Solved Paper 2022

CHEMISTRY (TERM II)

Time : 2 Hours **Class-XII** **Max. Marks : 35**

General Instructions :

Read the following instructions very carefully and strictly follow them:

*(i) This question paper contains **12** questions. **All** questions are compulsory.*

*(ii) This question paper comprises of **three** sections-**Section A, B** and **C.***

*(iii) **Section A – Q.** No. 1 to 3 are very short-answer type questions carrying **2** marks each.*

*(iv) **Section B – Q.** No. 4 to 11 are short-answer type questions carrying **3** marks each.*

*(v) **Section C – Q.** No 12 is case-based question carrying **5** marks.*

*(vi) Use of log tables and calculators is **not** allowed.*

Delhi Set-I, Series: AABB5/5, **56/5/1**

SECTION - A

1. Answer the following questions (Do any two): **1 × 2 = 2**

(a) Identify the order of reaction from the following unit for its rate constant: $Lmol^{-1}s^{-1}$

(b) The conversion of molecules A to B follow second order kinetics. If concentration of A is increased to three times, how will it affect the rate of formation of B?

(c) Write the expression of integrated rate equation for zero order reaction.

Ans. (a) The unit L mol^{-1} sec^{-1} for rate constant is the unit of second order reaction.

(b) For reaction A → B,

Rate of reaction (r)

$$= k[A]^2 \quad ...1$$

If the concentration of reactant increased to three times.

Rate of reaction (r')

$$= k[3A]^2 \quad ...2$$

Thus, on dividing eq. 1 and 2.

$$\frac{r}{r'} = \frac{k[A]^2}{k[3A]^2}$$

$$= \frac{1}{9}$$

Therefore, rate of formation of B increases to nine times.

(c) Integrated rate equation for zero order reaction is

$$k = \frac{[R_0 - R]}{t}$$

Where, k = rate constant

R_0 = Initial concentration of reactant

R = Final concentration of reactant

t = time taken **(Any two)**

2. Arrange the following in the increasing order of their property indicated: **1 × 2 = 2**

(a) Ethanal, Propanone, Propanal, Butanone (reactivity towards nucleophilic addition)

(b) 4-Nitrobenzoic acid, benzoic acid, 3,4-Dinitrobenzoic acid,

4-Methoxy benzoic acid (Acid strength)

Ans. (a) The increasing order towards nucleophilic addition of the following compounds is

Butanone < Propanone < Propanal < Ethanal (Due to +I effect).

(b) The increasing order of acidic strength of the following compounds is

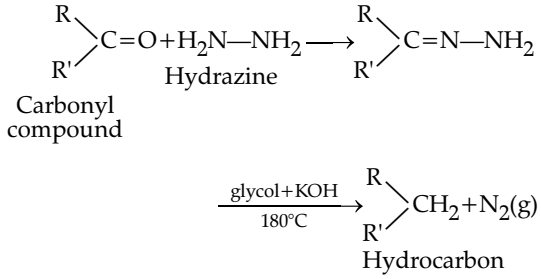
4-methoxy benzoic acid < benzoic acid < 4-nitrobenzoic acid < 3,4-dinitrobenzoic acid. (Due to presence of electron withdrawing group).

3. Explain the following reactions: **1 × 2 = 2**

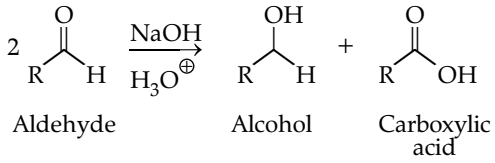
(a) Wolff-Kishner reduction

(b) Cannizzaro reaction

Ans. (a) Wolff-Kishner Reduction Reaction - In this reaction, the reduction of carbonyl compounds to hydrocarbons takes place by heating them with hydrazine and a base to form hydrazone which is further reduced to form methylene group along with nitrogen gas.

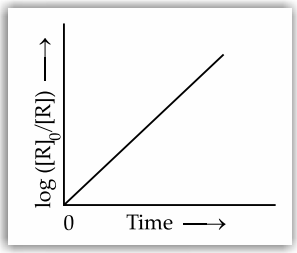


(b) Cannizzaro Reaction - The self-oxidation reduction (disproportionation) reaction of aldehydes having no α-hydrogens when reacts with concentrated alkali is known as the Cannizzaro reaction. In this reaction, two molecules of aldehydes react where one is reduced to alcohol and the other is oxidized to carboxylic acid.



SECTION - B

4. Observe the graph shown in figure and answer the following questions: 1 × 3 = 3



(a) What is the order of the reaction?

(b) What is the slope of the curve?

(c) Write the relationship between k and $t_{1/2}$ (half life period)

Ans. (a) The order of the reaction is first order reaction.

(b) Slope of the curve

$$\text{Slope} = \frac{k}{2.303}$$

(c) Half-life for the first order reaction is given by

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

5. (a) (i) Write the IUPAC name of the following complex: 1 × 3 = 3
$K_2[PdCl_4]$

(ii) Using crystal field theory, write the electronic configuration of d^5 ion, if $\Delta_0 > P$.

(iii) What are Homoleptic complexes?

OR

(b) (i) Why chelate complexes are more stable than complexes with unidentate ligands? 1

(ii) What is ''spectrochemical series''? What is the difference between a weak field ligand and a strong field ligand? 2

Ans. (a) (i) IUPAC name of $K_2[PdCl_4]$ is Potassium tetrachloro palladate (II).

(ii) If $\Delta_0 > P$, the electronic configuration of d^5 ion will be $t_{2g}^5\ e_g^0$ as it is associated with strong field and low spin situation. Thus, no electron will enter into e_g orbital.

(iii) The complex compounds in which all the ligand which are connected with central atom are same or identical are called homoleptic complexes. For example: $[Ni(CO)_4]$, $[Co(NH_3)_6]^{+3}$.

OR

(b) (i) Chelate complexes are more stable than unidentate ligand because chelate ligand forms a ring with the central metal ion and are held by strong force of attraction and are less likely to dissociate. However, unidentate ligands are attached to central metal at one point which involves less force of attraction and are more likely to dissociate.

(ii) A series in which ligands are arranged in the order of increasing magnitude of crystal field splitting energy (CFSE), is called spectrochemical series.

The ligands present on the R.H.S of the series are strong field ligands while that on the L.H.S are weak field ligands.

$I^- < Br^- < Cl^- < SCN^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO$

S. No.	Weak Field Ligand	Strong Field Ligand
1.	These are the ligands used in octahedral complexes in which the crystal field stabilization energy Δ° is less than pairing energy (P) in a single orbital.	These are the ligands used in octahedral complexes in which the crystal field stabilization energy Δ° is greater than pairing energy (P).
2.	Complexes formed by these ligands are also known as high spin complexes.	Complexes formed by these ligands are also known as low spin complexes

3.	The complexes formed are generally paramagnetic in nature.	The complexes formed are mostly diamagnetic or comparatively less paramagnetic in nature.

* **6. (a) (i) Define coagulation.** **1 × 3 = 3**

(ii) State Hardy-Schulze rule.

(iii) What is Electrophoresis?

OR

* **(b) Write three differences between Physisorption and Chemisorption.** **1 × 3 = 3**

7. (a) Write any two consequences of Lanthanoid Contraction.

(b) Name the element of 3*d* series which exhibits the largest number of oxidation states. Give reason. **2 + 1 = 3**

Ans. (a) The two consequences of lanthanide contraction are:

(i) Due to close similarity in electronic configuration and ionic radii, the lanthanides have identical chemical properties which makes their separation difficult.

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

(b) The element which shows largest number of oxidation states in 3*d* series is Manganese (Mn). It shows the following oxidation states + 2, + 3, + 4, + 5, + 6 and + 7. It is because it contains the maximum no. of unpaired e^- *s* in the outermost shell, *i.e.*, $3d^9 4s^2$.

8. Give reasons for the following statements: **1×3=3**

(a) Copper does not displace hydrogen from acids.

(b) Transition metals and most of their compounds show paramagnetic behaviour.

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

Ans. (a) Copper cannot displace hydrogen from an acid because copper is less reactive element than hydrogen and it is present below hydrogen in the activity series of metals.

(b) Transition metals and many other metals shows paramagnetic behaviour because they posses number of unpaired electrons in *d*-orbital.

(c) Metal atoms like Zn, Cd, Hg have completely filled *d*-orbitals (d^{10} configuration). Thus, *d*-electrons are not available for metallic bond formation. As a result, these metals are quite soft and also have low melting points.

9. (a) Account for the following: **1 × 3 = 3**

(i) pK_b of aniline is more than that of methylamine.

(ii) Aniline does not undergo Friedel-Crafts reaction.

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

OR

(b) (i) Arrange the following compounds in the increasing order of their basic strength in aqueous solution: **1 × 3 = 3**

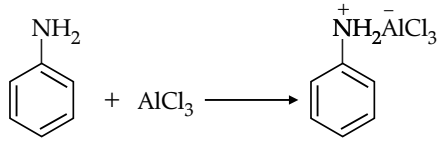
CH_3NH_2, $(CH_3)_3N$, $(CH_3)_2NH$

(ii) What is Hinsberg's reagent?

(iii) What is the role of pyridine in the acylation reaction of amines?

Ans. (a) (i) Aniline has higher pK_b than methylamine because aniline undergoes resonance and the electrons on N-atom are delocalized in benzene ring. Thus, electrons are less available to donate whereas in methylamine electron density on nitrogen atom is greater than aniline. As a result, the acidic character of methylamine is more than aniline and pK_b value is less.

(ii) Aniline does not undergo Friedel-Crafts reaction because aniline act as a strong base which reacts with $AlCl_3$ to form salt. Thus, due to the presence of positive charge on N–atom, electrophilic substitution is deactivated in benzene ring.



Aniline Salt

(iii) Boiling point of primary amines is higher than that of tertiary amines because tertiary amines do not form hydrogen bond due to absence of H–atoms. So, intermolecular forces between tertiary amines are weaker. On the other hand, in primary amines two hydrogen atoms are attached to electronegative N–atom. It leads to the greater magnitude of H-bonding and hence, larger intermolecular forces.

* Out of Syllabus

OR

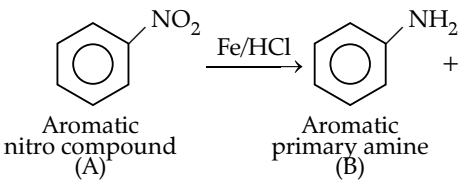
(b) (i) The increasing order of basic strength in aqueous solution of following amines is
$(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$
(Due to steric hindrance and +I effect of alkyl groups)

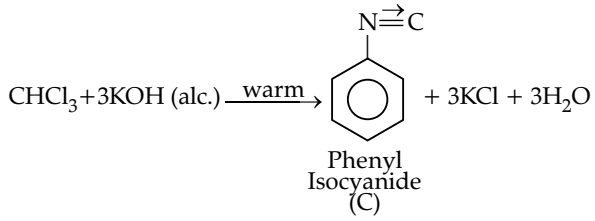
(ii) The benzene sulphonyl chloride ($C_6H_5SO_2Cl$) is called Hinsberg reagent.
- It is an organo-sulphur compound.
- It is used for detection and distinction of primary, secondary and tertiary amine in a given sample.

(iii) Pyridine is used in acylation of amines because it acts as a strong base which helps in removing the side product HCl from the reaction mixture. Therefore, it acts as an acceptor for the acid by-product formed during the reaction.

10. A compound 'A' on reduction with iron scrap and hydrochloric acid gives compound 'B' with molecular formula C_6H_7N. Compound 'B' on reaction with $CHCl_3$ and alcoholic KOH produces an obnoxious smell of carbylamine due to the formation of 'C'. Identify 'A', 'B' and 'C' and write the chemical reactions involved. 1 × 3 = 3

Ans.



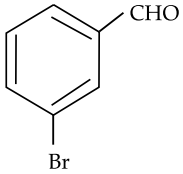


The compound A is Nitrobenzene, B is Aniline and C is Phenyl isocyanide.

11. (a) Complete the following: 1 × 3 = 3

(i) $CH_3CN \xrightarrow[2.\ H_2O]{1,\ AlH(i\text{-}Bu)_2}$ **'A'** $\xrightarrow[H^+]{H_2N\text{-}OH}$ **'B'**

(ii) Write IUPAC name of the following compound:



(iii) Write a chemical test to distinguish between the following compounds: Phenol and Benzoic acid

OR

(b) Convert the following: 1 × 2 = 2

(i) Benzoic acid to Benzaldehyde

(ii) Propan-1-ol to 2-Bromopropanoic acid

(iii) Acetaldehyde to But-2-enal

Ans. (a) (i) $CH_3C \equiv N + DIBAL\text{–}H + H_2O \rightarrow CH_3CHO + NH_2OH + H^+ \rightarrow CH_3CH = N\text{–}OH + H_2O$

A – Acetaldehyde B – Acetaloxide

(ii) The IUPAC name is 3-bromobenzaldehyde.

(iii) Phenol and Benzoic Acid can be distinguished by iron chloride ($FeCl_3$) test. As phenol gives violet colouration with neutral $FeCl_3$ solution while benzoic acid gives buff coloured precipitate of ferric benzoate.

$6C_6H_5OH + FeCl_3 \rightarrow [Fe(OC_6H_5)_6]^{3-} + 3H^+$

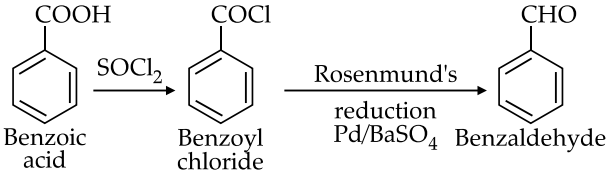
Violet complex + 3HCl

$3C_6H_5COOH + FeCl_3 \rightarrow (C_6H_5COO)_3Fe + 3HCl$

Benzoic acid Buff coloured ppt.

OR

(b) (i) Benzoic acid to benzaldehyde – Firstly benzoic acid is converted into benzoyl chloride by adding sulphonyl chloride and then by Rosenmund reduction reaction using Pd-$BaSO_4$ converted into benzaldehyde.



(ii) Propan-1-ol to 2-bromo propanoic acid -Firstly propanol is converted into propanoic acid by oxidizing in presence of alk. $KMnO_4$and then by using Red Phosphorous/ NaOH and Bromine gas is further converted into 2-Bromo-propanoic acid

$CH_3—CH_2—CH_2—OH \xrightarrow{\text{alkaline } KMnO_4}$

Propanol

$$CH_3—CH_2—\overset{\overset{O}{\|}}{C}—OH + Br_2 \xrightarrow[NaOH]{red\ P} CH_3—\underset{\underset{Br}{|}}{CH}—COOH$$

Propanoic acid — 2-Bromopropanoic acid

(iii) Ethanal or Acetaldehyde into But-2-en-1-al Aldol condensation (in presence of dil NaOH) followed by dehydration.

$$2CH_3CHO \xrightarrow{dil\ NaOH} CH_3—\underset{\underset{OH}{|}}{CH}—CH_2—CHO$$

Ethanal — 3-Hydroxybutanal

$$\xrightarrow[-H_2O]{\Delta} CH_3—CH=CH—CHO$$

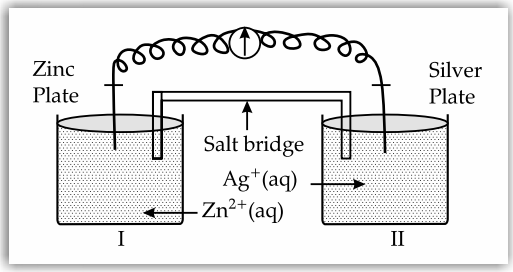
But-2-en-1-al

SECTION - C

12. Read the passage given below and answer the questions that follow: 1 + 1 + 1 + 2 = 5

Oxidation-reduction reactions are commonly known as redox reactions. They involve transfer of electrons from one species to another. In a spontaneous reaction, energy is released which can be used to do useful work. The reaction is split into two half reactions. Two different containers are used and a wire is used to drive the electrons from one side to the other and a Voltaic/Galvanic cell is created. It is an electrochemical cell that uses spontaneous redox reactions to generate electricity. A salt bridge also connects to the half cells. The reading of the voltmeter gives the cell voltage or cell potential or electromotive force. If E^0_{cell} is positive the reaction is spontaneous and if it is negative the reaction is non-spontaneous and is referred to as electrolytic cell. Electrolysis refers to the decomposition of a substance by an electric current. One mole of electric charge when passed through a cell will discharge half a mole of a divalent metal ion such as Cu^{2+}. This was first formulated by Faraday in the form of laws of electrolysis.

The conductance of material is the property of materials due to which a material allows the flow of ions through itself and thus conducts electricity. Conductivity is represented by k and it depends upon nature and concentration of electrolyte, temperature, etc. A more common term molar conductivity of a solution at a given concentration is conductance of the volume of solution containing one mole of electrolyte kept between two electrodes with the unit area of cross-section and distance of unit length. Limiting molar conductivity of weak electrolytes cannot be obtained graphically.



(a) Is silver plate the anode or cathode? 1

(b) What will happen if the salt bridge is removed? 1

(c) When does electrochemical cell behaves like an electrolytic cell? 1

(d) (i) What will happen to the concentration of Zn^{2+} and Ag^+ when $E_{cell} = 0$. 1 × 2 = 2

(ii) Why does conductivity of a solution decreases with dilution?

OR

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

Ans. (a) Silver plate acts as cathode.

(b) Salt bridge permits the flow of current by completing the circuit as well as it maintains the charge balance between anode and cathode by movement of electrons. If the salt bridge is removed no current will flow in the circuit and the voltage will drop to zero.

(c) An electrochemical cell behaves like an electrolytic cell when there is an application of an external opposite potential on the galvanic cell and reaction is not inhibited until the opposing voltage reaches the value 1.1 V. At this stage, no current flows through the cell and on increasing the external potential any further the reaction will function in the opposite direction.

$$E_{ext} > E_{cell}$$

(d) (i) When $E_{cell} = 0$, an equilibrium condition is reached and the concentration of Zn^{2+} and Ag^+ remains same.

(ii) Conductivity of a solution defined as the conductance of ions present in a unit volume of the solution. On dilution, the number of ions per unit volume decreases. Thus, the conductivity of the solution decreases on dilution.

OR

(d) Molar Conductivity (k)

$$= \frac{\text{Conductivity}}{\text{Concentration}}$$

$$\wedge_m = \frac{\kappa}{c}$$

$$= \frac{138.9\,\text{S cm}^2\text{mol}^{-1} \times 1.5\text{mol / L}}{1000\text{cm}^3 / l}$$

$$\text{Conductivity} = \wedge_m \times \text{C}$$

$$= 0.208\ \text{Scm}^{-1}$$

Delhi Set-II, Series: AABB5/5, 56/5/2

Note: Except these, all other questions are from Set-I.

SECTION - A

2. Explain the following reactions:

(a) Clemmensen reaction

(b) Stephen reaction **1 × 2 = 2**

Ans. (a) Clemmensen's reduction: This reaction is used to reduce carbonyl compounds to form simple hydrocarbons in presence of zinc amalgam and concentrated hydrochloric acid.

$$>\text{C}=\text{O} \xrightarrow[\text{HCl}]{\text{Zn-Hg}} >\text{CH}_2 + \text{H}_2\text{O}$$

(b) Stephen Reaction: This reaction is used to synthesize aldehydes from nitriles or cyanides. Firstly, nitriles or cyanides are reduced in the presence of stannous chloride and hydrochloric acid in ethyl acetate solvent to form imine intermediate. Then hydrolysis of this intermediate with water gives corresponding aldehyde.

$$\text{CH}_3\text{—C} \equiv \text{N} + 2[\text{H}] \xrightarrow[\text{Ether}]{\text{SnCl}_2/\text{HCl}}$$

$$\text{CH}_3\text{—CH} = \text{NH} + \text{HCl}$$

$$\downarrow \text{H}_2\text{O}/\text{H}^+$$

$$\text{CH}_3\text{CHO} + \text{NH}_4\text{Cl}$$

Acetaldehyde

5. (a) (i) Write the IUPAC name of the following complex: **1 × 3 = 3**

$[Pt(NH_3)_6]Cl_4$

(ii) On the basis of crystal field theory, write the electronic configuration of d^4 ion, if $\Delta_o < P$.

(iii) What are Heteroleptic complexes?

OR

(b) (i) Using IUPAC norms write the formulas for the follwing: **2 + 1 = 3**

(i) Pentaamminenitrito-N-Cobalt (III)

(ii) Tetrahydroxidozincate (II)

(ii) What is crystal field splitting energy?

Ans. (a) (i) The IUPAC name of $[Pt(NH_3)_6]Cl_4$ is Hexaammineplatinum (IV) chloride.

(ii) If $\Delta_0 < P$, the electronic configuration of d^4 ion will be $t_{2g}^3 e_g^1$ as it is associated with weak field and high spin situation. Thus, the fourth electron will enter into e_g orbital.

(iii) The complexes in which central atom or metal ion is surrounded by more than one type of ligands are called heteroleptic complexes. For example: $[Co(NH_3)_4Cl_2]^+$.

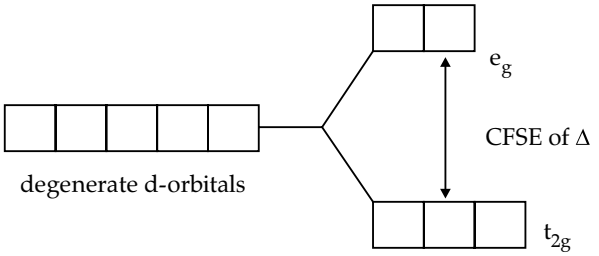
OR

(b) (i) (a)Pentaamminenitrito-N-cobalt(III) is

$[Co(NO_2)(NH_3)_5]^{2+}$

(b) Tetrahydroxidozincate(II) is $[Zn(OH)_4]^{-2}$

(ii) The difference of energy between the two sets of degenerated orbitals (t_{2g} and e_g) after crystal field splitting is known as crystal field splitting energy. It is denoted by Δ_o.



8. Give reason for the following statements: **1 × 3 = 3**

(a) Scandium (Z = 21) is a transition element but Zn (Z = 30) is not.

(b) $[Ti(H_2O)]^{3+}$ is coloured while $[Sc(H_2O_6]^{3+}$ is colourless.

(c) Physical and chemical properties of the 4*d* and 5*d* series of the transition elements are quite similar than expected.

Ans. (a) On the basis of incompletely filled 3*d*-orbitals in case of Scandium atom ($3d^1$) having one electron in its ground state, it is regarded as a transition element. On the other hand, zinc atom having completely filled *d*-orbitals ($3d^{10}$) in its ground state as well as in its oxidized state, it is not considered as a transition element.

(b) $[Ti(H_2O)_6]^{+3}$ is coloured because $Ti^{+3}(3d^1)$ has one unpaired electron which undergoes *d-d* transition so it is coloured. While $[Sc(H_2O)_6]^{+3}$ ($3d^0$) has no unpaired electrons so it will not undergo *d-d* transition so it is colourless.

(c) Physical and chemical properties of 4*d* and 5*d* series elements are similar because they have same atomic and ionic radii due to the lanthanide contraction. Due to equal atomic radii the size of Zr and Hf, Nb and Ta, Mo and W, etc., the two elements of each pair have the same properties.

10. A primary amine 'A' C_2H_7N reacts with alkyl halide (C_2H_5I) to give secondary amine 'B'. 'B' reacts with $C_6H_5SO_2Cl$ to give a solid 'C' which is insoluble in alkali. Identify 'A', 'B', 'C' and write all the chemical reactions involved. **3**

Ans. $CH_3CH_2NH_2 + CH_3CH_2I \rightarrow CH_3CH_2NHCH_3CH_2$

1° Amine (A) Ethyl iodide 2° Amine(B)

$+ C_6H_5SO_2Cl \rightarrow C_6H_5SO_2N(C_2H_5)$

N, N-diethyl benzene sulphonamide (C)

A = Ethyl amine,

B = Diethyl amine,

C = N, N-diethyl benzene sulphonamide.

Outside Delhi Set-I, Series: AABB4/3, 56/3/1

SECTION - A

1. Predict the reagent for carrying out the following transformations: **1 × 2 = 2**

(a) Benzoyl chloride to Benzaldehyde

(b) Ethanal to 3-hydroxy butanal

(c) Ethanoic acid to 2-chloroethanoic acid

Ans. (i) Rosenmund Reduction in presence of Lindlar's Catalyst (H_2/ Pd-$BaSO_4$).

(ii) Aldol Condensation in presence of dil. NaOH.

(iii) Hell – Volhard Zelinsky Reaction in presence of Cl_2/Red Phosphorous. (Any two)

2. (a) Why on dilution the $\wedge_m$ of CH_3COOH increases very fast, while that of CH_3COONa increases gradually?

(b) What happens if external potential applied becomes greater than E° to be in subscript of electrochemical cell? **1 × 2 = 2**

Ans. (i) On dilution $\wedge_m$ of CH_3COOH increases very fast because it is a weak electrolyte and the number of ions also increases due to increase in the degree of dissociation (less than 1). However,in CH_3COONa which is a strong electrolyte, the number of ions remains same but the intermolecular forces of attraction decreases and the degree of dissociation is equal to 1. Thus, $\wedge_m$ increases gradually in case of CH_3COONa.

(ii) If the external potential applied become greater than E°cell of electrochemical cell, then the reaction gets reversed and the electrochemical cell acts as an electrolytic cell and vice-versa.

3. An Organic compound (A) with molecular formula C_3H_7NO on heating with Br_2 and KOH forms a compound (B). Compound (B) on heating with $CHCl_3$ and alcoholic KOH produces a foul smelling compound (C) and on reacting with $C_6H_5SO_2Cl$ forms a compound (D) which is soluble in alkali. Write the structure of (A), (B), (C) and (D). **2**

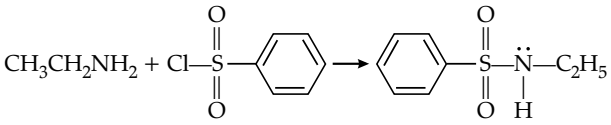
Ans. $CH_3CH_2CONH_2 + Br_2 + KOH \rightarrow CH_3CH_2NH_2$

(A) (B)

$CH_3CH_2NH_2 + CHCl_3 + KOH \rightarrow CH_3CH_2NC$

(B) (C)

$+ KCl + H_2O$



(B) N-ethyl benzene sulfonamide (soluble in alkali)

A = Propanaimde

B = Ethyl amine (1° amine)

C = Ethyl isocyanide

D = N-ethyl benzene sulphonamide

4. Account for the following: 1 × 3 = 3

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

(b) E° value of the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}.

(c) Transition metals form alloys

Ans. (i) Cu^{2+} salts are coloured whereas Zn^{2+} salts are white because Cu^{2+} ([Ar]3d^9) has one unpaired electron in *d*-orbital which allows electron transition in visible region which imparts colour whereas Zn^{2+} ([Ar]3d^{10}) do not possess any unpaired electron hence no electron transition takes place thus shows no colour.

(ii) E° values for Mn^{3+}/Mn^{2+} couple is much more positive than for Cr^{3+}/Cr^{2+} because the conversion of Mn^{2+} from Mn^{3+} possesses extra stability due to half filled valence electronic configuration (3d^5) whereas Cr ion changes from Cr^{3+} to Cr^{2+} undergoes change in outer configuration from 3d^3 to 3d^4 making it less stable comparatively.

(iii) Transition metals have very similar atomic sizes as a result one metal can easily replace the other metal from its lattice to form solid solution (alloy). Transition metals are also miscible with one another in the molten state. Thus, the molten state solution of two or more transition metals on cooling forms alloy.

5. (a) Calculate Δ_r G° and log K_c for the following cell: 3

Ni(*s*) + 2 Ag^+(*aq*) → Ni^{2+}(*aq*) + 2 Ag(s)

Given that E° cell = 1.05 V, 1 F = 96,500 C mol^{-1}

OR

(b) Calculate the e.m.f. of the following cell at 298 K: 3

Fe(*s*) | Fe^{2+} (0.001 M) || H^+ (0.01 M) | H_2(*g*) (1 bar) | Pt (*s*)

Given that E° cell = 0.44 V

[log 2 = 0.3010, log 3 = 0.4771, log 10 = 1]

Ans. According to the equation,

$Ni + 2Ag^+ \rightarrow Ni^{2+} + 2Ag$

$\Delta G = -nFE°$

where ΔG = Gibb's free energy

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

N = No. of electrons gain or lost = 2

$\Delta G = -202.650$ kJ

F = Faraday's constant = 96500

E° = Standard emf = 1.05V

The relation between Gibb's free energy and Equilibrium constant is given by equation

$$E° \text{ cell} = \frac{0.0591}{n} \log K_c$$

$$\log K_c = -\frac{1.05 \times 2}{0.0591} = 35.53$$

$$K_c = 3.39 \times 10^{35}$$

OR

According to the equation,

$Fe(s) + 2H^+ (aq) \rightarrow Fe^{+2} (aq) + H_2 (g)$

$E°_{cell} = E°_{cathode} - E°_{anode}$

$E°_{cell} = 0 - (-0.44)$ V

$E°_{cell} = +0.44$ V

By applying Nernst Equation,

$$E_{cell} = E°_{cell} - \frac{0.0591}{2} \log \frac{[Fe^{+2}]}{[H^+]^2}$$

$$E_{cell} = 0.44 \frac{-0.0591}{2} \log \frac{0.001}{(0.01)^2}$$

$$E_{cell} = 0.44 - \frac{0.0591}{2} \log 10$$

$E_{cell} = 0.44 - 0.0295 \times 1$

$E_{cell} = +0.410$V

6. (a) Using Valence Bond theory, predict the hybridization and magnetic character of following:

$[CoF_6]^{3-}$ [Atomic number of Co = 27]

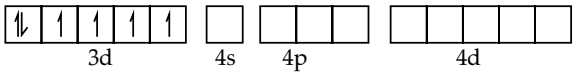
(b) Write IUPAC name of the following complex:

$[CoBr_2(en)_2]^+$

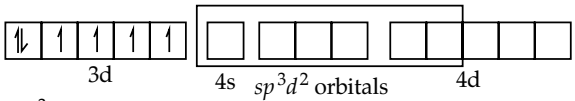
(c) How many ions are produced from the complex $[Co(NH_3)_6]Cl_2$ in solution? 1 ×3 = 3

Ans. (a) $[CoF_6]^{3-}$

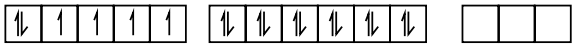
Orbitals of CO^{2+} ion



Co^{2+} undergoing $sp^3 d^2$ hybridisation



$CoF_6]^{3-}$ outer orbital or high spin complex



sp^3d^2 hybrid orbitals
six pairs of electrons from
six fluoride ions

Hybridization = sp^3d^2

Magnetic Nature = Paramagnetic

(b) $[CoBr_2(en)_2]^+$

IUPAC name of the complex is Dibromidobis-(ethane – 1,2 -diamine) cobalt(III) ion.

(c) In aqueous solution of the complex, 3 ions are produced.

$[Co(NH_3)_6]Cl_2 \rightleftharpoons [Co(NH_3)_6]^{+2} + 2Cl^-$

*** 7. (a) Differentiate between the following:**

(i) Adsorption and Absorption

(ii) Lyophobic Sol and Lyophilic Sol

(iii) Multimolecular Colloid and Macromolecular colloid. 1 × 3 = 3

OR

*** (b) (I) Define the following terms: 3**

(i) Zeta Potential

(ii) Coagulation

(II) Why a negatively charged sol is obtained when $AgNO_3$ solution is added to KI solution?

8. Define transition metals. Why Zn, Cd and Hg are not called transition metals? How is the variability in oxidation states of transition metals different from that of *p*-block elements 3

Ans. Transition metals : Elements having partially filled *d*-orbitals in ground state or in excited state, are known as transition elements.

The orbitals of the elements like Zn, Cd, Hg are completely filled when they are in their ground state as well as in their general oxidation state. Therefore, these elements are not considered as transition elements.

In transition elements, the variability in the oxidation state is due to the participation of $(n-1)$ *d* orbitals and ns orbitals. Thus, oxidation states differ by unity. For example, Fe^{+3} to Fe^{+2}, Cr^{+3} to Cr^{+2}, etc On the other hand, the variable oxidation states shown by some *p* block elements differ by two units. For example, Sn^{4+} to Sn^{2+}, Pb^{4+} to Pb^{2+}.

9. (a) What happens when 1 ×3 = 3

(i) Propanone is is treated with CH_3MgBr and then hydrolysed?

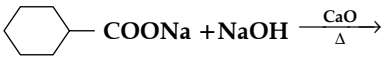
(ii) Ethanal is treated with excess ethanol and acid?

(iii) Methanal undergoes Cannizzaro reaction?

(b) Write the main product in the following reaction? 1 × 3 = 3

(i) $2CH_3COCl + (CH_3)_2Cd \rightarrow$

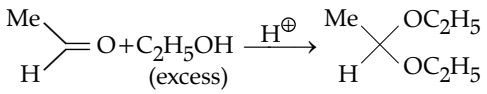
(ii) $CH_3CH_2CHO \xrightarrow{Zn(Hg)/Conc\ HCl}$

(iii)  **COONa +NaOH** $\xrightarrow[\Delta]{CaO}$

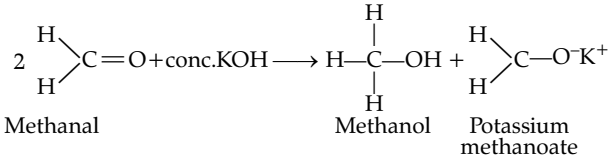
Ans. (a) (i) When propanone reacts with ethyl magnesium bromide (Grignard's reagent) and hydrolysed, it forms aldehyde.

$$(CH_3)_2CO + H_3CCH_2MgBr \xrightarrow[H_2O]{} (CH_3)_2\overset{CH_2CH_3}{\underset{|}{C}}OH + Mg(OH)Br$$

(ii) When ethanal reacts with excess ethanol and acid gives acetal.



(iii) Methanal will undergo Cannizzaro reaction as it possesses α-hydrogen to form methanol.



* Out of Syllabus

OR

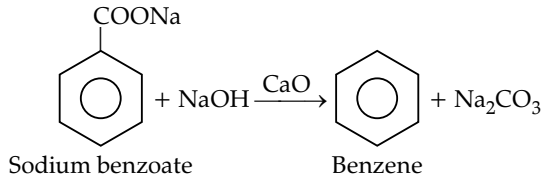
(b) (i) $2\,CH_3COCl + (CH_3)_2Cd \rightarrow 2CH_3COCH_3 + CdCl_2$

Propanone Cadmium Chloride

(ii) $CH_3CH_2CHO \xrightarrow[\text{Conc.HCl}]{\text{Zn – Hg}} CH_3CH_2CH_3$

Propane

(iii)



Sodium benzoate Benzene

10. Give reasons:

(a) Ammonolysis of alkyl halides is not a good method to prepare pure primary amines.

(b) Aniline does not give Friedel-Crafts reaction.

(c) Although —NH_2 group is *o/p* directing in electrophilic substitution reaction, yet aniline on nitration gives good yield of m-nitroaniline.

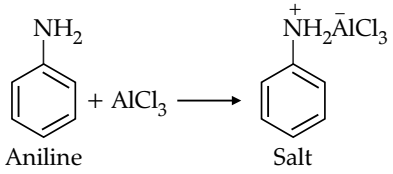
1 × 3 = 3

Ans. (i) Ammonolysis of alkyl halides leads to the formation of mixture of primary, secondary, tertiary amines and quaternary salts. It is because every time nucleophilic substitution reaction takes place in which amine acts as a nucleophile and form primary amine which further react and form secondary amine, which again react with the alkyl halide to form the tertiary amine, and further leads to the formation of quaternary salt. Thus, ammonolysis reaction forms a mixture of all the four compounds and it will be difficult to get the pure amine.

$$R—X \text{ Alkyl halide} \xrightarrow[-HX]{NH_3} R—NH_2 \xrightarrow[-HX]{R—X}$$

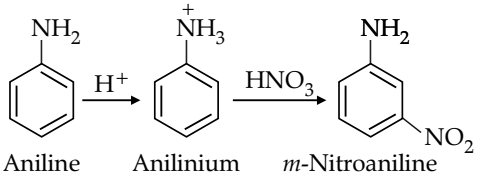
$$R_2NH \xrightarrow[-HX]{R—X} R_3N \xrightarrow{R—X} R_4\overset{+}{N}X^-$$

(ii) Aniline does not undergo Friedel-Crafts reaction because aniline act as a strong base which reacts with $AlCl_3$ to form salt. Thus, due to the presence of positive charge on N-atom electrophilic substitution is deactivated in benzene ring.



Aniline Salt

(iii) Nitration is carried out in an acidic medium. In a strongly acidic medium, aniline is protonated to give anilinium ion (which is meta-directing). For this reason, aniline on nitration gives a substantial amount of m-nitroaniline.



Aniline Anilinium ion *m*-Nitroaniline (47%)

*** 11 (a) (i) Which acid of the following pair would you except to be stronger?**

F—CH_2–COOH or CH_3—COOH

(ii) Arrange the following compounds in increasing order of their boiling points:

CH_3CH_2OH, CH_3—CHO. CH_3—COOH

(iii) Give simple chemical test to distinguish between Benzaldehyde and Acetophenone.

1 × 3 = 3

OR

(b) (i) Which will undergo faster nucleophilic addition reaction?

Acetaldehyde Propanone

(ii) What is the composition of Fehling's reagent?

(iii) Draw structure of the semicarbazone of Ethanal. **1 × 3 = 3**

Ans. (a) (i) Among FCH_2COOH and CH_3COOH, FCH_2COOH is stronger due to the presence of electron withdrawing group (–F). As Fluorine (halogens) is most electronegative element hence, electronegativity makes it stronger than acetic acid.

(ii) The increasing order of boiling point in the following compounds is

$CH_3CHO < CH_3CH_2OH < CH_3COOH$

Ethanoic acid and ethanol has comparatively higher boiling point than ethanal as they both are held by strong hydrogen bonds in between them whereas in ethanal there is dipole-dipole interaction in between them.

* Out of Syllabus

(iii) With ammoniacal silver nitrate solution (Tollen's reagent), benzaldehyde forms silver mirror but acetophenone does not give this test.

$C_6H_5CHO + 2[Ag(NH_3)^{2+} + 3OH^-$
$\rightarrow C_6H_5COO^- + 2Ag\downarrow + 4NH_3 + 2H_2O$

Acetophenone gives positive iodoform test whereas benzaldehyde do not give iodoform test.

$C_6H_5COCH_3 + 3\,NaOI \rightarrow C_6H_5COONa + CHI_3 + 2\,NaOH$

Acetophenone — Sodium hypoiodite — Sodium benzoate — Iodoform↓ (yellow ppt)

$C_6H_5CHO + NaOI \rightarrow$ No yellow ppt of CHI_3

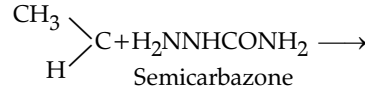
Benzaldehyde

OR

(b) (i) Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric hindrance. As the electron density at carbonyl carbon increases, +I effect increases which decreases the chances of attack by a nucleophile. Thus, acetaldehyde is more reactive than propanone.

(ii) Fehling's solution is a mixture of alkaline solution of copper(II) sulphate ($CuSO_4$) containing sodium potassium tartrate (Rochelle salt- $KNaC_4H_4O_6.4H_2O$).

(iii) Structure of semi carbazone from ethanal.



Ethanal — Semicarbazone

Ethanal — Semicarbazone

12. Read the following passage and answer the question that follow:

The rate of reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. A number of factors such as temperature, concentration of reactants, catalyst affect the rate of reaction. Mathematical representation of rate of a reaction is given by rate law:

$$\text{Rate} = k[A]^x\,[B]^y$$

x and y indicate how sensitive the rate is to change in concentration of A and B. Sum of $x + y$ gives the overall order of a reaction.

When a sequence of elementary reaction gives us the products, the reaction is called complex reaction. Molecularity and order of an elementary reaction are same. Zero order reaction are relatively uncommon but they occur under special condition. All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics. **1 + 1 +1 + 2**

(a) What is the effect of temperature on the rate constant of a reasons.

(b) For a reaction A + B → Product, the rate given by, rate $k[A]^2\,[B]^{½}$. What is the order of the reaction?

(c) How order and molecularity are different for complex reactions?

(d) A first order reaction has a rate constant $2 \times 10^{-3}\ s^{-1}$. How long will 6 g of this reactant take to reduce to 2g.

OR

The half life for radioactive decay of ^{14}C is 6930 years. An archaeological artifact containing wood had only 75% of the ^{14}C found in a living tree. Find the age of the sample.

[log 4 = 0.6021, log 3 = 0.4771, log 2 = 0.3010, log 10 = 1]

Ans. (a) The rate constant (k) for a reaction increases with increase in temperature and becomes almost double with every 10° rises in temperature. This effect is expressed by Arrhenius equation

$$k = \frac{Ae^{-Ea}}{RT}$$

(b) According to the equation, $r = k[A]^2[B]^{1/2}$

Order of the reaction $= 2 + \frac{1}{2} = \frac{5}{2}$

(c) Order of reaction is defined as the sum of the powers of the molar concentration of the

reaction species in the rate equation of the reaction. It is applicable for both elementary and complex reactions.

Molecularity of a reaction is defined as the total number of reacting species participating in an elementary reaction. It has no significance for complex reactions as applicable for only elementary reactions.

(d) $k = 2 \times 10^{-3}\ s^{-1}$

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

$$t = \frac{2.303}{2\times10^{-3}}\log\frac{6}{2}$$

$$t = 1151.5 \times 0.4771 = 549.3\ s$$

OR

According to first order reaction,

$$\text{Half-life } (t_{1/2}) = \frac{0.693}{k}$$

$$t_{1/2} = 6980 \text{ years}$$

$$k = 0.693/6980$$

However, the time taken can be calculated using first order rate of reaction when wood contain only 75% of C^{14}.

Initial concentration of C_{14}, $[R]_0 = 100$

Amount at time t s, $[R] = 75$

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

$$t = \frac{2.303}{\frac{0.693}{6980}}\log\frac{100}{75}$$

$$t = 2898 \text{ years}$$

Thus, the age of the sample is approximately 2898 years.

❑❑