SAMPLE
QUESTION
PAPER

BLUE PRINT

Time Allowed : 3 hours **Maximum Marks :** 70

S. No.	Chapter	Passage based/ MCQs/A & R (1 mark)	SA-I (2 marks)	SA-II (3 marks)	LA (5 marks)	Total
1.	The Solid State	1(1)	–	1(3)	–	**9(23)**
2.	Solutions	–	–	–	1(5)	
3.	Electrochemistry	–	1(2)	–	1(5)	
4.	Chemical Kinetics	–	1(2)	1(3)	–	
5.	Surface Chemistry	2(2)	–	–	–	
6.	The *p*-Block Elements	3(3)	1(2)	1(3)	–	**10(19)**
7.	The *d*- and *f*-Block Elements	2(2)	1(2)	1(3)	–	
8.	Coordination Compounds	1(4)	–	–	–	
9.	Haloalkanes and Haloarenes	3(3)	1(2)	–	–	**14(28)**
10.	Alcohols, Phenols and Ethers	2(2)	–	1(3)	–	
11.	Aldehydes, Ketones and Carboxylic Acids	1(1)	1(2)	–	1(5)	
12.	Amines	–	2(4)	–	–	
13.	Biomolecules	1(4)	1(2)	–	–	
	Total	**16(22)**	**9(18)**	**5(15)**	**3(15)**	**33(70)**

Subject Code : 043

CHEMISTRY

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

General Instructions : Read the following instructions carefully.

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

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

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

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

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

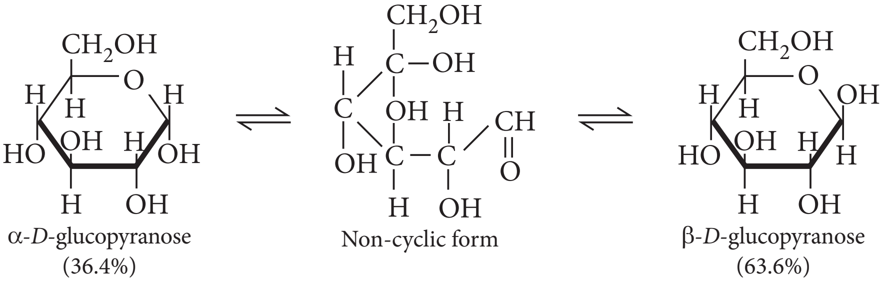
(f) There is no overall choice. However, internal choices have been provided.

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

SECTION - A (OBJECTIVE TYPE)

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

Formation of ring structure in monosaccharides results in creation of an additional asymmetric carbon called anomeric carbon (C-1 of an aldose, C-2 of a ketose). For an aldohexose, such as glucose, the number of asymmetric carbon atoms increases to 5 and the number of possible isomers, therefore increase to $2^5 = 32$. When the two forms differ in the arrangement of the substituents around the carbonyl carbon (*i.e.*, C-1) are called anomers.



The anomers are not stable under ordinary condition, tend to interconvert constantly. The interconversion of two anomeric forms is referred to as mutarotation. Both anomers are present in equilibrium with the open chain.

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

(i) Mutarotation is characteristic feature of

(a) epimers (b) enantiomers (c) anomers (d) ring chain isomers.

(ii) What percentage of β-*D*-(+) glucopyranose is found at equilibrium in the aqueous solution?

(a) 50% (b) ≈ 100% (c) 36% (d) 64%

(iii) α-*D*-(+)-glucose and β-*D*-(+)-glucose are
(a) enantiomers (b) conformers (c) epimers (d) anomers.

(iv) The rapid interconversion of α-*D*-glucose and β-*D*-glucose in solution is known as
(a) racemization (b) asymmetric induction
(c) functional isomerism (d) mutarotation.

OR

Mutarotation does not occur in
(a) sucrose (b) *D*-glucose (c) *L*-glucose (d) none of these.

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

The majority of coordination compounds that one encounters are size-coordinate, the structure adopted being that of a regular or slightly distorted octahedron. It is important to recognise that the octahedral geometry is found for complexes of both transition metal and main group elements. Example of octahedral complexes of main group elements are [Al(*acac*)$_3$], $[InCl_6]^{3-}$ and $[PCl_6]^-$. It is common for transition metal elements.

Tetrahedral arrangement of ligands is commonly exhibited by complexes with coordination number four. It is found for both transition metal and non-transition elements, for the latter it is rather common. The four coordinate arrangement in which the ligands lie at the vertices of a square (square planar complexes) is almost entirely confined to transition metal complexes (but XeF_4 also have this structure).
e.g., $[Pt\ Cl_4]^{2-}$, $[PdCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ etc.

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

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

(i) Assertion : In a mixture of Cd(II) and Cu(II), Cd^{2+} gets precipitated in presence of KCN by H_2S.
Reason : The stability constant of $[Cu(CN)_4]^{3-}$ is greater than $[Cd(CN)_4]^{2-}$.

(ii) Assertion : $[Fe(CN)_6]^{3-}$ has d^2sp^3 type hybridisation.
Reason : $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.

OR

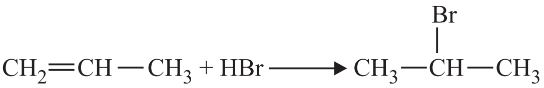
Assertion : F^- ion is a weak ligand and forms outer orbital complex.
Reason : F^- ion cannot force the electrons of d_{z^2} and $d_{x^2-y^2}$ orbitals of the inner shell to occupy d_{xy}, d_{yz} and d_{zx} orbitals of the same shell.

(iii) Assertion : $[Fe(H_2O)_5NO]SO_4$ is paramagnetic.
Reason : The Fe in $[Fe(H_2O)_5NO]SO_4$ has three unpaired electrons.

(iv) Assertion : Co when dissolve in conc. HCl give blue ion.
Reason : Formation of blue $[CoCl_4]^{2-}$ ion takes place.

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

3. The basic character of the transition metal monoxide follows the order
(a) TiO > VO > CrO > FeO (b) VO > CrO > TiO > FeO
(c) CrO > VO > FeO > TiO (d) TiO > FeO > VO > CrO



4. The reaction, $CH_2{=}CH{-}CH_3 + HBr \longrightarrow CH_3{-}\overset{\overset{\large Br}{|}}{C}H{-}CH_3$ is an example of
(a) nucleophilic addition
(b) free radical addition
(c) electrophilic addition
(d) electrophilic substitution.

5. The transition metal ion that has 'spin-only' magnetic moment value of 5.96 B.M. is
(a) Mn^{2+}
(b) Fe^{2+}
(c) V^{2+}
(d) Cu^{2+}

OR

Which of the following statements is incorrect?
(a) Iron belongs to 3*d*-transition series of the periodic table.
(b) Iron belongs to *f*-block of the periodic table.
(c) Iron belongs to first transition series.
(d) Iron belongs to group VIII of the periodic table.

6. How many layers are adsorbed in chemical adsorption?
(a) One
(b) Two
(c) Many
(d) Zero

OR

Adsorption is an exothermic process, because during adsorption
(a) surface energy increases
(b) surface energy decreases
(c) surface energy remains same
(d) residual forces of attraction increase.

7. Which of the following is not correctly matched?
(a) Acidic oxides - P_2O_5, NO_2, Cl_2O_7
(b) Basic oxides - Na_2O, CaO, MgO
(c) Neutral oxides - CO_2, CO, BeO
(d) Amphoteric oxides - ZnO, SnO, Al_2O_3

8. Which of the following will not yield acetic acid on strong oxidation?
(a) Butanone
(b) Propanone
(c) Ethyl ethanoate
(d) Ethanol

OR

X is heated with soda lime and gives ethane. *X* is
(a) ethanoic acid
(b) methanoic acid
(c) propanoic acid
(d) either (a) or (c).

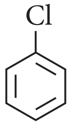
9. Phenol on reduction with H_2 in the presence of Ni catalyst gives
(a) benzene
(b) toluene
(c) cyclohexane
(d) cyclohexanol.

10. Amongst the following statements, which is incorrect?
(a) The ceaseless zig-zag motion of sol particles is due to the unbalanced bombardment of particles by the molecules of dispersion medium.
(b) The intensity of zig-zag motion increases with the increase in the size of the particles.
(c) The zig-zag motion of particles becomes intense at high temperature.
(d) This motion has a stirring effect which does not permit the particles to settle.

OR

Which of following statements is not true for a lyophobic sol?
(a) It carries charges.
(b) It can be easily solvated.
(c) It is less stable in a solvent.
(d) The coagulation of this sol is irreversible in nature.

11. Which one of the following does not give white precipitate with acidified silver nitrate solution?

(a) 

(b) $CH_2{=}CH{-}Cl$

(c) $CH_2{=}CH{-}CH_2{-}Cl$

(d) Both (a) and (b)

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

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

12. **Assertion :** The heavier p-block elements do not form strong π-bonds.

Reason : The heavier elements of p-block form $d\pi - d\pi$ or $p\pi - d\pi$ bonds.

13. **Assertion :** An alcohol does not react with halide ions as such but on dissolution in strong acids it does react smoothly forming an alkyl halide.

Reason : The strong acid accelerates the removal of proton from the –OH group of the alcohol.

14. **Assertion :** Both rhombic and monoclinic sulphur exist as S_8 but oxygen exists as O_2.

Reason : Oxygen forms $p\pi$-$p\pi$ multiple bond due to small size and small bond length but $p\pi$-$p\pi$ bonding is not possible in sulphur.

15. **Assertion :** Hydrides of group-16 elements show volatility in the order : $H_2O > H_2S > H_2Se > H_2Te$.

Reason : Electronegativity of group-16 elements decreases down the group from oxygen to tellurium.

OR

Assertion : N_2 is less reactive than P_4.

Reason : Nitrogen has more electron gain enthalpy than phosphorous.

16. **Assertion :** $CH_2{=}CH{-}CH_2{-}X$ is an example of allyl halides.

Reason : These are the compounds in which the halogen atom is bonded to an sp^2 hybridised carbon atom.

SECTION - B

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

17. Why on dilution the Λ_m of CH_3COOH increases drastically, while that of CH_3COONa increases gradually?

18. How do you account for the following :
(a) All scandium salts are white. (At. number of Sc = 21)
(b) The first ionisation energies of the 5d-transition elements are higher than those of the 3d-and 4d-transition elements in respective groups.

OR

(a) Why is the third ionization energy of manganese (At. number = 25) unexpectedly high?
(b) In which compound transition metals show very low oxidation states?

19. How will you obtain
(a) propanoic acid from ethyne
(b) 2-methylbutanoic acid from butan-2-ol ?

20. A reaction is of second order with respect to its reactant. How will its reaction rate be affected if the concentration of the reactant is (i) doubled (ii) reduced to half ?

21. (a) Predict all the alkenes that would be formed by dehydrohalogenation of the following halide with sodium ethoxide in ethanol and identify the major alkene :
2-Chloro-2-methylbutane

(b) Arrange each set of compounds in order of increasing boiling points :
1-Chloropropane, *iso*-Propyl chloride, 1-Chlorobutane

OR

(a) In the preparation of Grignard reagent, all the starting materials must be dry. Why?

(b) Electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions. Why ?

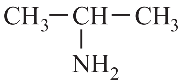
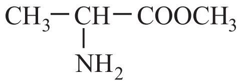
22. Explain the following observations :

(a) In aqueous solution, the K_b order is $Me_2NH > MeNH_2 > Me_3N$.

(b) Tertiary amines do not undergo acylation reaction.

OR

Which amine in each of the following pairs is a stronger base? Give reason.

(a)  $CH_3-\underset{NH_2}{\underset{|}{CH}}-CH_3$ and  $CH_3-\underset{NH_2}{\underset{|}{CH}}-COOCH_3$

(b) $CH_3CH_2CH_2NH_2$ and $CH_3NHCH_2CH_3$

23. (i) Why cannot primary aromatic amines be prepared by Gabriel phthalimide synthesis?

(ii) Arrange the following compounds in increasing order of solubility in water :
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$

24. Explain : Oxygen is a gas, but sulphur is a solid at room temperature.

25. Write Haworth structure of α and β-*D* – (–) fructose.

SECTION - C

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

26. Complete the reactions :

(i) $Cl_2 + NaOH$ (cold and dil.) $\rightarrow$

(ii) $F_2 + NaOH$ (dil.) $\rightarrow$

(iii) $F_2 + H_2O \rightarrow$

27. Prove that half-life period of a zero order reaction is directly proportional to initial concentration of the reactant.

28. (a) Name the reagents and write the chemical equations for the preparation of the following compounds by Williamson's synthesis :

(i) Ethoxybenzene (ii) 2-Methyl-2-methoxypropane

(b) Why do phenols not give the protonation reaction readily?

OR

(i) The $C\overset{:\ddot{O}:}{\smile}H$ bond angle in alcohol is slightly less than the tetrahedral angle. Why?

(ii) Why the dehydration reaction of alcohols to give ethers is mainly applicable to primary alcohols?

(iii) Why are ethers *o*-, *p*-directing?

29.

$E^\circ_{(M^{2+}/M)}$	Cr	Mn	Fe	Co	Ni	Cu
	–0.91	–1.18	–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.

30. Silver crystallises with face-centred cubic unit cell. Each side of this unit cell has a length of 409 pm. What is the radius of silver atom? Assume the atoms just touch each other on the diagonal across the face of the unit cell.

OR

The density of lead is 11.35 g cm^{-3} and crystallise with *fcc* unit cell. Estimate the radius of lead atom.
(At. mass of lead = 207 g mol^{-1} and $N_A = 6.02 \times 10^{23}$ mol^{-1})

SECTION - D

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

31. (i) How will you convert acetic acid to
(a) malonic acid (b) *tert*-butyl alcohol?
(ii) Give chemical tests to distinguish between the following pairs of compounds :
(a) Methyl acetate and ethyl acetate (b) Benzaldehyde and benzoic acid
(c) Phenol and benzoic acid

OR

(i) State reasons for the following :
(a) Monochloroethanoic acid has a higher pK_a value than dichloroethanoic acid.
(b) Ethanoic acid is a weaker acid than benzoic acid.
(ii) How will you convert acetic acid to
(a) glycine (b) acetylene (c) ethylamine?

32. (i) 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. 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})
(ii) Which of the two, molarity or molality, is a better way to express the concentration of a solution and why?
(iii) An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molecular mass of the solute?

OR

(i) Differentiate between molarity and molality in a solution. What is the effect of temperature change on molarity and molality in a solution?
(ii) Give reasons for the following :
(a) Measurement of osmotic pressure method is preferred for the determination of molar masses of macromolecules such as proteins and polymers.
(b) Elevation of boiling point of 1 M KCl solution is nearly double than that of 1 M sugar solution.

33. (a) Calculate standard emf of the cell in which following reaction takes place at 25°C.
$Cu_{(s)} + Cl_{2(g)} \rightleftharpoons Cu^{2+} + 2Cl^-$
$E^\circ_{Cl_2/Cl^-} = +1.36$ V, $E^\circ_{Cu^{2+}/Cu} = +0.34$ V
Also calculate standard free energy change and equilibrium constant of the reaction.
(b) The emf of a galvanic cell composed of two hydrogen electrode is 0.16 volt at 25°C. Calculate pH of the anode solution if the cathode is in a solution with pH = 1.

OR

Calculate e.m.f and ΔG for the following cell :

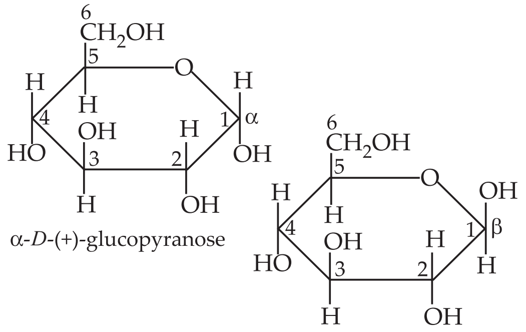
$Mg_{(s)} \mid Mg^{2+}$ (0.001 M) $\|$ Cu^{2+} (0.0001 M) $\mid Cu_{(s)}$; $E^\circ_{(Mg^{2+}/Mg)} = -2\cdot 37$ V, $E^\circ_{(Cu^{2+}/Cu)} = +0.34$ V

SOLUTIONS

1. (i) (c)

(ii) (d) : Ordinary glucose is α-glucose, with a fresh aqueous solution having specific rotation, $[\alpha]_D = +111°$. On keeping the solution for sometime, α-glucose slowly changes into an equilibrium mixture of α-glucose (36%) and β-glucose(64%) and the mixture has specific rotation + 52.5°.

(iii) (d) : Structures of α-*D*-(+)-glucose and β-*D*-(+)-glucose are :



α-*D*-(+)-glucopyranose

β-*D*-(+)-glucopyranose

A pair of stereoisomers which differ in configuration at C-1 are known as anomers.

(iv) (d) : Spontaneous rapid interconversion of α-*D* glucose and β-*D*-glucose in solution is known as mutarotation.

OR

(a) : Sucrose does not show mutarotation since there is no hemiacetal structure in sucrose.

2. (i) (a) : $Cd^{2+} + 2CN^- \rightarrow Cd(CN)_2$

$Cd(CN)_2 + 2CN^- \rightarrow [Cd(CN)_4]^{2-}$

$[Cd(CN)_4]^{2-}$ is colourless compound and not too stable. When hydrogen sulphide gas is added, cadmium sulphide is precipitated.

$[Cd(CN)_4]^{2-} + H_2S \rightarrow CdS\downarrow + 2H^+ + 4CN^-$

But in case of Cu^{2+},

$Cu^{2+} + 2CN^- \rightarrow Cu(CN)_2\downarrow$

$2Cu(CN)_2 \xrightarrow[\text{decomposes}]{\text{Quickly}} 2CuCN\downarrow + (CN)_2\uparrow$

$CuCN\downarrow + 3CN^- \rightarrow [Cu(CN)_4]^{3-}$

This complex is so stable (*i.e.*, $[Cu^+]$ is too low) that H_2S cannot precipitate Cu(I) sulphide (Cu_2S).

(ii) (c) : $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to one unpaired electron.

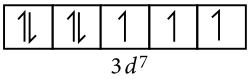
OR

(a) : F^- ion is a weak field ligand and it doesn't help in pairing of unpaired electron.

(iii) (a) : Fe^+ : [Ar] $3d^6\,4s^1$

When the weak field ligand H_2O and strong field ligand NO attack, the configuration changes as follows :

Fe^+ : [Ar] $3d^7\,4s^0$



∴ Fe^+ has 3 unpaired electrons.

(iv) (a)

3. (a) : Basic character of oxides decreases from left to right in a period of periodic table.

4. (c) : Alkenes undergo electrophilic addition with hydrogen halide.

5. (a) : Mn^{2+} with electronic configuration $3d^5 4s^0$ has 5 unpaired electrons.

Spin-only magnetic moment (μ) = $\sqrt{n(n+2)}$

For Mn^{2+} : $3d^5\,4s^0$

$\mu = \sqrt{5(5+2)} = 5.916 \approx 5.92$ B.M.

This is the calculated value of μ. Experimental μ for Mn^{2+} is 5.96. While the calculated μ for

$Fe^{2+} = 4.90$ B.M.

$V^{2+} = 3.87$ B.M. ; $Cu^{2+} = 1.73$ B.M.

OR

(b) Iron is a *d*-block element ($3d^6 4s^2$).

6. (a)

OR

(b) : During adsorption, there is always a decrease in residual forces of the surface, *i.e.*, there is decrease in surface energy which appears as heat, therefore adsorption is an exothermic process.

7. (c) : CO_2 is an acidic oxide, CO is neutral and BeO is an amphoteric oxide.

8. (c)

OR

(c) $X \xrightarrow{\text{NaOH/CaO}} C_2H_6$

$$\underset{\text{Propanoic acid}}{C_2H_5COOH} \xrightarrow{\text{NaOH/CaO}} \underset{\text{Ethane}}{C_2H_6}$$

9. (d)

10. (b) : The zig-zag motions are faster with smaller size.

OR

(b) : Lyophobic sols are not solvated hence, less stable in solvent.

11. (d) : In case of (a) and (b), there is partial double bond character in C—Cl bond and C-atom is sp^2-hybridised *i.e.*, C—Cl bond is stronger and hence, chlorine cannot be easily replaced.

12. (a)

13. (c) : The strong acid protonates the –OH group thereby making it a good leaving group.

14. (a)

15. (d) OR (c)

16. (c)

17. In case of CH_3COOH, which is a weak electrolyte, the number of ions increase on dilution due to an increase in degree of dissociation.
$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$
In case of strong electrolyte the number of ions remains same but the interionic attraction decreases.

18. (a) Sc^{3+} has d^0 configuration, no d-d transitions are possible. So, all scandium salts are white.
(b) The first ionisation energy of 5d-transition elements is higher due to their higher effective nuclear charge. This is due to poor shielding effect of 4f-electrons.

OR

(a) The bivalent ion Mn^{2+} ([Ar] $3d^5$) has stable half-filled configuration. So, the third ionisation energy of manganese is unexpectedly high.
(b) Compounds having ligand capable of π-acceptor character in addition to the σ-bonding show very low oxidation state, *e.g.*, CO, NO.

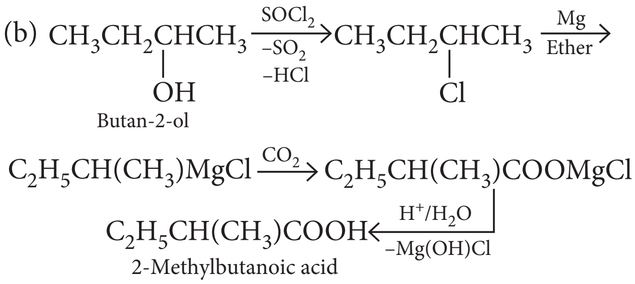
19. (a)

$$\underset{\text{Ethyne}}{HC\equiv CH}\xrightarrow[Hg^{2+}]{HCl}H_2C=CHCl\xrightarrow[\text{Ether}]{Mg}$$

$$H_2C=CHMgCl\xrightarrow{CO_2}H_2C=CHCOOMgCl\xrightarrow{H^+}$$

$$H_2C=CHCOOH\xrightarrow{H_2/Pd}\underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

(b)



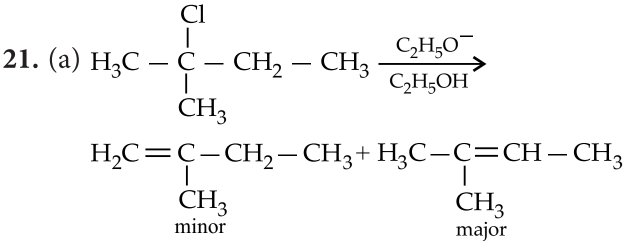
$$\underset{\text{Butan-2-ol}}{CH_3CH_2\underset{\substack{|\\OH}}{C}HCH_3}\xrightarrow[\substack{-SO_2\\-HCl}]{SOCl_2}CH_3CH_2\underset{\substack{|\\Cl}}{C}HCH_3\xrightarrow[\text{Ether}]{Mg}$$

$$C_2H_5CH(CH_3)MgCl\xrightarrow{CO_2}C_2H_5CH(CH_3)COOMgCl$$

$$\underset{\text{2-Methylbutanoic acid}}{C_2H_5CH(CH_3)COOH}\xleftarrow[-Mg(OH)Cl]{H^+/H_2O}$$

20. Let the concentration of the reactant $[A] = a$
Order of reaction = 2
so rate of reaction $= k\,[A]^2 = ka^2$ ...(1)
(i) Given that concentration of the reactant is doubled
So, $[A] = 2a$,
Putting the value in equation (1) we get
New rate of reaction, $R_1 = k(2a)^2 = 4ka^2$
Hence, rate of reaction will increased to 4 times.
(ii) Given that concentration of the reactant is reduced to half
So, $[A] = (1/2)a$
Putting the value in equation (1), we get
New rate of reaction $R_2 = k((1/2)a)^2 = (1/4)ka^2$
Hence, rate of reaction will reduce to 1/4.

21. (a)



$$H_3C-\overset{\substack{Cl\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_2-CH_3\xrightarrow[C_2H_5OH]{C_2H_5O^-}$$

$$\underset{\text{minor}}{H_2C=\underset{\substack{|\\CH_3}}{C}-CH_2-CH_3}+\underset{\text{major}}{H_3C-\underset{\substack{|\\CH_3}}{C}=CH-CH_3}$$

(b) As mass increases, boiling point increases. Amongst molecules with same mass, it is the size of the molecule that determines the boiling point. Branched compounds are more compact and therefore have less surface area as compared to their straight chain counterparts and therefore lower boiling point. The order of boiling point is, *iso*-propyl chloride < 1-chloropropane < 1-chlorobutane.

OR

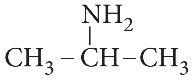
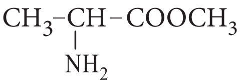
(a) Grignard reagents are highly reactive and react with any source of proton to give hydrocarbon. Therefore, if any starting material contains moisture then Grignard reagent is converted into alkane.

$RMgX + H_2O \longrightarrow RH + Mg(OH)X$

(b) Due to $-I$ effect, halogen withdraws electron density towards it and overall deactivation of the ring takes place. Therefore, for better yield drastic conditions are required.

22. (a) In alkyl amines, a combination of $+I$ effect of alkyl groups, steric factors and H-bonding factors determine the stability of ammonium cations in aqueous solution. All these factors are favourable for 2° amines and for smaller alkyl group, stability due to hydrogen bonding predominates over the stability due to $+I$ effect. Consequently, we get the following K_b order : $Me_2NH > MeNH_2 > Me_3N$
(b) Tertiary amines do not undergo acylation reaction because they do not contain any H-atom on the nitrogen atom.

OR

(a)  $CH_3-\overset{\substack{NH_2\\|}}{C}H-CH_3$ is more basic than  $CH_3-\underset{\substack{|\\NH_2}}{C}H-COOCH_3$ because $-COOCH_3$ is an electron withdrawing group which decrease the electron density on nitrogen atom.

(b) 2° amines are more basic than 1° amines, because in 2° amine there are two electron releasing groups and in 1° amine only one electron releasing group is present, so, $CH_3NHCH_2CH_3$ is more basic than $CH_3CH_2CH_2NH_2$.

23. (i) Aromatic amines cannot be prepared by Gabriel phthalimide synthesis because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

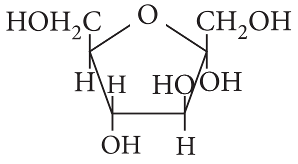
(ii) 1° amines are more soluble in water than 2° amines. Aniline due to large hydrophobic benzene ring is least soluble.

$$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$$

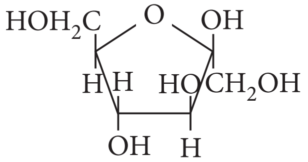
24. Due to small size and six electrons in the valence shell, oxygen atom forms a double bond, and exists as a diatomic molecule. These molecules exhibit van der Waals' forces of attraction and thus oxygen exists as a gas at room temperature.

Due to large atomic size of sulphur atom, does not form multiple bonds with itself. Sulphur exists as S_8 molecule with covalent bonds, forming a puckered eight membered ring structure. These S_8 molecules have high molecular mass and thus exhibit strong van der Waal's forces of attraction and thus sulphur exists as a solid at room temperature.

25. **(b)**



α-*D*-(–)-Fructose



β-*D*-(–)-Fructose

26. (i) $Cl_2 + 2NaOH \text{ (cold and dil.)} \rightarrow NaOCl + NaCl + H_2O$

(ii) $2F_2 + 2NaOH \text{ (dil.)} \rightarrow 2NaF + H_2O + OF_2$

(iii) $2F_2 + 2H_2O \rightarrow 4H^+ + 4F^- + O_2$

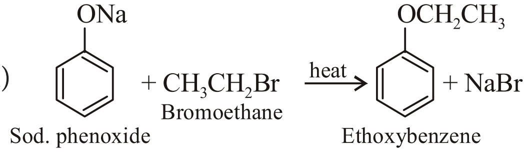
27. For zero order reaction, rate constant is given by :

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

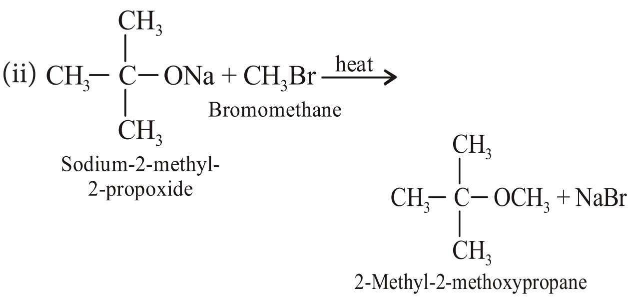
$$k = \frac{[R]_0 - \frac{[R]_0}{2}}{t_{1/2}} \Rightarrow k = \frac{[R]_0}{2t_{1/2}} \Rightarrow t_{1/2} = \frac{[R]_0}{2k}$$

In zero order reaction, $t_{1/2}$ is directly proportional to $[R]_0$.

28. (a) (i)



(ii)



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-ONa + CH_3Br \xrightarrow{heat} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OCH_3 + NaBr$$

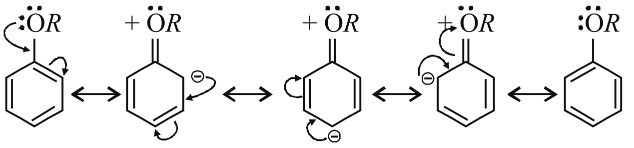
(b) In phenols, the lone pairs of electron on the oxygen atom are delocalised over the benzene ring due to resonance and hence are not easily available for protonation.

OR

(i) The bond angle $C\overset{:\ddot{O}:}{\frown}H$ in alcohol is slightly less than tetrahedral angle due to the repulsion between the unshared electron pairs of oxygen.

(ii) Dehydration of alcohol to yield ether is a S_N2 reaction and we know that 2° and 3° alcohol rarely show S_N2 reaction due to steric reason.

(iii)



Due to presence of electron releasing group on benzene ring, electron density at *ortho* and *para* position increases, So, an electrophile easily attacks on it.

29. (i) Electrode potential ($E°$) value is the sum of three factors :

(a) Enthalpy of atomisation; Δ_aH for $Cu_{(s)} \rightarrow Cu_{(g)}$

(b) Ionisation enthalpy; Δ_iH for $Cu_{(g)} \rightarrow Cu^{2+}_{(g)}$

(c) Hydration enthalpy; $\Delta_{hyd}H$ for $Cu^{2+}_{(g)} \rightarrow Cu^{2+}_{(aq)}$

In case of copper the sum of enthalpy of atomisation and ionisation enthalpy is greater than enthalpy of hydration.

This is why $E°_{M^{2+}/M}$ for Cu is positive.

(ii) Mn^{2+} ion has stable half-filled ($3d^5$) electronic configuration. Its ionisation enthalpy value is lower in comparison to hydration enthalpy. Hence $E°_{Mn^{2+}/Mn}$ is more negative.

(iii) Cr^{2+} is a stronger reducing agent than Fe^{2+}.

$E°_{Cr^{3+}/Cr^{2+}}$ is negative (–0.41 V) whereas $E°_{Fe^{3+}/Fe^{2+}}$ is positive (+ 0.77 V). Thus, Cr^{2+} is easily oxidized to Cr^{3+} but Fe^{2+} cannot be easily oxidized to Fe^{3+}. Hence, Cr^{2+} is stronger reducing agent than Fe^{2+}.

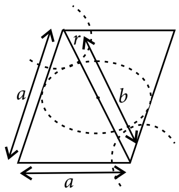
30. As the atoms just touch each other on the diagonal across the face of unit cell, therefore

$b^2 = a^2 + a^2 = 2a^2$

$b = \sqrt{2}a$ ...(i)

Also $b = r + 2r + r = 4r$ ...(ii)

From (i) and (ii), we get



$$4r = \sqrt{2}a \Rightarrow r = \frac{\sqrt{2}}{4}a;$$

$$r = \frac{1.414 \times 409\text{ pm}}{4}$$

$= 144.58$ pm

OR

$$d = \frac{Z \times M}{a^3 \times N_A} \Rightarrow a^3 = \frac{Z \times M}{d \times N_A} \quad ...(i)$$

For *fcc* unit cell, $Z = 4$

Given, $M = 207\text{ g mol}^{-1}$, $N_A = 6.02 \times 10^{23}\text{ mol}^{-1}$

$d = 11.35\text{ g cm}^{-3}$

Substituting these values in equation (i), we get

$$a^3 = \frac{4 \times 207\text{ g mol}^{-1}}{11.35\text{ g cm}^{-3} \times 6.02 \times 10^{23}\text{ mol}^{-1}}$$

$$a^3 = \frac{4 \times 207 \times 10}{11.35 \times 6.02 \times 10^{24}}\text{ cm}^3$$

$$\Rightarrow a = \left(\frac{8280}{11.35 \times 6.02}\right)^{1/3} \times 10^{-8}\text{ cm}$$

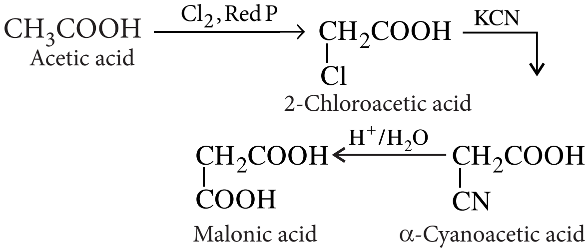
$\therefore\ a = 4.949 \times 10^{-8}\text{ cm} \Rightarrow a = 494.9\text{ pm}$

For *fcc*, $r = \dfrac{a}{2\sqrt{2}}$

$$\therefore\ r = \frac{494.9}{2\sqrt{2}}\text{ pm} = \frac{494.9\sqrt{2}}{4}\text{ pm} = \frac{494.9 \times 1.414}{4}\text{ pm}$$

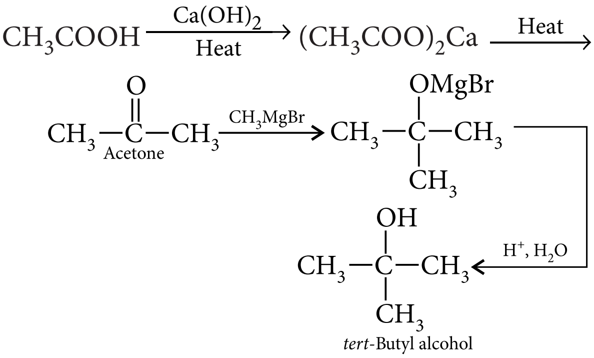
$\therefore\ r = 174.95$ pm

31. (i) (a) Acetic acid to malonic acid :



$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{Cl_2,\text{Red P}} \underset{\text{2-Chloroacetic acid}}{\underset{\displaystyle Cl}{CH_2COOH}} \xrightarrow{KCN} \underset{\alpha\text{-Cyanoacetic acid}}{\underset{\displaystyle CN}{CH_2COOH}} \xrightarrow{H^+/H_2O} \underset{\text{Malonic acid}}{\underset{\displaystyle COOH}{CH_2COOH}}$$

(b) Acetic acid to *tert*-butyl alcohol :



$$CH_3COOH \xrightarrow[\text{Heat}]{Ca(OH)_2} (CH_3COO)_2Ca \xrightarrow{\text{Heat}} \underset{\text{Acetone}}{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3} \xrightarrow{CH_3MgBr} CH_3-\overset{\displaystyle OMgBr}{\underset{\displaystyle CH_3}{C}}-CH_3 \xrightarrow{H^+,\ H_2O} \underset{\textit{tert}\text{-Butyl alcohol}}{CH_3-\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}-CH_3}$$

(ii) (a) Ethyl acetate is hydrolysed slowly by water to form ethyl alcohol while methyl acetate gives methyl alcohol.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \longrightarrow CH_3COOH + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

$$\underset{\text{Methyl acetate}}{CH_3COOCH_3} + H_2O \longrightarrow CH_3COOH + \underset{\text{Methyl alcohol}}{CH_3OH}$$

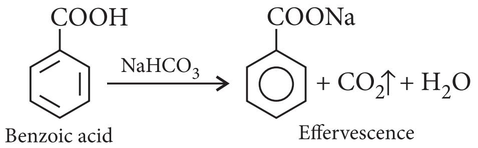
The hydrolysis product of ethyl acetate *i.e.*, ethanol undergoes iodoform test with iodine and alkali. Methanol does not give iodoform test.

(b) Benzaldehyde when treated with ammoniacal silver nitrate gives silver mirror.

$$C_6H_5CHO + 2[Ag(NH_3)_2]^+OH^- \longrightarrow C_6H_5COOH + \underset{\substack{\text{Silver}\\ \text{mirror}}}{2Ag} + 4NH_3 + 2H_2O$$

Benzoic acid does not give silver mirror test.

(c) Phenol and benzoic acid can be distinguished by their reactions with sodium bicarbonate solution. Benzoic acid will give effervescence with $NaHCO_3$ but phenol will not react.



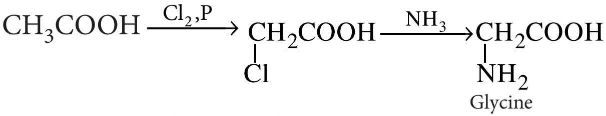
OR

(i) (a) The strength of an acid is indicated by pK_a value, where, $pK_a = -\log K_a$

Since, monochloroethanoic acid is weaker acid than dichloroethanoic acid so, it has lower value of dissociation constant K_a. Therefore, it has higher value of pK_a.

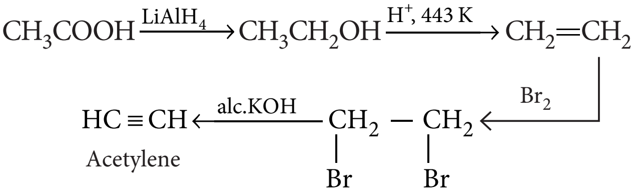
(b) —COOH group in benzoic acid is attached to sp^2-carbon of the phenyl ring and is more acidic than acetic acid in which —COOH group is attached to sp^3-carbon atom of $—CH_3$ group.

(ii) (a) Acetic acid to glycine :



$$CH_3COOH \xrightarrow{Cl_2,P} \underset{\displaystyle Cl}{CH_2COOH} \xrightarrow{NH_3} \underset{\text{Glycine}}{\underset{\displaystyle NH_2}{CH_2COOH}}$$

(b) Acetic acid to acetylene :



$$CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{H^+,\ 443\text{ K}} CH_2{=}CH_2 \xrightarrow{Br_2} \underset{\displaystyle Br \qquad Br}{CH_2 - CH_2} \xrightarrow{\text{alc.KOH}} \underset{\text{Acetylene}}{HC\equiv CH}$$

(c) Acetic acid to ethylamine :

$$CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{PCl_5} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow{NH_3} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

32. (i) $M_2 = \dfrac{K_b \times w_2 \times 1000}{\Delta T_b \times w_1} = \dfrac{2.53 \times 0.30 \times 1000}{0.0633 \times 100}$

$\approx 120 \text{ g mol}^{-1}$

Molar mass of CH_3COOH = 60 g/mol

$$i = \frac{M_{2(\text{calculated})}}{M_{2(\text{observed})}} = \frac{60}{120} = \frac{1}{2} = 0.5$$

As $i = 0.5$, therefore the solute (acetic acid) is dimerised in benzene.

(ii) Molarity of a solution is the number of moles of the solute dissolved per litre of the solution. The volume changes with temperature, *i.e.*, molarity changes with change in temperature. However, molality is independent of temperature as it is the number of moles of the solute dissolved per kg of the solvent and mass does not vary with temperature. Thus, it is better to express concentration in terms of molality.

(iii) Vapour pressure of pure water at its boiling point (p^o) = 1 atm = 1.013 bar

Vapour pressure of solution (p_s) = 1.004 bar

Let mass of solution be 100 g, then,

Mass of solute (w_2) = 2 g

Mass of solvent (w_1) = 100 – 2 = 98 g

By Raoult's law for dilute solution,

$$\frac{p^o - p_s}{p_s} = \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1} = \frac{w_2}{M_2} \times \frac{M_1}{w_1}$$

$$\frac{1.013 - 1.004}{1.004} = \frac{2}{M_2} \times \frac{18}{98}$$

$$M_2 = \frac{2 \times 18}{98 \times 8.96 \times 10^{-3}} = 40.998 \simeq 41 \text{ g mol}^{-1}$$

OR

(i)

Molarity	**Molality**
Number of moles of solute dissolved in one litre solution is called molarity.	Number of moles of solute dissolved in one kg solvent is called molality.
$M = \dfrac{\text{No. of moles of solute}}{\text{Volume of solution in litre}}$	$m = \dfrac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$
Molarity depends on temperature as volume depends on temperature. Molarity decreases with rise in temperature.	Molality is independent of temperature as mass does not change with temperature.

(ii) (a) In osmotic pressure method, pressure measured around the room temperature and the molarity of the solution is used instead of molality. That is why this method is used for determination of molar masses of macromolecules as they are generally not stable at higher temperatures.

(b) i for 1 M KCl = 2; i for sugar solution = 1

$\therefore \ \Delta T_b = iK_b m = 2K_b$ (for KCl);

$\Delta T_b = K_b$ (for sugar)

$\therefore \ \Delta T_b$ of 1 M KCl solution is double than that of 1 M sugar solution.

33. (a) The given cell may be represented as :

$Cu_{(s)} | Cu^{2+} || Cl_2 | Cl^-$

(i) $E^\circ_{\text{cell}} = E^\circ_c - E^\circ_a = (+1.36\text{ V}) - (+0.34\text{ V}) = 1.02\text{ V}$

(ii) $\Delta G^\circ = -nFE^\circ = -2 \times 96500\text{ C} \times 1.02\text{ V} = -196.86\text{ kJ}$

(iii) $E^\circ_{\text{Cell}} = \dfrac{0.0591}{n} \log K$

$$K = \text{antilog}\frac{2 \times 1.02\text{ V}}{0.0591} = \text{antilog}(34.51)$$

$K = 3.236 \times 10^{34}$

(b) The given cell may be represented as

Pt, H_2 (1 atm) | H^+ (pH = ?) || H^+ (pH = 1) | H_2 (1 atm)

Using formula, $E_{\text{cell}} = \dfrac{0.0591}{1} \log \dfrac{[H^+]_c}{[H^+]_a}$

or, $0.16\text{ V} = 0.0591\,[\log [H^+]_c - \log [H^+]_a]$

or, $0.16\text{ V} = 0.0591\,[pH_a - pH_c]$, $0.16\text{ V} = 0.0591\,[pH_a - 1]$

or, $pH_a - 1 = \dfrac{0.16}{0.0591} = 2.70$ or, $pH_a = 2.70 + 1 = 3.70$

OR

$Mg_{(s)} | Mg^{2+}(0.001\text{ M}) || Cu^{2+}(0.0001\text{ M}) | Cu_{(s)}$

Reactions :

Anode : $Mg_{(s)} \longrightarrow Mg^{2+}_{(aq)} + 2e^-$

Cathode : $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$

Net cell reaction : $Mg_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$

$\therefore \ n = 2$

Using Nernst equation :

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303RT}{nF} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$$

For the given cell,

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

$= E^\circ_{Cu^{2+}/Cu} - E^\circ_{Mg^{2+}/Mg}$

$= 0.34\text{ V} - (-2.37\text{ V}) = 2.71\text{ V}$

Given, $[Mg^{2+}] = 0.001\text{ M}$, $[Cu^{2+}] = 0.0001\text{ M}$

Putting in Nernst equation at 298 K

$$E_{\text{cell}} = 2.71\text{ V} - \frac{0.059}{2} \log \frac{0.001}{0.0001}$$

$E_{\text{cell}} = 2.71 - 0.0295 \log 10 = 2.68\text{ V}$

$\Delta_r G = -nFE_{\text{cell}} = -2 \times 96500\text{ C mol}^{-1} \times 2.68$

$= -517.240\text{ J mol}^{-1} = -517.24\text{ kJ mol}^{-1}$

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