2011

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Part I *(Answer all questions)*

Question: 1

a. Fill in the blanks by choosing the appropriate word/words from those given in the brackets:

(concentrated sulphuric acid, methylamine, ethylamine, sp^2, 2-propanol, s^{-1}, sp^3, glycol, Cannizzaro's reaction, pyramidal, mol l^{-1} s^{-1}, Hofmann's degradation, glycerol, concentrated nitric acid, square planer, octahedral, concentrated hydrochloric acid.) [5]

i. Nitrogen atom in ammonia undergoes_____hybridisation and the geometry of the molecule is_____.

Answer: *sp^3, pyramidal*

ii. For a first order reaction, the unit of rate is _____and that of rate constant is _____.

Answer: *mol l^{-1} s^{-1}, s^{-1}*

iii. When acetamide is treated with bromide and caustic soda, it gives _____as the main product and the reaction is called_____.

Answer: *methylamine, Hofmann's degradation*

iv. _____is an example of trihydric alcohol and _____is an example of dihydric alcohol.

Answer: glycerol, glycol

v. Aqua regia is a mixture of _____and_____in the ratio of 3:1.

Answer: *concentrated hydrochloric acid, concentrated nitric acid.*

b. Complete the following statements by selecting the **correct alternative** from the choices given: [5]

1. Out of the following solutions, the one having the highest boiling point will be:

   0.1 M NaCl

   0.1 M $BaCl_2$

   0.1 M KNO_3

   0.1 M K_4 $[Fe(CN)_6]$ *Answer*

2. 75% of a first order reaction was completed in 32 minutes. When was 50% of the reaction completed?

   24 minutes

16 minutes *Answer*

8 minutes

4 minutes

3. When zinc granule is dipped into copper sulphate solution, copper is precipitated because:

   Both copper and zinc have a positive reduction potential

   Reduction potential of copper is higher than that of zinc *Answer*

   Reduction potential of zinc is higher than that of copper

   Both zinc and copper have a negative reduction potential.

4. Among the following compounds, the one showing geometric isomerism is:

   2-chloro propane

   2-bromo-2-chlorobutane

   1,2 dichloro ethane *Answer*

   Glycine

5. Of the following compounds, the one which is a Lewis acid is:

   PCl_3

   $AlCl_3$ *Answer*

   NCl_3

   $AsCl_3$

c. Answer the following questions: [5]

i. 0.1 M urea solution shows less depression in freezing point than 0.1 M $MgCl_2$ solution. Explain.

Answer: *Depression in freezing point is a colligative property which depends upon number of particles present in the solution.*

MgCl2 when dissolved in water gives three particles per molecules (MgCl2 Mg++ + 2 Cl-) while urea remains dissociated.

ii. What is the pH of a solution whose hydroxyl ion concentration is 10^{-2} M?

Answer: *pH = 14 – pOH*

= 14 – (-log 10^{-2})

= 14 -2

= 2

iii. If neutral litmus solution is added to sodium acetate solution, what will you observe and why?

Answer: *Litmus solution will turn blue because sodium acetate is a salt of weak acid-strong bases. When dissolved in water it undergoes anionic hydrolysis and solution turns basic.*

iv. State why the boiling point of HF is very high.

Answer: *This is because of intermolecular H-bonding between HF molecules.*

v. Define piezoelectricity and give one use of piezoelectric crystals.

Answer: *When electricity is produced in insulators due to displacement of ion by mechanical stress, it is called piezoelectricity. Piezoelectric crystals are used as pick ups in record players.*

d. Match the following:

i. Biuret	a. DNA
ii. Urotropine	b. Amines
iii. Purine	c. Urea
iv. Frasch process	d. Formaldehyde
v. Hinsberg's reagent	e. Sulphur

Answer: *(i) (c)*
(ii) (d)
(iii) (a)
(iv) (e)
(v) (b)

Part II *(Answer six questions choosing two from section A, two from section B. And two from section C)*

Section A *(Answer any two questions)*

Question: 2

a.

i. 46 gms of ethyl alchohol is dissolved in 18 gms of water. Calculate the mole fraction of ethyl alcohol (at. Wt of C = 12, O =16, H = 1) $[1\frac{1}{2}]$

Answer: $X_{alc} = \frac{nalc}{n_{alc} + n_{water}} = \frac{46/46}{46/46 + 18/18} = \frac{1}{2} = 0.5$

ii. The osmotic pressure of 0.01 molar solution of an electrolyte is found to be 0.65 atm at 27^0C. Calculate the Vant Hoff factor. What conclusion can you draw about the molecular state of the solute in the solution? $[2\frac{1}{2}]$

Answer: *Given π = 0.65 atm; c = 0.01 M*
R = 0.0821 l atm K-1 Mol-1, T = 273 + 27 = 300 K
Now π = i x CRT
0.65 = i x 0.01 x 300 x 0.0821

$$i = \frac{0.65}{0.01 \times 300 \times 0.0821} = 2.639$$

b.

i. State Faraday's First Law of Electrolysis. [1]

Answer: *Faraday's laws of electrolysis*

ii. How many electrons will flow when a current of 5 amperes is passed through a solution for 200 seconds? [1]

Answer: *1 F = charge on 1 mole of e-*
or 96500 coulumbs = charge on 6.023 x 10^{23} electrons

$$\therefore 5 \times 2000 = \frac{6.023 \times 10^{23}}{96500}$$

= 6.24 x 10^{21} electrons
= 6.24 x 10^{21} electrons will flow.

c. Give reasons for the following:

i. A reaction / process will be spontaneous when it is exothermic and randomness is increasing. [2]

Answer: *A process is spontaneous when its free energy change, ΔG is negative and $\Delta G = \Delta H - T\Delta S$*

ΔG will be negative when ΔH is negative (for exothermic reaction ΔH is negative) and further when randomness i.e ΔS is positive (randomness is increasing).

ii. The number of hydronium ions increase when one litre of water is added to 1 M acetic acid. [2]

Answer: *Acetic acid, is a weak electrolyte and according to Ostwalds dilution law degree of dissociation, α of a weak electrolyte is proportion to the square root of dilution accordingly.*
$\alpha = \sqrt{KV}$ where K is dissociation constant of weak electrolyte and V is dilution.

Question: 3

a.

i. What are semiconductors? What is the effect of increasing temperature on the conductivity of a semiconductor? [$1\frac{1}{2}$]

Answer: *These are the crystals which allow only partial conduction of current through them. Their conductivities are intermediate between those of conductors and insulators. Their conductivity increases with increase in temperature.*

ii. A compound AB has a cubic structure and molecular mass 99. Its density is 3.4 g cm^{-3}. What is the length of the edge of the unit cell? [3]

Answer: *Given: Density ρ = 3.4 g cm-3, M.mass = 99*
Z = 1(cubic structure), NA = 6.023 x 10^{23}

Now $\rho = \frac{Z \times M.Mass}{a3 \times N_A}$

$3.4 = \frac{1 \times 99}{a3 \times 6.023 \times 10^{23}}$

$a = \sqrt[3]{99 / 3.4 \times 6.023 \times 10^{23}}$

Edge length a = 3.64 x 10-8 cm.

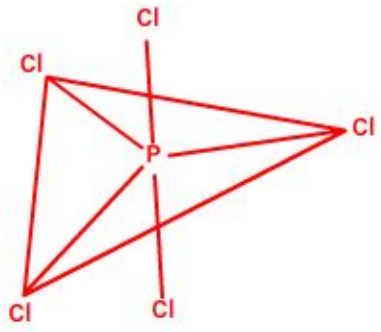
b.

i. What is the maximum work that can be obtained by the isothermal expansion of one mole of an ideal gas at 273 K form 2.24 dm^3 to 22.4 dm^3? [$2\frac{1}{2}$]

Answer: *Given n = 1, R = 8.314 JK-1 Mol-1, T = 273K*
V_1 = 2.24 dm^3, V_2 = 22.4 dm^3
Now $W_{max} = -2.303\ nRT \log \frac{V_2}{V_1}$

ii. State the geometry of PCl_5 molecule. Draw its structure. [1]

Answer:



c. Give two differences between a sigma bond and a pie bond. [2]

Answer:

	Sigma bond	*Pi bond*
i.	*A σ bond is formed by head on overlap of two atomic orbitals along the nuclear axis.*	*A π bond is formed by side ways overlap of atomic orbitals along a line perpendicular to nuclear axis.*
ii	*Since the extent of overlapping is greater a σ bond is a stronger bond.*	*Extent of overlapping is only partial, therefore a π bond is a weaker bond.*

Question: 4

a. i. What is meant by common ion effect? [2]

Answer: *See topics on ' Common-ion effect'.*

ii. Give the conjugate acid and the conjugate base for NH_3.

Answer: *NH_4^+ is the conjugate acid. NH_3 is the conjugate base of ammonia.*

b. Consider the reaction $2Ag^+ Cd \rightarrow 2Ag + Cd^{2+}$. The standard reduction potentials of Ag^+/Ag and Cd^{2+} / Cd are + 0.80 vot and -0.40 volt respectively. [4]

i. Give the cell representation.

Answer: $\xrightarrow{e^-} Cd / Cd^{++}_{(aqu)} \; \| \; Ag^+_{(aqu)} / Ag \xrightarrow{e^-}$

ii. What is the standard cell emf E^0?

Answer: *Given Eo Ag^+/Ag = +0.80 V, Eo cd++ / Cd = -0.40V.*
Now, $E^o_{Cell} = E^o_{Cathode} - E^o_{anode} = 0.80 - (-0.40) = 1.20$ V

iii. What will be the emf of the cell if concentration of Cd2+ is 0.1 M and Ag+ is 0.2 M?

Answer: $E_{Cell} = E^o_{Cell} - = \frac{0.0591}{n} log \frac{[Product]}{[Reactant]}$

$= 1.20 - \frac{0.0591}{2} log \frac{[0.1]}{[0.2]^2}$

$= 1.20 - \frac{0.0591}{2} x .3979$

$= 1.20 - 0.01175$

$= 1.188$ V

iv. Will the cell work spontaneously for the condition given in (iii) above?

Answer: *Cell will work spontaneously because E_{cell} is a positive value.*

c.

i. What is meant by promoter? Give example. [1]

Answer: *These are substances which when added to substrate in very small accounts along with the catalyst, enhance the effectiveness of the catalyst. These are not catalysts themselves. Example: In Haber's process iron powder acts as catalyst while Al_2O_3 is s promoter.*

ii. The solubility product of $BaSO_4$ is 1.5×10^{-9}. Find out its solubility in pure water. [1]

Answer: *Given: K_{sp} ($BaSO_4$) = 1.5 x 10-9*
$BaSO_4$ ⇌ $Ba^{++} + SO4^{--}$

If solubility of $BaSO_4$ is 's' then
Ksp =$[Ba^{++}]$ $[SO4^{--}]$
1.5 NO^{-9} = S x S
$S = \sqrt{1.5 \times 10^{-9}} = 3.87 \times 10^{-5}$

iii. What is the dissociation constant of 0.1 M solution of a weak acid HA which is 4.5 % ionized at 20^0C? [2]

Answer: *Given C = 0.1 M, α = 0.1 M, α = 4.5 / 100*
Then $\alpha = \sqrt{K_a / C}$

$$\left(\frac{4.5}{100}\right)^2 = \frac{K_a}{0.1}$$
$K_a = 2.025 \times 10^{-4}$

Section B *(Answer any two questions)*

Question: 5

a. Give the IUPAC names for the following: [2]
i. $Na_3[AlF_6]$

Answer: *Sodium hexafluoroaluminate (III)*

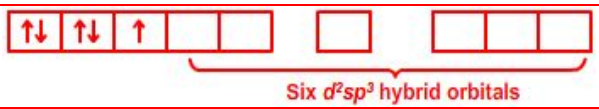
ii. $[CO(NH3)_6Cl_3$

Answer: *Hexaamminecobalt (III) chloride*

b. For the complex ion of $[Fe(CN)_6]^{3-}$ [3]

i. Show the hybridization diagrammatically.

Answer: *In $[Fe(CN)_6]^{3-}$ oxidation state of Fe is +3.*

Fe atom in (Z = 26) ground state	
Fe^{+++} ion	
d^2sp^3 hybridisation in presence of CN^- ligands	

ii. Is it an inner orbital complex or an outer orbital complex?

Answer: *It is an inner orbital complex.*

iii. State its magnetic property.

Answer: *The ion is paramagnetic due to the presence of an unpaired electron.*

Question: 6

a. Give balanced chemical equation for the following:
   i. Chlorine gas is passed through cold, dilute NaOH [3]

Answer: *$2NaOH + Cl_2 \rightarrow NaCl + NaClO + H_2O$*

   ii. Sulphur dioxide gas is passed through NaOH solution.

Answer: *$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$*

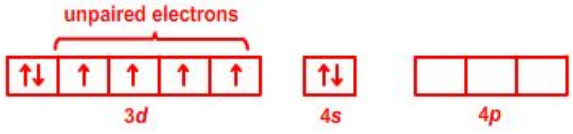
   iii. Zinc is added to sodium argentocyanide solution.

Answer: *$Zn + 2Na\,[Ag\,(CN)_2] \rightarrow Na_2[Zn(CN)_4] + 2Ag \downarrow$*

b. Iron is ferrogmagnetic in nature. Explain why. [2]

Answer: *Ferromagnetic substances have a larger number of unpaired electrons and are attracted strongly in a magnetic field.*
$Fe2_6$ has $4s^2 3d^6$ valence shell configuration with four unpaired electrons in 3d. So it is ferromagnetic when all four unpaired electrons get aligned in the same direction in a given magnetic field.

Fe_{26} atom's valence shell



Question 7

a. State the common oxidation state of : [1]
   i. Lanthanides

Answer: *Oxidation state of lanthanides is +3. Some lanthanide show +2, +4 as well.*

   ii. Actinides

Answer: *Oxidation state of Actinides is +3 but many actinides also show +2, +4 and some +5, +6, +7 also.*

b. In a given transition series, there is no significant change in the atomic radii of elements with increase in atomic number. Explain why. [2]

Answer: *In a transition series, the electrons are filled in inner d orbitals so there is no increase in the number of shells but there is an increase in the nuclear charge and also an increase in the repulsion between inner orbital electrons. The two opposite forces i.e. increased attraction by the nucleus and increased repulsion between electrons counter*

balance each other, as a result there is no significant change in atomic radii of transition element.

Give reactions and the conditions required for preparation of the following compounds:

i. XeF_6

Answer: $Xe + 3F_2 \xrightarrow[300^0\,C,\ 50\ atm.]{1:20\ ratio,\ Ni\ vessel} XeF_6$

ii. $XeOF_4$ [2]

Answer: $XeF_6 + H_2O \xrightarrow[with\ water]{Partial\ hydrolysis} XeOF_4 + 2HF$

Section C *(Answer any two questions)*

Question: 8

a. Carry out the following conversions:

i. Methyl chloride to acetic acid [3]

Answer:

$$\underset{methyl\ chloride}{CH_3Cl} \xrightarrow[-KCl]{+KCN} CH_3CN \xrightarrow{+2H_2O} CH_3COONH_4 \xrightarrow[-NH_4Cl]{+HCl} \underset{acetic\ acid}{CH_3COOH}$$

ii. Benzene to benzoic acid [3]

Answer: $C_6H_6 + CH_3Cl \xrightarrow[-HCl]{AlCl_3} C_6H_5CH_3$

$$2C_6H_5CH_3 + 3O_2 \xrightarrow[(CH_3COO)_2Mn]{443 - 573\,K} 2C_6H_5COOH + 2H_2O$$

iii. Ethanol to acetone [2]

Answer:

$$\underset{ethanol}{2C_2H_5OH} \xrightarrow[-2H_2O]{+2O} 2CH_3COOH \xrightarrow[-2H_2O]{+Ca(OH)_2} (CH_3COO)_2Ca \xrightarrow{\Delta} \underset{acetone}{CH_3COCH_3} + CaCO_3$$

b. Deficiency of what vitamins will cause the following diseases:

i. Night blindness [1]

Answer: *Vitamin A*

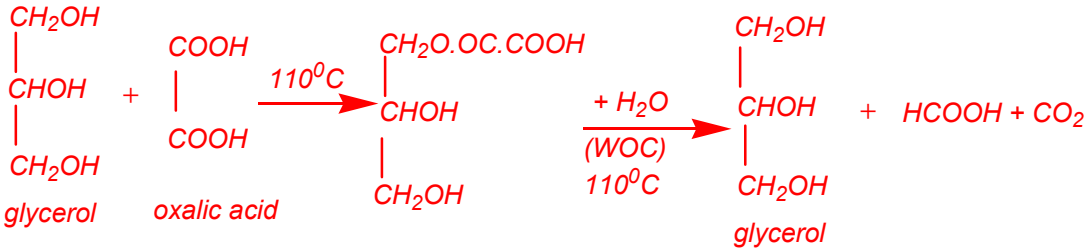
ii. Scurvy [1]

Answer: *Vitamin C*

c. Give balanced equations for the following:

i. Glycerol is heated with oxatic acid 110^0C (383K)

Answer:



ii. Acetamide is heated with sodium hydroxide

Answer: $CH_3CONH_2 + NaOH \xrightarrow{\Delta} CH_3COONa + NH_3 \uparrow$
acetamide

iii. Acetone reacts with hydrogen in the presence of heated copper.

Answer: $CH_3COCH_3 + NaOH \xrightarrow{\Delta} CH_3CHOHCH_3$

Question: 9

a. Identify A to F. [3]

$$A \xrightarrow{LiAlH_4} C_2H_5OH \xrightarrow{PBr_3} B \xrightarrow{KCN} C \xrightarrow{D} C_3H_7NH_2 \xrightarrow{HNO_2} E \xrightarrow[K_2Cr_2O_7H^+]{[O]}$$

Answer: *A → CH_3CHO, B → C_2H_5Br, C → C_2H_5CN, D → $LiAlH_4$, E → C_3H_7OH, F → C_2H_5COOH*

b. Give one good chemical test to distinguish between the following pairs of compounds:

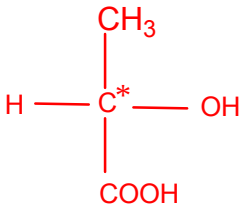
i. Benzaldehyde and acetone

Answer: *Benzaldehyde gives silver mirror when heated with Tollens reagent. Acetone does not give this test.*

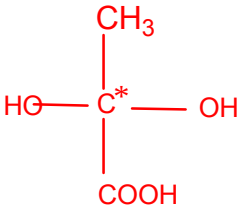
ii. Methylamine and dimethylamine

Answer: *Methylamine gives offensive smell of methyl isocyanide when heated with chloroform and alcoholic KOH dimethylamine does not give this test.*

c. Draw the isomers of 2-hydroxy prop ionic acid



dextro - 2 - hydroxy propionic acid



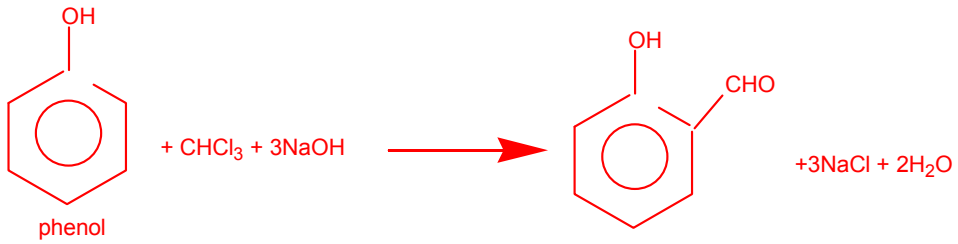
leavo - 2 - hydroxy propionic acid

Answer: * C is an assymetric carbon atom

d. Give an example(equation) for each of the following name reactions:
   i. Aldol condensation

Answer: *Carbon nucleophiles*

   ii. Reamer-Tiemann reaction



Answer:

   iii. Rosemund's reduction

Answer: $CH_3COCl + H_2 \xrightarrow{Pd/BaSO_4} CH_3CHO + HCl$

Question: 10

a. An organic compound A has the molecular formula of C_7H_6O. When A is treated with NaOH followed by acid hydrolysis, it gives two products, B and C. When B is oxidized, it gives A. When A and C are each treated separately with PCl_5, they give two different organic products D and E.
   i. Identify A to E. [3]

Answer: *A → C_6H_5CHO, B → $C_6H_5CH_2OH$, C → C_6H_5COOH D → $C_6H_5CHCl_2$, E → C_6H_5COCl*

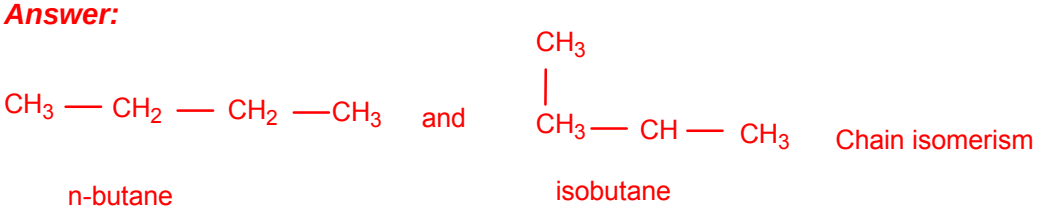
   ii. Give the chemical reaction when A is treated with NaOH and name the reaction. [2]

Answer: *$2C_6H_5CHO + NaOH \rightarrow C_6H_5COONa + C_6H_5CH_2OH$*
This is Cannizzaro's reaction.

b. Draw a pair of isomers for each of the following and name the type of isomerism:

   i. C_4H_{10}

Answer:



ii. $C_2H_2Cl_2$

Answer: *CHCl = CHCl and CH_2CCl_2 → positive isomerism*

iii. CH_3COCH_3

Answer: *Introduction*

iv. $C_4H_{10}O$

Answer: *Introduction*

c. What are polyamides? Give one example of a polyamide and name its monomers. [2]

Answer: *Polyamides are condensation polymers formed from acids and amines. Nylon 6,6 is a polyamide. Monomer units present in it are hexamethylene diamine and adipic acid.*