CBSE Delhi 2012

Chemistry (Theory)

Time: 3 Hrs | Max. Marks: 70

General Instructions

(a) *All questions are compulsory*.

(b) *Question numbers 1 to 8 are very short answer questions and carry 1 mark each.*

(c) *Question numbers 9 to 18 are short answer questions and carry 2 marks each.*

(d) *Question numbers 19 to 27 are also short answer questions and carry 3 marks each.*

(e) *Question numbers 28 to 30 are long answer questions and carry 5 marks each.*

(d) *Use log tables if necessary. Use of calculators is not allowed.*

1. What is meant by doping in a semiconductor?

Solution

To increase the conductivity of intrinsic semiconductors, an appropriate amount of impurity is added to them. This process is called doping.

2. What is the role of graphite in the electrometallurgy of aluminium?

Solution

In the electrometallurgy of aluminium, graphite anode is used for the reduction of the metal oxide to metal.

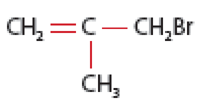
$$2Al_2O_3 + 3C \text{ (graphite)} \rightarrow 4Al + 3CO_2$$

3. Which one of PCl_4^- and PCl_4^+ is not likely to exist and why?

Solution

In PCl_4^+, the oxidation state of P is +3. Phosphorous is less stable in +3 oxidation state of PCl_4^- is not likely to exist.

4. Give the IUPAC name of the following compound.



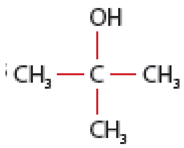
Solution

IUPAC name is 3-bromo-2-methylpropene.

5. Draw the structural formula of 2-methyl 2-propanol.

Solution

The structure is



6. Arrange the following compounds in increasing order of their reactivity towards nucleophilic addition reaction: ethanol, propanal, propanone, butanone.

Solution

The order is ethanol > propanal > propanone > butanone.

7. Arrange the following in decreasing order of their basic strength in aqueous solution:

CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ and NH_3

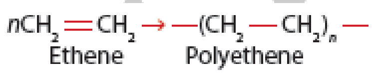
Solution

The order is $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

8. Define the term "homopolymerization" giving an example.

Solution

The addition polymerization reaction that involves polymerization of a single monomeric unit is called homopolymerization. For example, polymerization of ethene to give polyethene.



9. A 1.0 molal aqueous solution of trichloroacetic acid (CCl_3COOH) is heated to its boiling point. The solution has a boiling point of 100.18°C. Determine the value of van't Hoff factor for trichloroacetic acid. (Given that K_b for water is 0.512 kg mol^{-1}.)

Solution

Given that molality of solution (m) = 1.0 molal

Boiling point of solution (T_b) = 100.18°C = 100.18 + 273 = 373.18 K

Boiling point of pure solvent (water) (T_b^o) = 100°C = 100 + 273 = 373 K

Using the formula of elevation in boiling point, we have

$$\Delta T_b = T_b - T_b^o = 373.18 - 373 = 0.18 \text{ K (observed)}$$

Given that K_b (given) = 0.512 kg mol^{-1}. So,

$\Delta T_b = K_b \cdot m = 0.512 \times 1 = 0.512$ K (calculated)

van't Hoff factor

$$i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}} = \frac{0.18}{0.512} = 0.35$$

OR

Define the following terms: (a) mole fraction, (b) isotonic solutions, (c) van't Hoff factor and (d) ideal solution.

Solution

(a) Mole fraction: It is defined as the ratio of number of moles of a component to the total number of moles of all components present in the mixture.

Mole fraction of component A, $x_A = \dfrac{n_A}{n_A + n_B}$

(b) Isotonic solutions: These are the solutions having same osmotic pressure at a given temperature, that is, $\pi_1 = \pi_2$.

(c) van't Hoff factor: It is defined to account for the extent of association or dissociation in a molecule. The van't Hoff factor can be calculated in the following ways:

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}};\; i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}};\; i = \frac{\text{Total number of moles of particles after association / dissociation}}{\text{Number of particles before association / dissociation}}$$

(d) Ideal solutions: The solutions which obey Raoult's law over the entire range of concentration are called ideal solutions. The change in volume as well as enthalpy after mixing is zero, that is, $\Delta H_{mix} = 0$ and $\Delta V_{mix} = 0$.

10. What do you understand by the order of a reaction? Identify the reaction order from each of the following units of reaction rate constant: (a) L^{-1} mol s^{-1} and (b) L mol^{-1} s^{-1}.

Solution

The sum of the powers of the concentration terms of the reactants in the final rate law expression is called the order of the reaction.

$$A + B \rightarrow C$$

The rate = $k[A]^x[B]^y$ and the overall order is $x + y$.

(a) The units of rate are L^{-1} mol s^{-1}. For k to have the same units as rate, the reaction must be of zero order.

(b) If the units of k are L mol^{-1} s^{-1}, then from the rate expression, we have

$$L^{-1}\ \text{mo1}\ s^{-1} = L\ mol^{-1}s^{-1} \times (mol\ L^{-1})^{x+y}$$

$$(mol\ L^{-1})^{x+y} = \frac{L^{-1}mol\ s^{-1}}{L\ mol\ s^{-1}} = L^{-2}mol^{2} \Rightarrow x + y = 2$$

So, the reaction is of second order.

11. Name the two groups in which the phenomenon of catalysis can be divided. Give an example of each group with the chemical equation involved.

Solution

The phenomenon of catalysis can be divided into two groups:

Homogeneous catalysis: In this type of catalysis, the reactants, products and the catalyst all are present in the same phase. For example,

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

Heterogeneous catalysis: In this type of catalysis, the phase of reactants, products and the catalyst will be different. For example,

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

12. What is meant by coagulation of a colloidal solution? Describe briefly any three methods by which coagulation of lyophobic sols can be carried out?

Solution

The phenomenon of the precipitation of a colloidal solution by the addition of excess of an electrolyte is called coagulation or flocculation.

The coagulation of the lyophobic sols can be carried out by following methods:

(a) By electrophoresis: In electrophoresis, the colloidal particles move towards oppositely charged electrodes. When these come in contact with the electrode for long, these are discharged and precipitated.

(b) By mixing two oppositely charged sols: When oppositely charged sols are mixed in almost equal proportions, their charges are neutralized. Both sols may be partially or completely precipitated as the mixing of ferric hydroxide (positive sol) and arsenious sulphide (negative sol) bring them in precipitated form. This type of coagulation is called mutual coagulation.

(c) By boiling: When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of dispersion medium. This reduces the charge on the particles and ultimately they settle down to form a precipitate.

(d) By persistent dialysis: On prolonged dialysis, the traces of the electrolyte present in the sol are removed almost completely and the colloids become unstable.

(e) By addition of electrolytes: The particles of the dispersed phase, that is, colloids bear some charge. When an electrolyte is added to sol, the colloidal particles take up ions carrying opposite charge from the electrolyte. As a result, their charge gets neutralized and this causes the uncharged particles to come closer and get coagulated or precipitated. For example, if $BaCl_2$ solution is added to As_2S_3 sol the Ba^{2+} ions are attracted by the negatively charged sol particles and their charge gets neutralized. This leads to coagulation.

13. Describe the principle involved in each of the following processes:

(a) Mond process for refining of nickel.

(b) Column chromatography for purification of rare elements.

Solution

(a) Mond's process is used in the refining of nickel. Impure Ni is heated with CO to form a volatile complex, that is, nickel teracarbonyl complex, which then undergoes thermal decomposition to give pure nickel metal.

$$Ni + 4CO \rightarrow Ni(CO)_4$$

$$Ni(CO)_4 \xrightarrow{\text{Heat}} \underset{\text{Pure}}{Ni} + 4CO$$

(b) Column chromatography is based on the principle that different components present in a mixture are adsorbed differently on an adsorbent. The metal to be purified is dissolved in minimum amount of solvent and loaded on a column. When the solvent is passed through the column at atmospheric pressure, it elutes metal and different impurities present based on adsorption or partition. The polarity of the sample is increased stepwise and the eluant is collected in small fractions, each of which is concentrated and checked by TLC for purity. It is very useful in the purification of the elements which are available in minute quantities and the impurities do not differ in chemical properties from those of the element to be purified.

In case of Al_2O_3, the column of Al_2O_3 is the stationary phase and the mobile phase can be a solid, liquid or gas in which the sample is dissolved. The mobile phase is then forced to move through the stationary phase. The component which is more strongly adsorbed will take more time to travel than the component that is weakly adsorbed.

14. Explain the following giving an appropriate reason in each case:

(a) O_2 and F_2 both stabilize higher oxidation states of metals, but O_2 exceeds F_2 in doing so.

(b) Structures of xenon fluorides cannot be explained by valence bond approach.

Solution

(a) This is because O_2 has −2 charge and can form multiple bonds with metals due to larger intermolecular force, whereas F_2 has −1 charge and cannot form multiple bonds.

(b) As xenon has fully filled orbitals, and the formation of covalent bonds takes place by the overlapping of half-filled orbitals, that is why, valence bond approach cannot deduce structure of xenon fluorides, whereas VSEPR can.

15. Complete the following chemical equations:

(a) $Cr_2O_7^{2-} + H^+ + I^- \rightarrow$

(b) $MnO_4^- + NO_2^- + H^+ \rightarrow$

Solution

(a) $Cr_2O_7^{2-} + H^+ + I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

(b) $MnO_4^- + NO_2^- + H^+ \rightarrow Mn^{2+} + 5NO_3^- + 3H_2O$

16. What is meant by (a) peptide linkage and (b) biocatalysts?

Solution

(a) Peptide linkage: It is the amide linkage formed between – COOH group of one amino acid –NH_2 group of the other. For example,

$$NH_2 - CH_2 - COOH + H_2N - CH(CH_3) - COOH \xrightarrow{H_2O}$$

$$NH_2 - CH_2 - CO - NH - CH(CH_3) - COOH$$

(b) Biocatalysts: These are substances also known as enzymes which catalyze the rate of a chemical reaction inside living systems. For example, the enzyme maltase catalyzes the hydrolysis of maltose into glucose.

17. Write any two reactions of glucose which cannot be explained by the open chain structure of glucose molecule.

Solution

The following observations cannot be accounted for by the open chain structure of glucose:

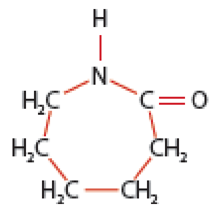
(a) Despite having aldehyde group, it does not give precipitate with 2,4-DNP solution nor does it give Schiff's reagent test.

(b) The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free –CHO group.

18. Draw the structure of the monomer for each of the following polymers: (a) Nylon-6 and (b) polypropene.

Solution

(a) The monomer of nylon-6 is caprolactum.



Caprolactum

(b) The monomer of polypropene is propene, $CH_3-CH=CH_2$.

19. Tungsten crystallizes in body centred cubic unit cell. If the edge of the unit cell is 316.5 pm, what is the radius of tungsten atom?

Solution

Given that edge length (a) = 316.5 pm. Since it has bcc structure, the relationship between *r* and *a* is $r=\frac{\sqrt{3}a}{4}$.

Substituting values, we get

$$r=\frac{\sqrt{3}(316.5)}{4}=137.04\text{ pm}$$

OR

Iron has a body centred cubic unit cell with a cell dimension of 286.65 pm. The density of iron is 7.874 g cm^{-3}. Use this information to calculate Avogadro's number (atomic mass of Fe = 55.845 u).

Solution

Given that edge length (a) = 286.65 pm = 286.65 × 10^{-10} cm; density ρ = 7.874 g cm^{-3}; Z = 2 (for bcc); M (atomic mass) for Fe = 55.845 u. Using the formula of density, we get

$$\rho=\frac{Z\times M}{a^3\times N_A}\Rightarrow 7.874=\frac{2\times 55.845}{(286.65\times 10^{-10})N_A}$$

or $$N_A=\frac{2\times 55.845}{(286.65\times 10^{-10})^3\times 7.874}=\frac{111.69}{1.85\times 10^{-22}}=6.03\times 10^{23}$$

20. Calculate the amount of KCl with must be added to 1 kg of water so that the freezing point is depressed by 2 K. (K_f for water = 1.86 k kg mol^{-1}).

Solution

Let the subscripts 1 and 2 represent KCl and water, respectively. Given that W_2 = 1 kg = 1000 g, ΔT_f = 2K, K_f = 1.86 k kg mol^1, M_2 = molar mass of KCl = 39.09 + 35.5 = 74.54u.

Using the formula from depression in freezing point, we have

$$\Delta T_b=K_1\times\frac{W_2\times 1000\times M_1}{W_1\times M_2}\Rightarrow 2=1.86\times\frac{W_2\times 1000\times 18}{1000\times 74.54}$$

or $$W_2=\frac{2\times 1000\times 74.54}{1.86\times 1000\times 18}=4.45\text{ g}$$

21. For the reaction $2NO(g) + Cl_2(g) \rightarrow 2NOCl$, the following data was collected. All the measurements are taken at 263 K.

Experiment No.	Initial [NO] concentration (M)	Initial [Cl_2] concentration (M)	Initial Rate of Disappearance of Cl_2 (M min^{-1})
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	2.40
4	0.25	0.25	?

(a) Write the expression for rate law.

(b) Calculate the value of rate constant and specify its units.

(c) What is the initial rate of disappearance of Cl_2 in expt. 4?

Solution

(a) The expression for rate law is

$\text{Rate} = k[\text{NO}]^x[\text{Cl}_2]^y$ (1)

where $x + y$ is the overall order of the reaction. Putting all the values from experiment 1 in Eq. (1), we get

$0.60 = k(0.15)^x (0.15)^y$ (2)

Putting the values from experiment 2 in Eq. (1), we get

$1.20 = k(0.15)^x(0.30)^y$ (3)

Diving Eq.(2) by Eq.(3), we get $0.5 = (0.5)^y \Rightarrow y = 1$.

Now, put all the values from experiment 3 in Eq.(1), we get

$2.40 = k(0.30)^x (0.15)^y$ (4)

Now, dividing Eq. (2) by Eq. (4), we get $0.25 = (0.5)^x \Rightarrow x = 2$. Thus, the order of the reaction with respect to NO is 2, whereas that with respect to Cl_2 it is 1. So, the rate law becomes Rate = $k[\text{NO}]^2[\text{Cl}_2]^1$.

(b) To calculate the value of k: Using Eq. (2) and putting values $x = 2$ and $y = 1$, we get

$0.60 = k(0.15)^2(0.15)^1$

or $k = \dfrac{0.60}{0.15 \times 0.15 \times 0.15} = 177.77 \text{ mol}^{-1}\text{L}^2 \text{ min}^{-1}$

(c) To calculate the rate of disappearance of Cl_2 in experiment 4: The rate expression is

$\text{Rate} = k[\text{NO}]^2[\text{Cl}_2]^1$

Substituting all the values, we get

$\text{Rate} = 177.77\ (0.25)^2(0.25)^1 = 2.78 \text{ M min}^{-1}$

22. How would you account for the following?

(a) Many of the transition elements are known to form interstitial compounds.

(b) The metallic radii of the third (5*d*) series of transition metals are virtually the same as those of the corresponding group member of the second (4*d*) series.

(c) Lanthanoids primarily form +3 ions, whereas the actinoids usually have higher oxidation states in their compounds, +4 or even +6 being typical.

Solution

(a) Interstitial compounds are formed when small atoms like H, C or N are trapped inside the crystal lattice of the metals. For example, TiC, Fe_3H, etc. As the size of the transition metals is large, they can trap small atoms easily and thus form interstitial compounds.

(b) The metallic radii of the third (5*d*) series of transition metals are virtually the same as those of the corresponding group member of the second (4*d*) series. This is because of lanthanoid contraction. The filling of 4*f* orbitals before 5*d* orbitals results in gradual decrease in atomic radii which compensates the increase in size with increase in atomic number.

(c) The actinoids can form greater range of oxidation states because the 5*f*, 6*d*, 7*s* orbitals are of comparable energies, whereas in the case of lanthanoids these levels are not of comparable energies.

23. Give the formula of each of the following coordination entities:

(a) Co^{3+} ion is bound to one Cl^{-}, one NH_3 molecule and two bidentate ethylenediamine molecules (en).

(b) Ni^{2+} is bound to two water molecules and two oxalate ions.

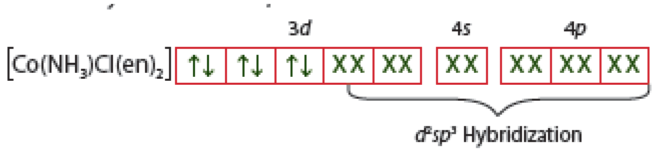
(c) Write the name and magnetic behavior of each of the above coordination entities (atomic number of Co = 27 u, Ni = 28 u.)

Solution

(a) $[Co(NH_3)Cl(en)_2]^{2+}$

IUPAC: Amminechloridobis(ethane-1, 2-diamine) cobalt(III) ion.

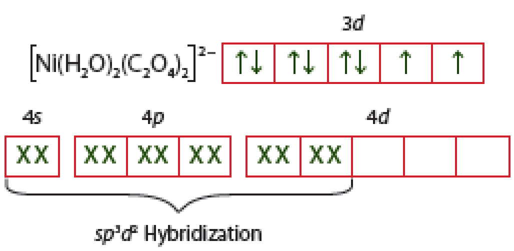
Electronic configuration is Co(27) = $3d^7\ 4s^2$ and Co(III) = $3d^6$. As NH_3 and en are strong field ligands, pairing takes place, so the complex is diamagnetic with hybridization d^2sp^3.



(b) $[Ni(H_2O)_2\ (C_2O_4)_2]^{2-}$

IUPAC: Diaquadioxalatonickelate(II)

Electronic configuration is Ni(28) = $3d^8\ 4s^2$ and Ni(II) = $3d^8$. As H_2O and $C_2O_4^{2-}$ are weak field ligands, no pairing takes place, so the complex is paramagnetic with hybridization sp^3d^2.

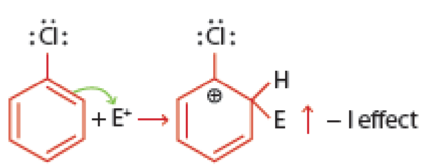


As the number of unpaired electrons = 2, the complex is paramagnetic.

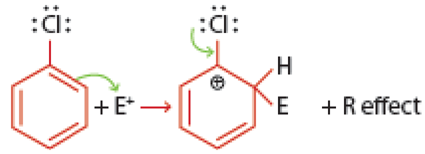
24. Although chlorine is an electron withdrawing group, yet it is *ortho-para* directing in electrophilic aromatic substitution reactions. Why is it so?

Solution

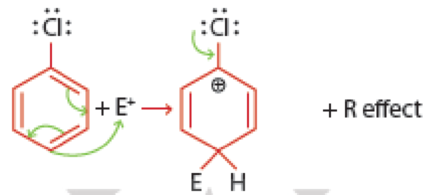
The mechanism of electrophilic aromatic substitution reactions is as follows:



Attack of electrophile at ortho position



Attack of electrophile at para position



Chlorine has –I effect, due to which it withdraws electrons and it has +R effect as well due to which it releases electrons in the ring through resonance. As the inductive effect is stronger than the resonance effect, there is net deactivation. So, we can say that reactivity is controlled by strong inductive effect and the orientation is controlled by resonance effect.

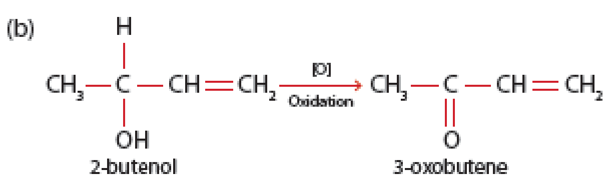
25. Draw the structure and name the product formed if the following alcohols are oxidized. Assume that an excess of oxidizing agent is used.

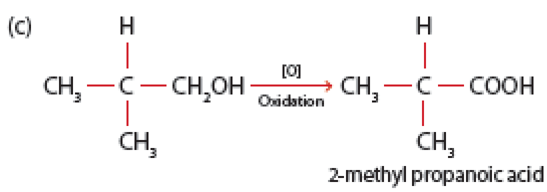
(a) $CH_3CH_2CH_2CH_2OH$

(b) 2-butenol

(c) 2-methyl-1-propanol

Solution





26. Write chemical equation for the following conversions:

(a) Nitrobenzene to benzoic acid

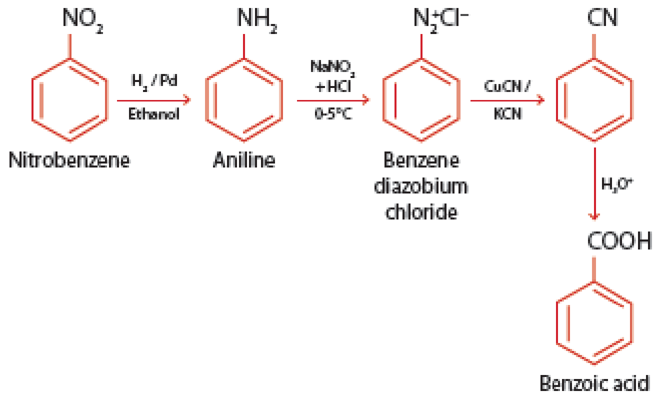
(b) Benzyl chloride to 2-phenylethanamine

(c) Aniline to benzylalcohol

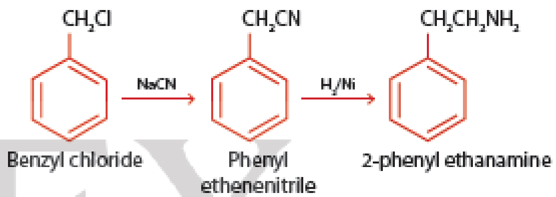
Solution

The reactions are as follows:

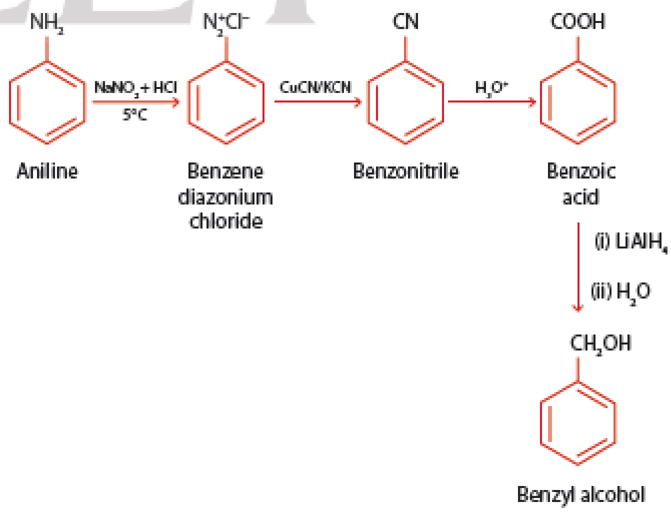
(a)



(b)



(c)



27. What are the following substances? Give one example of each of them:

(a) Tranquilizers

(b) Food preservatives

(c) Synthetic detergents

Solution

(a) These are the drugs given to the patients suffering from anxiety and mental tension. For example, noradrenaline is an antidepressant drug.

(b) These are the chemical substances added to the food to prevent the spoilage of food due to microbial growth. For example, salt, sugar, sodium benzoate, etc.

(c) These are the cleansing agents having the properties of soap but do not contain soap. They can work in soft as well as hard water. For example, sodium dodecylbenzenesulphonate.

28. (a) What type of a battery is lead storage battery? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery when current is drawn from it?

(b) In a button cell, widely used in watches, the following reaction takes place:

$Zn(s) + Ag_2O(s) + H_2O(l) \longrightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$

Determine $E°$ and $\Delta G°$ for the reaction. (Given: $E^o_{Ag^+/Ag} = +0.80V$; $E^o_{Zn^{2+}/Zn} = -0.76V$)

Solution

(a) Lead storage battery is a type of secondary battery. The cell reactions when the battery is in use are:

At the anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

At the cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

The overall reaction: $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

(b) Reaction at anode: $Zn \longrightarrow Zn^{2+} + 2e^-$

At the cathode: $Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^-$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0.80 - (-0.76) = 1.56V$$

Hence, $\Delta G = -nFE^o_{cell} = 2 \times 1.56 \times 96500$

$= -301080 \text{ J mol}^{-1}$

OR

(a) Define molar conductivity of a solution and explain how molar conductivity changes with change in concentration of solution for a weak and a strong electrolyte.

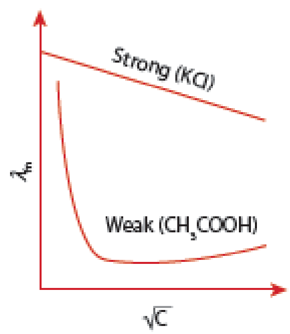
(b) The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}?

Solution

(a) Molar conductivity of a solution is the conductance of volume *V* of a solution containing 1 mol of electrolyte kept between two electrodes with the area of cross-section *A* and a distance of unit length.

Variation of molar conductivities with dilution: For strong electrolytes, molar conductivity increases slowly with dilution while for weak electrolytes, molar conductivity increases steeply on dilution.

This can be explained from the graph



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(b) Given that the conductivity (k) = 0.146×10^{-3} S cm^{-1}; resistance R = 1500 Ω. Therefore, the cell constant (l/A) = $k \times R = 0.146 \times 10^{-3} \times 1500 = 0.219$ cm^{-1}.

29. (a) Complete the following chemical reaction equations:

(i) $P_4 + SO_2Cl_2 \rightarrow$

(ii) $XeF_4 + H_2O \rightarrow$

(b) Predict the shape and the asked angle (90° or more or less) in each of the following cases:

(i) SO_3^{2-} and the angle O–S–O

(ii) ClF_3 and the angle F–Cl–F

(iii) XeF_2 and the angle F–Xe–F

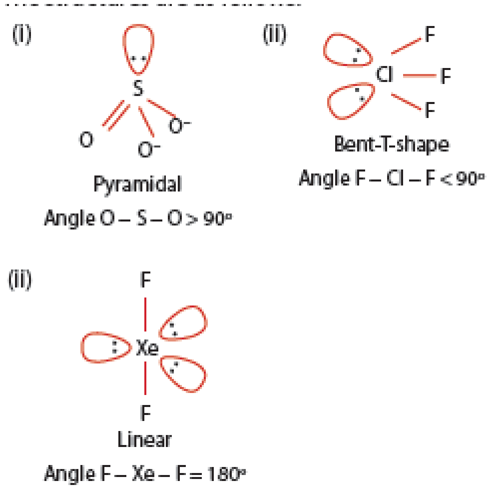
Solution

(a) (i) $P_4 + 2SO_2Cl_2 \rightarrow 4PCl_3 + 10SO_2$

(ii) $XeF_6 + 3H_2O \xrightarrow{\text{Complete hydrolysis}} XeO_3 + 6HF$

$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

(b) The structures are as follows:



OR

(a) Complete the following chemical equations:

(i) NaOH (hot and conc.) + $Cl_2 \rightarrow$

(ii) $XeF_2 + O_2F_2 \rightarrow$

(b) Draw the structures of the following molecules:

(i) H_3PO_2

(ii) $H_2SO_2O_7$ and

(iii) $XeOF_4$

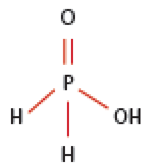
Solution

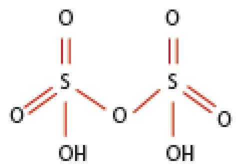
(a) The reactions involved are

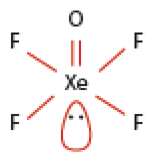
(i) $6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$

(ii) $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$

(b) The structures are as follows:

(i)  H_3PO_2 (Hypophosphorous acid)

(ii)  $H_2S_2O_7$ (Pyrosulphuric acid) (Oleum)

(iii)  $XeOF_4$ (Square pyramidal)

Aldehydes, Ketones and Carboxylic Acids

30. (a) Illustrate the named reaction giving example in each case: (i) Clemmensen reduction and (ii) Hell-Volhard-Zelinsky reaction.

(b) How are the following conversions carried out?

(i) Ethylcyanide to ethanoic acid

(ii) Butan-1-ol to butanoic acid

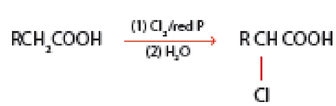
(iii) Benzoic acid to *m*-bromobenzoic acid

Solution

(a) (i) Clemmenson reduction: On treatment with zinc amalgam and conc. HCl, the carbonyl group of aldehydes and ketones is reduced to CH_2 group. This reaction is known as Clemmensen reduction. For example,

$$CH_3 - CH_2 - CHO + Zn - Hg / \text{conc.HCl} \rightarrow CH_3CH_3CH_3$$

(ii) Hell-Volhard-Zelinsky reaction: In this reaction, the carboxylic acid group having α-hydrogen are halogenated with halogens (Cl_2 or Br_2) in presence of red phosphorus. The halogenation takes place at α-hydrogen only. For example,



(b) The reactions are

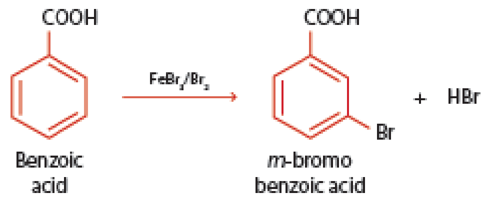
(i)

$$\underset{\text{Ethyl cyanide}}{C_2H_5CN} \xrightarrow{H_2O/H^+} \underset{\text{Propanoic acid}}{C_2H_5COOH} \xrightarrow[\Delta]{NH_3} \underset{\text{Propananide}}{C_2H_5CONH_2} \xrightarrow{Br_2/KOH}$$

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} \xrightarrow{HNO_2} \underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow{\text{alk.KMnO}_4} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

(ii) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{(ii) Dil } H_2SO_4]{\text{(i) } K_2Cr_2O_7/H_2SO_4} CH_3CH_2CH_2COOH$

(iii)



OR

(a) Illustrate the following reactions giving suitable example in each case: (i) Cross-aldol condensation and (ii) decarboxylation.

(b) Give simple tests to distinguish between the following pairs of compounds

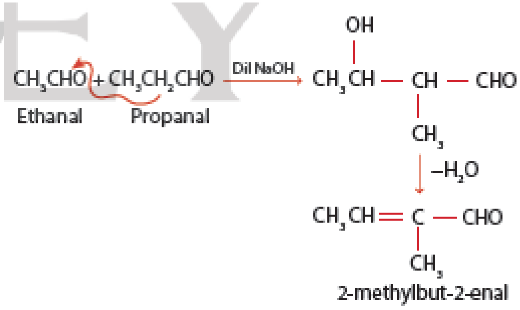
(i) Pentan-2-one and pentan-3-one

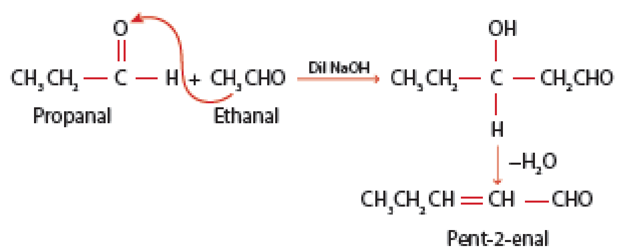
(ii) Benzaldeyde and acetophenone

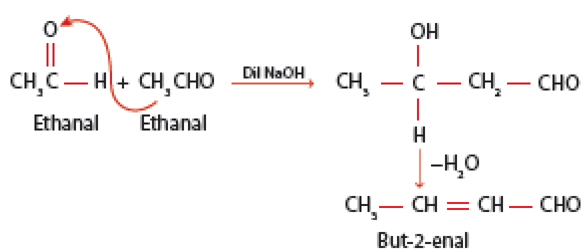
(iii) Phenol and benzoic acid

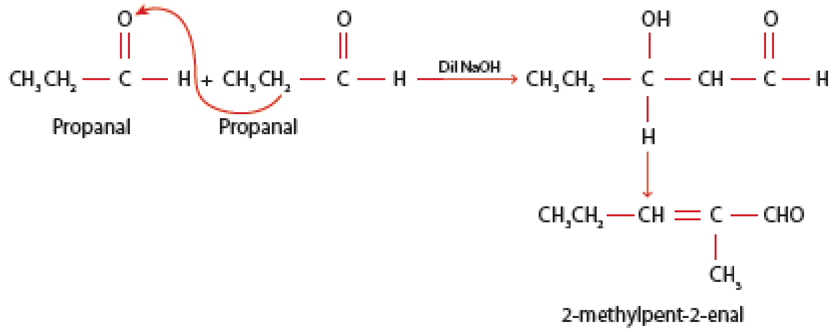
Solution

(a) (i) Cross-aldol condensation: When aldol condensation is carried out between two different aldehydes or ketones, it is called cross-aldol condensation. In case, both the aldehydes and ketones have α-hydrogens, we get a mixture of four products. For example,









(ii) Decarboxylation: In this reaction, carboxylic acids lose CO_2 to form hydrocarbons when they are heated with NaOH and CaO in the ratio 3:1 (also called soda-lime). This reaction is used for stepping down the series as in the product we get one carbon less than that of the reactant.

$$C_6H_5COONa \xrightarrow[\text{CaO, Heat}]{\text{NaOH}} C_6H_6 + Na_2CO_3$$

(b) (i) Pentan-2-one and pentan-3-one can be distinguished by iodoform test. Since pentan-2-one is a methyl ketone, it will give a positive iodoform test whereas pentan-3-one will not.

$$\underset{\text{pentan-2-one}}{CH_3CH_2CH_2COCH_3} + 3NaOI \rightarrow CH_3CH_2CH_2COONa + \underset{\text{(yellow ppt.)}}{CHI_3} + 2NaOH$$

(ii) Benzaldehyde and acetophenone can be distinguished by iodoform test. Acetophenone is a methyl ketone, therefore, it will give a positive iodoform test whereas benzaldehyde will not.

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 3NaOI \rightarrow C_6H_5COONa + \underset{\text{(Yellow ppt.)}}{CHI_3} + 2NaOH$$

(iii) Phenol gives violet coloration with neutral $FeCl_3$ solution, whereas benzoic acid gives a buff colored ppt.

$$\underset{\text{Phenol}}{3C_6H_5OH} + FeCl_3 \rightarrow \underset{\text{(Violet coloration)}}{(C_6H_5O)_3Fe} + 3HCl$$

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + FeCl_3 \rightarrow \underset{\text{(Buff colored)}}{(C_6H_5COOH)_3Fe} + 3HCl$$