Chemistry 2018

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

1. **Analysis shows that FeO has a non-stoichiometric composition with formula $Fe_{0.95}O$. Give reason.**** [1]

2. **CO(g) and H_2(g) react to give different products in the presence of different catalysts. Which ability of the catalyst is shown by these reactions ?** [1]

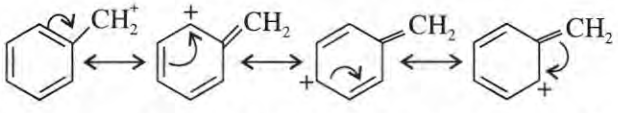
   Answer : CO(g) and H_2(g) react in presence of different catalysts to give different products, this shows that action of a catalyst is highly selective in nature.

3. **Write the coordination number and oxidation state of Platinum in the complex $[Pt(en)_2 Cl_2]$.**[1]

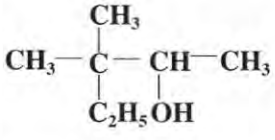
   Answer : Coordination number : 6; Oxidation state : +2

4. **Out of chlorobenzene and benzyl chloride, which one gets easily hydrolysed by aqueous NaOH and why ?** [1]

   Answer : Benzyl chloride would be easily hydrolysed compared to chlorobenzene. In the given reaction condition, hydrolysis proceeds by nucleophilic substitution mechanism and the benzylic carbonium ion formed after losing the leaving group (—Cl) is better stabilized (through resonating structures) hence reacts easily.



5. **Write the IUPAC name of the following :** [1]



   Answer : The IUPAC name would be 3, 3-Dimethy1-pentan-2-o1.

6. **Calculate the freezing point of a solution containing 60 g of glucose (Molar mass = 180 g mol^{-1}) in 250 g of water.**
   (K_f of water = 1.86 K kg mol^{-1}) [2]

   Answer : Molality (m) of given solution of Glucose :

$$m = [(60/180)\ g\ mol^{-1}/250\ g] \times 1000$$
$$= 1.33\ mol\ kg^{-1}$$

Now, depression in freezing point is given by,
$\Delta T_f = K_f m$
Putting the given values,

$$\Delta T_f = K_f m$$
$$= 1.86 \times 1.33$$
$$= 2.5$$

So, freezing point of the solution would be
273.15 K – 2.5 K = 270.65 K.

7. **For the reaction** [2]

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

the rate of formation of NO_2(g) is 2.8×10^{-3} Ms^{-1}. Calculate the rate of disappearance of N_2O_5(g).

Answer : Rate of reaction for the given reaction can be given as,

$$\text{Rate} = 1/2\ \{-\Delta[N_2O_5]/\Delta t\}$$

or $\{-\Delta[N_2O_5]/\Delta t\} = 1/2\ \{[NO_2/\ \Delta t]\}$

So, rate of disappearance of N_2O_5 would be half of rate of production of NO_2 (given $2.8 \times 10^{-3} Ms^{-1}$). So, the rate of disappearance of N_2O_5 is 1.4×10^{-3} Ms^{-1}.

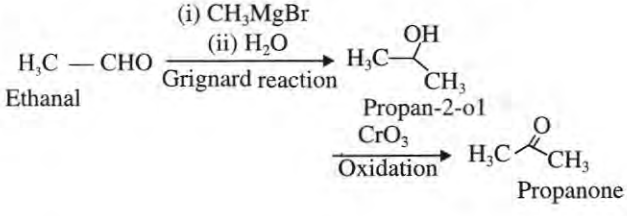
8. **Among the hydrides of Group-15 elements, which have the****
   (a) lowest boiling point ? [2]
   (b) maximum basic character ?
   (c) highest bond angle ?
   (d) maximum reducing character ?

9. **How do you convert the following ?** [2]
   (a) Ethanal to Propanone
   (b) Toluene to Benzoic acid

   OR

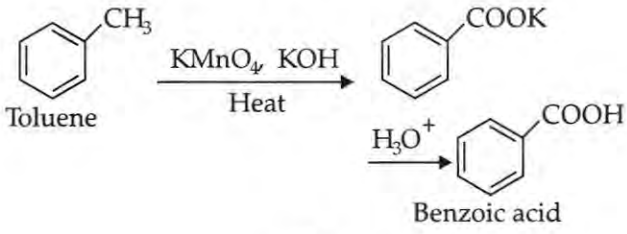
   Account for the following :
   (a) Aromatic carboxylic acids do not undergo Friedel- Crafts reaction.
   (b) pK_a value of 4-nitrobenzoic acid is lower than that of benzoic acid.

Answer : (a) Conversion of ethanal to Propanone :



** Answer is not given due to change in present syllabus.

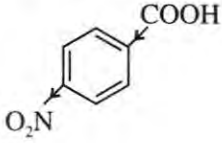
(b) Conversion of toluene to benzoic acid :



OR

(a) Aromatic carboxylic acids do not undergo Friedel-Crafts reaction because the carboxyl group is deactivating for electrophilic substitution reaction, secondarily, the catalyst aluminium chloride gets bonded to the carboxyl group.

(b) pK_a value of 4-Nitrobenzoic acid is lower than benzoic acid, which means 4-Nitrobenzoic acid is more acidic than the benzoic acid. Being an electron withdrawing group, the—NO_2 group withdraws electrons towards itself resulting in ease of carboxylic proton release, hence increasing the acidity.



10. Complete and balance the following chemical equations :

(a) $Fe^{2+} + MnO_4^- + H^+ \rightarrow$

(b) $MnO_4^- + H_2O + I^- \rightarrow$ [2]

Answer :

(a) $5\,Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

(b) $2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2\,OH^- + IO_3^-$

11. Give reasons for the following : [3]

(a) Measurement of osmotic pressure method is preferred for the determination of molar masses of macromolecules such as proteins and polymers.

(b) Aquatic animals are more comfortable in cold water than in warm water.

(c) Elevation of boiling point of 1 M KCl solution is nearly double than that of 1 M sugar solution.

Answer :

(a) Molar masses of macromolecules like polymers and proteins are measured through osmotic pressure method. The osmotic pressure method uses 'molarity' of solution (instead of molality) which has a large magnitude even for dilute solutions, given that polymers have poor solubility, osmotic pressure measurement is used for determination of their molar masses. Macromolecules such as proteins are not stable at high temperatures and because measurement of osmotic pressure is done at around room temperature, it is useful for determination of molar masses of proteins.

(b) Solubility of gases in liquid decreases on increasing the temperature. Hence, the availability of dissolved oxygen in water is more at lower temperatures hence, the aquatic animals feel more comfortable at lower temperatures than at the higher temperatures.

(c) Elevation of boiling point is a colligative property and hence depends on the number of solute particles in the solution. Now, 1 M KCl would have twice the number of solute particles, as KCl dissociates into K^+ and Cl^-, compared to sugar solution (as sugar does not undergo any dissociation). So, elevation of boiling point is nearly double for 1 M KCl solution compared to 1 M sugar solution.

12. An element 'X' (At. mass = 40 g mol^{-1}) having f.c.c. structure, has unit cell edge length of 400 pm. Calculate the density of 'X' and the number of unit cells in 4 g of 'X'. ($N_A = 6.022 \times 10^{23}\ mol^{-1}$)** [3]

13. A first order reaction is 50% completed in 40 minutes at 300 K and in 20 minutes at 320 K. Calculate the activation energy of the reaction. (Given : log 2 = 0.3010, log 4 = 0.6021, R = 8.314 $JK^{-1}\ mol^{-1}$) [3]

Answer : Rate constant for a first order reaction is given by,

$$k = \frac{2.303}{t} \log \frac{[R_0]}{[R_1]}$$

So, at 300 K,

$$k_{300} = \frac{2.303}{40} \log \left(\frac{100}{50}\right)$$

$$= 0.058 \times \log 2$$

$$= 0.058 \times 0.301$$

$$= 0.017$$

$$k_{320} = \frac{2.303}{20} \log \left(\frac{100}{50}\right)$$

** **Answer is not given due to change in present syllabus.**

$$= 0.11 \times \log 2$$

$$= 0.11 \times 0.3010 = 0.034$$

Now, $$\log \frac{k_{320}}{k_{300}} = \left(\frac{E_a}{2.303R}\right)\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Putting the values,

$$\log \frac{0.034}{0.017} = \left(\frac{E_a}{2.303 \times 8.314 JK^{-1}mol^{-1}}\right)$$

$$\left[\frac{320-300}{320\times 200}\right] K$$

$$0.3010 = \frac{E_a}{19.14(0.0002)}$$

$$E_a = 28{,}805.7 \text{ J mol}^{-1} = 28.80 \text{ kJ mol}^{-1}$$

14. What happens when [3]

(a) a freshly prepared precipitate of $Fe(OH)_3$ is shaken with a small amount of $FeCl_3$ solution ?

(b) persistent dialysis of a colloidal solution is carried out ?

(c) an emulsion is centrifuged ?

Answer :

(a) When $FeCl_3$ is added to a freshly prepared precipitate of $Fe(OH)_3$, a positively charged sol of hydrated ferric oxide is formed due to adsorption of Fe^{3+} ions.

(b) When persistent dialysis of colloidal solution is carried out, traces of electrolytes present in the sol are removed almost completely leaving the colloids unstable and finally coagulation takes place.

(c) Emulsions are centrifuged to separate them into constituent liquids.

15. Write the chemical reactions involved in the process of extraction of Gold. Explain the role of dilute NaCN and Zn in this process. [3]

Answer : Extraction of gold involves leaching the metal with dilute solution of NaCN or KCN in the presence of air (for O_2) from which the metal is obtained later by replacement method (using Zinc).

The reactions involved are :

$$4Au(s) + 8CN^-(aq) + 2\,H_2O(aq) + O_2(g) \rightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$$

$$2\,[Au(CN)_2]^-(aq) + Zn(s) \rightarrow 2Au(s) + [Zn(CN)_4]^{2-}(aq)$$

16. Give reasons :

(a) E^o value for Mn^{3+}/Mn^{2+} couple is much more positive than that for Fe^{3+}/Fe^{2+}.

(b) Iron has higher enthalpy of atomization than that of copper .

(c) Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured. [3]

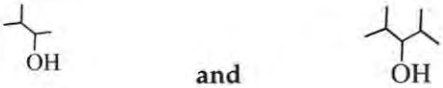
Answer :

(a) Mn^{2+} has a d^5 configuration, and the extra stability of half filled d-orbitals is compromised when another electron is taken out to give Mn^{3+}, On the contrary Fe^{3+} attains a half filled orbital configuration when Fe^{2+} gets oxidized to Fe^{3+}. Hence, the E° value for Mn^{3+}/Mn^{2+} couple has more positive E° value.

(b) Fe has a $3d^6 4s^2$ outer electronic configuration whereas Cu has $3d^{10}\ 4s^1$ configuration. Now, more the number of unpaired electrons in d-orbital, more favourable are interatomic attractions and thus higher atomization enthalpies. Hence, Fe having 4 unpaired d-electrons has more enthalpy of atomization than copper having no unpaired d-electron.

(c) Sc^{3+} has a $3d^0$ configuration whereas Ti^{3+} has a $3d^1$ configuration. As there are no electrons in d orbital for Sc^{3+} ion, there is no transition of electrons by absorption of energy and hence no emission in visible range imparting colour to the Sc^{3+} ion.

17. (a) Identify the chiral molecule in the following pair : [3]



(i) **(ii)**

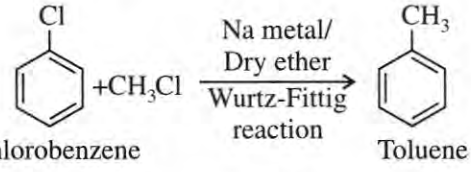
(b) Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.

(c) Write the structure of the alkene formed by dehydrohalogenation of 1-bromo-1 methylcyclohexane with alcoholic KOH.

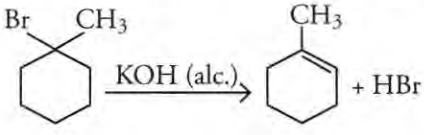
Answer :

(a) The molecule **(i)** is a chiral molecule.

(b) Chlorobenzene reacts with methyl chloride in presence of sodium metal and dry ether to give toluene. This reaction is known as Wurtz-Fittig reaction.



(c) In the 1-bromo-1-methylcyclohexane, all β-hydrogen atoms are equivalent. Thus dehydrohalogenation takes place, in the reaction of this compound with KOH.



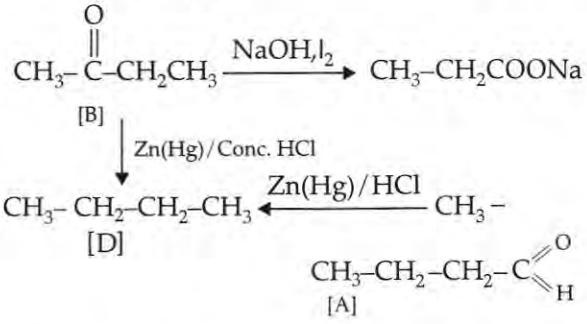
18. (A), (B) and (C) are three non-cyclic functional isomers of a carbonyl compound with molecular formula C_4H_8O. Isomers (A) and (C) give positive Tollen's test whereas isomer (B) does not give Tollen's test but gives positive Iodoform test. Isomers (A) and (B) on reduction with Zn (Hg)/conc. HCl give the same product (D).

(a) Write the structures of (A), (B), (C) and (D).

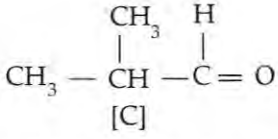
(b) Out of (A), (B) and (C) isomers, which one is least reactive towards addition of HCN ? [3]

Answer :

(a) Compound A and C give positive Tollen's test which indicates that they are aldehydes. Compound C gives Iodoform test which means it contains a carbonyl group with a methyl group attached to the carbonyl carbon so, with formula C_4H_8O the structure of compound would be $CH_3COCH_2CH_3$ (Butanone). Now upon reduction with Zn(Hg)/conc. HCl, the corresponding alkanes are obtained, so reduction of B gives Butane (D), so the isomer A have to be a linear chain aldehyde (Butanal), giving Butane (compound D) on reduction. So, the last isomer possible is compound C, 2-Methyl propanaldehyde. The reactions involved are shown below with the structures of compounds :

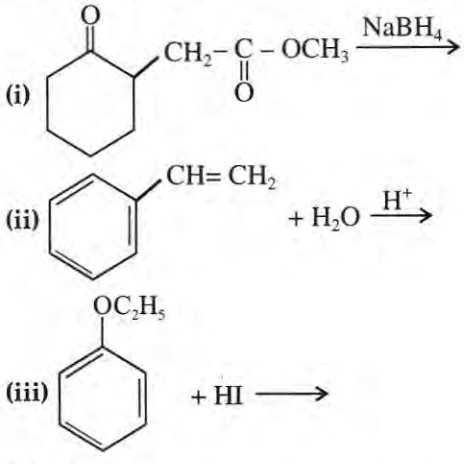


isomer of [A] is compound [C] whose structure is



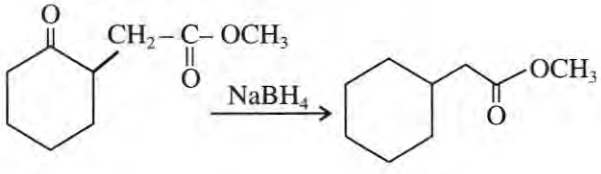
(b) Out of the three isomers A, B and C, compound B (Butanone) would be least reactive towards addition of HCl as the carbonyl carbon is sterically hindered and most reactive would be compound A (Butanal) towards addition of HCN.

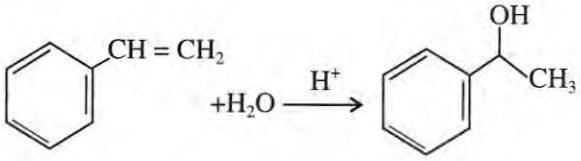
19. Write the structures of the main products in the following reactions : [3]

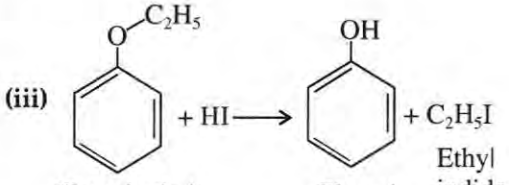


Answer :

(i) Sodium borohydride doesn't reduce esters, so product would be,



(ii) 

(iii) 

20. (a) Why is bithional added to soap ? [3]

(b) What is tincture of iodine ? Write its one use.

(c) Among the following, which one acts as a food preservative ?

Aspartame, Aspirin, Sodium Benzoate, Paracetamol

Answer :

(a) Bithional is added to soaps to impart antiseptic properties to soap.

(b) Tincture of iodine is 2-3 percent mixture of iodine in alcohol water mixture. It is used as an antiseptic.

(c) Sodium benzoate is used as a food preservative.

21. Define the following with an example of each : [3]

(a) Polysaccharides

(b) Denatured protein

(c) Essential amino acids

OR

(a) Write the product when D-glucose reacts with conc. HNO_3.

(b) Amino acids show amphoteric behaviour. Why ?

(c) Write one difference between α–helix and β-pleated structures of proteins.

Answer :

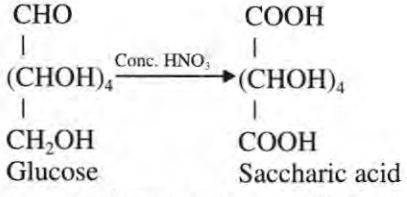
(a) Polysaccharides : Polysaccharides are food storage materials and most commonly found carbohydrates in nature. These are the compound which are formed of large number of monosaccharide units joined together by glycosidic linkages. Example. Starch, main storage polysaccharide of plants.

(b) Denatured protein : Proteins have an unique three dimensional structure in their native form. If the native form of protein is subjected to any physical change (such as temperature change) or any chemical change (such as change in pH), the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled due to which protein loses its biological activity. This is called denaturation of protein. During denaturation 2° and 3° structures of proteins are destroyed but 1° structure remains intact. Coagulation of egg white is an example of denaturation of protein.

(c) Essential amino acids : The amino acids which are not synthesized in our body and have to be obtained through diet are known as essential amino acids. Example : Tryptophan

OR

(a) D-Glucose gets oxidized to give saccharic acid, a dicarboxylic acid on reacting with nitric acid.



(b) Amino acids show amphoteric behaviour due to the presence of both acidic (carboxylic group) and basic (amino group) in the same molecule. So, in basic medium the carboxyl group can lose a proton and in acidic medium amino group can accept a proton.

(c) In α -helix structure the polypeptide chain forms all possible hydrogen bonds by twisting into a right handed screw (helix) with the —NH group of each amino acid residue gets hydrogen bonded to the —C = O of an adjacent turn of the helix (intra.molecular bonding), whereas in

β -structure all peptide chains are stretched out to nearly maximum extension and then laid side by side which are held together by intermolecular hydrogen bonds (intermolecular bonding).

22. (a) Write the formula of the following coordination compound :
Iron (III) hexacyanoferrate (II)

(b) What type of isomerism is exhibited by the complex $[Co(NH_3)_5 Cl]SO_4$?

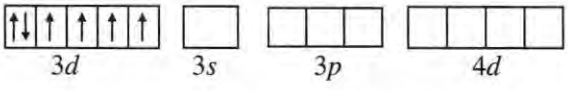
(c) Write the hybridisation and number of unpaired electrons in the complex $[CoF_6]^{3-}$. (Atomic number of Co =27) [3]

Answer :

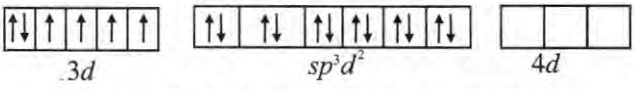
(a) Molecular formula of Iron(III) α – cyanoferrate(II) is $Fe_4[Fe(CN)_6]_3$

(b) $[Co(NH_3)_5Cl]SO_4$ will show Ionisation isomerism and the possible isomers are $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$

(c) Electronic configuration of Co^{3+} ion is,



Electronic configuration of sp^3d^2 hybridized (as F^- is a weak field ligand) orbitals of Co^{3+}, with six pairs of electrons from six F^- ions.



There are 4 unpaired electrons in $[CoF_6]^3$.

23. Shyam went to a grocery shop to purchase some food items. The shopkeeper packed all the items in polythene bags and gave them to Shyam. But Shyam refused to accept the polythene bags and asked the shopkeeper to pack the items in paper bags. He informed the shopkeeper about the heavy penalty imposed by the government for using polythene bags. The shopkeeper promised that he would use paper bags in future in place of polythene bags. [4]

Answer the following :

(a) Write the values (at least two) shown by Shyam.**

(b) Write one structural difference between low-density polythene and high-density polythene.

(c) Why did Shyam refuse to accept the items in polythene bags ?

(d) What is a biodegradable polymer ? Give an example.

Answer :

(b) Low density polythene has branched chain structure, whereas the high density polythene has linear chain structure.

(c) Shyam refused to take the items in polythene bags as polythene is non-biodegradable neither recyclable,

(d) Biodegradable polymers contain functional groups similar to functional groups present in biopolymers, so they get degraded in environment by certain microorganisms and thus are environment friendly. For example : Poly β -hydroxybutyrate-co- β - hydroxyvalerate (PHBV).

24. (a) Give reasons : [5]

(i) H_3PO_3 undergoes disproportionation reaction but H_3PO_4 does not.

(ii) When Cl_2 reacts with excess of F_2, ClF_3 is formed and not FCl_3.

(iii) Dioxygen is a gas while Sulphur is a solid at room temperature.

(b) Draw the structures of the following :

(i) XeF_4

(ii) $HClO_3$

OR

(a) When concentrated sulphuric acid was added to an unknown salt present in a test tube a brown gas (A) was evolved. This gas intensified when copper turnings were added to this test tube. On cooling, the gas (A) changed into a colourless solid (B).

(i) Identify (A) and (B).

(ii) Write the structures of (A) and (B).

(iii) Why does gas (A) change to solid on cooling ?

(b) Arrange the following in the decreasing order of their reducing character :
HF, HCl, HBr, HI

(c) Complete the following reaction :
$XeF_4 + SbF_5 \rightarrow$

Answer :

(a) (i) In H_3PO_3 (orthophosphorus acid) oxidation state of phosphorus is +3 and it contains one P-H bond in addition to P=O and P–OH bonds. These type of oxoacids tend to undergo disproportionation to give orthophosphoric acid (P has +5 state) and phosphine (P has +3 state). Whereas in H_3PO_4 (orthophosphoric

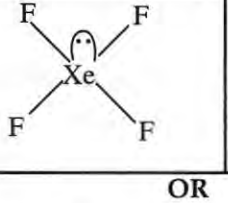
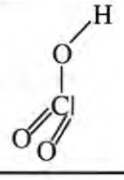
****Answer is not given due to the change in present syllabus.**

acid), Phosphorus is in +5 state hence no disproportionation takes place in H_3PO_4.

(ii) When Cl_2 reacts with excess of F_2, ClF_3 is formed-and not FCl_3 because Fluorine can't expand its valency and can show only –1 oxidation state, whereas Cl can expand its valency due to the availability of *d*-orbitals.

(iii) Dioxygen is a gas while sulphur is a solid at room temperature this is because sulphur have S_8 molecules and these are packed to give different crystal structure, whereas dioxygen is a diatomic molecule (O_2) and it does not have enough intermolecular attraction and thus exists in gaseous form.

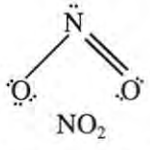
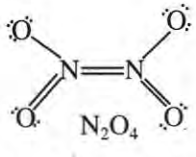
(b)

(i) XeF_4 is square planar in structure	(ii) $HClO_3$ or chloric acid
	

OR

(a) (i) The brown gas A is NO_2 or nitrogen dioxide. On cooling it dimerises to N_2O_4 and solidifies as a colourless solid.

$$2NO_2 \underset{\text{Heat}}{\overset{\text{Cool}}{\rightleftharpoons}} N_2O_4$$

(ii)  

NO_2 N_2O_4

(iii) Compoud A, that is, NO_2 contains odd number of valence electrons. It behaves as a typical odd molecule. On dimerization, it is converted to stable N_2O_4 molecule with even number of electrons (thus colourless) and have better intermolecular forces to get solidified. Thus, it changes to solid on cooling.

(b) Decreasing order of reducing character-

$$HI > HBr > HCl > HF$$

(c) $XeF_4 + SbF_5 \rightarrow [XeF_3]^+ + [SbF_6]^-$

25. (a) Write the cell reaction and calculate the e.m.f. of the following cell at 298 K : [5]

Sn(s) | Sn^{2+} (0.004 M) || H^+ (0.020 M) | H_2(g) (1 bar) | Pt (s)

(Given : $E^\circ_{Sn^{2+}/Sn} = -0.14V$)

(b) Give reasons :

(i) On the basis of E° values, O_2 gas should be liberated at anode but it is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl.

(ii) Conductivity of CH_3COOH decreases on dilution.

OR

(a) For the reaction

2 AgCl(s) + H_2(g) (1 atm) → 2Ag(s) + 2H^+ (0.1M) + 2Cl^- (0.1M),

$\Delta G^\circ = -43600$ J at 25°C.

Calculate the e.m.f. of the cell.

[log $10^{-n} = -n$]

(b) Define fuel cell and write its two advantages.

Answer :

(a) The half cell reactions can be written as;

$$Sn^{2+} + 2e^- \rightarrow Sn$$

$$E_{cell} = -0.14 + \frac{0.0591}{2} (\log [Sn^{2+}])$$

$$= -0.11 \times (\log 0.004)\ V$$

$$= 0.26\ V \quad \text{.....(i)}$$

$$2H^+ + 2e^- \rightarrow H_2$$

$$E_{cell} = 0.0 + 0.0591\ (\log [H^+])$$

$$= 0.0591 \times (-1.7)$$

$$= -0.10V \quad \text{.....(ii)}$$

Considering,

$2H^+(aq) + Sn(s) \rightarrow Sn^{2+}(aq) + H_2(g)$, as the cell reaction

So, E_{cell} will be,

$$E_{cell} = 0.26\ V - (-0.10)\ V$$

$$= 0.36\ V$$

(b) (i) During the electrolysis of aqueous NaCl, there are two possible reactions at anode,

$$Cl^-(aq) \rightarrow \tfrac{1}{2} Cl_2(g) + e^-;\ E_{cell} = 1.36\ V$$

$$2\ H_2O(I) \rightarrow O_2\ (g) + 4H^+\ (aq) + 4e^-;\ E_{cell} = 1.23\ V$$

The reaction at anode with lower value of E_{cell} is preferred and therefore, water

should get oxidized to give O_2 but on account of over potential of oxygen, Cl^- gets oxidized preferably, liberating Cl_2 gas.

(ii) Conductivity of CH_3COOH decreases on dilution because the number of ions per unit volume that carry the current in a solution decreases on dilution.

OR

(a) E°_{cell} can be obtained from the formula, $\Delta G^\circ = -nE^\circ_{cell}$

$$E^\circ_{cell} = \frac{\Delta G^\circ}{nF}$$

$$= \frac{-43600\ J}{1 \times 96487\ C\ mol^{-1}}$$

$$= -0.45\ V$$

Now, let us consider the given reaction equation,

$2AgCl(s) + H_2(g)\ (1\ atm) \rightarrow 2Ag(s) + 2H^+\ (0.1\ M) + 2\ Cl^-\ (0.1\ M)$

or $AgCl(s) + \frac{1}{2} H_2\ (g)\ (1\ atm) \rightarrow Ag\ (s) + H^+\ (0.1\ M) + Cl^-\ (0.1\ M)$

According to Nernst equation :

$$E_{cell} = E^\circ_{cell} - \frac{2.303\,RT}{nF} \log \frac{[product]}{[reactant]}$$

$$E_{cell} = E^\circ_{cell} - \frac{2.303\,RT}{nF} \log \frac{[H^+][Cl^-][Ag]}{[AgCl][H_2]^{1/2}}$$

As the activity of solid and H_2 gas at 1 atm is taken unity, the equation becomes,

$$E_{cell} = E^\circ_{cell} - \frac{2.303\,RT}{nF} \log ([H^+]\ [Cl^-]) \quad .....(i)$$

Now, putting the values in equation (i) above,

$$E_{cell} = -0.45 - (0.059) \log (0.1 \times 0.1)$$

$$= -0.51 \log (10^{-2})$$

$$= -0.51 \times (-2)$$

$$= 1.02\ V$$

So, EMF of the given cell is 1.02 V

(b) Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol etc. directly into electrical energy are called fuel cells.

Advantages of fuel cells are :

1. Fuel cells produce electricity with an efficiency of about 70% compared to thermal plants whose efficiency is about 40%.
2. Fuel cells are pollution free.

26. (a) Write the reactions involved in the following : [5]

(i) Hofmann bromamide degradation reaction

(ii) Diazotisation

(iii) Gabriel phthalimide synthesis

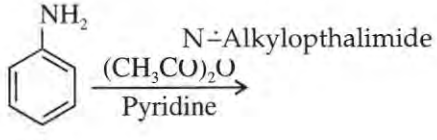
(b) Give reasons :

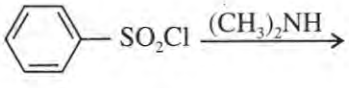
(i) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.

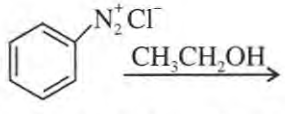
(ii) Aromatic diazonium salts are more stable than aliphatic diazonium salts.

OR

(a) Write the structures of the main products of the following reactions :.

(i) 

(ii) 

(iii) 

(b) Give a simple chemical test to distinguish between Aniline and N, N-dimethylaniline.

(c) Arrange the following in the increasing order of their pK_b values :

$C_6H_5NH_2$, $C_2H_5NH_2$, $C_6H_5NHCH_3$

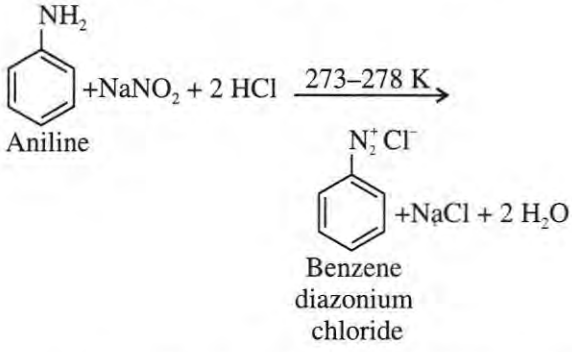
Answer :

(a) (i) Hofmann bromamide degradation reaction : Acetamide can be considered for example. In this reaction, Acetamide (CH_3CONH_2) undergoes Hofmann degradation in presence of Bromine and NaOH to give Methanamine.

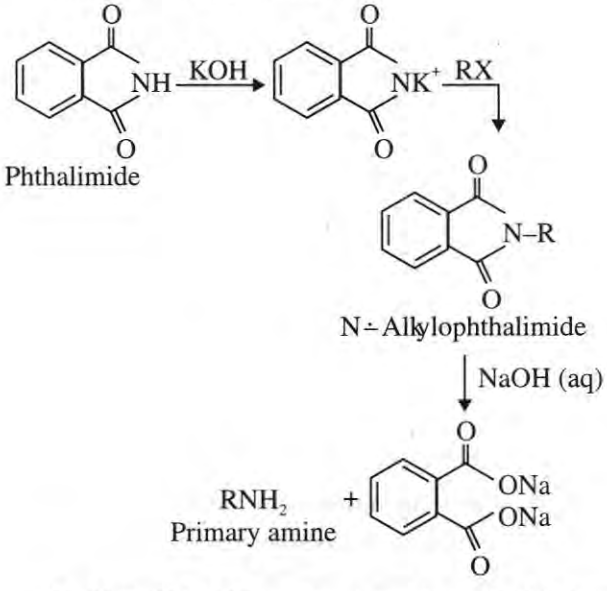
$CH_3CONH_2 + Br_2 + 4NaOH \rightarrow CH_3NH_2$

$Na_2CO_3 + 2NaBr + 2H_2O$

(ii)Diazotisation : The conversion of primary aromatic amines into diazonium salts is known as diasotisation.



(iii) Gabriel phthalimide synthesis : This reaction is used for the preparation of primary amines. Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.

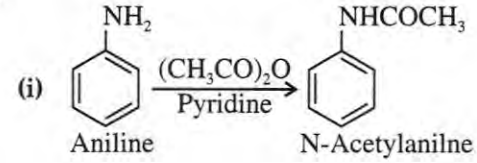


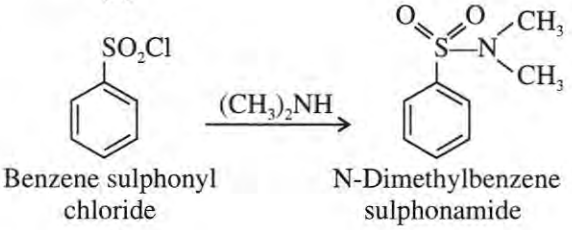
(b) (i) $(CH_3)_2$ NH is more basic than $(CH_3)_3N$ in aqueous solutions because, in $(CH_3)_3N$ the lone pair of electrons on nitrogen atom is responsible for its basicity are quite hindered by the three methyl groups, hence are less available. Due to which it is less basic as compared to $(CH_3)_2NH$.

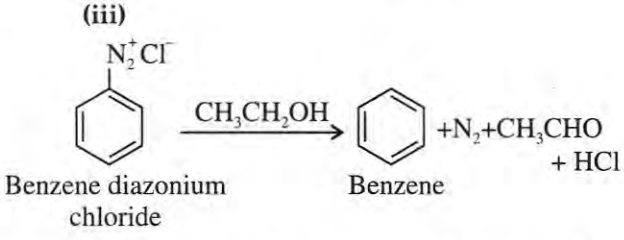
(ii) Aromatic diazonium salts are more stable than aliphatic diazonium salts because the positive charge on nitrogen atom is stabilized by the resonance with attached phenyl group.

OR

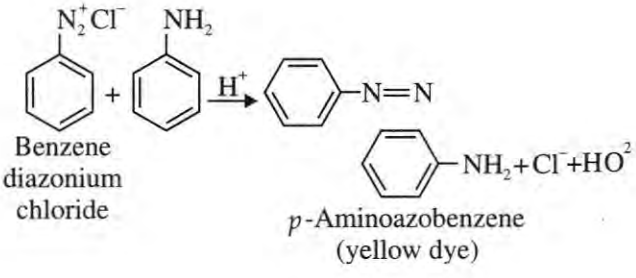
(a)

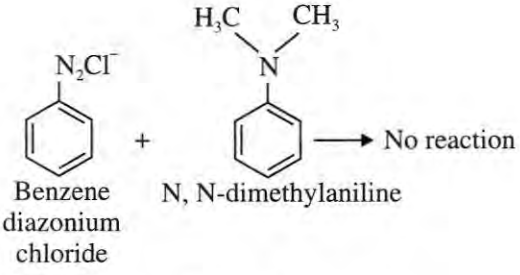






(b) Aniline can be distinguished from N, N-dimethyl aniline by diazo coupling reaction. Aniline would react with benzene diazonium chloride to give a yellow dye, whereas N, N-dimethyl aniline won't undergo this reaction.





(c) Increasing order of pK_b values is

$C_2H_5NH_2 < C_6H_5NH_2 < C_6H_5NH_2CH_3$