 2, 4, 6-tribromofluorobenzene

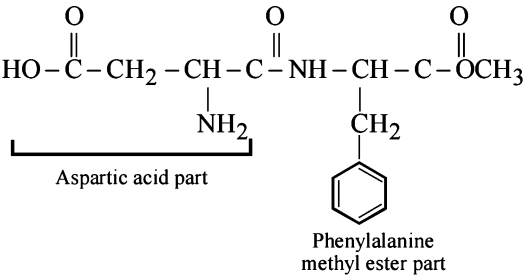


(3 marks)

SECTION - D

23. (a) Raveena preferred sucralose over aspartame because sucralose does not provide calorie. **(1 mark)**

(b)



(1 mark)

(c) Helping and caring behavior, sensitivity and awareness towards health **(1 mark)**

SECTION - E

24. (a) (i) + 2 oxidation state of Mn is most stable. In this oxidation state, it has exactly half-filled *d*-orbitals.

(ii) Osmium, (Os) shows highest oxidation state in osmium tetraoxide (OsO_4).

(iii) Osmium (Os) is the densest transition element.

(1 + 1 + 1 = 3 marks)

(b) Balanced ionic equations for the reactions are given below:

(i) $[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$

$$\left[\begin{array}{l} COO^- \\ | \\ COO^- \end{array} \longrightarrow 2CO_2 + 2e^-\right] \times 5$$

$$2MnO_4^- + 5\begin{array}{l} COO^- \\ | \\ COO^- \end{array} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

(1 mark)

(ii)

$$6e^- + 14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$2I^- \longrightarrow I_2 + 2e^-] \times 3$$

$$14H^+ + Cr_2O_7^{2-} + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$$

(1 mark)

OR

(a) (i) It is due to poor shielding effect of 4f-electrons. As effective nuclear charge increases, ionic size decreases. **(1 mark)**

(ii) Ionic character of metal halide depends upon the electronegativity difference between the metal and halogen. F is more electronegative than Cl, Br, therefore fluorides are ionic whereas chlorides and bromides are covalent in nature. **(1 mark)**

(b) The information suggests that the gas (A) is H_2S while the gas (B) is SO_2. Both turn acidified $K_2Cr_2O_7$ paper green.

(1 mark)

$$K_2Cr_2O_7 + 4H_2SO_4 + \underset{\text{(Gas A)}}{3H_2S} \longrightarrow K_2SO_4 + \underset{\text{(green)}}{Cr_2(SO_4)_3} + 7H_2O + 3(S)$$

(½ mark)

$$K_2Cr_2O_7 + H_2SO_4 + \underset{\text{(Gas B)}}{3SO_2} \longrightarrow K_2SO_4 + \underset{\text{(green)}}{Cr_2(SO_4)_3} + H_2O$$

(½ mark)

$$\underset{\text{(Gas A)}}{H_2S} + (CH_3COO)_2Pb \longrightarrow \underset{\text{(Black ppt.)}}{PbS} + 2CH_3COOH$$

(½ mark)

$$\underset{\text{(Gas A)}}{2H_2S} + \underset{\text{(Gas B)}}{SO_2} \longrightarrow 2H_2O + \underset{\text{(Yellowish turbidity)}}{3S}$$

(½ mark)

25. (a) **Step I.**

Calculation of the Van't Hoff factor (i)

Calcium nitrate dissociates in aqueous solution as :

$$Ca(NO_3)_2 \rightleftharpoons Ca^{2+}(aq) + 2NO_3^-(aq)$$ **(¼ mark)**

$$\alpha = \frac{i-1}{n-1}$$ **(¼ mark)**

$$0.7 = \frac{i-1}{3-1}$$ **(¼ mark)**

or $i = 0.7 \times 2 + 1 = 2.4$ **(¼ mark)**

Step II

Calculation of vapour pressure of the solution

According to Raoult's Law,

$$\frac{P_A^\circ - P_S}{P_S} = ix_B = i\frac{n_B}{n_A}; \frac{P_A^\circ - P_S}{P_S} = \frac{i \times W_B \times M_A}{M_B \times W_A}$$ **(½ mark)**

$P_A^\circ = 760$ mm, $i = 2.4$, $W_B = 7.0$ g, $M_B = 164$ g mol^{-1} (for calcium nitrate)

$W_A = 100$ g, $M_A = 18$ g mol^{-1}

$$\therefore \frac{760 - P_S}{P_S} = \frac{2.4 \times (7.0\text{g}) \times (18\text{g mol}^{-1})}{(164\text{ g mol}^{-1}) \times (100\text{ g})} = 0.0184$$ **(½ mark)**

$$\text{or } \frac{760 - P_S}{P_S} = 0.0184 \quad \text{or} \quad \frac{760}{P_S} - 1 = 0.0184;$$

$$P_S = \frac{760}{1.0184} = 746.3 \text{ mm}$$ **(1 mark)**

(b) Three, $Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$ **(1 mark)**

(c) Ethylene glycol ($C_2H_6O_2$). This is because, it has lower molecular weight and hence contains more moles for the same mass of glycerine. **(1 mark)**

OR

(a) **In case of naphthalene**

Mass of naphthalene (W_B) = 0.5126 g

Mass of carbon tetrachloride (W_A) = 50.0 g = 0.050 kg

Molar mass of naphthalene (M_B) = 128 g mol^{-1}

Elevation in boiling point (ΔT_b) = 0.402 K

$$K_b = \frac{M_B \times \Delta T_b \times W_A}{W_B}$$ **(¼ mark)**

$$= \frac{(128\text{g mol}^{-1}) \times (0.402\text{ K}) \times (0.050\text{ kg})}{(0.5126\text{ g})}$$ **(¼ mark)**

$$= 5.019 \text{ K kg mol}^{-1}$$ **(½ mark)**

In case of unknown solute,

Mass of solute (W_B) = 0.6216 g

Mass of solvent (W_A) = 50.0 g = 0.05 kg

Elevation in b.p (ΔT_b) = 0.647 K

Molal elevation constant (K_b) = 5.019 K kg mol^{-1}

$$M_B = \frac{K_b \times W_B}{\Delta T_b \times W_A}$$ **(¼ mark)**

$$= \frac{(5.019 \text{ K kg mol}^{-1}) \times (0.6216 \text{ g})}{(0.647 \text{ K}) \times (0.05 \text{ kg})}$$ **(¼ mark)**

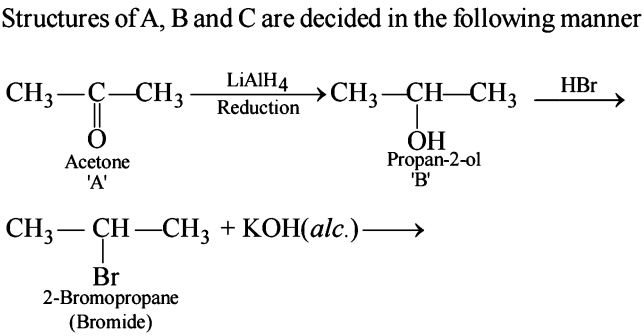
$$= 96.44 \text{ g mol}^{-1}$$ **(½ mark)**

(b) Both elevation in boiling point temperature and depression in freezing point temperature are not so useful for determining the molar mass of macro-molecules because ΔT is very small in both the cases. Moreover some macro-molecules, proteins in particular break at elevated temperatures. Under the circumstances, osmotic pressure is most widely used. It can be determined even at room temperature. **(2 marks)**

(c) The elevation in boiling point will become four times because

$$\Delta T_b = K_b \frac{W_2 \; 1000}{M_2 \; W_1}$$ **(1 mark)**

26. (a) Structures of A, B and C are decided in the following manner:



$$CH_3-\underset{\text{Propene 'C'}}{CH=CH_2} + KBr + H_2O$$

(1+1+1 = 3 marks)

(b) (i) **Propanal and propanone :** The two compounds can be distinguished by iodoform test. Propanone contains CH_3CO- group and gives iodoform test while propanal (CH_3CH_2CHO) does not give iodoform test.

$$CH_3COCH_3 + 3NaOI \longrightarrow CH_3COONa + 2NaOH + \underset{\text{Iodoform}}{CHI_3}$$

(1 mark)

(ii) **Phenol and benzoic acid :** The two compounds can be distinguished as under:

Ferric chloride test : Phenol gives a violet colour with aqueous $FeCl_3$, while benzoic acid gives buff coloured ppt. of ferric benzoate. **(1 mark)**

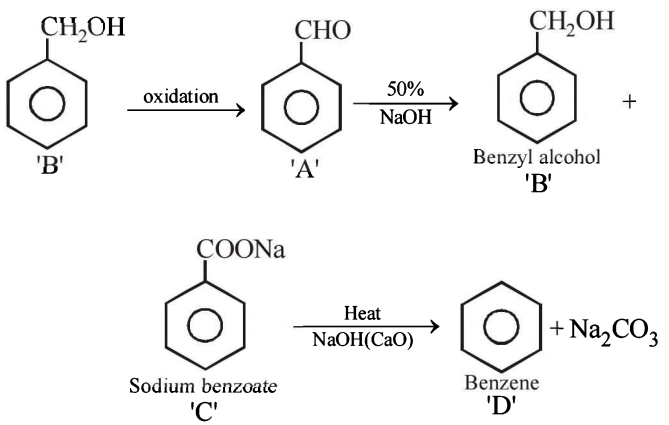
$$\underset{\text{Phenol}}{3C_6H_5OH} + FeCl_3 \longrightarrow \underset{\text{Violet colour}}{(C_6H_5O)_3Fe} + 3HCl$$

$$\underset{\text{Benzoic acid}}{3C_6H_5COOH} + FeCl_3 \longrightarrow \underset{\substack{\text{Ferric benzoate}\\ \text{(Buff coloured ppt.)}}}{(C_6H_5COO)_3Fe} + 3HCl$$

Alternatively, benzoic acid gives effervescences of CO_2 with $NaHCO_3$ solution, while phenol does not give.

OR

(a)



(1 + ½ + ½ + 1 = 3 marks)

(b) (i) 4-Chloropentan-2-one.

(ii) 3-Bromo-2-methylbutanal. **(1 + 1 = 2 marks)**

Sample Paper 2

SECTION - A

1. This is because in $CHCl_3$, all the three chlorine atoms are bonded to carbon atom by covalent bonds and there is no free chloride ions; $AgNO_3$ gives white precipitate only when free chloride ions are present in solution. **(1 mark)**

2. Rate $= k\,[A]^0[B]^0$ or Rate $= k$ **(1 mark)**

3. (a) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$ **(½ mark)**

(b) $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$ **(½ mark)**

4. Gelatin is a better protecting colloid as it has lesser gold number than haemoglobin. **(1 mark)**

5. 4-Bromo-3-chloro-2-methylpentan-1-ol. **(1 mark)**

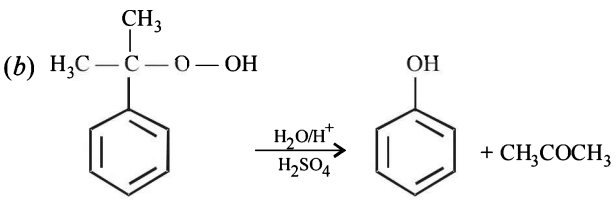
SECTION - B

6. (a) It is because nitric acid decomposes to NO_2 which is brown in colour and makes HNO_3 yellow. **(1 mark)**

(b) As we move down a group in *p*-block, metallic character increases, Bi being the last element in Group 15 is metallic in nature. Oxides of metals are basic. **(1 mark)**

7. (*a*) $CH_3CH_2CH_2OH + SOCl_2 \xrightarrow{\Delta} CH_3CH_2CH_2CH_2Cl + SO_2 + HCl$

(*b*)



8. In the lead storage battery, the oxidising agent, PbO_2, and the reducing agent, Pb, as well as their oxidation and reduction products, $PbSO_4$ are solids. **(2 marks)**

Thus, all the reagents can be placed in the same cell.

OR

$$Zn(s) + Cl_2(g) \xrightarrow{K} Zn^{2+}{}^{M} + 2Cl^{-}{}^{C}$$

Here Zn is oxidised as zinc is anode.

Anode reaction : $Zn\,(s) \longrightarrow Zn^{2+} + 2e^-$

$1\text{ mol} = 65g \qquad 2F = 2 \times 96500C$

As can be seen from above reaction, 65g of Zn produces = 2× 96500C **(½ mark)**

∴ 6·5g of Zn will produces

$= \frac{2\times96500}{65}\times6{\cdot}5\,C = 19300\text{ C of charge}$ **(½ mark)**

We know that, $Q = I \times t \Rightarrow 19300 = 0{\cdot}2 \times t$

Time, $t = \frac{19300}{0{\cdot}2} = 96500$ sec. **(½ mark)**

Time for which it can deliver 0·2 A = 96500 sec. = $\frac{19600}{60\times60}$ hours

= 26·80 hours. **(½ mark)**

9. (a) For a face centred cubic lattice (fcc).

Radius (r) = $\frac{a}{2\sqrt{2}}$ **(¼ mark)**

$a = r \times 2\sqrt{2} = 125 \times 10^{-12} \times 2\sqrt{2}\,m$ **(¼ mark)**

$= 125 \times 2 \times 1.414 \times 10^{-12} = 354 \times 10^{-12}$ m **(½ mark)**

(b) Volume of unit cell $(a)^3 = (354 \times 10^{-12})^3 m^3 = 4.436 \times 10^{-29} m^3$ **(½ mark)**

No. of unit cells in 1.0 m^3 of Al

$= \frac{(1.0\,m^3)}{(4.436\times10^{-29}\,m^3)} = 2.25\times10^{28}$ **(½ mark)**

10. (a) $[PtCl(NH_3)_5]Cl_3$ **(1 mark)**

(b) Coordination isomerism. **(1 mark)**

SECTION - C

11. (a) (i) $[Fe(CN)_3(NH_3)_3]^-$ **(1 mark)**

(ii) $[Fe(OH)(NH_3)_2Cl_3]^{2-}$ **(1 mark)**

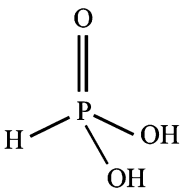
(b) The complex contains ambidentate ligand, SCN which is capable of linking itself through either S (as – SCN) or N (as – NCS), following two isomers are possible:

$[Pt(NH_3)_3(-SCN)](SCN)$ and $[Pt(NH_3)_3(-NCS)](SCN)$

These are linkage isomers. **(1 mark)**

12. (a) Both nitrogen and fluorine atoms do not have any vacant d-orbitals to accept electron pairs from the oxygen atom in H_2O molecule. Therefore, NF_3 cannot be hydrolysed. However, in case of NCl_3 chlorine has vacant d-orbitals which can take up electron pairs from H_2O molecules. Therefore, NCl_3 can be hydrolysed $NCl_3 + 3H_2O \longrightarrow NH_3 + 3HClO$ **(1 mark)**

(b) In the structural formula, phosphorus acid (H_3PO_3) has only two OH groups and therefore, there are only two ionisable hydrogen atoms. Since the third hydrogen atom is attached directly to the phosphorus atom, it is not ionisable. Thus the acid is diprotic in nature. **(1 mark)**



(c) In the vapour state sulphur partly exists as S_2 molecules similar to O_2 molecules. Just like oxygen, sulphur molecule has also two unpaired electrons in the antibonding π^* orbitals. Therefore, it exhibits paramagnetic character in the vapour state.

(1 mark)

OR

(a) SF_6 is colourless, odourless and non-toxic gas at room temperature. It is thermally stable and chemically inert. Because of its inertness and high tendency to suppress internal discharges, it is used as a gaseous electrical insulator in high voltage generators and switch gears. **(1 mark)**

K M C

(b) NO readily combines with O_2 of the air to form NO_2 which has brown colour.

$$\underset{\text{(Colourless)}}{2NO} + O_2 \longrightarrow \underset{\text{(Brown)}}{2NO_2}$$ **(1 mark)**

(c) NO has an odd number of valance electrons, five of N & six of oxygen (total 11) and hence all the electrons are not paired. One electron remains unpaired so it is paramagnetic in the gaseous state. But in liquid and solid states, it exists as a symmetrical or asymmetrical dimer (N_2O_4) and hence is diamagnetic in these states with 34 electrons. **(1 mark)**

13. (*i*) Copper wire at 30 °C will have greater conductance. This is because metallic conduction decreases with increase in temperature due to vibration of kernels.

(*ii*) KCl solution at 50 °C will have greater conductance. This is because ionic mobilities increases with increase in temperature.

(*iii*) 0·1 M NH_4OH at 25 °C. This is because dissociation increases with dilution.

14. (a) It may be remembered that higher the value of the C.N., more will be forces of attraction in the closely packed cations and anions and, thus, greater will be the stability of the crystal lattice. Ceasium chloride has higher C.N. (8 : 8) than sodium chloride (6 : 6) and is therefore, more stable in nature.

(1½ marks)

(b) When $CdCl_2$ is added to the crystals of AgCl, the replacement of one Ag^+ ion with Cd^{2+} ion necessitates the removal of second Ag^+ ion from the lattice to maintain the electrical neutrality of the crystal. However, the same does not take place in case of NaCl because both Ag^+ and Na^+ ions are monovalent. Thus, Schottky defects are caused by the addition of $CdCl_2$ and not by NaCl. **(1½ marks)**

15. (a) (i) Chromium and manganese

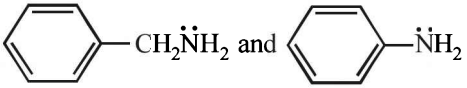
(ii) Sodium and mangnesium

(iii) Tin and lead

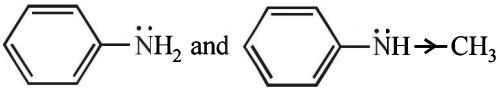
(iv) Copper and silver **(½ + ½ + ½ + ½ = 2 marks)**

 Approved: 0777 023 444

(b) In the blast furnace, iron ore is reduced by carbon monoxide (CO). So, reducing agent which reduces iron ore to iron is carbon monoxide. **(1½ marks)**

16. (i) 

Benzylamine is more basic than aniline because in aniline the electron pair on the nitrogen atom is involved in conjugation with the π-electrons of the ring, hence involved in resonance and not easily available for protonation. As no such conjugation is possible in benzylamine, its electron pair donating tendency is more. Thus, it is a stronger base than aniline. **(1½ marks)**

(ii) 

N-Methylaniline is more basic than aniline because the $-CH_3$ group with + I effect increases the electron density on the nitrogen atom. As a result, its electron releasing tendency is more than that of aniline, hence it is more basic. **(1½ marks)**

17. As compound A gives NH_3 and carboxylic acid on hydrolysis with NaOH, it must be an organic cyanide. This is also indicated by the fact that A on reduction gives C which has four H-atom more than A. The compound C is primary amine as it reacts with HNO_2 forms an alcohol D. The sequence of reactions are: **(2 marks)**

$$\underset{\substack{\text{Propananitrile}\\(A)}}{CH_3CH_2C\equiv N} \xrightarrow[\text{Heat}]{\text{Alkali}} \underset{\substack{\text{Propanoic}\\\text{acid (B)}}}{CH_3CH_2COOH} + NH_3$$

$$\downarrow \text{Reduction}$$

$$\underset{\substack{\text{1-aminopropane}\\(C)}}{CH_3CH_2CH_2NH_2} \xrightarrow{HONO} \underset{\substack{\text{1-propanol}\\(D)}}{CH_3CH_2CH_2OH} + N_2 + H_2O$$

(½ + ½ + ½ + ½)

18. (i) This is because drugs work on different receptor. For example, secretion of histamine causes allergy. It also causes acidity due to release of hydrochloric acid in the stomach. Since antiallergic and antacids drugs work on different receptors, therefore, antihistamines remove allergy while antacids remove acidity. **(2 marks)**

(ii) Macromolecules such as proteins, nucleic acids, carbohydrates and lipids are called drug targets. **(1 mark)**

K M C

19. (a) According to Frendlich adsorption isotherm, the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature is given by the following equation :

$$\frac{x}{m} = kp^{1/n} \quad (n > 1)$$

where x→is mass of the gas adsorbed on mass m of the adsorbent at pressure P

k and n → constants **(1 mark)**

(b) Lyophilic sols are liquid-loving and can be prepared by directly mixing the dispersed phase and dispersion medium. An improtant characteristic of these sols is that if dispersion medium is separated from dispersed phase, the sol can be reconstituted by simply remixing the dispersion medium. **(1 mark)**

(c) An example of

(i) multimolecular colloid : gold sol, sulphur sol

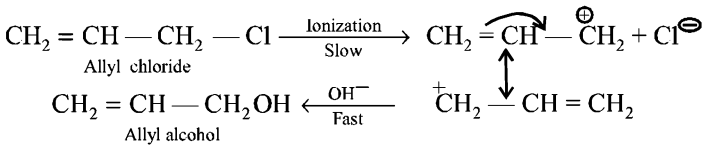
(ii) associated colloid : soaps, synthetic detergents **(1 mark)**

20. (*i*) $CH_2=CHCl$ **(1 mark)**

(*ii*) $F_2C=CF_2$ **(1 mark)**

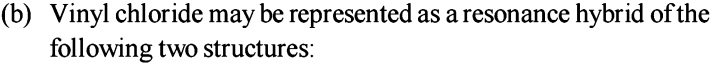
(*iii*) $CH_2=C(COOCH_3)(CH_3)$ **(1 mark)**

21. (a) Allyl chloride readily undergoes ionization to produce resonance stabilized allyl carbocation. Since carbocations are reactive species, therefore, allyl cation readily combines with OH^- ions to form allyl alcohol. Corresponding formation of *n*-propyl carbocation is not easy because of its less stability. So *n*-propyl chloride does not hydrolyse easily.



(1½ marks)

(b) Vinyl chloride may be represented as a resonance hybrid of the following two structures:



As a result of resonance, the carbon-chlorine bond acquires some double bond character, hence it is stronger and difficult to cleave. In contrast, in ethyl chloride the carbon-chlorine bond is a pure single bond. Thus, vinyl chloride undergoes hydrolysis more slowly than ethyl chloride. **(1½ marks)**

22. The rate law may be expressed as :

$$\text{Rate} = k[A]^p[B]^q$$

$$(\text{Rate})_1 = k[0.1]^p[1.0]^q = 2.1 \times 10^{-3} \quad \text{... (i)}$$

(¼ mark)

$$(\text{Rate})_2 = k[0.2]^p[1.0]^q = 8.4 \times 10^{-3} \quad \text{...(ii)}$$

(¼ mark)

$$(\text{Rate})_3 = k[0.2]^p[2.0]^q = 8.4 \times 10^{-3} \quad \text{...(iii)}$$

(¼ mark)

Dividing equation (iii) by (ii),

$$\frac{(\text{Rate})_3}{(\text{Rate})_2} = \frac{k[0.2]^p[2.0]^q}{k[0.2]^p[1.0]^q} = \frac{8.4\times10^{-3}}{8.4\times10^{-3}}$$ **(½ mark)**

$$[2]^q = [2]^0;\ q = 0$$ **(½ mark)**

Dividing equation (ii) by (i),

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{k[0.20]^p[1.0]^q}{k[0.10]^p[1.0]^q} = \frac{8.4\times10^{-3}}{2.1\times10^{-3}} = 4$$ **(½ mark)**

$$[2]^q = [2]^2;\ p = 2$$ **(½ mark)**

Order w.r. t. A = 2 ; B = 0 ; Overall order = 2. **(¼ mark)**

SECTION - D

23. (a) Vitamin D **(1 mark)**

(b) This is because sunlight is a richest source of vitamin D.

(c) Awareness towards health, helpful to others, presence of mind, understand his moral duty etc. are some values displayed by Ramendra's supervisor.

SECTION - E

24. (i) Positive test with 2, 4-DNP and negative tests with Tollen's reagent and Fehling solution suggest that the compound [A] is a ketone. Since it responds to iodoform test (I_2/NaOH), it must be a methyl ketone (CH_3COR). **(1 mark)**

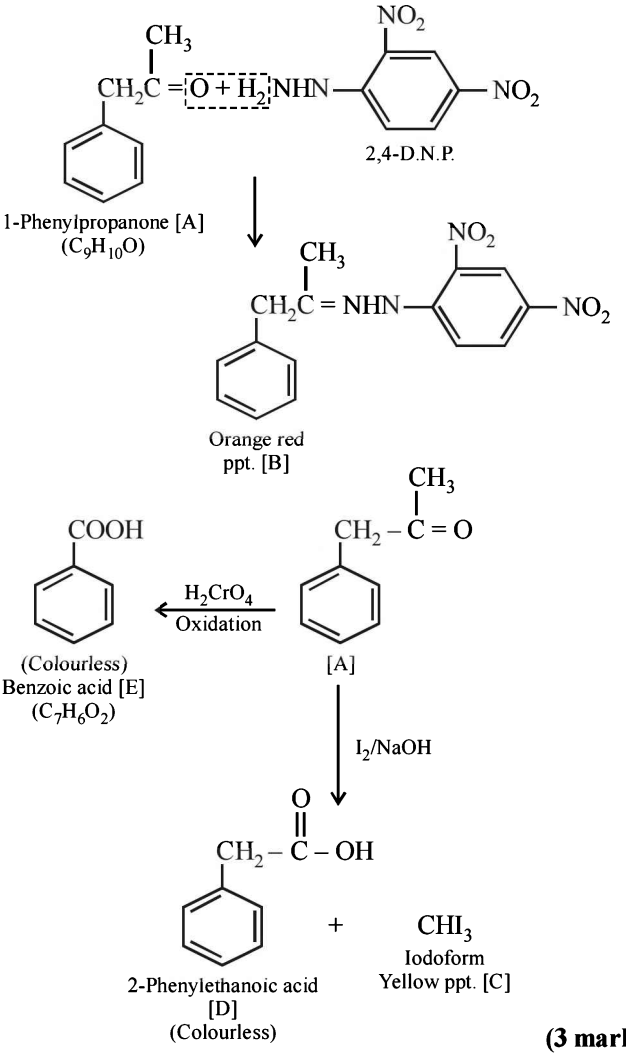
K M C

(ii) The molecular formula suggests a high degree of unsaturation which is ruled out because it does not decolourise either bromine water or Baeyer's reagent. Thus, we may conclude that it is an aromatic compound and the side chain has $-COCH_3$ group.

(1 mark)

(iii) Thus, the compound [A] is $C_6H_5CH_2COCH_3$ (1– phenylpropanone).

The reactions involved are as follows :



(3 marks)

(a) (i) Schiff's reagent, or Fehling solution **(1 mark)**

(ii) I_2/NaOH **(1 mark)**

(iii) I_2/NaOH. **(1 mark)**

(b) (i) Formaldehyde to acetaldehyde

$$\underset{\text{Formaldehyde}}{HCHO} \xrightarrow{CH_3MgBr} \underset{\text{[Addition compound]}}{CH_3CH_2OMgBr} \xrightarrow{H_2O}$$

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{\text{Oxidation}} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

(1 mark)

(ii) Acetaldehyde to formaldehyde

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{\text{Oxidation}} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[-H_2O]{NH_3/\text{Heat}}$$

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{Br_2/KOH} \underset{\text{Methyl amine}}{CH_3NH_2} \xrightarrow{HONO}$$

$$\underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{\text{oxide}} \underset{\text{Formaldehyde}}{HCHO}$$

(1 mark)

25. (a) These elements do not fulfill the condition or definition of a transition element and do not show any characteristic of the property of a transition element. It is because neither, these elements nor their ions have incompletely filled d-orbitals.

(1 mark)

(b) Transition metal atoms or their ions have generally partially filled d-orbitals and thus can undergo d-d transitions by absorbing light from visible region and radiate complimentary colour. **(1 mark)**

(c) Due to lanthanide contraction, their atomic and ionic sizes are almost equal. **(1 mark)**

(d) 4f-orbitals are progressively filled in lanthanides whereas in actinides 5f-orbitals are progressively filled up. **(1 mark)**

(e) Atomic size does not very much due to shielding effect of $(n-1)$ *d*-electrons on nucleus. Thus, effective nuclear charge does not very much. **(1 mark)**

OR

(a) Steps involved in the preparation of $K_2Cr_2O_7$ and $KMnO_4$ are explained with the help of following equations:

(i) $2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$ **(1 mark)**

(ii) $MnO_4^{2-} \xrightarrow{\text{electrolysis}} MnO_4^- + e^-$ **(1 mark)**

(b) The decrease in atomic and ionic size with the increase in atomic number in lanthanoids is called lanthanoid contraction. **(1 mark)**

It has the following effects:

(i) The ionisation energy in 5d series is more than that in 3d and 4d series. **(1 mark)**

(ii) There is resemblance between properties of elements 4d and 5d transition series. **(1 mark)**

26. (a)

	Ideal Solution		Non-ideal solution
(i)	The interactions between components are similar to those in pure components.	(i)	The interactions between components are different from those in pure components.
(ii)	There is no volume change and enthalpy change on mixing the components. ($\Delta V = 0$, $\Delta H = 0$)	(ii)	$\Delta V \neq 0$, $\Delta H \neq 0$ on mixing the components.
(iii)	Each component obeys Raoult's law at all temperatures and concentrations i.e, $P_A = x_A P_A°$ and $P_B = x_B P_B°$	(iii)	They do not obey Raoult's law. They show positive or negative deviations from Raoult's law, i.e., P_A ? $x_A P_A°$ and P_B ¹ $x_B P_B°$
(iv)	They do not form azeotropes.	(iv)	They form azeotropes.

(2 marks)

(*b*) By Raoult's Law,

$P_A = P_A^o X_A$ and $P_B = P_B^o X_B$

Total vapour pressure, *i.e.*, $P = P_A + P_B = P_A^o X_A + P_B^o X_B$

We know that $X_A = 1 - X_B$

$P_A = P_A^o (1 - X_B) + P_B^o X_B$

$= P_A^o - P_A^o X_B + P_B^o X_B = P_A^o + (P_B^o - P_A^o) X_B$. **(1½ marks)**

(*c*) Consider 1 litre of pure water, *i.e.*, 1000 mL

Weight of 1000 mL of water = Volume × Density

= 1000 × 1 = 1000 g.

$$\text{Moles of water} = \frac{1000}{18} = 55{\cdot}55 \text{ moles}$$

Hence, 55·55 moles of water are present in one litre of water

∴ Molarity of water = 55·55 M. **(1½ marks)**

OR

(*a*) In a solution, sum of mole fractions of all components is unity.

∴ $X_A + X_B + X_C = 1$

∴ $X_B = 1 - (X_A + X_C) = 1 - (0{\cdot}5 + 0{\cdot}2) = 0{\cdot}3$. **(1½ marks)**

(*b*) $M = \dfrac{n_B}{V \text{ in litres}}$ and $m = \dfrac{n_B}{W \text{ in kg}}$

Where M is molarity and m is molality.

M and m will be equal if 1 litre of solution has mass of 1 kg.

This is generally true in case of very dilute aqueous solutions at room temperature when density of solution can be taken as 1 g cm^{-3}. **(1½ marks)**

(c) Total volume of solution $= V = 100 + 100 = 200\,mL = 0{\cdot}2\,L$

After mixing of two solutions, 6g of urea is present in 200 mL solution.

$$\therefore \pi_1 = \frac{n_B}{V} RT = \frac{6/60}{0{\cdot}2} \times \frac{0{\cdot}0821 \times 300}{1} = 12{\cdot}315\,atm$$

(When molar mass of urea NH_2CONH_2

$= 2 \times 14 + 12 + 16 + 4 \times 1 = 60$)

Similarly, 18g of glucose ($C_6H_{12}O_6$) is present in 200 mL solution. **(2 marks)**

Osmotic pressure due to glucose,

$$\pi_2 = \frac{n_B}{V} RT = \frac{18 \times 0{\cdot}0821 \times 300}{180 \times 0{\cdot}2}\,atm = 12{\cdot}315\,atm$$

The two solutes behave independently and total osmotic pressure is the sum of two.

$\therefore$ Osmotic pressure of mixture, $\pi = \pi_1 + \pi_2$

$= 12{\cdot}315 + 12{\cdot}315 = 24{\cdot}630\,atm.$

Sample Paper 3

SECTION-A

1. It is the unbalanced bombardment of molecules of dispersed phase with molecules of dispersion medium which causes Brownian movement. **(1 mark)**

2. $CH_3-\overset{*}{C}H(Cl)-CH_2-CH_3$ **(1 mark)**

2-chlorobutane

3. $(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$ **(1 mark)**

4. No, they don't provide energy to the body.

5. $CH_3-C(CH_3)=CH-COCH_3$

6. From the value of reduction potentials we can arrange the reducing agents as: Ag < Zn < Al < Na. **(1 mark)**

Na is the strongest reducing agent and Ag is the weakest reducing agent. **(1 mark)**

7. (a) Alkali halides like NaCl and KCl show this type of defect. **(1 mark)**

(b) When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of crystals. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. The electron released in this process, $(Na + Cl^- \longrightarrow NaCl + e^-)$ diffuses into the crystal and occupies anionic site. **(1 mark)**

8. Edge length of unit cell (a) = 3.5 Å = 3.5×10^{-8} cm.

Volume of unit cell $(a^3) = (3.5 \times 10^{-8})^3$ cm^3

Density of Li (ρ) = 0.53 g cm^3

Avogadro's no. $(N_0) = 6.023 \times 10^{23}$ mol^{-1}

Atomic mass of Li (M) = 6.94 g mol^{-1}

We know that $\rho = \dfrac{Z \times M}{a^3 \times N_0}$ or $Z = \dfrac{\rho \times a^3 \times N_0}{M}$ **(½ mark)**

$$Z = \frac{(0.53 g\ cm^{-3}) \times (3.5 \times 10^{-8})^3 cm^3 \times (6.023 \times 10^{23} mol^{-1})}{(6.94\ g\ mol^{-1})} \simeq 2$$

(½ mark)

$\therefore$ No. of atoms in a unit of Li = 2 **(Body centred unit cell)**

(1 mark)

OR

We know that $\rho = \frac{Z \times M}{a^3 \times N_0 \times 10^{-30}}$ or $N_0 = \frac{Z \times M}{a^3 \times \rho \times 10^{-30}}$

(½ mark)

Edge length of NaCl (a) = 2 ($r_{Na^+} + r_{Cl^-}$) = 2 × 281 = 562 pm = 562

($\because$ NaCl has F_{CC} structure)

No. of atoms per unit cell (Z) = 4

Density of NaCl (ρ) = 2.165 g cm^{-3}

Gram molecular mass of NaCl (M) = 23 + 35.5 = 58.5 g mol^{-1}

(½ mark)

$\therefore$ Avogadro's Number (N_0)

$$= \frac{4 \times (58.5\ g\ mol^{-1})}{(562)^3 \times (2.165 g\ cm^{-3}) \times (10^{-30} cm^3)}$$

$= 6.089 \times 10^{23}\ mol^{-1}$ **(1 mark)**

9. $$\log \frac{k_2}{k_1} = \frac{E_a}{2{\cdot}303\ R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$E_a = \frac{2{\cdot}303\ R \times T_1\ T_2}{T_2 - T_1} \log \frac{k_2}{k_1}$$ **(½ mark)**

$$= \frac{2{\cdot}303 \times 8{\cdot}314 \times 298 \times 308}{308 - 298} \log 4$$ **(½ mark)**

$= 175444{\cdot}2 \log 4$

$= 175444{\cdot}2 \times 0{\cdot}6021$

$= 105635\ J = 105{\cdot}635\ kJ.$ **(1 mark)**

10. (a) $P_4 (s) + 3NaOH (aq) + 3H_2O (l)$

$\longrightarrow 3NaH_2PO_2 (aq) + PH_3 (g)$ **(1 mark)**

Sod. hypophosphite.

(b) $2I^- (aq) + H_2O (l) + O_3 (g) \longrightarrow I_2 (s) + O_2 (g) + 2OH^- (aq)$

(1 mark)

11. Calculation of cell constant

Resistance of KCl solution (R) = 100 ohm

Conductivity (specific conductance) (κ) = 1.29×10^{-2} ohm^{-1} cm^{-1}

Specific conductance (κ) = $\frac{1}{R} \times$ cell constant

Cell constant = $\kappa \times R = \left(1.29 \times 10^{-2}\ ohm^{-1}\ cm^{-1}\right) \times (100\ ohm)$

= 1.29 cm^{-1}, **(1 mark)**

Specific conductance of 0.02 M KCl solution

Resistance of KCl solution (R) = 520 ohm

Cell constant of the cell (l / a) = 1.29 cm^{-1}

Specific conductivity (κ) = $\frac{1}{R} \times$ cell constant

$= \left(\frac{1}{520}\ ohm^{-1}\right) \times \left(1.29\ cm^{-1}\right)$

$= 2.49 \times 10^{-3}\ ohm^{-1}\ cm^{-1}$ **(1 mark)**

Molar conductivity of 0.02 M KCl solution

Concentration (C) = 0.02 M=0.02 mol

$L^{-1} = \frac{0.02 mol}{1L} = \frac{0.02\ mol}{1000\ cm^3}$

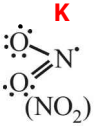
$= 2.0 \times 10^{-5}$ mol cm^{-3}

Molar conductance ($\wedge_m$) = $\frac{\kappa}{C} = \frac{(2.49 \times 10^{-3} ohm^{-1}(cm^{-1})}{(2.0 \times 10^{-5} mol(cm^{-3})}$

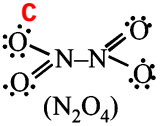
$= 124.5\ ohm^{-1}\ cm^2\ mol^{-1}$ **(1 mark)**

12. (a) Carbon and nitrogen atoms have comparable sizes. They can be linked to each other by triple bond to form $C \equiv \overset{\ominus}{N}$ ion in which $p_\pi - p_\pi$ bonding is possible. However, similar $p_\pi - p_\pi$ bonding is not possible between carbon and phosphorus atoms because of comparatively large atomic size of phosphorus. Therefore, $C \equiv \overset{\ominus}{P}$: ion does not exist. **(1 mark)**

(b) NO_2 is an odd electron molecule and has 17 valence electrons (5 due to N and 12 due to two O atoms). Upon dimerisation, it changes into a stable N_2O_4 molecule with even number of electrons (34). **(1 mark)**



(NO_2)



(N_2O_4)

(c) ICl is polar $(\overset{\delta+}{I}—\overset{\delta-}{Cl})$ due to the electronegativity difference between the two participating halogen atoms. It is therefore, more reactive than I_2 which is completely non-polar. **(1 mark)**

OR

(a) The balanced equation for the reaction is as follows : **(1 mark)**

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

(b) Similarities :

(i) N and P both have 5 valence electrons and both form N^{3-} and P^{3-} ions. **(½ mark)**

(ii) N_2O_5 and P_2O_5 both are acidic oxides. **(½ mark)**

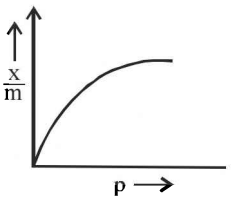
Dissimilarities :

(i) N_2 is a gas, phosphorus (P_4) is a solid. **(½ mark)**

(ii) NCl_5 does not exist, PCl_5 exists. **(½ mark)**

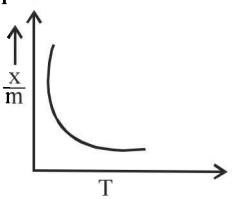
13. (a) (i) The amount of gas absorbed varies with pressure and is given by the expression

$$\frac{x}{m} = kp^{1/n} \text{ when } n > 1$$



(1 mark)

(ii) Increase in temperature decreases amount of gas adsorbed. This is because, adsorption is a exothermic process.



(1 mark)

(b) Charcoal **(1 mark)**

14. (a) The value for the redox couple Zn^{2+}/Zn (– 0·76 V) is more negative than that of Fe^{2+}/Fe (– 0·44 V) redox couple. Therefore, zinc is more reactive than iron and hence reduction will be faster in case if zinc scraps are used. But zinc is a costlier metal than iron so using iron scraps would be more economical. **(1 + 1 = 2 marks)**

(b) Reduction of oxides is easier than that of the carbonates and sulphides for obtaining corresponding metals. **(1 mark)**

15. (i) (a) HF attacks sodium silicate which is the main constituent of glass. As a result, the glass bottles are slowly corroded or eaten up. Therefore, HF cannot be stored in glass bottles. It is normally kept in wax bottles.

$$Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O$$ **(1 mark)**

(b) Bonds in the interhalogen compounds (X–Y) are generally weaker and also more polar than the bonds in the pure halogens (X–X). Therefore, interhalogen compounds are more reactive than halogens. **(1 mark)**

(ii) $$\underset{\text{Phosphorus acid}}{4H_3PO_3} \xrightarrow{\text{Heat}} \underset{\text{Phosphoric acid}}{3H_3PO_4} + PH_3$$ **(1 mark)**

16. (a) Rate = $k[NO]^2[O_2]$ **(½ mark)**

Suppose initially, moles of NO = a, moles of O_2 = b, volume of the vessel = VL. Then $[NO] = a/V$ M, $[O_2] = b/V$ M

$$\therefore \quad \text{Rate}(r_1) = k\left(\frac{a}{V}\right)^2\left(\frac{b}{V}\right) = k\frac{a^2b}{V^3} \quad \text{....(i)}$$

(½ mark)

New volume = V/3.

$$\therefore \quad \text{New concentrations}: [NO] = \frac{a}{V/3} = \frac{3a}{V}$$

$$[O_2] = \frac{b}{V/3} = \frac{3b}{V}$$

$$\therefore \quad \text{New rate}(r_2) = k\left(\frac{3a}{V}\right)^2\left(\frac{3b}{V}\right) = \frac{27\,k\,a^2b}{V^3} \quad \text{...(ii)}$$

(½ mark)

$$\therefore \quad \frac{r_2}{r_1} = 27 \text{ or } r_2 = 27\,r_1,$$ *i.e.*, rate becomes 27 times

There is no effect on the order of reaction **(½ mark)**

(b) $$\frac{dx}{dt} = k[N_2O_5] = 6.2\times10^{-4}\ s^{-1}\times1.25\ mol\ L^{-1} = 7.75\times10^{-4}\ mol\ L^{-1}\ s^{-1}.$$

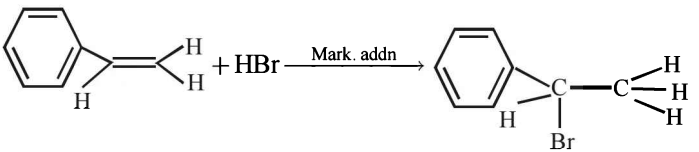
(1 mark)

17. (i) (a) The complex $\left[Ni(CN)_4\right]^{2-}$ is square planar while $\left[Ni(CO)_4\right]$ is tetrahedral in nature. But since all the electrons in the orbitals of the central metal atom/ion in these complexes are paired, both are therefore, diamagnetic in nature. **(1mark)**

(b) In square planar complexes $M_2X_2L_2$, the two identical ligands (X_2 or L_2) can occupy either adjacent positions or opposite positions in the co-ordination polyhedron representing square plane. Therefore, cis and trans isomers are possible. In tetrahedral complexes, all the four positions are identical and no spatial isomerism can be shown. **(1 mark)**

(ii) The magnitude of crystal field splitting is larger in the octahedral complex than in the tetrahedral complex. **(1 mark)**

18. (a)



(1 mark)

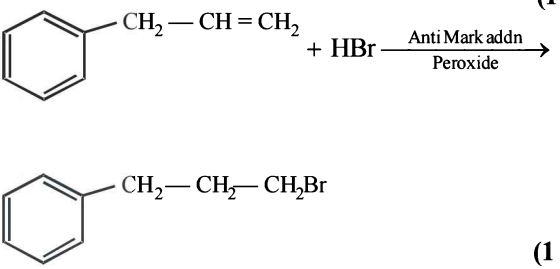
1-Bromo-1-phenylethane

(b) $CH_3CH_2CH=CH_2 + HCl \xrightarrow{\text{Mark. addn}} CH_3-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_3$

2-chlorobutane

(1 mark)

(c)



(1 mark)

1-Bromo-3-phenylpropane

19. (a) As compound A gives NH_3 and carboxylic acid on hydrolysis with NaOH, it must be an organic cyanide. This is also indicated by the fact that A on reduction gives C which has four H-atom more than A. The compound C is primary amine as it reacts with HNO_2 forms an alcohol D. The sequence of reactions are:

$$\underset{\text{Propanenitrile (A)}}{CH_3CH_2C\equiv N} \xrightarrow[\text{Heat}]{\text{Alkali}} \underset{\text{Propanoic acid (B)}}{CH_3CH_2COOH} + NH_3$$

↓Reduction

$$\underset{\text{1-aminopropane (C)}}{CH_3CH_2CH_2NH_2} \xrightarrow{HONO} \underset{\text{1-propanol (D)}}{CH_3CH_2CH_2OH} + N_2 + H_2O$$

(½ + ½ + ½ + ½ = 2 marks)

(b) Aromatic amines are much less basic than alkyl amines because in aromatic amines, the electron density from the unshared pair of electrons on the N atom is delocalised at ortho and para positions of the ring. In cyclohexylamine, the electron density is localised and hence more basic than aniline.

(1 mark)

20. (a) Vitamin B_1. **(1 mark)**

(b) (i) $OHC-(CHOH)_4-CH_2OH \xrightarrow{(CH_3CO)_2O}$

$OHC-(CHOCOCH_3)_4-CH_2OCOCH_3$ **(1 mark)**

Glucose pentaacetate

(ii) $HOH_2C-(CHOH)_4-CHO$

$\xrightarrow{HCN} HOH_2C-(CHOH)_4-CH(OH)CN$ **(1 mark)**

Glucose cyanohydrin

21. (a) Phenol and formaldehyde (b) Vinyl chloride

(c) chloroprene **(1 + 1 + 1 = 3 mark)**

22. (a) One main reason for the heart attack is blood clotting. Aspirin checks the blood clotting to large extent. It is therefore, recommended for heart patients. A low potency of aspirin is generally suitable. **(1 mark)**

(b) The natural sweetner which is commonly used is sugar (sucrose). Being a carbohydrate, it has high calorific value. Since diabetic patients are to be given low calorie diet, sugar is therefore not suitable. A number of artificial synthetic sweetners are available which are not carbohydrates and have low calorific value. They can be safely used by diabetic patients also. **(1 mark)**

(c) Detergents are generally non-biodegradable due to the presence of long chain of hydrocarbons with branching. Since soaps normally contain straight chain of hydrocarbons, these are biodegradable and do not cause any pollution problem.

(1 mark)

23. (a) The orange coloured solution is due to $Cr_2O_7^{2-}$ (dichromate ion). Ethanol reacts with dichromate ion in acidic solution according to the chemical equation as shown below. In this reaction, dichromate ion is converted to chromium ion. This reaction is easily observed because the orange color disappears as dichromate ion is used up, and the blue-green color appears due to formation of chromium ion.

$$\underset{\text{dichromate ion}}{2Cr_2O_7^{2-}} + \underset{\text{ethanol}}{3C_2H_5OH} + 16H^+ \longrightarrow \underset{\text{chromium ion}}{4Cr^{3+}} + \underset{\text{acetic acid}}{3CH_3COOH} + 11H_2O$$

(2 marks)

(b) For estimating blood alcohol content (BAC) from a breath sample. **(1 mark)**

(c) Honest, disciplined, sincerity towards his duties, Alert.

(1 mark)

24. (a) $\pi V = nRT$ **(½ mark)**

Substituting the values, we get

$$\pi \times 0.2 = \left(\frac{0.25 + 0.10}{2}\right)(0.082) \times 293$$ **(½ mark)**

(As volume becomes double, number of moles becomes half)

or $\pi = \dfrac{0.175 \times 0.082 \times 293}{0.2}$

or $\pi = \dfrac{4.20455}{0.2} = 21.02275$ atm. **(1 mark)**

(b) The molecular mass obtained with the help of colligative property is sometimes different from normal molecular mass, it is called abnormal molecular mass. **(1 mark)**

The factors which bring abnormality in molecular mass are :

(i) **Association :** When solute particles undergo association, number of particles become less and molecular mass determined with the help of colligative property will be more. **(1 mark)**

(ii) **Dissociation :** When solute particles undergo dissociation there is an increase in the number of particles. Therefore, increase in colligative property or decrease in molecular weight is observed. **(1 mark)**

OR

(a) Using Raoult's law equation of lowering of vapour pressure :

$$\frac{p_A^o - p_A}{p_A^o} = x_B$$ **(½ mark)**

or $$\frac{31.82 - 30.95}{31.82} = \frac{27/M_B}{100/18}$$ **(½ mark)**

or $$\frac{0.87}{31.82} = \frac{27}{M_B} \times \frac{18}{100} \text{ or } M_B = \frac{27 \times 18 \times 31.82}{0.87 \times 100} \text{ or } 177.75 \text{ g mol}^{-1}$$

(1 mark)

Hence, molecular mass of the solute = 177.75 g mol^{-1}.

(b) (i) Non-ideal solutions are those solutions which do not follow Raoult's Law.

Also $\Delta H_{mix} \neq 0$ and $\Delta V_{mix} \neq 0$. **(1 mark)**

The force of attraction between A–A and B–B is not equal to that between A – B.

(ii) (1) In alcohol and acetone solution, force of attraction is less between alcohol and acetone molecules than in pure alcohol molecules as well as in pure acetone molecules, therefore, vapour pressure increases. **(1 mark)**

(2) In chloroform and acetone, force of attraction increases due to intermolecular H-bonding therefore, vapour pressure decreases. **(1 mark)**

25. (a) (i) $\underset{\text{(Chromite ore)}}{4FeCr_2O_4} + 16NaOH + 7O_2 \longrightarrow$

$\underset{\text{(Sodium chromate)}}{8Na_2CrO_4} + 2Fe_2O_3 + 8H_2O$ **(1 mark)**

(ii) $\underset{\text{(Pyrolusite)}}{2MnO_2} + 4KOH + O_2 \longrightarrow \underset{\text{(Potassium manganate)}}{2K_2MnO_4} + 2H_2O$

(1 mark)

(iii) $\underset{\text{(Potassium permanganate)}}{2KMnO_4} + H_2O \longrightarrow 2MnO_2 + 2KOH + \underset{\text{Nascent oxygen}}{3[O]}$

(1 mark)

(b) (i) Mn^{2+} is more stable $\left(4s^0\ 3d^5\right)$, because of half-filled *d*-orbitals than Mn^{3+} $\left(4s^0\ 3d^4\right)$ while $Fe^{3+}\left(4s^0\ 3d^5\right)$ is more stable than $Fe^{2+}\left(4s^0\ 3d^6\right)$ again because of half filled *d*-orbitals. Therefore, Mn^{3+} can be easily reduced to Mn^{2+} whereas Fe^{3+} is not easily reduced to Fe^{2+}, rather Fe^{2+} is more easily oxidised to Fe^{3+}. **(1 mark)**

(ii) Ce^{4+} is more stable than Ce^{3+} because of stable electronic configuration and higher hydration energy of Ce^{4+}, hence Ce^{3+} is easily oxidised to Ce^{4+}. **(1 mark)**

OR

(a) (i) $Cr_2O_7^{2-}(aq) + 3H_2S(g) + 8H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(aq) + 3S(s)$

(1 mark)

(ii) $2Cu^{2+}(aq) + 4I^-(aq) \rightarrow Cu_2I_2(s) + I_2(s)$ **(1 mark)**

(iii) $2MnO_4^-(aq) + 3S_2O_3^{2-}(aq) + H_2O(\ell) \rightarrow 2OH^-(aq) + 2MnO_2(s) + 3SO_4^{2-}(aq) + 3S(s)$

(1 mark)

K M C

(b) (i) *d*-orbitals are influenced more by ligands as they can project out and so they have greater tendency to form complexes. Comparatively, *f*-orbitals lie deep inside the atom and thus, *f*-electrons do not come in contact with ligands. Therefore, *f*-block elements form lesser complexes. **(1 mark)**

(ii) The strength of metallic bond in transition metals depend upon number of unpaired electrons in valence shell, *i.e.*, (n – 1)d and *ns* orbitals. As there are no unparied electrons is these metals, the bond strength is quite weak and thus they are soft and have very low melting points. Hg is liquid at ordinary temperature. **(1 mark)**

26. (a) (i) Formation of ammonia derivatives (oximes, hydrazone, semi-carbazone, etc.) proceeds via the attack of carbonyl carbon with proton to form the conjugate acid.

$$>C=\ddot{O}+H^+ \longrightarrow >C=\overset{+}{O}H \longleftrightarrow >\overset{+}{C}-OH$$

Therefore, presence of an acid is a must for preparing these derivatives. However, in strongly acidic medium, the proton attacks the unshared pair of electrons on nitrogen to form the species RNH_3 which cannot attack the carbonyl carbon.

$$H^+ + :NH_2R \longrightarrow \overset{\oplus}{N}H_3R$$

In basic medium, there is no protonation of carbonyl group, and hence no reaction.

$$>C=O \xrightarrow{\text{Basic medium}} \text{No protonation , No reaction}$$

Therefore, preparation of ammonia derivatives requires slightly acidic medium (pH $\simeq 3\cdot5$) and its careful control is essential. **(2 marks)**

(ii) Due to resonance between lone pairs of electrons on the O-atom of the OH group and C = O, the carboxyl carbon is less electrophilic than carbonyl carbon in aldehyde and ketones. Therefore, nucleophilic addition of NH_2OH to the C = O group of carboxylic acids does not occur and hence carboxylic acids do not form oximes. **(1 mark)**

(b) (i) $$C_6H_6 \xrightarrow[\text{Anhy } AlCl_3 / CuCl]{CO / HCl} C_6H_5CHO$$

(ii) $$2C_6H_5CHO \xrightarrow{\text{Conc. NaOH}} C_6H_5CH_2OH + C_6H_5COONa$$

(1 + 1 = 2 marks)

OR

(a) HCOOH has an aldehydic (CHO) group in addition to carboxyl group (COOH). Therefore, it is expected to behave as reducing agent also and reduces Tollen's reagent to form a shining mirror.

$$\underset{\text{Formic acid}}{HCOOH} + \underset{\text{Tollen's reagent}}{2[Ag(NH_3)_2]^+OH^-} \longrightarrow \underset{\text{Silver mirror}}{2Ag} + 2H_2O + CO_2 + 4NH_3$$

(1 mark)

(b) In the carboxylic acids, the carboxylic groups are involved in the intermolecular hydrogen bonding. However, it is absent in the aldehydes and ketones. Therefore, aldehydes and ketones have lower boiling point than the corresponding acids of comparable molecular mass. **(1 mark)**

(c) The K_a value of benzoic acid (6.3×10^{-5}) is more than that of acetic acid (1.75×10^{-5}). Actually, C_6H_5 group with –I effect facilitates the release of H^+ from benzoic acid while CH_3 group with + I effect tends to retard it. **(1 mark)**

(d) (i) 3-methyl butanoyl chloride

(ii) Ethanoic propanoic anhydride **(1 + 1 = 2 marks)**