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CHEMISTRY MODEL QUESTION PAPER – I

CLASS: XII **MARKS: 150**
SUB: CHEMISTRY **TIME: 3 Hrs.**

PART – I **(30 x 1 = 30)**

i).All questions are compulsory.

ii). Each question carries 1 mark.

iii).Choose the most suitable answer from the given four alternatives.

1. $E_n = \frac{-313.6}{n^2}$, If the value of E_n = -34.84 to which value 'n' corresponds

(a) 1 (b) 2 (c) 3 (d) 4

Answer: (c) 3

2. Which is not a characteristic property of particle nature of an electron?

(a) striking ZnS screen (b) J.J. Thomson experiment
(c) Black body radiation (d) Interference

Answer: (d) Interference

3. The electronegativity of Cl according to Pauling's scale is

(a) 2.1 (b) 1.77 (c) 3.87 (d) 4.22

Answer: (c) 3.87

4. Which is used for preventing dental cavities?

(a) CaF_2 (b) SF_6 (c) UF_6 (d) NaF

Answer: (d) NaF

5. The number of unpaired electrons in Fe^{+3} ion is

(a) 2 (b) 3 (c) 4 (d) 5

Answer: (d) 5

6. The outermost electronic configuration of chromium is

(a) $3d^6$ (b) $3d^5 4s^1$ (c) $3d^4 4s^2$ (d) $3d^3 4s^2 4p^1$

Answer: (b) $3d^5 4s^1$

7. ---------- is used in gas lamp material.

(a) CeO_2 (b) PuO_2 (c) ThO_2 (d) both a and c

Answer: (a) CeO_2

8. The oxidation state of central metal ion $[Pt(NH_3)_2(NO_3)_2]SO_4$ is

(a) +1 (b) +2 (c) +3 (d) +4

Answer: (d) +4

9. In cigarette lighters ……..is used
   (a) mish-metal (b) CeO_2 (c) Mg-alloy (d) Pyrophoric alloy
   Answer: (d) Pyrophoric alloy

10. Which of the following is used as neutron absorber in the nuclear reactor?
   (a) Water (b) Dueterium (c) some compound (d) cadmium
   Answer: (d) cadmium

11. Semi conductors are used as
   (a) rectifiers (b) transistors (c) solar cells (d) all the above
   Answer: (d) all the above

12. When a liquid boils, there is
   a) an increase in entropy b) a decrease in entropy
   c) an increase in heat of vapourisation d) an increase in free energy
   Answer: a) an increase in entropy

13. Which one of the following is having high ΔH_{vap} value
   a) acetone b) ethyl alcohol c) CCl_4 d) $CHCl_3$
   Answer: b) ethyl alcohol

14. In the equilibrium $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$, the maximum yield of ammonia will be obtained with the process having
   (a) low pressure and high temperature (b) low pressure and low temperature
   (c) high pressure and low temperature (d) high pressure and high temperature
   Answer: (c) high pressure and low temperature

15. Forward reaction takes place when,
   a) Q<Kc b) Q >Kc c) Q= Kc d) none of these
   Answer: b) Q >Kc

16. $2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$, $\frac{d[N_2O_5]}{dt} = k_1[N_2O_5]$, $\frac{d[NO_2]}{dt} = k_2\ [N_2O_5]$ and $\frac{d[O_2]}{dt} = k_3\ [N_2O_5]$,
   the relation between k_1,k_2 and k_3 is
   (a) $2k_1=k_2=k_3$ (b) $2k_1 =k_2=4k_3$ (c) $2k_1 =4k_2=k_3$ (d) $k_1=k_2=k_3$
   Answer: (b) $2k_1 =k_2=4k_3$

17. The phenomenon of Tyndall's effect is not observed in
   (a) emulsion (b) colloidal solution (c) true solution (d) None
   Answer: (c) true solution

18. Emulsion is a colloidal solution of
   (a) solid in gas (b) gas in liquid (c) liquid in liquid (d) gas in solid
   Answer: (c) liquid in liquid

19. The catalyst used in Bergius process is
   (a) $CuCl_2$ (b) Cr_2O_3 (c) Fe_2O_3 (d) V_2O_5
   Answer: (c) Fe_2O_3

20. The pH of a solution containing 0.1N NaOH solution is
   (a) 1 (b) 10^{-1} (c) 13 (d)10^{-13}
   Answer: (c) 13

21. When glycol is heated with conc. H_2SO_4 it gives
    (a) Diethylene glycol (b) Acetaldehyde
    (c) Ethylene oxide (d) Dioxan
    Answer: (d) Dioxan

22. Pick out the incorrect statement.
    (a) The formula of diethyl oxonium chloride is (C_2H_5)-O^+Cl^-
    (b) Diethyl ether reacts with chlorine in presence of sunlight forms $(C_2Cl_5)_2O$
    (c) Ether is used as solvent for Grignard reagent
    (d) In anisole oxygen is strongly bonded to benzene ring
    Answer: (c) Ether is used as solvent for Grignard reagent

23. The number of ether isomers possible for $C_4H_{10}O$ is
    (a) 3 (b) 4 (c) 7 (d) 2
    Answer: (c) 7

24. A cyanohydrin of a compound X on hydrolysis gives lactic acid. The X is
    (a) HCHO (b) CH_3CHO
    (c) $(CH_3)_2$ CO (d) CH_3CH_2CHO
    Answer: (b) CH_3CHO

25. The concentrated solution of sodium acetate on electrolysis gives
    (a) Acetone (b) Acetic acid
    (c) Methane (d) Ethane
    Answer: (d) Ethane

26. The most reactive compound towards electrophillic nitration is
    (a) Methyl benzene (b) Nitro benzene
    (c) Amino benzene (d) Benzene
    Answer: (a) Methyl benzene

27. The organic compound that undergoes carbylamine reaction is
    (a) $(C_2H_5)_2$ NH (b) $(C_2H_5)_3$ N (c) C_2H_5 NH_2 (d) C_6H_5 N_2Cl
    Answer: (c) C_2H_5 NH_2

28. The product obtained when nitro benzene is treated with $SnCl_2$/NaOH is
    (a) Aniline (b) Phenyl hydroxylamine
    (c) Hydrazo benzene (d) Azo benzene
    Answer: (d) Azo benzene

29. Sucrose is not ……
    (a) a disaccharide (b) a non – reducing sugar
    (c) hydrolysed to only glucose (d) hydrolysed to glucose & fructose
    Answer: (c) hydrolysed to only glucose

30. Which one of the following serves to prevent loss of heat from the body?
    (a) Wax (b) Cephalin (c) Lecithin (d) Fat
    Answer: (d) Fat

PART – II **(15x3=45)**

Note: i) Answer any *fifteen* questions.
ii) Answer in *one or two* sentences.

31. What is nodal surface?

The orbital where the probability of finding the electron is zero (nearly). This is called a node or nodal surface.

32. Why is electron affinity of fluorine less than that of chlorine?

- Small size of fluorine
- Electron-electron repulsion

33. Prove that Phosphorous Pentoxide is a powerful dehydrating agent.

Phosphorus pentoxide extracts water from many inorganic compound including sulphuric acid, nitric acid and several organic compounds. It is therefore, used as a powerful dehydrating agent.

$$H_2SO_4 \xrightarrow[-H_2O]{P_4O_{10}} SO_3$$

$$2HNO_3 \xrightarrow[-H_2O]{P_4O_{10}} N_2O_5$$

$$\underset{\text{Amide}}{RCONH_2} \xrightarrow[-H_2O]{P_4O_{10}} \underset{\text{Nitrile}}{RCN}$$

34. Write the preparation of ClF, BrF_3 and IF_7.

$$Cl_2 + F_2 \text{ (equal volume)} \xrightarrow{473K} 2ClF \text{ (AX type)}$$

$$Br_2 + 3F_2 \text{ (diluted with nitrogen)} \rightarrow 2Br F_3$$

$$IF_5 + F_2 \text{ (Excess)} \xrightarrow{573K} IF_7 \text{ (AX}_7 \text{ Type)}$$

35. Why do transition elements form complexes?

Complex formation:

- Small size and high positive charge density.
- Presence of vacant (n-1)d orbitals which are of appropriate energy to accept lone pair and unshared pair of electrons from the ligands for bonding with them.
- Examples of some complex compounds are,
$[Cu(NH_3)_4]^{2+}$, $[Ag(NH_3)^2]^+$, $[Fe(CN)_6]^{4-}$,....etc.

36. What is matte?

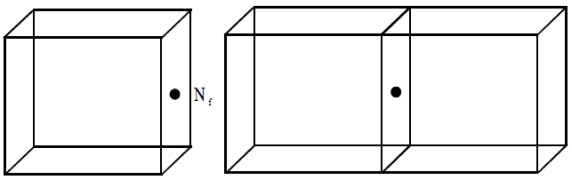
As a result of smelting, two separate molten layers are formed at the bottom of the furnace. The upper layer consists of slag and is removed as a waste while the lower layer is called matte. It chiefly consists of cuprous sulphide and some unchanged ferrous sulphide.

37. Neutron bombardment fragmentation of U^{235} occurs according to the equation. $_{92}U^{235} + {}_{0}n^{1} \rightarrow {}_{42}Mo^{95} + {}_{57}La^{139} + X\ {}_{-1}e^{0} + Y\ {}_{0}n^{1}$. Calculate the values of X and Y.

X value-2

Y value-7

38. Write a note on the assignment of atoms per unit cell in fcc.



N_f = Number of atoms at the faces

The number of atoms per unit cell in fcc $= \frac{N_c}{8} + \frac{N_f}{2} = \frac{8}{8} + \frac{6}{2} = 1 + 3 = 4$

N_f = Number of atoms at the faces.

39. Calculate the change of entropy for the process, water (liq) to water (vapour, 373K) involving ΔH_{vap} = 40850 J. mol^{-1} at 373K.

$$\Delta S_{vap} = \frac{\Delta H_{vab}}{Tb\,(K)} = \frac{40850\,J/mol}{373K} = 109.517\,J.K.^{-1}mol^{-1}$$

$$\Delta S_{vap} = 109.52\ J\ mole^{-1}\ K^{-1}$$

40. State Le Chatelier's principle.

According to this principle, if a system at equilibrium is subjected to a disturbance or stress, then the equilibrium shifts in the direction that tends to nullify the effect of the disturbance or stress.

41. Write any three characteristics of order of reaction.

(i) When the concentration of the reactant is increased by '*n*' times, the rate of reaction is also increased by n times. That is, if the concentration of the reactant is doubled, the rate is doubled.

(ii) The unit of rate constant of a first order reaction is sec^{-1} or $time^{-1}$.

$$k_1 = \frac{\text{rate}}{(a-x)} = \frac{\text{mol.lit}^{-1}\,\text{sec}^{-1}}{\text{mol.lit}^{-1}} = \text{sec}^{-1}$$

(iii)The time required to complete a definite fraction of reaction is independent of the initial concentration, of the reactant if $t_{1/u}$ is the time of one 'u'th fraction of reaction to take place then from equation

$$x = \frac{a}{u} \quad \text{and} \quad t_{1/u} = \frac{2.303}{k_1} \log \frac{a}{a - \frac{a}{u}}$$

42. Write a note on consecutive reactions. Give an example.

The reactions in which the reactant forms an intermediate and the intermediate forms the product in one or many subsequent reactions are called as consecutive or sequential reactions.

Example of consecutive reactions

Saponification of a diester in presence of an alkali :

$$R'OOC-(CH_2)_n-COOR \xrightarrow{k_1} R'OOC-(CH_2)_n-COOH \xrightarrow{k_2} HOOC-(CH_2)_n-COOH$$

43. What is electro dialysis?

In this process, dialysis is carried under the influence of electric field. Potential is applied between the metal screens supporting the membranes. This speeds up the migration of ions to the opposite electrode. Hence dialysis is greatly accelerated. Evidently electrodialysis is not meant for non electrolyte impurities like sugar and urea.

44. What is meant by Buffer solution? Mention its types.

A buffer solution is one which maintains its pH fairly constant even upon the addition of small amounts of acid or base,solution of acetic acid and sodiumacetate (CH_3COOH/CH_3COONa).

1. a weak acid together with a salt of the same acid with a strong base.
   These are called Acid buffers. (e.g.,) $CH_3COOH + CH_3COONa$.
2. a weak base and its salt with a strong acid. These are called Basic buffers.
   (e.g.,) $NH_4OH + NH_4Cl$.

45. Meso tartaric acid is an optically inactive compound with asymmetric carbon atoms. Justify your answers.

- Though the Meso isomer has two asymmetric carbon atoms the configuration of one carbon is the mirror image of the other, the net result being the molecule as a whole becomes symmetric.
- This molecule is said to have a symmetric plane, which divides the molecule into two equal halves.

- The molecule becomes ‘‘achiral’’. It has configuration which is superimposable on its mirror image.
- The optical inactivity of the ‘Meso’ isomer is due to the internal compensation. It is due to the inherent symmetry in the molecule.

46. What is Saponification reaction? Give suitable equation.

Esters are hydrolysed by warming with dil. acids or alkali.

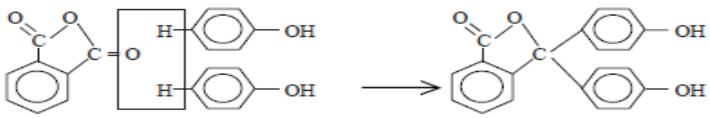
$$CH_3COOCH_3 \xrightarrow{H^+/H_2O} CH_3COOH + CH_3OH$$

$$CH_3COOCH_3 + NaOH \longrightarrow \underset{\text{sodium acetate}}{CH_3COONa} + CH_3OH$$

(Saponification)

47. How will you convert phenol into Phenolphthalein ?

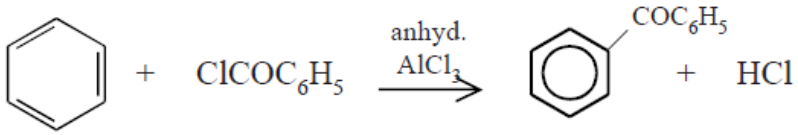
Phenols are heated with phthalic anhydride and con. H_2SO_4 to give Phenolphthalein. This can be tested by the formation of pink colour when it is treated with sodium hydroxide.



Phenolphthalein

48. How is acetophenone prepared by Friedal -Craft’s method?

. Benzoylation of benzene takes place in presence of **anhydrous aluminium chloride** as a catalyst. Benzoyl cation ($C_6H_5CO^+$) is the electrophile.



49. What are the uses of oxalic acid?

1. For removing ink stains and iron stains.
2. as mordant in dyeing and calico printing.
3. in manufacture of ink and metal polishes.
4. Redox titration

50. $CH_4 \xrightarrow[400^\circ C]{HNO_3} A \xrightarrow{Sn/HCl} B \xrightarrow[HgCl_2]{CS_2} C$. Identify A, B and C

A-CH_3NO_2
B-CH_3NH_2
C–CH_3NCS

51. Why are Iodoform and phenolic solutions called antiseptic?

Iodoform, CHI_3 is used as an antiseptic and its 1% solution is a disinfectant.

PART – III **(7x 5 = 35)**

Note: (i) Answer any *seven* questions

(ii) Choosing atleast *two* questions from each section.

Section – A

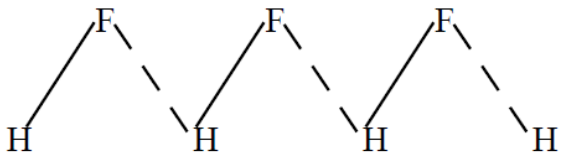
52. Explain inter and intra molecular hydrogen bonding with suitable examples.

i) Intermolecular hydrogen bonding:

This type of bond is formed between the two molecules of the same or different compounds. Some examples of the compounds exhibiting intermolecular hydrogen bonds are:

1. Hydrogen fluoride, H - F.

In the solid state, hydrogen fluoride consists of long zig-zag chains of molecules associated by hydrogen bonds as shown below:

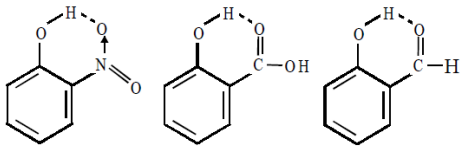


inter molecular hydrogen bonding

Therefore, hydrogen fluoride is represented as (HF)n

ii) Intramolecular hydrogen bonding:

This type of bond is formed between hydrogen atom and N, O or F atom of the same molecule. This type of hydrogen bonding is commonly called chelation and is more frequently found in organic compounds. Intramolecular hydrogen bonding is possible when a six or five membered rings can be formed.



O-Nitrophenol **Salicylic Acid** **Salicylaldehyde**

53. Discuss the salient features of oxidation states of transition elements.

Salient features:

- The elements which exhibit the maximum number of oxidation states occur either in or near the middle of the series. For example, in the first transition series manganese exhibits maximum number of oxidation states (+2 to +7).

- The elements in the beginning of the series exhibit fewer oxidation states because they have less number of d-electrons which they can lose or contribute for sharing. The elements at the end of the series exhibit fewer oxidation states, because they have too many d electrons and hence fewer vacant d-orbitals can be involved in bonding.
- The transition elements in lower oxidation states (+2 and +3) generally form ionic bonds and in higher oxidation state form covalent bonds.
- The highest oxidation state shown by any transition metal is +8. For example, ruthenium and osmium show highest oxidation states of +8 in some of their compounds.
- Some transition metals show oxidation state of zero in their compounds. $Ni(CO)_4$ and $Fe(CO)_5$ are common examples.

54. What are the consequences of lanthanide contraction?

consequences:

i) Basicity of ions:

Due to lanthanide contraction, the size of Ln^{3+} ions decreases regularly with increase in atomic number. According to Fajan's rule, decrease in size of Ln^{3+} ions increase the covalent character and decreases the basic character between Ln^{3+} and OH^- ion in $Ln(OH)_3$. Since the order of size of Ln^{3+} ions

$La^{3+} > Ce^{3+} \ldots\ldots\ldots\ldots > Lu^{3+}$

ii) There is regular decrease in their ionic radii.

iii) Regular decrease in their tendency to act as reducing agent, with increase in atomic number.

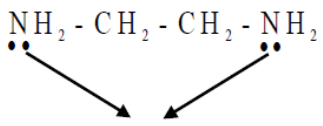
iv) Due to lanthanide contraction, second and third rows of d-block transistion elements are quite close in properties.

v) Due to lanthanide contraction, these elements occur together in natural minerals and are difficult to separate.

55. Explain the types of ligands with suitable examples.

Types of ligands:

When a ligand is bound to a metal ion through a single donor atom, as with Cl-, H_2O or NH_3, the ligand is said to be unidentate. Whenever a single coordinating group (or) ligand occupies two (or) more coordination position on the same central metal ions, a complex possessing a closed ring is formed. Such ligands are called polydentate ligands. When a single ligand has two coordinating positions, it is called bidentate ligand and when there are three coordinating positions available, it is called a tridentate ligand and so on. For example, ethylenediamine is a bidentate ligand because it has two amino groups each of which can donate a pair of electrons.



Name of the ligands:

Positive ligands:

The positive ligands are named with an ending -ium.

NH_2 - NH_3^+

hydrazinium

This ligand, though positive can bind through the uncharged nitrogen.

Neutral ligands:

The neutral ligands are named as such without any special name. But water is written as 'aqua : Ammonia is written as ammine. Note that two m's to distinguish from organic amine CO-Carbonyl, NO-Nitrosyl, NH_2 - CH_2 - CH_2 - NH_2-ethylenediamine (en), Pyridine C_5H_5N.

Negative Ligands:

Negative ligands end in suffix 'O'.

Example;

F--Fluoro, Cl--Chloro, $C_2O_4^{2}$--Oxalato, CN--Cyano,

Section – B

56. Write the statements of second law of thermodynamics.

STATEMENTS OF SECOND LAW OF THERMODYNAMICS:

i) "It is impossible to construct an engine which operated in a complete cycle will absorb heat from a single body and convert it completely to work without leaving some changes in the working system". This is called as the Kelvin – Planck statement of II law of thermodynamics.

ii) "It is impossible to transfer heat from a cold body to a hot body by a machine without doing some work". This is called as the clausius statement of II law of thermodynamics.

iii) 'A process accompanied by increase in entropy tends to be spontaneous". This statement is called as the entropy statement of II law of thermodynamics. Entropy is a measure of randomness or disorder of the molecules of a system and it is a thermodynamic state function. A system always spontaneously changes from ordered to a disordered state. Therefore entropy of a spontaneous process is constantly increasing.

iv) "Efficiency of a machine can never be cent percent".

v) The heat Efficiency of any machine is given by the value of ratio of output to input energies. Output can be in the form of any measurable energy or temperature change while input can be in the form of heat energy or fuel amount which can be converted to heat energy. Thus

% efficiency = input/output x 100

The machine can be a heat engine also. Consider a heat engine which has an initial temperature T1 and final temperature as T2, then if T1>T2 then when some amount of heat is being converted into work, T2 is the lowered temperature. The efficiency 'η' is given by,

$$\% \text{ efficiency} = \left(\frac{T_1 - T_2}{T_1} \right) \text{x } 100$$

According to II law of thermodynamics it is impossible to have a machine or heat engine which converts the input energy completely into output energy or output work without any amount of heat or energy being absorbed by the machine.

Hence, % efficiency can never be achieved as cent percent

$$\therefore \%\ \text{efficiency} = \left(1 - \frac{T_2}{T_1}\right) \text{x } 100$$

By II law, T2<T1 % efficiency less than 100.

57. Explain the dependance of dissociation constant with formation.

Dependance of dissociation constant with formation equilibrium Constant:

In a formation equilibrium reaction, the reactants and products are written at the LHS and RHS of the equilibrium sign respectively. For the same reaction, the dissociation equilibrium consists of the products in the place of reactants and reactants in the place of products being written at the LHS and RHS of the equilibrium sign respectively.

In such cases, the equilibrium constant of the dissociation equilibrium reaction which is also known as the dissociation constant, is found to be the reciprocal value of the equilibrium constant for the formation equilibrium reaction. For example, consider the formation equilibrium reaction of SO_3, from SO_2 and O_2 gases,

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

The equilibrium constant of the dissociation equilibrium is Kc, given by

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}\ dm^3/mole$$

$$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$$

$$K_c' = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{1}{K_c}\ mole/dm^3$$

Kc is considered as the dissociation constant of SO_3 gas. Usually, the equilibrium constant of the dissociation equilibrium is the reciprocal of the equilibrium constant of the formation equilibrium reaction.

58. Compound A reacts by first order kinetics at 25°C the rate constant of the reaction is 0.45 sec.What is the half-life of A at 25° C . What is the time required to have 12.5% unreacted A for first order reaction.

$$t_{½} = \frac{0.693}{k_1} = \frac{0.693}{0.45}$$

$$= 1.54 \text{ secs}$$

No. of $t_{½}$	Amount unreacted from 100%
1	50%
2	25%
3	12.5%

$\therefore$ Time of three half-life periods $= 3 \times 1.54$

$= 4.62$ secs

59. Write an account on cell terminology.

Current is the flow of electrons through a wire or any conductor.

Electrode is the material : a metallic rod/bar/strip which conducts electrons into and out of a solution.

Anode is the electrode at which oxidation occurs. It sends electrons into the outer circuit. It has negative charge and is shown as (–) in cell diagrams.

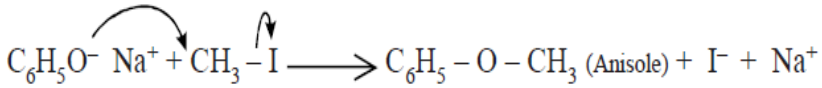
Cathode is the electrode at which electrons are received from the outer circuit. It has a positive charge and is known as (+) in the cell diagrams.

Electrolyte is the salt solution in a cell.

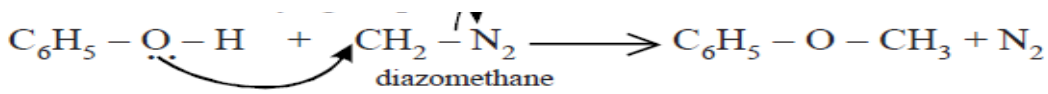
Section - C

60. Give three methods of preparation of anisole.

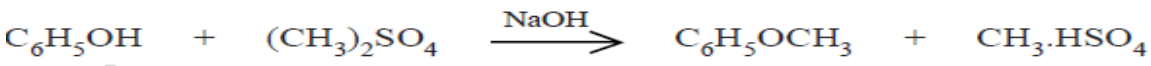
1. Williamsons synthesis



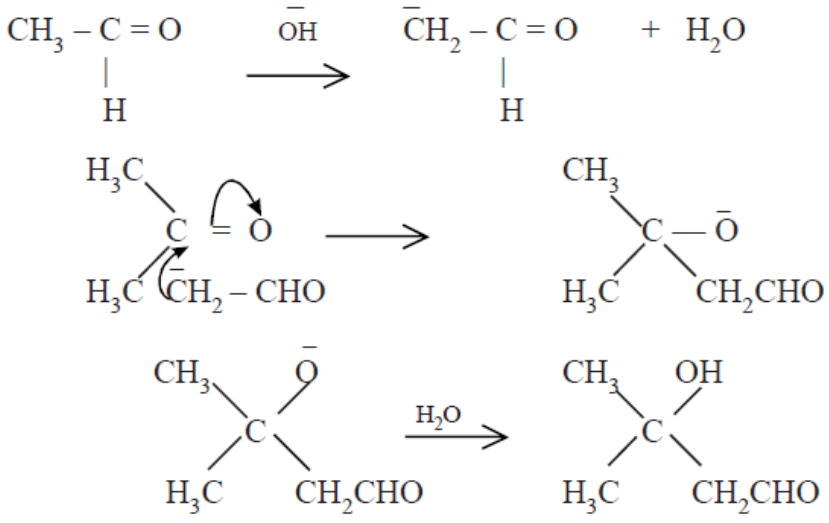
2. Using diazomethane :



3. Manufacture of ether :

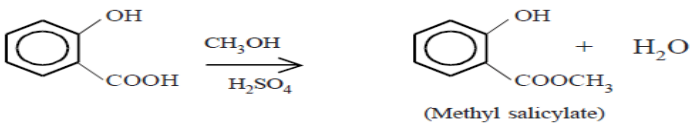


61. Write the mechanism of crossed Aldol condensation of acetone.



62. How are the following conversions take place?
(i) Salicylic acid → Methyl salicylate (ii) Methyl acetate → Ethyl acetate
(iii) Lactic acid → Pyruvic acid

i) Salicylic acid → methyl salicylate



(Methyl salicylate)

ii) Methyl acetate →Ethyl acetate

$CH_3COOCH_3 + C_2H_5OH \rightarrow CH_3COOC_2H_5 + CH_3OH$

iii) Lactic acid → Pyruvic acid

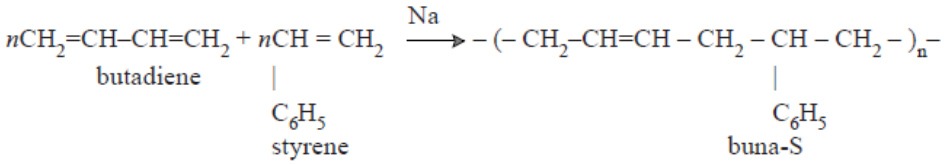
Mild oxidising agent like Fenton's reagent Fe^{2+}/H_2O_2 forms **pyruvic acid** with lactic acid

$$\underset{\text{Lactic acid}}{CH_3CH(OH)COOH} \xrightarrow[H_2O_2/Fe^{2+}]{(O)} \underset{\text{Pyruvic acid}}{CH_3COCOOH}$$

63. How are the following obtained? Mention one use for each.
i) Buna S ii) Nylon 6,6

Buna S

It is obtained by the polymerization of butadiene and styrene in presence of sodium metal.

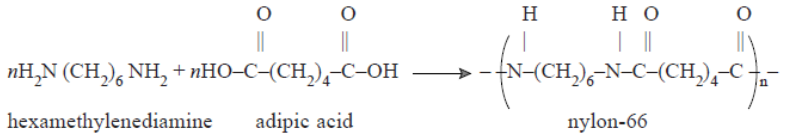


Uses:

Neoprene and Buna-S are extremely resistant towards wear and tear and used for the manufacture of tyres, rubber tubes and other mechanical rubber goods.

Nylon-6,6

It is obtained by condensing adipic acid with hexamethylenediamine with the elimination of water molecule. The chain length depends upon the temperature and time for which the process is carried out.



The polyamides are identified by numbers. These numbers refer to the number of carbon atoms in diamine and in the dibasic acid. As in the above case, the carbon atoms are 6 in each case, therefore, the product is described as nylon-66.

Uses; Crinkled nylon fibres are used for making elastic hosiery.

PART – IV **(4 x 10 = 40)**

Note: <u>Question No. 70 is compulsory and answer any *three* from the remaining questions.</u>

64. (a) Explain the change of electron affinity along a group.

a) **Change of Electron Affinity along a Group**

On moving down a group,the size of atom increases significantly and hence, the effective nuclear attraction for the electron decreases. Consequently the atom will possess less tendency to attract additional electrons towards itself. It means that electron affinity would decrease as we move down a group. In case of halogens the decrease in electron affinity from chlorine to iodine is due to steady increase in atomic radii from chlorine to iodine.

On moving down a group the electron affinity decreases. Thus, the electron affinity of Cl should be less than F. But actually the electron affinity of F (320 kJ mol-1) is less than Cl (348 kJ mol-1). The reason for this is probably due to small size of fluorine atom. The addition of an extra electron produces high electron density which increases strong electron-electron repulsion. The repulsive forces between electrons results in low electron affinity.

Electron affinities of noble gases are zero. As these atoms possess ns_2np_6 configuration in their valence shells, these are stablest atoms and there are no chances for the addition of an extra electron. Thus, the electron affinities of noble gases are zero.

Electron affinities of beryllium and nitrogen are almost zero. This may be due to the extra stability of the completed 2s-orbital in beryllium and of the exactly half-filled p-orbital in nitrogen. As these are stable electronic configurations, they do not have tendency to accept electrons and therefore, the electron affinities for beryllium and nitrogen are zero.

(b) Illustrate (i) tri basic nature of ortho phosphoric acid
(ii) reducing property of phosphorous acid

i)It is a tribasic acid. It combines with alkalies like NaOH to form three series of salts.

$$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$$
Sodium Di hydrogen Phosphate

$$H_3PO_4 + 2NaOH \rightarrow Na_2HPO_4 + 2H_2O$$
Disodium hydrogen Phosphate

$$H_3PO_4 + 3NaOH \rightarrow Na_3PO_4 + 3H_2O$$
Sodium Phosphate

ii) It is a powerful reducing agent because it has P-H bond. It reduces silver nitrate solution into silver.

$$2AgNO_3 + H_3PO_3 + H_2O \rightarrow 2Ag + H_3PO_4 + 2HNO_3$$

65. (a) In the coordination complex $K_3[Cr(C_2O_4)_3].3H_2O$ Mention the following
a) IUPAC name of the complex b) Central metal ion c) Ligands
d) Coordination number e) Geometry

a) IUPAC name of the complex - Potassium tris oxalate chromate(III) trihydrate
b) Central metal ion - Chromium
c) Ligands - oxalate
d) Coordination number -6
e) Geometry -Octahedral

(b) Discuss the controlled fission.

Nuclear Power Generator

A nuclear reactor or nuclear power generator is a kind of furnace for carrying out the controlled fission of a radioactive material like U^{235} for producing power. The core of the nuclear reactor produces heat through nuclear fission. Heavy water at high pressure takes heat away from the core. In the heat exchanger, the heavy water inside the reactor gives up its heat to water outside the reactor, which boils to form steam. The steam is taken away to drive turbines that make electricity. In Tamilnadu atomic power stations generating electricity are situated at Kalpakkam and another one is being constructed at Koodamkulam.

66. (a) Explain the types of ionic crystals.

a) **Ionic Crystals:**

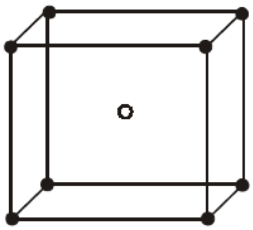
In ionic crystals, the units occupying lattice points are positive and negative ions. Each ion of a given sign is held by coulombic forces of attraction to all ions of opposite sign. The forces are very strong. The ionic crystals have the following characteristics.

Types of Ionic Crystals:

The structure of ionic crystals is determined by the ratio of the numbers, the ratio of the sizes and the structural units. In general, ionic crystals are classified into AB and AB_2 type.
Substance of the general formula AB mostly crystallise in one of the following six forms.
Lattice type : CsCl NaCl FeS ZnO ZnS BN
Coordination number : 8 6 6 4 4 3

AB Type:

Let us discuss the structure of CsCl for AB type. It is body centered cubic system. The chloride ions are at the corners of a cube where as Cs^+ ion is at the centre of the cube or vice versa. Each Cs^+ ion is connected with eight Cl^- ion and Cl^- is connected with eight Cs+ ions.



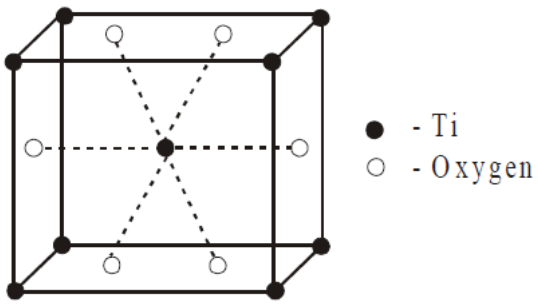
$$\text{Number of chloride ions per unit} = \frac{N_c}{8} = \frac{8}{8} = 1$$

$$\text{Number of cesium ion per unit} = \frac{N_b}{1} = \frac{1}{1} = 1$$

Thus number of CsCl units per unit cell is one.

AB_2 Type:

Compounds having the general formula AB_2 generally crystallise in forms based on the following eight typical lattices like CO_2, SiO_2, TiO_2, CaF_2, Cu_2O, FeS_2, CdI_2 and MoS_2. For example Rutile (TiO_2) has the following structure.



(b) Discuss the technical application of colloids.

(i) Electrical precipitation of smoke: Smoke is a colloidal solution of solid particles such as carbon, arsenic compounds, dust, etc., in air. The smoke, before it comes out from the chimney, is led through a chamber containing plates having a charge opposite to that carried by smoke particles.The particles on coming in contact with these plates lose their charge and get precipitated. The particles thus settle down on the floor of the chamber. The precipitator is called **Cottrell precipitator.**

(ii) Purification of drinking water: The water obtained from natural sources often contains bacteria and suspended impurities. Alum is added to such water so as to destroy the bacteria as well as to coagulate the suspended impurities and make water fit for drinking purposes.

(iii) Medicines: Most of the medicines in use are colloidal in nature. For example, argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing kalazar. Colloidal gold is used for intramuscular injection. Milk of magnesia, an emulsion, is used for stomach disorders. Colloidal medicines are more effective because these are easily assimilated.

(iv) Tanning: Animal hides are colloidal in nature. When a hide, which has positively charged particles, is soaked in tannin, which contains negatively charged colloidal particles, mutual coagulation takes place, which results in the hardening of leather. The process is termed as **tanning.** Chromium salts have been used in place of tannin.

(v) Photographic plates and films : The photographic plates or films are prepared by coating an emulsion of the light sensitive silver bromide in gelatin over glass plates or celluloid films.

67. (a) Derive Henderson equation.

a) **Henderson equation :** The pH of an acid buffer can be calculated from the dissociation constant, Ka, of the weak acid and the concentrations of the acid and the salt used.

The dissociation expression of the weak acid, HA, may be represented as

$$HA \rightleftharpoons H^+ + A^-$$

and
$$K_a = \frac{[H^+][A^-]}{[HA]}$$

or
$$[H^+] = \frac{[HA]K_a}{[A^-]} \quad \ldots (1)$$

$$[H^+] = K_a \times \frac{[acid]}{[salt]} \quad \ldots (2)$$

$$-\log [H^+] = -\log K_a - \log \frac{[acid]}{[salt]} \quad \ldots (3)$$

But $-\log [H^+] = pH$ and $-\log K_a = pK_a$

Thus from (3) we have

$$pH = pK_a - \log \frac{[acid]}{[salt]} = pKa + \log \frac{[salt]}{[acid]}$$

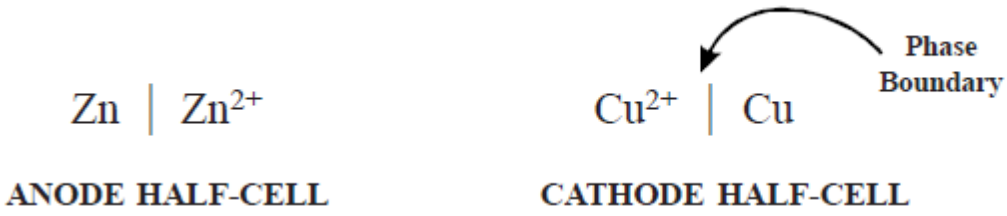
Hence, $$pH = pK_a + \log \frac{[salt]}{[acid]}$$

This relationship is called the **Henderson-Hasselbalch equation** or **simply Henderson equation.**

(b) Write notes on IUPAC conventions of representation of a cell.

IUPAC Conventions:

(1) a single vertical line (|) represents a phase boundary between metal electrode and ion solution (electrolyte). Thus the two half-cells in a voltaic cell are indicated as

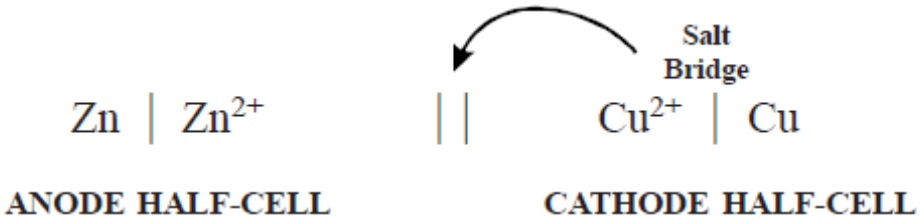


It may be noted that the metal electrode in anode half-cell is on the left, while in cathode half-cell it is on the right of the metal ion.

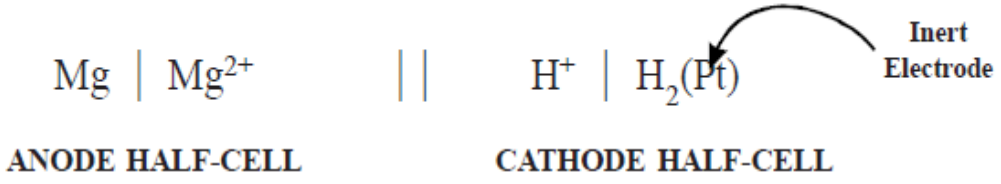
(2) A double vertical line represents the salt bridge, porous partition or any other means of permitting ion flow while preventing the electrolyte from mixing.

(3) Anode half-cell is written on the left and cathode half-cell on the right.

(4) In the complete cell diagram, the two half-cells are separated by a double vertical line (salt bridge) in between. The zinc-copper cell can now be written as



(5) The symbol for an inert electrode, like the platinum electrode is often enclosed in a bracket. For **example**,

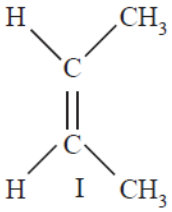


68. (a) Explain Geometrical isomerism with example.

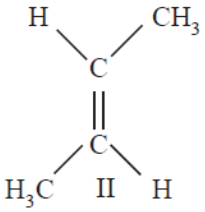
Geometrical Isomerism :

Isomerism that arises out of difference in the spatial arrangement of atoms or groups about the doubly bonded carbon atoms is called **Geometrical isomerism**. These isomers are not mirror images of each other. Rotation about C=C is not possible at normal conditions and hence the isomers are isolable.

If different atoms or groups are bonded to the 'C=C' bond in a molecule, more than one spatial arrangement is possible. For example, 2-butene exists in two isomeric forms.



Cis isomer



Trans isomer

This isomerism arises out of the hindrance to rotation about the C=C bond in such molecules. The cis-trans isomers do not differ much in chemical properties. They differ in physical properties like boiling point, melting point, crystal structure, solubility and refractive index. Highly substituted olefin is more stable than less substituted olefin. Among substituted olefins, trans olefin is more stable than cisolefin. In the cis isomer because similar groups are very near each other, Vander Waals repulsion and steric hindrance make the molecule much unstable. In the trans isomer, similar groups are diagonally opposite to each other. Hence there is no such steric interaction. Generally trans isomer is more stable than cis isomer. Hence reactivity of cis isomer may be little higher than the trans isomer. The energy of the cis isomer is greater than that of trans isomer. Though at room temperature, cis and trans isomers are stable and are not interconvertible, on heating to a certain temperature, trans isomer can be converted to cis isomer and vice-versa. 'Breaking of carbon-carbon bond and its reformation is responsible for the interconversion.'

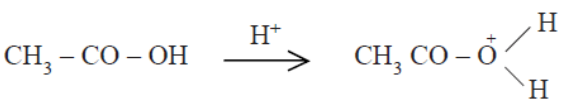
Trans isomer ↔Cis isomer

(b) Give the mechanism involved in the esterification of a carboxylic acid with alcohol.

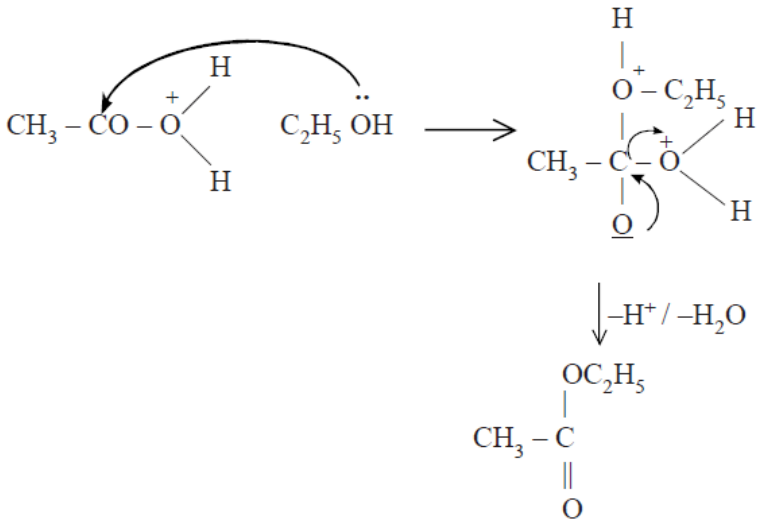
Mechanism of esterification:

Protonation of the –OH group of the acid, enhances the nucleophilic attack by alcohol to give the ester.

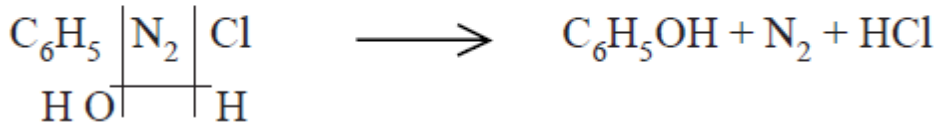
Step 1. Protonation of carboxylic acid

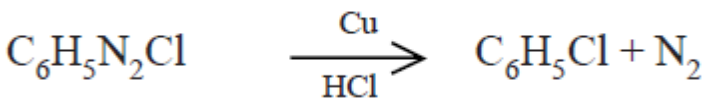


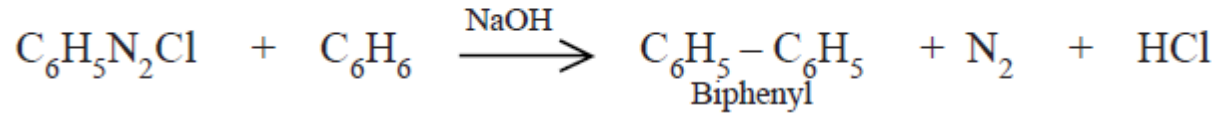
Step 2. Attack by nucleophile.

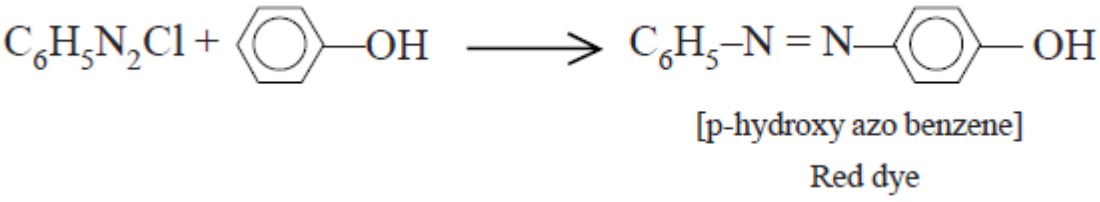


69. (a) How are (i) phenol (ii) biphenyl (iii) Chlorobenzene (iv) p-hydroxyazobenzene prepared by using benzene diazonium chloride?







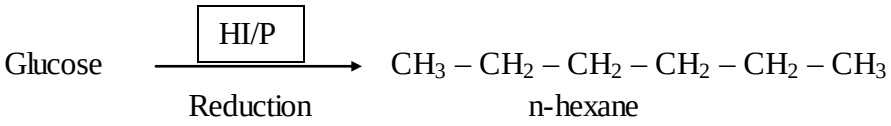


(b) How is the structure of glucose determined?

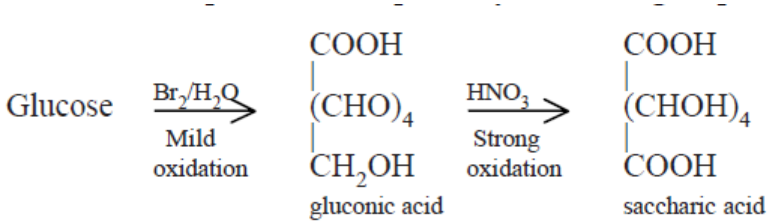
The structure of glucose has been derived from the following facts.

- Elemental analysis and molecular weight determination show that the molecular formula of glucose is $C_6H_{12}O_6$.

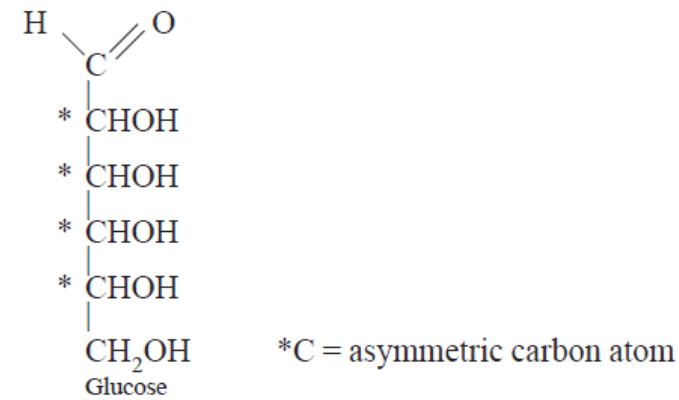
- Complete reduction of glucose with concentrated hydriodic acid in the presence of red phosphorous produces n-hexane as the major product. This indicates that the six carbon atoms in the glucose molecule form a unbranched chain of six carbon atoms



- Glucose readily dissolves in water to give a neutral solution. This indicates that the glucose molecule does not contain a carboxyl group.
- Glucose reacts with hydroxylamine to form a monoxime or adds only one mole of HCN to give a cyanohydrin. This reaction indicates the **presence of either an aldehyde**
- Mild oxidation of glucose with bromine water gives gluconic acid. This indicates the **presence of an aldehyde group** since only the aldehyde group can be oxidised to an acid, containing same number of carbon atoms. Since the six carbon atoms in glucose form a consecutive unbranched chain, the aldehyde group, must occupy one end of this chain.
- Further oxidation of gluconic acid with nitric acid gives saccharic acid. This indicates the **presence of a primary alcoholic group.**



- Glucose **reduces** an ammoniacal solution of silver nitrate (Tollen's reagent) to metallic silver or a basic solution of cupric ion (Fehling's solution) to red cuprous oxide. These reactions further confirm the **presence** of a **aldehyde group.**
- Glucose reacts with acetic anhydride in the presence of pyridine to form a penta acetate. This reaction indicates the **presence of five hydroxyl groups** in a glucose molecule.
- From the above evidences we conclude that glucose is a penta hydroxyl Z hexanal (an aldohexose) and can be represented by the following structure.



(2,3,4,5,6 penta hydroxy hexanal)

70. (a) An element (A) belongs to Group No. 11 and Period No. 4. (A) reacts with oxygen at two different temperatures forming compounds (B) and (C). (A) also reacts with dil. HNO_3 to give the compound (D). Find out (A), (B) , (C) and (D). Explain the reactions.

$$2Cu + O_2 \xrightarrow{\text{Below } 1370\,K} 2CuO$$

A B

$$4Cu + O_2 \xrightarrow{\text{Above } 1370\ K} 2Cu_2O$$

A C

$$3Cu + 8HNO_3(dil) \rightarrow 3Cu(NO_3)_2 + 2NO\uparrow + 4H_2O$$

A D

S.no	Compound	Molecular formula	Name of the compound
1.	A	Cu	Copper
2.	B	CuO	Cupric oxide
3.	C	Cu_2O	Cuprous oxide
4.	D	$Cu(NO_3)_2$	Copper nitrate

(b) Compound (A) of molecular formula C_7H_8 is treated with chlorine and then treated with NaOH to give aromatic alcohol (B) of molecular formula C_7H_8O which liberates H_2 with Metallic Na. Compound (B) on reaction with CH_3COCl gives the compound (C) of molecular Formula $C_9H_{10}O_2$which has the fragrance of jasmine. Identify (A),(B) and (C). Explain the reactions.

$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[-HCl]{Cl_2} \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow{NaOH} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + NaCl$$

A B

$$C_6H_5CH_2OH + CH_3COCl \rightarrow C_6H_5CH_2COOCH_3$$

A C

S.no	Compound	Molecular formula	Name of the compound
1.	A	$C_6H_5CH_3$	Toluene
2.	B	$C_6H_5CH_2OH$	Benzyl alcohol
3.	C	$C_6H_5CH_2COOCH_3$	Benzyl acetate

(c) An organic compound A (C_2H_4O) with HCN gives B (C_3H_5ON), B on hydrolysis gives C ($C_3H_6O_3$) which is an optically active compound. C also undergoes iodoform test. What are A,B,C ? Explain the reactions.

$$CH_3CHO + HCN \rightarrow CH_3CHOHCN$$

A B

$$CH_3 - \underset{\underset{OH}{|}}{CH} - CN \xrightarrow[\Delta]{H^+/H_2O} CH_3 - \underset{\underset{OH}{|}}{CH} - COOH$$

Acetaldehyde cyanohydrin Lactic acid

B C

no	Compound	Molecular formula	Name of the compound
1.	A	CH_3CHO	Acetaldehyde
2.	B	$CH_3CHOHCN$	Acetaldehyde cyano hydrin
3.	C	$CH_3 - \underset{\underset{OH}{\|}}{CH} - COOH$	Lactic acid

(d) What current strength in ampere will be required to liberate 10 gm of Iodine from Potassium iodide solution in one hour? (Equivalent mass of iodine is 127).

Solution : 127 g of iodine (1g eqvt) is liberated by = 96,500 coulomb

10 g of iodine is liberated by $= \frac{96,500}{127} \times 10$ coulomb

Let the current strength be = I

Time in seconds = $1 \times 60 \times 60$

We know that the quantity of electricity, Q, used is given by the expression

$Q = I \times$ time in seconds

Curernt strength, $I = \frac{Q}{t} = \frac{96,500 \times 10}{127 \times 60 \times 60}$

= 2.11 ampere.