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CHEMISTRY

EVALUATION PLAN

1. (a) Theory / Written examination (3 hours) : **70 marks**
   (b) Practical examination (3 hours) : **30 marks**
   Total : 100 marks

2. **Question paper pattern for the theory / written examination :**

Section	Question Type	Question No.	Internal Choice	Total Marks	Marks with Option
A	Multiple Choice Questions (MCQ)	Q. 1. [(i) to (x)]	–	10	10
	Very Short Answer Questions (VSA)	Q. 2. [(i) to (viii)]	–	8	8
B	Short Answer Questions (SA) – I	Q. 3. to Q. 14.	8 out of 12 Qs.	16	24
C	Short Answer Questions (SA) – II	Q. 15. to Q. 26.	8 out of 12 Qs.	24	36
D	Long Answer Questions (LA)	Q. 27. to Q. 31.	3 out of 5 Qs.	12	20
				70	**98**

3. **Chapterwise distribution of marks in the question paper :**

Chapter No.	Name of the Chapter	Marks	Marks with Option
1	Solid State	3	5
2	Solutions	4	6
3	Ionic Equilibria	4	6
4	Chemical Thermodynamics	6	8
5	Electrochemistry	5	7
6	Chemical Kinetics	4	6
7	Elements of Groups 16, 17 and 18	6	8
8	Transition and Inner Transition Elements	6	8
9	Coordination Compounds	5	7
10	Halogen Derivatives	5	7
11	Alcohols, Phenols and Ethers	4	6
12	Aldehydes, Ketones and Carboxylic Acids	6	8
13	Amines	3	4
14	Biomolecules	3	4
15	Introduction to Polymer Chemistry	3	4
16	Green Chemistry and Nanochemistry	3	4
	Total	**70**	**98**

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NON-EVALUATIVE PORTION FOR THE ACADEMIC YEAR 2020-21
AS DECLARED ON 22-07-2020

Chapter No. & Name	Non-evaluative portion
1. Solid State	1.2.1 : Crystalline solids
	1.2.2 : Amorphous solids
	1.7.3 : Packing efficiency of metal crystal in fcc lattice
	Table 1.3 : Edge length and particle parameters in cubic system
	Table 1.4 : Point no. 3 fcc/hcp only
	1.9 : Electrical properties of solids
	1.10 : Magnetic properties of solids
2. Solutions	Demonstration and Exceptions to Henry's Law
	2.11.1 : Van't Hoff factor(i)
	2.11.2 : Modification of expressions of colligative property
	2.11.3 : Van't Hoff factor and degree of dissociation
	Problems : 2.10 to 2.12 and 2.14
3. Ionic Equilibria	3.1 : Introduction
	3.6.2 : Acidity, basicity and neutrality of aqueous solutions
4. Chemical Thermody	
	4.11.6 : Gibbs energy and spontaneity
	4.11.7 : Spontaneity and ΔH or ΔS
	4.11.8 : Temperature of equilibrium
	4.11.9 : Gibbs function and equilibrium constant
	Problems : 4.16 to 4.20
5. Electrochemistry	5.1 : Introduction
	5.2.2 : Ionic conduction
	5.2.3 : Measurement of conductivity of solution
	Significance of molar conductivity
	5.4.1 : Electrochemical reactions
	5.4.2 : Electrodes
	5.10.1 : Dry cell
	5.10.2 : Lead accumulator
	5.11 : Fuel cells

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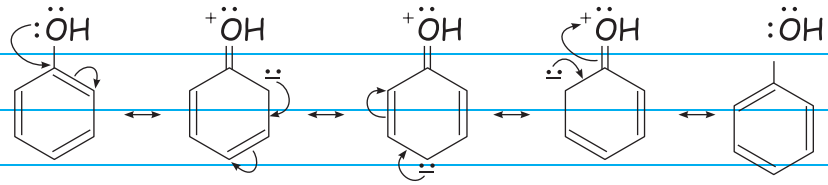


(VI) (VII) (VIII) (IX) (X) (1 mark)

The delocalization of charge in phenol (structures VI to X), the resonating structures have charge separation (where oxygen atom of OH group to be positive and delocalization of negative charge over the ortho and para positions of aromatic ring) due to which phenol molecule is less stable than phenoxide ion. This favours ionization of phenol. Thus phenols are more acidic than ethyl alcohol. ($\frac{1}{2}$ mark)

Q. 8. Consider 'n' moles of an ideal gas enclosed in an ideal cylinder.

Let V be the volume of the gas at a pressure P and a temperature T.

When pressure changes from P to $P - dP$ and volume increases from V to $V + dV$, then the work obtained is

$dW = -(P - dP)\, dV$

$= -PdV + dPdV$ ($\frac{1}{2}$ mark)

Since dP.dV is negligibly small relative to PdV

$dW = -PdV$

Let the state of the system change from $A(P_1, V_1)$ to $B(P_2, V_2)$ isothermally and reversibly, at temperature T involving number of infinitesimal steps.

Then the total work or maximum work in the process is obtained by integrating above equation.

$$W_{max} = \int_A^B dW$$

$$= \int_A^B -PdV$$

$\because PV = nRT$ ($\frac{1}{2}$ mark)

$$\therefore P = \frac{nRT}{V}$$

$W_{max} = \int_{V_1}^{V_2} -nRT \frac{dV}{V}$ ($\frac{1}{2}$ mark)

$= -nRT \int_{V_1}^{V_2} \frac{dV}{V}$

$= -nRT (\ln V_2 - \ln V_1)$

$= -nRT \log_e \frac{V_2}{V_1}$

$\therefore W_{max} = -2.303\ nRT \log_{10} \frac{V_2}{V_1}$

At constant temperature,

$\because P_1 \times V_1 = P_2 \times V_2 \quad \therefore \frac{V_2}{V_1} = \frac{P_1}{P_2}$

$\therefore W_{max} = -2.303\ nRT \log_{10} \frac{P_1}{P_2}$ ($\frac{1}{2}$ mark)

Q.9. Given : $C = 0.1$ M, Dissociation $= 5\%$, $K_a = ?$

$\alpha = \frac{\text{Percent dissociation}}{100}$ ($\frac{1}{2}$ mark)

$= \frac{5}{100} = 0.05$

$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.1 \times (0.05)^2}{1 - 0.05}$ (1 mark)

$= \frac{0.1 \times (0.05)^2}{0.95}$

$= 2.63 \times 10^{-4}$ ($\frac{1}{2}$ mark)

Ans. Dissociation constant of acid $= K_a = 2.63 \times 10^{-4}$

Q.10. The conversion of amides into amines in the presence of bromine and alkali is known as Hofmann degradation of amides. An important characteristic of this reaction is that an amine with one carbon less than those in the amide is formed. Thus, decreasing the length of carbon chain. This reaction is an example of molecular rearrangement and involves the migration of an alkyl or aryl group from the carbonyl carbon to the adjacent nitrogen atom. (1 mark)

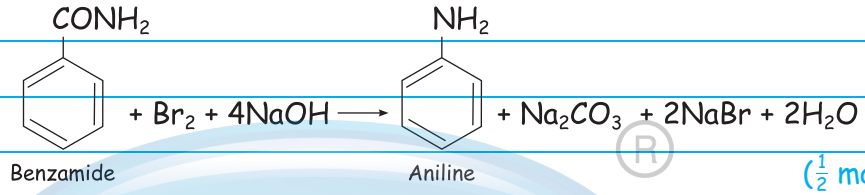
For example,

(1) When propanamide is treated with bromine and aqueous or alcoholic sodium hydroxide, ethanamine is obtained which has one carbon atom less.

$$\underset{\text{Propanamide}}{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-NH_2} + Br_2 + 4NaOH \longrightarrow \underset{\text{Ethanamine}}{CH_3-CH_2-NH_2} + Na_2CO_3 + 2NaBr + 2H_2O$$

($\frac{1}{2}$ mark)

(2) When benzamide is treated with bromine and aqueous or alcoholic sodium hydroxide, aniline is obtained.



Benzamide Aniline

($\frac{1}{2}$ mark)

Q. 11.

(1) Atom economy is a measure of the amount of atoms from the starting material that are present in the final product at the end of a chemical process. Good atom economy means most of the atoms of the reactants are incorporated in the desired products. Only small amount of waste is produced, hence lesser is problem of waste disposal. (1 mark)

(2) The atom economy of a process can be calculated using the following formula.

$$\% \text{ atom economy} = \frac{\text{Formula weight of the desired product}}{\text{Sum of formula weight of all the reactants used in the reaction}} \times 100$$

Consider the conversion of Butan-1-ol to 1-bromobutane

$$CH_3-CH_2-CH_2-CH_2\,OH + NaBr + H_2SO_4 \longrightarrow CH_3-CH_2-CH_2-CH_2-Br + NaHSO_4 + H_2O$$

$$\% \text{ atom economy} = \frac{\text{mass of 1-Bromobutane}}{\text{sum of mass of 1-Butanol + sodium bromide}} \times 100$$

$$= \frac{\text{mass of } (4C + 9H + 1Br) \text{ atoms}}{\text{mass of } (4C + 12H + 5O + 1Br + 1Na + 1S) \text{ atoms}} \times 100$$

$= \frac{137\,u}{275\,u} \times 100 = 49.81\%$

The atom economy of the above reaction is less than 50% and hence waste produced is higher. (1 mark)

Q.12. Given : $E^0_{Ni^{2+}/Ni} = -0.25$ V; $E^0_{Al^{3+}/Al} = -1.66$ V; $E^0_{cell} = ?$

Since Ni is oxidised and Al^{3+} is reduced,

$E^0_{cell} = E^0_{Al^{3+}/Al} - E^0_{Ni^{2+}/Ni}$ ($\frac{1}{2}$ mark)

$= -1.66 - (-0.25)$ ($\frac{1}{2}$ mark)

$= -1.41$ V (1 mark)

Ans. $E^0_{cell} = -1.41$ V

Q.13.

Order	Molecularity
1. It is the sum of the exponents to which the concentration terms in rate law expression are raised.	1. It is the number of molecules (or atoms or ions) of the reactants taking part in the elementary reaction.
2. It is experimentally determined and indicates the dependence of the reaction rate on the concentration of particular reactants.	2. It is theoretical property and indicates the number of molecules of reactant in each step of the reaction.
3. It may have values which are integer, fractional or zero.	3. It is always an integer.
4. Its value depends upon experimental conditions.	4. Its value does not depend upon experimental conditions.
5. It is the property of elementary and complex reactions.	5. It is the property of elementary reactions only.
6. Rate law expression describes the order of the reaction.	6. Rate law does not describe molecularity.

Q. 14.

Double salt	Coordination compound (complex)
1. Double salts exist only in the solid state and dissociate into their constituent ions in the aqueous solutions.	1. Coordination compounds exist in the solid state as well as in the aqueous or non-aqueous solutions.
2. Double salts lose their identity in the solution.	2. They do not lose their identity completely.
3. The properties of double salts are same as those of their constituents.	3. The properties of coordination compounds are different from their constituents.
4. Metal ions in the double salts show their normal valence.	4. Metal ions in the coordination compounds show two valences namely primary valence and secondary valence satisfied by anions or neutral molecules called ligands.
5. In $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$. the ions K^+, Al^{3+} and SO_4^{2-} show their properties.	5. In $K_4[Fe(CN)_6]$, the ions K^+ and $[Fe(CN)_6]^{4-}$ show their properties.

(Any four points : $\frac{1}{2}$ mark each)

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SECTION-C

Note : There are 12 Short Answer Type questions from Q. 15 to Q. 26 carrying three marks each. You have to attempt any **eight** questions. This section includes ten theory questions and two numerical problems. Write appropriate units for each calculated value.

Q.15. (i) As the dilution of an electrolytic solution increases, the dissociation of the electrolyte increases, hence the total number of ions increases, therefore, the molar conductivity increases. ($\frac{1}{2}$ mark)

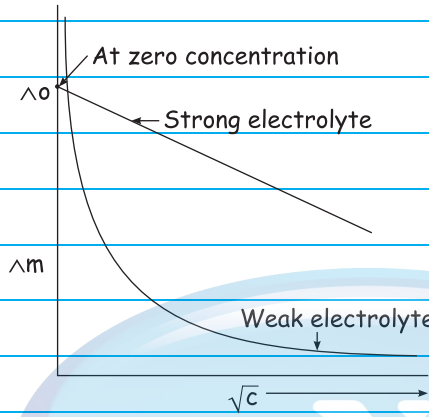

Fig. : Variation of molar conductivity with $\sqrt{c}$ (1 mark for figure)

(ii) The increase in molar conductivity with increase in dilution or decrease in concentration is different for strong and weak electrolytes. ($\frac{1}{2}$ mark)

(iii) On dilution, the molar conductivity of strong electrolytes increases rapidly and approaches to a maximum limiting value at infinite dilution or zero concentration and represented as $\wedge_\infty$ or $\wedge_0$ or $\wedge_m^0$. In case of weak electrolytes which dissociate less as compared to strong electrolytes, the molar conductivity is low and increases slowly in high concentration region, but increases rapidly at low concentration or high dilution. This is because the extent of dissociation increases with dilution rapidly. ($\frac{1}{2}$ mark)

(iv) $\wedge_0$ values for strong electrolytes can be obtained by extrapolating the linear graph to zero concentration (or infinite dilution). However $\wedge_0$ for the weak electrolytes cannot be obtained by this method, since the graph increases exponentially at very high dilution and does not intersect $\wedge_m$ axis at zero concentration. ($\frac{1}{2}$ mark)

Q.16. (1) Atomic and ionic radii :

(i) As compared to group 15 elements, the atomic and ionic radii of group 16 elements are smaller due to higher nuclear charge. ($\frac{1}{2}$ mark)

(ii) The atomic and ionic radii increase down the group from oxygen to polonium. This is due to the addition of a new shell at each successive elements on moving down the group.

The atomic radii increases in the order $O < S < Se < Te < Po$ ($\frac{1}{2}$ mark)

(2) Ionisation enthalpy :

(i) The ionisation enthalpy of group 16 elements has quite high values.

(ii) Ionisation enthalpy decreases down the group from oxygen to polonium. This is due to the increase in atomic volume down the group. ($\frac{1}{2}$ mark)

(iii) The first ionisation enthalpy of the lighter elements of group 16 (O, S, Se) have lower values than those of group 15 elements in the corresponding periods. This is due to difference in their electronic configurations.

Group 15 : (valence shell) $ns^2\ np_x^1\ np_y^1\ np_z^1$

Group 16 : (valence shell) $ns^2\ np_x^2\ np_y^1\ np_z^1$

Group 15 elements have extra stability of half filled and more symmetrical orbitals, while group 16 elements acquire extra stability by losing one of paired electrons from np_x-orbital forming half filled p-orbitals.

Hence group 16 elements have lower first ionisation enthalpy than group 15 elements. ($\frac{1}{2}$ mark)

(3) Electronegativity :

(i) The electronegativity values of group 16 elements have higher values than corresponding group 15 elements in the same periods.

(ii) Oxygen is the second most electronegative elements after fluorine. ($O = 3.5$, $F = 4$)

(iii) On moving down the group electronegativity decreases from oxygen to polonium.

(iv) On moving down the group atomic size increases, hence nuclear attraction decreases, therefore electronegativity decreases.

(1 mark)

Q.17. The salient features of valence bond theory (VBT) are as follows :

(1) According to this theory, a central metal atom or ion present in a complex provides a definite number of vacant orbitals (s, p, d and f) to accommodate the electrons from the ligands for the formation coordinate bonds with the metal ion / atom.

(2) The number of vacant orbitals provided by the central metal atom or ion is the same as the coordination number of the metal.
For example : Cu^{2+} provides 4 vacant orbitals in the complex.
$[Cu(NH_3)_4]^{2+}$.

(3) The vacant orbitals of metal atom or ion undergo hybridisation forming the same number of hybridised orbitals, since the bonding with the hybrid orbitals is stronger.

(4) Each ligand has one or more orbitals containing one or more lone pairs of the electrons.

(5) The shape or geometry of the complex depends upon the type of hybridisation of the metal ion / atom.

(6) When inner orbitals namely $(n-1)d$ orbitals in transition metal atom or ion hybridise, the complex is called inner complex and when outer orbitals i.e., nd orbitals hybridise then the complex is called outer complex.

(7) When the central metal atom or ion in the complex contains one or more unpaired electrons the complex is paramagnetic while if all the electrons are paired, the complex is diamagnetic.

(Any six points : $\frac{1}{2}$ mark each)

Q. 18. Given : Molar mass $= M = 27\ g\ mol^{-1}$

Nature of crystal = cubic unit cell

Edge length $= a = 405\ pm = 4.05 \times 10^{-8}\ cm$

Density $= \rho = 2.7\ g\ cm^{-3}$

Nature of unit cell = ?

$$\rho = \frac{n \times M}{a^3 \times N_A}$$ ($\frac{1}{2}$ mark)

$$\therefore n = \frac{\rho \times a^3 \times N_A}{M}$$

$$= \frac{2.7 \times (4.05 \times 10^{-8})^3 \times 6.022 \times 10^{23}}{27}$$ ($\frac{1}{2}$ mark)

$$= 3.997$$

$$\cong 4$$ (1 mark)

Hence the nature of unit cell = face-centred cubic unit cell (1 mark)

Ans. The nature of cubic unit cell is fcc.

Q. 19. (a) Since cations are deficient of electrons they accept a pair of electrons, hence they are Lewis acids. (1 mark)

(b) Since ammonia molecule, $\ddot{N}H_3$ has a lone pair of electrons to donate it acts as a Lewis base. (1 mark)

(c) $AlCl_3$ is a molecule with incomplete octet hence it is electron deficient and acts as a Lewis acid. (1 mark)

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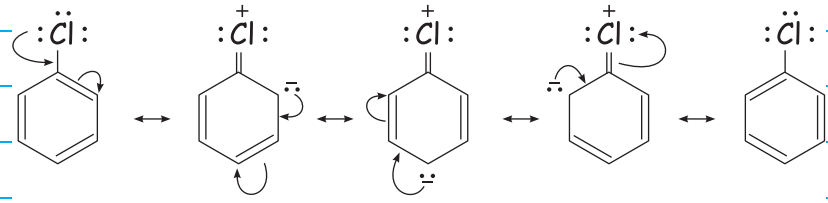
Q. 20. Haloarenes (Aryl halides) are less reactive than (alkyl halides) haloalkanes due to the following reasons :

(1) Resonance effect : In haloarenes, the electron pairs on halogen atom are in conjugation with π-electrons of the benzene ring. The delocalization of these electrons C-Cl bond acquires partial double bond character.



Due to partial double bond character of C-Cl bond in aryl halides, the bond cleavage in haloarene is difficult and are less reactive. On the other hand, in alkyl halides, carbon is attached to chlorine by a single bond and it can be easily broken. (1 mark)

(2) Aryl halides are stabilized by resonance but alkyl halides are not. Hence, the energy of activation for the displacement of halogen from aryl halides is much greater than that of alkyl halides. (1 mark)

(3) Different hybridization state of carbon atom in C-X bond :

(i) In alkyl halides, the carbon of C-X bond is sp^3-hybridized with less s-character and greater bond length of 178 pm, which requires less energy to break the C-X bond.

(ii) In aryl halides, the carbon of C-X bond is sp^2-hybridized with more s-character and shorter bond length which requires more energy to break C-X bond. Therefore, aryl halides are less reactive than alkyl halides.

(iii) Polarity of the C-X bond : In aryl halide C-X bond is less polar than in alkyl halides. Because sp^2-hybrid carbon of C-X bond has less tendency to release electrons to the halogen than a sp^3-hybrid carbon in alkyl halides. Thus halogen atom in aryl halides cannot be easily displaced by nucleophile. (1 mark)

Q. 21. (a) The smallest constituents or particles of various solids are atoms, ions or molecules. (1 mark)

(b) Intensive property : It is defined as a property of a system whose magnitude is independent of the amount of matter present in the system. ($\frac{1}{2}$ mark)

Intensive property is characteristic of the system. e.g., refractive index, density, viscosity. ($\frac{1}{2}$ mark)

(c) Enthalpy of fusion ($\Delta_{fus}H$) : The enthalpy change that accompanies the fusion of one mole of a solid into a liquid at constant temperature and pressure is called enthalpy of fusion.

For example,

$$H_2O_{(s)} \xrightarrow{1\ atm,\ 273\ K} H_2O_{(l)} \quad \Delta_{fus}H = 6.01\ kJ\ mol^{-1}$$ (1 mark)

Q. 22. (1) Ethanol : When ethanol is treated with PCl_3, ethyl chloride is obtained.

$$3CH_3CH_2\text{-}OH + PCl_3 \longrightarrow 3CH_3\text{-}CH_2Cl + H_3PO_3$$

Ethanol Ethyl chloride (1 mark)

(2) Propan-1-ol : When propan-1-ol is treated with PCl_3, n-propyl chloride is obtained.

$$3CH_3\text{-}CH_2\text{-}CH_2\text{-}OH + PCl_3 \longrightarrow 3CH_3\text{-}CH_2\text{-}CH_2\text{-}Cl + H_3PO_3$$

Propan-1-ol n-Propyl chloride (1 mark)

(3) Propan-2-ol : When propan-2-ol is treated with PCl_3, 2-Chloro-propane is obtained.

$$3CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 + PCl_3 \longrightarrow 3CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3 + H_3PO_3$$

Propan-2-ol 2-Chloropropane (1 mark)

Q. 23. An ethereal solution of a nitrile is reduced to imine hydrochloride by $SnCl_2$ in the presence of HCl gas. Further, imine hydrochloride on acid hydrolysis gives aldehyde. This reaction is called Stephen reaction.

$Sn + 2HCl \rightarrow SnCl_2 + 2(H)$ (1 mark)

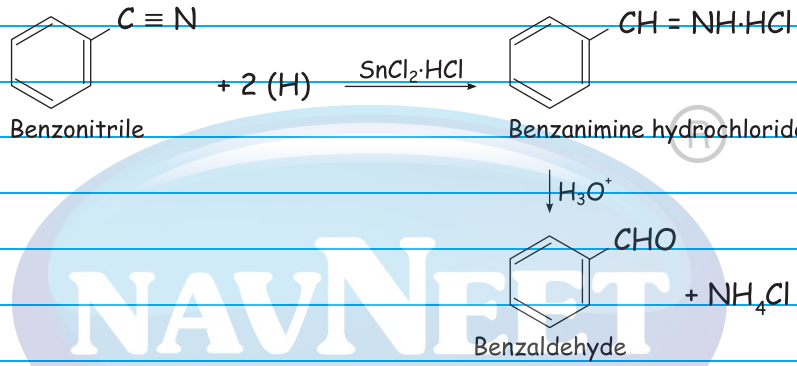
$R\text{-}C \equiv N + 2(H) \xrightarrow{SnCl_2 / dil.HCl} R\text{-}CH = NHHCl \xrightarrow{H_3O^+} R\text{-}CHO + NH_4Cl$

Alkyl nitrite — Imine hydrochloride — Aldehyde

$CH_3\text{-}C \equiv N + 2(H) + HCl \xrightarrow[SnCl_2]{\text{Dry ether}} CH_3CH = NH{\cdot}HCl \xrightarrow{H_3O^+} CH_3CHO + NH_4Cl$

Ethanenitrile — Acetaldimine hydrochloride

(1 mark)



Benzonitrile — Benzanimine hydrochloride — Benzaldehyde

(1 mark)

Q. 24. (a) Diamagnetic property : When a species has all electrons paired and repelled by magnetic field is said to be diamagnetic. (1 mark)

Example : Zn^{2+}, La^{3+} ($\frac{1}{2}$ mark)

(b) Paramagnetic property : When a species has one or more unpaired electrons and attracted towards applied magnetic field is said to be paramagnetic. (1 mark)

Example : Ni^{2+}, Pr^{3+}. ($\frac{1}{2}$ mark)

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Q. 25. Given : $[A]_0 = 20$ mmol dm^{-3}; $[A]_t = 8$ mmol dm^{-3}; $t = 38$ min; $t_{1/2} = ?$

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$ ($\frac{1}{2}$ mark)

$$= \frac{2.303}{38} \log_{10} \frac{20}{8}$$

$$= \frac{2.303}{38} \times 0.3979$$

$$= 0.02411 \text{ min}^{-1}$$ (1 mark)

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

$$= \frac{0.693}{0.02411} = 28.74 \text{ min}$$

Ans. Half-life period = 28.74 min (1 mark)

Q. 26. (i) A complex with the coordination number of central metal ion equal to 4 may be tetrahedral or square planar. (1 mark)

(ii) $CH_3\text{-}C \equiv N + 4[^-H] \xrightarrow{Na/C_2H_5OH} CH_3\text{-}CH_2\text{-}NH_2$ (1 mark)

Acetonitrile — Ethanamine

(iii) Proteins are the polymers of α-amino acids and they are connected to each other. The bond that connects α-amino acids to each other is called peptide bond (peptide linkage, $-CONH-$). (1 mark)

SECTION - D

Note : This section has five long Answer Type Questions from Q. 27 to Q. 31 carrying four marks each. This section includes theory questions and one numerical problem. You have to attempt any **three** questions.

Q. 27. (a) The freezing point depression, ΔT_f of a solution is directly proportional to molality (m) of the solution.

$\therefore \Delta T_f \propto m$

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

where K_f is a molal depression constant. ($\frac{1}{2}$ mark)

The molality of a solution is given by,

$$m = \frac{\text{Number of moles of the solute}}{\text{Weight of the solvent in kg}}$$

If W_1 grams of a solvent contain W_2 grams of a solute of the molar mass M_2, then the molality m of the solution is given by,

$$m = \frac{W_2 \times 1000}{W_1 M_2} = \frac{W_2}{W_1 \times M_2}\ \text{mol kg}^{-1}$$ ($\frac{1}{2}$ mark)

$$\therefore \Delta T_f = K_f \times \frac{W_2 \times 1000}{W_1 M_2}$$ ($\frac{1}{2}$ mark)

If the weights are expressed in kg then,

$$\Delta T_f = K_f \times \frac{W_2}{W_1 M_2}$$

The unit of K_f is K kg mol^{-1}. ($\frac{1}{2}$ mark)

(b) Given : $V_1 = 8.0\ \text{dm}^3$; $V_2 = 4.0\ \text{dm}^3$; $P_{ex} = 43$ bar

$W = ?$ What direction work energy flows?

$W = -P_{ex}\,(V_2 - V_1)$ ($\frac{1}{2}$ mark)

$= -43\,(4 - 8)$ ($\frac{1}{2}$ mark)

$= 172\ \text{dm}^3$ bar

$= 172 \times 100$ J

$= 17200$ J $\quad = 17.2$ kJ (1 mark)

In this compression process, the work is done on the system and work energy flows into the system.

Q. 28. (1) Consider alkaline hydrolysis of methyl bromide (Bromomethane), CH_3Br with aqueous NaOH or KOH.

$$CH_3-Br + OH^- \rightarrow CH_3-OH + Br^-$$

Bromomethane (substrate) — nucleophile — Methanol

(2) Stereochemistry and Kinetics of the reaction (R.D.S.) : This hydrolysis reaction takes place only in one step which is a rate determining step i.e. R.D.S. The rate of hydrolysis reaction depends on the concentration of CH_3Br and OH^- which are present in the R.D.S. of the reaction.

Rate $= R = k\,[CH_3Br]\,[OH^-]$ ($\frac{1}{2}$ mark)

where k is rate constant of the reaction.

SN^2 reaction : The reaction between methyl bromide and hydroxide ion to form methanol follows a second order kinetics, since the rate of the reaction depends on the concentrations of two reacting species, namely methyl bromide and hydroxide ion it is bimolecular second order (2nd) Nucleophilic Substitution reaction denoted by SN^2.

($\frac{1}{2}$ mark)

(3) Mechanism of the reaction :

(i) It is a single step mechanism. The reaction takes place in the following steps :

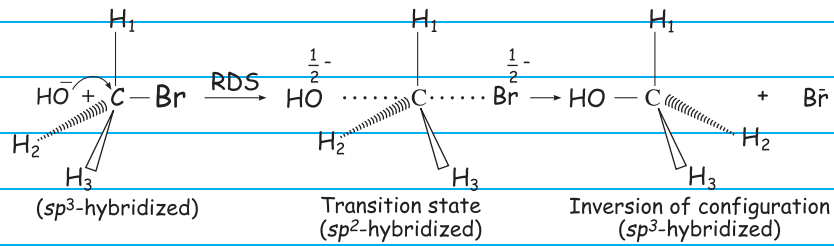

Fig. : Backside attack of nucleophile in SN^2 mechanism (1 mark)

(ii) Backside attack of the nucleophile : Nucleophile, OH^- attacks carbon atom of CH_3Br from back side i.e. from opposite side to that of the leaving group i.e. Br^- to experience minimum steric repulsion and electrostatic repulsion between the incoming nucleophile (OH^-) and leaving Br^-. ($\frac{1}{2}$ mark)

(iii) Transition state : When a nucleophile, OH^- approaches carbon atom of CH_3Br, the potential energy of the system increases until a transition state (T.S.) of maximum potential energy is formed in which $C-Br$ bond is partially broken and $C-OH$ bond is partially formed. The negative charge is equally shared by both incoming nucleophile $-OH^-$ and outgoing, leaving group $-Br^-$. (Thus, the total negative charge is diffused.) ($\frac{1}{2}$ mark)

(iv) In CH_3Br, carbon atom is sp^3-hybridized and CH_3Br molecule is tetrahedral. The hybridisation of carbon atom changes to sp^2 hybridization. The transition state contains pentacoordinate carbon having three δ (sigma) bonds in one plane making bond angles of 120° with each other i.e., H_1, H_2 and H_3 atoms lie in one plane while two partial covalent bonds containing Br and OH lie collinear and on opposite sides perpendicular to the plane. ($\frac{1}{2}$ mark)

(v) Inversion of configuration : The transition state decomposes fast by the complete breaking of the C-Br bond and the new C-OH bond is formed on the other side. The breaking of C-Br bond and the formation of C-OH bond take place simultaneously. The energy required to break the C-Br bond is partly obtained from the energy released when C-OH bond is formed. The formation of product CH_3OH is accompanied by complete or 100% inversion of configuration forming again sp^3-hybridized carbon atom giving tetrahedral CH_3OH molecule. But in this structure the positions of H_2 and H_3 atoms in the reactant (CH_3Br) and in product are on the opposite side. This inversion of configuration is called Walden inversion. ($\frac{1}{2}$ mark)

Q. 29. (a) (i) Halogens have outer electronic configuration $ns^2\ np^5$.

(ii) Halogens have tendency to gain or share one electron to attain the stable configuration of nearest inert element with configuration ns^2np^6. ($\frac{1}{2}$ mark)

(iii) Hence they are monovalent and show oxidation state -1.

(iv) Since fluorine does not have vacant d-orbital, it shows only one oxidation state of -1 while all other halogens show variable oxidation states from -1 to $+7$. These oxidation states are, -1, $+1$, $+3$, $+5$ and $+7$. Cl and Br also show oxidation states $+4$ and $+6$ in their oxides and oxyacids.

($\frac{1}{2}$ mark for each point)

(b) (i) The electrochemical cell from above reactions is

$Au^{3+}_{(aq)} + 3e^- \longrightarrow Au_{(s)}$ (Cathode reduction reaction)

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

$Mg_{(s)} \mid Mg^{2+}_{(aq)}\,1\,M \parallel Au^{3+}_{(aq)}\,1\,M \mid Au$

(ii) (1) The atomic or ionic radii of 3-d series transition elements are smaller than those of representative elements, with the same oxidation states. ($\frac{1}{2}$ mark)

(2) For the same oxidation state, there is an increase in nuclear charge and a gradual decrease in ionic radii of 3d-series elements is observed.

Thus ionic radii of ions with oxidation state $+2$ decreases with increase in atomic number. ($\frac{1}{2}$ mark)

(3) There is slight increase observed in Zn^{2+} ions. With the higher oxidation states, effective nuclear charge increases. Therefore ionic radii decrease with increase in oxidation state of the same element. For example, Fe^{2+} ion has ionic radius 77 pm whereas Fe^{3+} has 65 pm. (1 mark)

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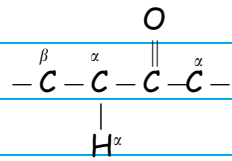
Q. 30. (1) The carbon atom adjacent to carbonyl carbon atom is called α-carbon atom ($\alpha - C$) and the hydrogen atom attached to α-carbon atom is called α-hydrogen atom ($\alpha - H$).

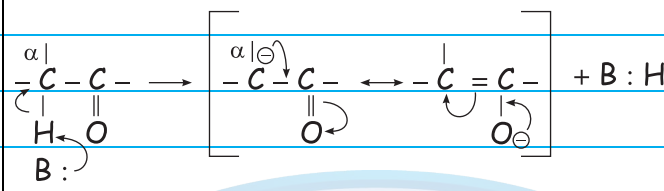


($\frac{1}{2}$ mark)

(2) The α-hydrogen of aldehydes and ketones is acidic in nature due to

(i) the strong-I effect of carbonyl group

(ii) resonance stabilization of the carbanion.



($\frac{1}{2}$ mark)

(3) Aldol condensation reaction is characteristic reaction of aldehydes and ketones containing active α-hydrogen atom. ($\frac{1}{2}$ mark)

(4) When aldehydes or ketones containing $\alpha - H$ atoms are warmed with a dilute base or dilute acid, two molecules of them undergo self condensation to give β-hydroxy aldehyde (aldol) or β-hydroxy ketone (ketol) respectively. The reaction is known as Aldol addition Reaction.

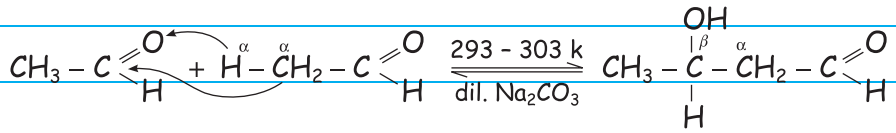
($\frac{1}{2}$ mark)

(5) In aldol condensation, the product is formed by the nucleophilic addition of α-carbon atom of a second molecule which gets attached to carbonyl carbon atom of the first molecule and α-hydrogen atom of the second molecule gets attached to carbonyl oxygen atom of the first molecule forming ($-OH$) group to give β-hydroxy aldehyde or ketone.

($\frac{1}{2}$ mark)

(6) This is a reversible reaction, establishing an equilibrium favouring aldol formation to a greater extent than ketol formation. ($\frac{1}{2}$ mark)

(7) For aldehyde :

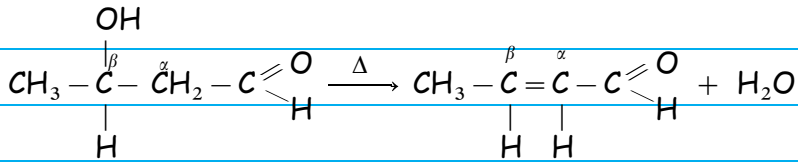


Acetaldehyde (first molecule) | Acetaldehyde (second molecule) | Acetaldol (β-hydroxy butyraldehyde)

($\frac{1}{2}$ mark)

Acetaldol on heating undergoes subsequent elimination of water giving rise to α, β unsaturated aldehyde.

Q. 31.



($\frac{1}{2}$ mark)

Crotonaldehyde (But-2-enal)

(1) HDP means high density polyethylene. It is a linear polymer with high density due to close packing. (1 mark)

$$n CH_2 = CH_2 \xrightarrow[6\text{-}7 \text{ atm catalyst}]{333 \text{ K} - 343 \text{ K}} \underset{\text{HDP}}{\{CH_2 - CH_2\}_n}$$ (1 mark)

HDP is obtained by polymerization of ethene in presence of Zieglar-Natta catalyst which is a combination of triethyl aluminium with titanium tetrachloride at a temperature of 333K to 343K and a pressure of 6-7 atm.

Properties of HDP :

(i) HDP is crystalline, melting point in the range of $144 - 150\ ^\circ C$.

(ii) It is much stiffer than LDP and has high tensile strength and hardness.

(iii) It is more resistant to chemicals than LDP. ($\frac{1}{2}$ mark)

Uses of HDP :

(i) HDP is used in manufacture of toys and other household articles like buckets, dustbins, bottles, pipes, etc.

(ii) It is used to prepare laboratory wares and other objects where high tensile strength and stiffness is required. ($\frac{1}{2}$ mark)

(2) Gerd Bining and Heinrich Rohrer. (Nobel Prize 1986) (1 mark)

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