

Chemistry 2015 (Outside Delhi)

SET I

Time allowed : 3 hours

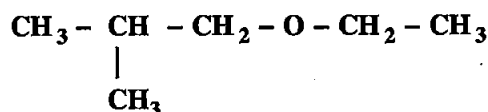
Maximum Marks : 70

1. Write the formulae of any two oxoacids of sulphur. [1]

Answer : Oxoacids of sulphur are chemical compounds that contain sulphur, oxygen and hydrogen. Two oxoacids of sulphur are :

1. Peroxodisulphuric acid : $\text{H}_2\text{S}_2\text{O}_8$
2. Dithionic acid : $\text{H}_2\text{S}_2\text{O}_6$.

2. Write the IUPAC name of the given compound : [1]

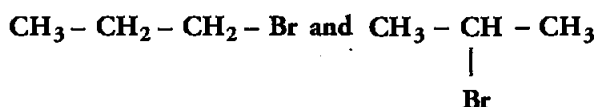


Answer : Ethoxy-2-methyl propane.

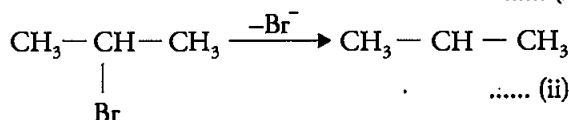
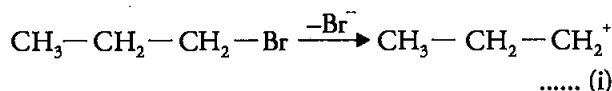
3. A delta is formed at the meeting point of sea water and river water. Why ? [1]

Answer : River water is the negatively charged colloidal solution whereas sea water contains a number of electrolytes the meeting point of sea water and river water, the electrolytes present in sea water coagulate the colloidal solution of clay resulting in its deposition with the formation of delta.

4. Which would undergo $\text{S}_{\text{N}}1$ reactions faster in the following pair : [1]

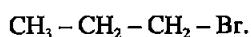


Answer :



During $\text{S}_{\text{N}}1$ reaction carbocation (i) and (ii) are formed. Out of (i) and (ii), (ii) is more stable due to +I effect of two methyl group.

Thus $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ | \\ \text{Br} \end{array}$ gives faster $\text{S}_{\text{N}}1$ reaction than



5. What is the formula of a compound in which the element Y forms ccp lattice and atoms of X occupy $2/3^{\text{rd}}$ of tetrahedral voids ? [1]

6. Write one similarity and one difference between the chemistry of lanthanoids and that of actinoids. [2]

Answer : Similarity

1. Both involve the filling of *f*-orbital (i.e. 4*f* and 5*f*)
2. Both show contraction i.e. Lanthanoid contraction and actinoid contraction.

Difference between lanthanoids and Actinoids :

	Lanthanoids	Actinoids
1.	Except Pm (promethium) all lanthanoids are non-radioactive.	Actinoids are radioactive.
2.	Lanthanoids do not show wide range of oxidation state.	Actinoids shows the wide range of oxidation state.
3.	Lanthanoids ions are generally coloured.	Actinoid ions are colourless

7. (i) Write down the IUPAC name of the following complex : $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$

(ii) Write the formula for the following complex: Potassium tetrachloridonickelate (II). [2]

Answer :

(i) $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$: Pentaamminechlorocobalt (III) ion

(ii) Potassium tetrachloridonickelate(II) : $\text{K}_2[\text{NiCl}_4]$

8. Write the reagents required in the following reactions :

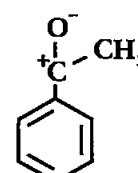
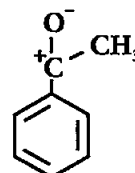


OR

Arrange the following compounds in increasing order of their property as indicated :

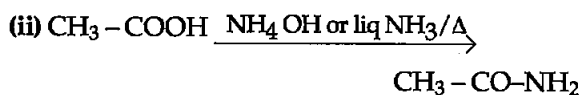
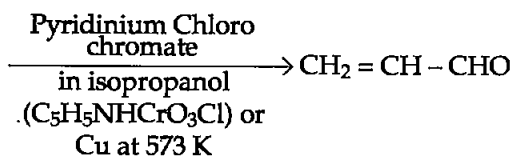
(i) CH_3COCH_3 , $\text{C}_6\text{H}_5\text{COCH}_3$, CH_3CHO (reactivity towards nucleophilic addition reaction)

(ii) $\text{Cl} - \text{CH}_2 - \text{COOH}$, $\text{F} - \text{CH}_2 - \text{COOH}$, $\text{CH}_3 - \text{COOH}$ (acidic character).

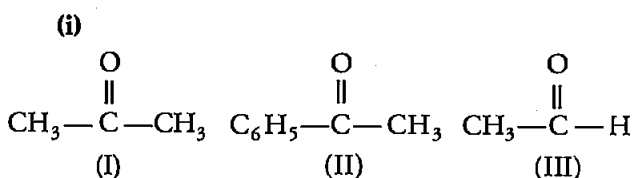


Answer : (i) $\text{CH}_2 = \text{CH} - \text{CH}_2\text{OH}$ [2]

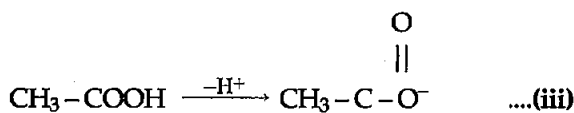
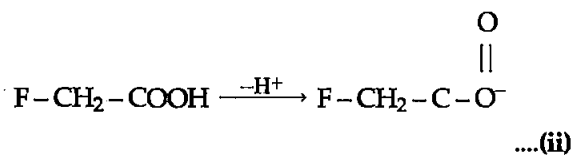
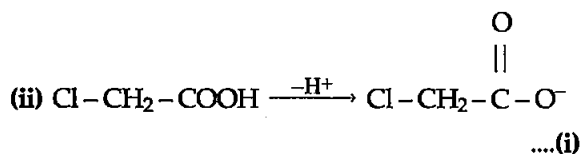
** Answer not given due to change in present syllabus



OR



Nucleophiles are negatively charged entity, positivity of carbon in carbonyl group facilitates nucleophilic addition. Thus positivity of carbon in carbonyl group is in order III > I > II. Due to +I effect of -CH₃ group and benzene ring π-cloud, positivity of carbonyl carbon is decreased so much than (I) and (II). Thus nucleophilic addition order III > I > II.



The stability order II > I > III. Due to +I effect of -CH₃ group electron density of oxygen is more. But in (I) and (II), -I effect of -F is more than -Cl. Thus II is more stabilized than I. Thus acidity order is II > I > III.

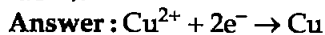
9. (i) On mixing liquid X and liquid Y, volume of the resulting solution decreases. What type of deviation from Raoult's law is shown by the resulting solution? What change in temperature would you observe after mixing liquids X and Y?
- (ii) What happens when we place the blood cell in water (hypotonic solution)? Give reason. [2]

Answer : (i) Negative deviation of Raoult's law occurred. There is a elevation of boiling point *i.e.*, temperature of the solution increases.

(ii) When blood cell is placed in water (hypotonic solution), water penetrate to blood cell and blood cell gets bulged and then disrupt.

10. Calculate the time to deposit 1.27 g of copper at cathode when a current of 2A was passed through the solution of CuSO₄.

(Molar mass of Cu = 63.5 g mol⁻¹, 1 F = 96500 C mol⁻¹). [2]



63.5 g of copper deposited by 2 × 96500 C

∴ 1.27 g of copper will be deposited by

$$\frac{2 \times 96500 \times 1.27}{63.5} \text{ C} = 3860 \text{ C}$$

We know $Q = It$

Here I = 2A and Q = 3860 C

$$t = \frac{Q}{I} = \frac{3860}{2} = 1930 \text{ s.}$$

11. A solution is prepared by dissolving 10 g of non-volatile solute in 200 g of water. It has a vapour pressure of 31.84 mm Hg at 308 K. Calculate the molar mass of the solute.

(Vapour pressure of pure water at 308 K = 32 mm Hg). [3]

Answer : According to Raoult's law,

$$\frac{P^\circ - P}{P^\circ} = \frac{w \times M}{m \times W}$$

Where

P^o → Vapour pressure of pure water

P → Vapour pressure of solution

w → Weight of solute

m → Molecular weight of solute

W → Weight of solvent

M → Molecular weight of solvent

$$\text{Thus, } \frac{32 - 31.84}{32} = \frac{10 \times 18}{m \times 200}$$

$$\text{or, } 0.005 m = 0.9 \text{ or, } m = 180$$

Thus molar mass of the solute 180 gm./mol

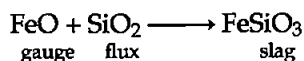
12. (i) Name the method of refining to obtain silicon of high purity.

(ii) What is the role of SiO₂ in the extraction of copper?

(iii) What is the role of depressants in froth floatation process? [3]

Answer : (i) Zone refining is the method of refining to obtain silicon of high purity.

(ii) SiO_2 combined with the iron in the copper ore to form iron(II) silicate slag which is easily removed. Thus it (SiO_2) acts as a flux to remove the impurity of Iron oxide.



(iii) In froth flotation process, depressant prevents the formation of froth. It is used to separate two sulphide ore by preventing the formation of froth of one sulphide ore and allowing the other to form the froth e.g., NaCN a depressant selectively prevents ZnS from coming in froth but allows PbS to come with the froth.

13. (i) Which one of the following is a polysaccharide :

Starch, maltose, fructose, glucose.

(ii) Write one difference between α -helix and β -pleated sheet structures of protein.

(iii) Write the name of the disease caused by the deficiency of vitamin B_{12} . [3]

Answer : (i) Starch is a polysaccharide.

(ii)

	α -helix	β -pleated
1.	It is rod like structure.	It is sheet like structure.
2.	It is stabilized by intramolecular hydrogen bonding.	It is stabilized by intermolecular hydrogen bonding.

(iii) Pernicious Anaemia caused by the deficiency of Vitamin B_{12} .

14. (i) What type of isomerism is shown by the complex $[\text{Cr}(\text{H}_2\text{O})_6] \text{Cl}_3$?

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

(iii) Write the hybridization and shape of $[\text{CoF}_6]^{3-}$.

(Atomic number of Co = 27). [3]

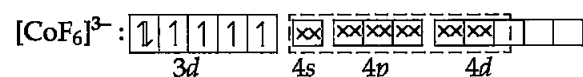
Answer : (i) Hydration isomerism is shown by the complex $[\text{Cr}(\text{H}_2\text{O})_6] \text{Cl}_3$.

$[\text{Cr}(\text{H}_2\text{O})_5 \text{Cl}] \text{Cl}_2 (\text{H}_2\text{O})$;

$[\text{Cr}(\text{H}_2\text{O})_3 \text{Cl}_3] 3(\text{H}_2\text{O})$.

(ii) Since $\Delta_o > P$ it is on splitting $t_{2g}^4 e_g^0$

(iii) $[\text{CoF}_6]^{3-}$: sp^3d^2 hybridisation and the shape is octahedral.



$[\text{CoF}_6]^{3-}$ has four unpaired electron. Thus it is paramagnetic.

15. How can the following conversion be carried out :

(i) Aniline to bromobenzene

(ii) Chlorobenzene to 2-chloroacetophenone

(iii) Chloroethane to butane. [3]

OR

What happens when

(i) Chlorobenzene is treated with $\text{Cl}_2/\text{FeCl}_3$

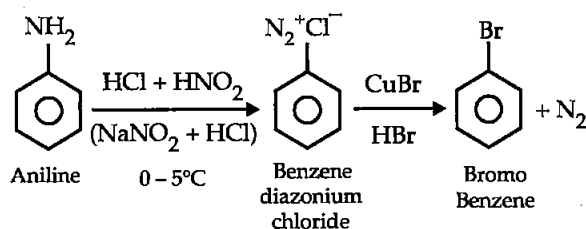
(ii) Ethyl chloride is treated with AgNO_2

(iii) 2-bromopentane is treated with alcoholic KOH ?

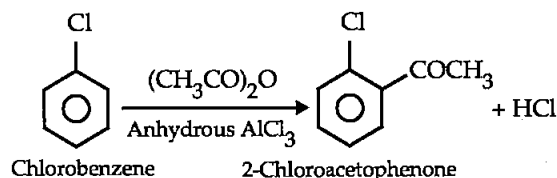
Write the chemical equations in support of your answer.

Answer :

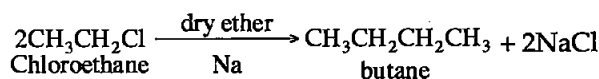
(i)



(ii)

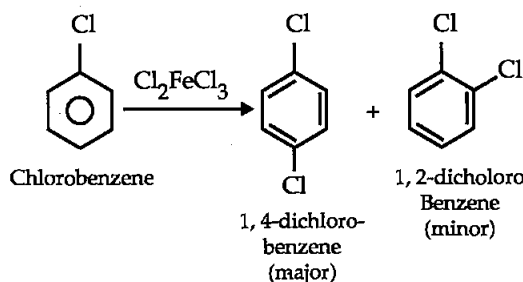


(iii)

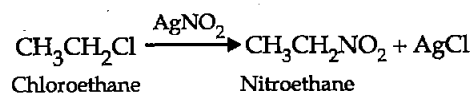


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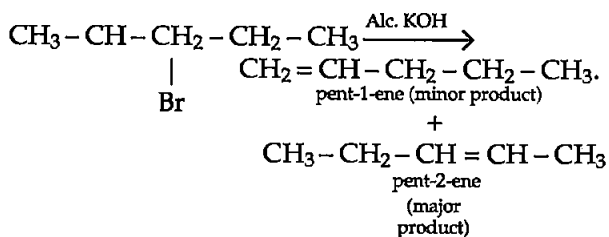
(i)



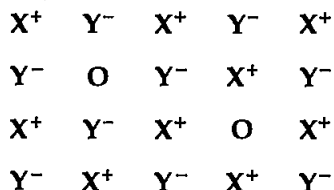
(ii)



(iii)



16. Examine the given defective crystal : **



Answer the following questions :

- Is the above defect stoichiometric or non-stoichiometric?
 - Write the term used for this type of defect. Give an example of the compound which shows this type of defect.
 - How does this defect affect the density of the crystal? [3]
17. Conductivity of 2.5×10^{-4} M methanoic acid is 5.25×10^{-5} S cm^{-1} .

Calculate its molar conductivity and degree of dissociation.

Given : $\lambda_{\text{H}^+} = 349.5 \text{ S cm}^2 \text{ mol}^{-1}$ and $\lambda_{\text{HCOO}^-}^0 = 50.5 \text{ S cm}^2 \text{ mol}^{-1}$. [3]

Answer : We know molar conductivity

$$\therefore \lambda_m = \frac{1000 \times \text{conductivity (k)}}{\text{concentration (c)}}$$

$$\therefore \lambda_m = \frac{1000 \times 5.25 \times 10^{-5}}{2.5 \times 10^{-4}} = 210 \text{ cm}^2 \text{ Mol}^{-1}$$

$$\lambda^0 \text{HCOOH} = \lambda_{\text{H}^+}^0 + \lambda_{\text{HCOO}^-}^0 = (349.5 + 50.5) = 400 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\therefore \alpha = \frac{\lambda_m}{\lambda_0} = \frac{210}{400} = 0.52$$

or, $\alpha = 52.5 \%$

18. Write any three differences between Physisorption and Chemisorption. [3]

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

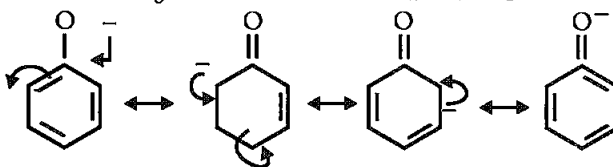
Answer :

	Physisorption	Chemisorption
1.	It forms multimolecular layers	It forms unimolecular layers
2.	It is reversible	It is irreversible
3.	Its does not require activation energy	It requires activation energy
4.	It is not very specific	It is very specific
5.	Force of attraction are Vander Waals forces	Force of attraction are chemical bond

19. Give reasons for the following :

- Phenol is more acidic than methanol.
- The C - O - H bond angle in alcohols is slightly less than the tetrahedral angle ($109^{\circ}28'$).
- $(\text{CH}_3)_3\text{C} - \text{O} - \text{CH}_3$ on reaction with HI gives $(\text{CH}_3)_3\text{C} - \text{I}$ and $\text{CH}_3 - \text{OH}$ as the main products and not $(\text{CH}_3)_3\text{C} - \text{OH}$ and $\text{CH}_3 - \text{I}$. [3]

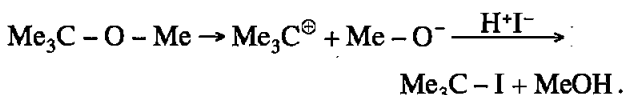
Answer : (i) Phenoxide ion is more stabilized than $\text{CH}_3 - \text{O}^-$ ion because of resonance :



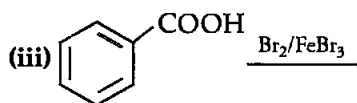
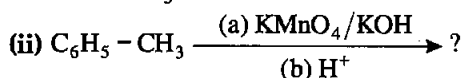
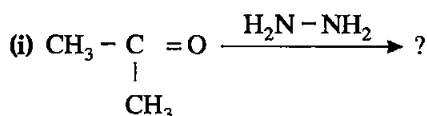
Thus phenol is more acidic than $\text{CH}_3 - \text{OH}$.

(ii) Due to presence of lone pair on oxygen which causes repulsion, the bond angle in alcohol is slightly less than tetrahedral angle ($109.28'$).

(iii) Since $(\text{CH}_3)_3\text{C}^{\oplus}$ is more stabilized through +I effect of three methyl group thus $(\text{CH}_3)_3\text{C} - \text{I}$ and $\text{CH}_3 - \text{OH}$ formed on treatment of HI with $(\text{CH}_3)_3\text{C} - \text{O} - \text{CH}_3$.



20. Predict the products of the following reactions : [3]



(iii) Nitrogen does not form pentahalide.**

(b) Draw the structures of the following :

(i) ClF_3

(ii) XeF_4

[5]

OR

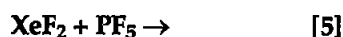
(i) Which allotrope of phosphorus is reactive and why?*

(ii) How are the supersonic jet aeroplanes responsible for the depletion of ozone layer?

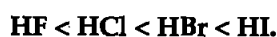
(iii) F_2 has lower bond dissociation enthalpy than Cl_2 . Why?

(iv) Which noble gas is used in filling balloons for meteorological observations?

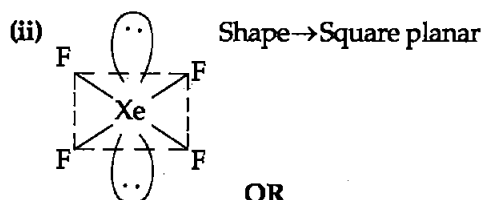
(v) Complete the following equation :



Answer : (a) (i) Size of halide ions is of the order $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$ with increase in size negative charge is dispersed throughout ions and ions gets stabilized. Thus acidity order



(ii) Due to presence of vacant *d*-orbital and combining forms of sulphur (S_8) which is not present in oxygen, the cohesive energy of sulphur is more than oxygen leading to large melting point and boiling point.

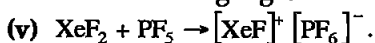


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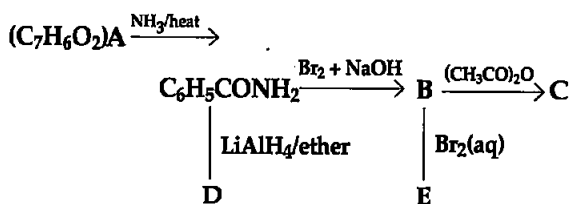
(ii) The exhaust emitted from supersonic jet aeroplane contains CO_2 , NO and other particles which are the killers of stratospheric ozone layer along with the supersonic sound produced by these aeroplanes are destroy ozone layer.

(iii) Due to smaller size and high electro-negativity of fluorine, more energy is required to break the bond of F_2 than Cl_2 . Thus F_2 has lower bond dissociation energy than Cl_2 .

(iv) Helium (He) gas is used in filling balloons for meteorological observations because it is non-inflammable and light gas.



25. An aromatic compound 'A' of molecular formula $\text{C}_7\text{H}_6\text{O}_2$ undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions : [5]



OR

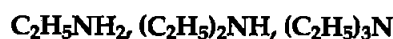
(a) Write the structures of main products when benzene diazonium chloride reacts with the following reagents :

(i) $\text{H}_3\text{PO}_2 + \text{H}_2\text{O}$

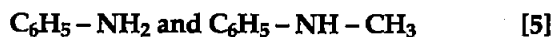
(ii) CuCN/KCN

(iii) H_2O

(b) Arrange the following in the increasing order of their basic character in an aqueous solution :



(c) Give a simple chemical test to distinguish between the following pair of compounds :



Answer :

A : $\text{C}_6\text{H}_5\text{COOH}$ (Benzoic acid)

B : $\text{C}_6\text{H}_5\text{NH}_2$ (Aniline)

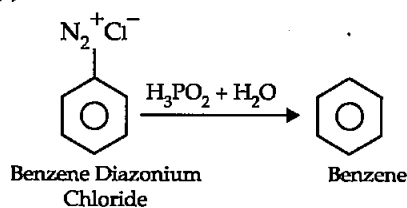
C : $\text{C}_6\text{H}_5\text{NHCOCH}_3$ (N-phenyl ethanamide)

D : $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ (Benzylamine)

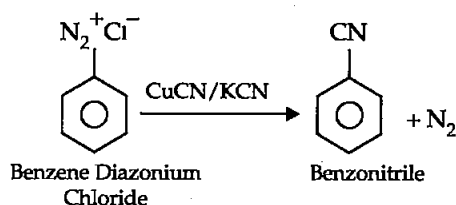
E : $\text{C}_6\text{H}_4(\text{Br})_3(\text{NH}_2)$ (2, 4, 6-Tribromoaniline)

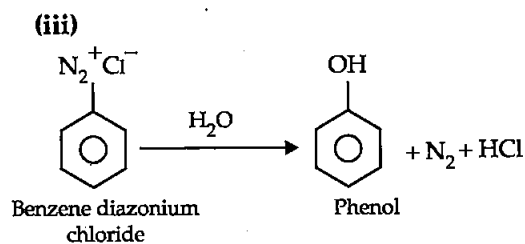
OR

(a) (i)



(ii)





(b) $\text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_3\text{N} < (\text{C}_2\text{H}_5)_2\text{NH}$

+I effect of three C_2H_5 group increases the enormous availability of lone pair of nitrogen atom than +I effect of 2 ethyl group. Thus the order of basicity is I < III < II.

(c) $\text{C}_6\text{H}_5 - \text{NH}_2$ (Primary amine) and

$\text{C}_6\text{H}_5 - \text{NH} - \text{CH}_3$ (Secondary amine) can be distinguished by Hinsberg's test. In this test amines are allowed to react with Hinsberg's reagent, benzenesulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$). Primary amines reacts with this reagent to form N-alkylbenzene sulphonyl amide which is soluble in alkali but secondary amines gives sulphonamide which is insoluble in alkali.

26. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained :

t/s	0	10	20
$[\text{CH}_3\text{COOCH}_3]/\text{mol L}^{-1}$	0.10	0.05	0.025

(a) Show that it follows pseudo first order reaction, as the concentration of water remains constant.

(b) Calculate the average rate of reaction between the time interval 10 to 20 seconds.

(Given : $\log 2 = 0.3010$, $\log 4 = 0.6021$). [5]

OR

(a) For a reaction $\text{A} + \text{B} \rightarrow \text{P}$, the rate is given by

$$\text{Rate} = k[\text{A}][\text{B}]^2$$

(i) How is the rate of reaction affected if the concentration of B is doubled ?

(ii) What is the overall order of reaction if A is present in large excess ?

(b) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction.

Answer : (a) $[\text{A}]_0 = 0.01 \text{ Mol/L}$

$$[\text{A}] = 0.05 \text{ Mol/L at time } t = 10 \text{ s.}$$

$$k = \frac{2.303}{10} \log \frac{0.10}{0.05}$$

$$k = \frac{2.303}{10} \log \frac{0.10}{0.05}$$

$$k = 0.0693 \text{ s}^{-1}$$

$$t = 20 \text{ s}$$

$$k = \frac{2.303}{t} \log \frac{[\text{A}]_0}{[\text{A}]} = \frac{2.303}{10} \log \frac{0.10}{0.05}$$

$k = 0.0693 \text{ s}^{-1}$, Thus its pseudo first order reaction.

(b) The average rate constant is

$$\begin{aligned} \frac{-\Delta[\text{R}]}{\Delta t} &= \frac{\Delta[\text{CH}_3\text{COOCH}_3]}{\Delta t} \\ &= \frac{[0.025 \text{ mol L}^{-1} - 0.05 \text{ mol L}^{-1}]}{20 \text{ s} - 10 \text{ s}} = \frac{0.025}{10 \text{ s}} \\ &= 0.0025 \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

OR

(a) (i) Since the given reaction has order two with respect to reactant B, thus if the concentration of B is doubled in the given reaction, then the rate of reaction will become four times.

(ii) If the concentration of B is doubled i.e.; $[\text{B}]^2$ the overall reaction will be two, because if A is present in large excess, then the reaction will be independent of the concentration of A and will be dependent only on the concentration of B. Order of reaction = 2.

(b) $t_{1/2} = 30 \text{ min}$

$$[\text{R}] = [\text{R}]_0 - 90\% \text{ of } [\text{R}]_0$$

$$= [\text{R}]_0 - \frac{90[\text{R}]_0}{100}$$

$$[\text{R}] = \frac{[\text{R}]_0}{10}$$

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{30} = 0.0231 \text{ min}^{-1}$$

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

$$t = \frac{2.303}{0.0231} \log \frac{[\text{R}]_0}{[\text{R}]} = \frac{2.303}{0.0231} \log 10$$

$$t = 99.7 \text{ min}$$

Note : All questions are same in outside Delhi Set II and III.

Chemistry 2015 (Delhi)

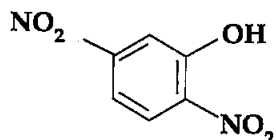
SET I

Time allowed : 3 hours

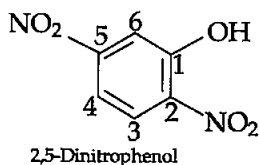
Maximum Marks : 70

1. What is the basicity of H_3PO_4 ? ** [1]

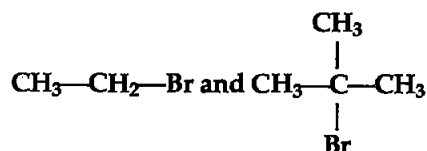
2. Write the IUPAC name of the given compound : [1]



Answer :



3. Which would undergo $\text{S}_{\text{N}}2$ reaction faster in the following pair and why? [1]



Answer : Primary alkyl halides will undergo $\text{S}_{\text{N}}2$ reactions faster than tertiary alkyl halides because of less steric hindrance experienced by the approaching nucleophile. Hence, out of the given pair, primary alkyl halide ($\text{CH}_3\text{CH}_2\text{Br}$) would undergo $\text{S}_{\text{N}}2$ reaction faster.

4. Out of BaCl_2 and KCl , which one is more effective in causing coagulation of a negatively charged colloidal sol? Give reason. [1]

Answer : According to the Hardy-Schulze rule, greater the valency of a flocculating ion, the greater is its power to cause precipitation. Between Ba^{2+} (from BaCl_2) and K^+ (from KCl), Ba^{2+} has greater valency. Therefore, BaCl_2 will be more effective in causing the coagulation of a negatively charged colloidal sol.

5. What is the formula of a compound in which the element Y forms ccp lattice and atoms of X occupy $\frac{1}{3}$ rd of tetrahedral voids? ** [1]

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

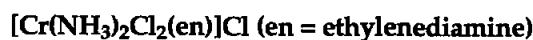
6. What are the transition elements? Write two characteristics of the transition elements. [2]

Answer : Elements which in their ground state or in any of their oxidation state have partially filled d -orbital are called transition elements. The name 'transition' given to the elements of d -block is only because of their position between s -block and p -block elements.

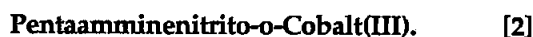
The two characteristics of transition elements are :

1. They show variable oxidation states.
2. They generally form coloured compounds.

7. (i) Write down the IUPAC name of the following complex :



(ii) Write the formula for the following complex :

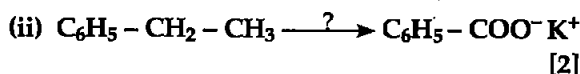
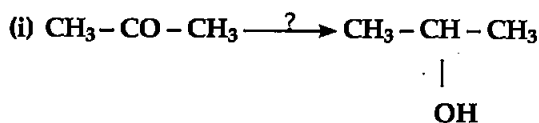


Answer :

(i) Diamminedichloridoethylenediaminechromium(III) chloride.

(ii) $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$.

8. Name the reagents used in the following reactions :



Answer :

(i) Sodium borohydride (NaBH_4)/ LiAlH_4 / H_2 , Pt.

(ii) Alkaline potassium permanganate (KMnO_4 , KOH).

9. What is meant by positive deviations from Raoult's law? Give an example. What is the sign of $\Delta_{\text{mix}}H$ for positive deviation? [2]

OR

Define azeotropes. What type of azeotrope is formed by positive deviation from Raoult's law? Give an example.

Answer : Positive deviation from Raoult's law means that the observed vapour pressure is greater than expected, and it occurs when the A – B attractions are weaker than the average of the attractions in the pure component of the mixture. For example : A mixture of ethanol and acetone shows a positive deviation from Raoult's law.

In case of solutions showing positive deviations, absorption of heat takes place; i.e., $\Delta_{\text{mix}}H$ has a positive (+) sign.

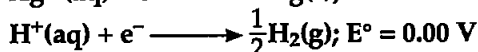
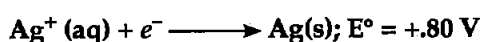
OR

Azeotropes are the binary mixtures which have the same composition in liquid and vapour phases and boil at a constant temperature.

A minimum-boiling azeotrope is formed by solutions showing a large positive deviation from Raoult's law at a specific composition.

Example : $C_2H_5OH + H_2O$ (An ethanol-water mixture)

10. (a) Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution :



On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why ?

- (b) Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with decrease in concentration ?

[2]

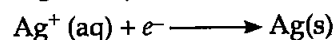
Answer : (a) The relationship between the standard free energy change and emf of a cell reaction is given by :

$$\Delta G^\circ = -nFE^\circ$$

Thus, more positive the standard reduction potential of a reaction, the more negative is the standard free energy change associated with the process and consequently, the higher is the feasibility of the reaction.

Since $E^\circ_{Ag^+/Ag}$ has a greater positive value than $E^\circ_{H^+/H}$, the reaction which is feasible at the

cathode is given by



- (b) The limiting molar conductivity of an electrolyte is defined as its molar conductivity when the concentration of the electrolyte in the solution approaches zero.

The conductivity of an electrolyte solution is the conductance of ions present in a unit volume of the solution. The number of ions (responsible for carrying current) decreases when the solution is diluted or the concentration is decreased. As a result, the conductivity of an electrolyte solution decreases with the decrease in concentration.

11. 3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression in freezing point of 1.62 K. Calculate the Van't Hoff factor and predict the nature of solute (associated or dissociated).

(Given : Molar mass of benzoic acid = 122 g mol⁻¹, K_f for benzene = 4.9 K kg mol⁻¹) [3]

Answer : We know that the depression in freezing point by

Given : Mass of solute (W_B) i.e., $C_6H_5COOH = 3.9 g$

$$\text{Mass of solvent } (W_A) = 49 g = \frac{49}{1000} \text{ kg}$$

Molar mass of $C_6H_5COOH(M_S) = 122 g/mol$

$$K_f = 4.9 \text{ K kg/mol}$$

$$\Delta T_f = 1.62 \text{ K}$$

To find : Van't Hoff factor ($i = ?$)

We know that the depression in freezing point is given by :

$$\Delta T_f = i \times K_f \times m$$

$$\Delta T_f = i \times K_f \times \frac{W_B}{M_S} \times \frac{1}{W_A (\text{kg})}$$

$$i = \frac{\Delta T_f \times M_S \times W_A (\text{kg})}{K_f \times W_B}$$

$$i = \frac{1.62 \times 122 \times 49}{4.9 \times 3.9 \times 1000}$$

Since, $i < 1$, hence solute benzoic acid (C_6H_5COOH) will undergo association in benzene.

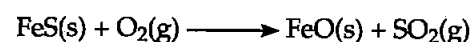
12. (i) Indicate the principle behind the method used for the refining of zinc.

(ii) What is the role of silica in the extraction of copper ?

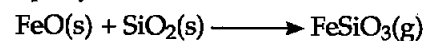
(iii) Which form of the iron is the purest form of commercial iron ? [3]

Answer : (i) Zinc is a metal having low boiling point and it is refined by distillation method which is used for metals having low boiling points.

(ii) During extraction of Copper, FeS or FeO is present as impurity hence SiO₂ is added as flux to form silicate (slag) which can be removed easily as it floats over molten copper (Cu)



impurity



impurity flux

Iron silicate (slag)

(iii) Wrought iron is purest form of commercial iron.

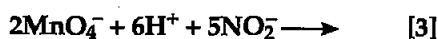
13. An element with molar mass 27 g mol⁻¹ forms a cubic unit cell with edge length 4.05 × 10⁻⁸ cm. If its density is 2.7 g cm⁻³, what is the nature of the cubic unit cell ?** [3]

14. (a) How would you account for the following :

(i) Actinoid contraction is greater than lanthanoid contraction.

(ii) Transition metals form coloured compounds.

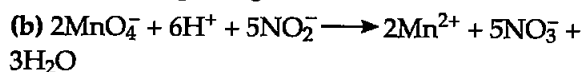
(b) Complete the following equation :



Answer : (a) (i) The 5 f-orbitals (in case of actinoids) have a poorer shielding effect than 4 f-orbitals (in lanthanoids). Thus, the effective nuclear charge experienced by electrons in valence shells in case of actinoids is much more than that experienced by electrons in valence shells in case of lanthanoids. Hence, the contraction in size in actinoids is greater than that in lanthanoids.

(ii) In the presence of ligands, the d-orbitals of transition metal ions split up into two sets of orbitals having different energies. Thus, the transition of electrons takes place from one set to

another. The energy required for these transitions is quite less and falls in the visible region of radiation. The ions of transition metals absorb the radiation of a particular wavelength and the rest is reflected, imparting colour to the solution.



15. (i) Draw the geometrical isomers of complex [Pt(NH₃)₂Cl₂].

(ii) On the basis of crystal field theory, write the electronic configuration for d⁴ ion if Δ₀ < P.

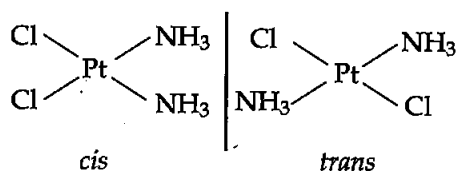
(iii) Write the hybridization and magnetic behaviour of the complex [Ni(CO)₄].

(At. no. of Ni = 28).

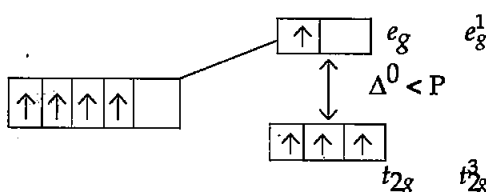
[3]

Answer :

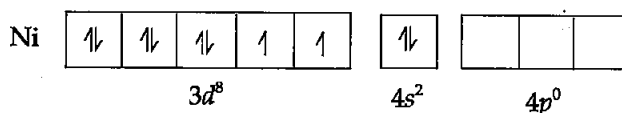
(i) Geometrical isomers of complex [Pt(NH₃)₂Cl₂].



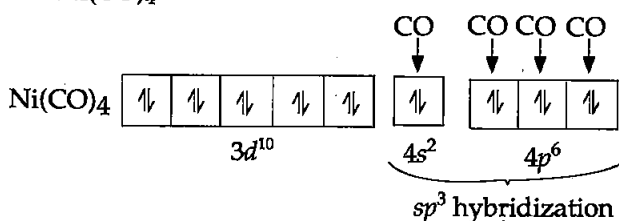
(ii) On the basis of crystal field theory, for a d⁴ ion if Δ₀ < P. then complex is a high spin complex formed by association of weak field ligands with the metal ion. As a result, the fourth electron enters one of the e_g orbitals, thereby, exhibiting the electronic configuration t_{2g}³e_g¹.



(iii) Outer electronic configuration of Ni atom in ground state.



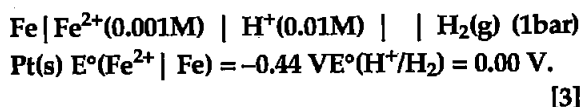
Outer electronic configuration of Ni atom in Ni(CO)₄



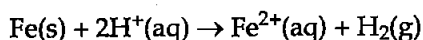
** Answer is not given due to change in present syllabus.

Carbonyl, CO being a strong field ligand causes the pairing of valence electrons in the Ni atom against the Hund's Rule of Maximum Multiplicity. This results in the formation of an inner orbital complex, $[\text{Ni}(\text{CO})_4]$. Since the complex $[\text{Ni}(\text{CO})_4]$ has no unpaired electron, it is diamagnetic in nature and possesses tetrahedral shape.

16. Calculate emf of the following cell at 25°C :



Answer : For the given cell representation, the cell reaction will be



The standard emf of the cell will be

$$E^\circ_{\text{cell}} = E^\circ_{\text{H}^+/\text{H}_2} - E^\circ_{\text{Fe}^{2+}/\text{Fe}}$$

$$E^\circ_{\text{cell}} = 0 - (-0.44) = 0.44 \text{ V}$$

The Nernst equation for the cell reaction at 25°C will be

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2}$$

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

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

$$= 0.44 - \frac{0.0591}{2}$$

Answer :

	Polymer	Name of Monomer(s)	Structure of Monomer(s)
(i)	Nylon-6, 6	Hexamethylenediamine and adipic acid	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$ Hexamethylenediamine $\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$ Adipic acid
(ii)	PHBV	3-Hydroxypentanoic acid and 3-Hydroxybutanoic acid.	$\text{CH}_3-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{COOH}$ 3-Hydroxypentanoic acid $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2-\text{COOH}$ 3-Hydroxybutanoic acid
(iii)	Neoprene	Chloroprene	$\text{H}_2\text{C}=\text{C}(\text{Cl})-\text{C}(\text{H})=\text{CH}_2$ Chloroprene

$$E_{\text{cell}} = 0.4105 \text{ V}^2 \approx 0.41 \text{ V}$$

17. Give reasons for the following observations :

- Leather gets hardened after tanning.
- Lyophilic sol is more stable than lyophobic sol.
- It is necessary to remove CO when ammonia is prepared by Haber's process. [3]

Answer : (i) Animal skin (hide) is colloidal in nature and has positively charged colloidal particles. When a hide is soaked in tanning, mutual coagulation takes place and as a result, leather gets hardened.

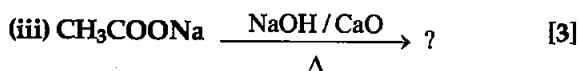
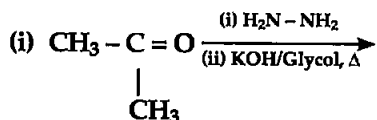
(ii) The stability of lyophilic solution depends on the two factors, the presence of a charge and the solvation of colloidal particles. On the other hand, the stability of lyophobic solutions is only because of the presence of a charge. Thus, lyophilic solution is more stable than lyophobic solution due to the extensive solvation.

(iii) It is necessary to remove CO when ammonia is prepared by Haber's process because in this process the CO acts as a poison and adversely affects the activity of iron catalyst, used in the process.

18. Write the names and structures of the monomers of the following polymers :

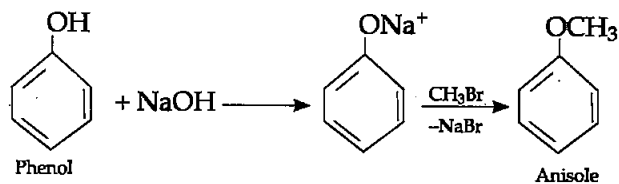
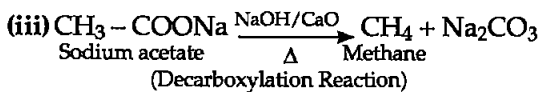
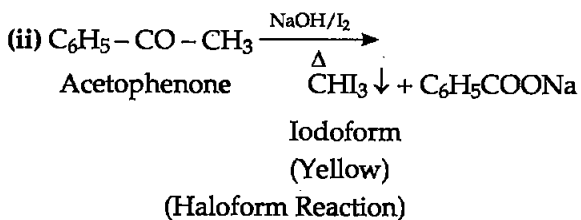
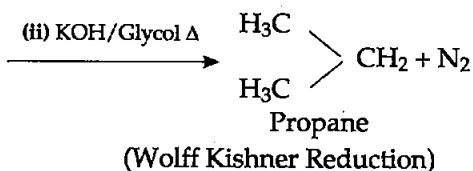
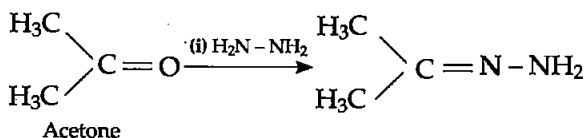
- Nylon-6, 6
- PHBV
- Neoprene. [3]

19. Predict the products of the following reactions :

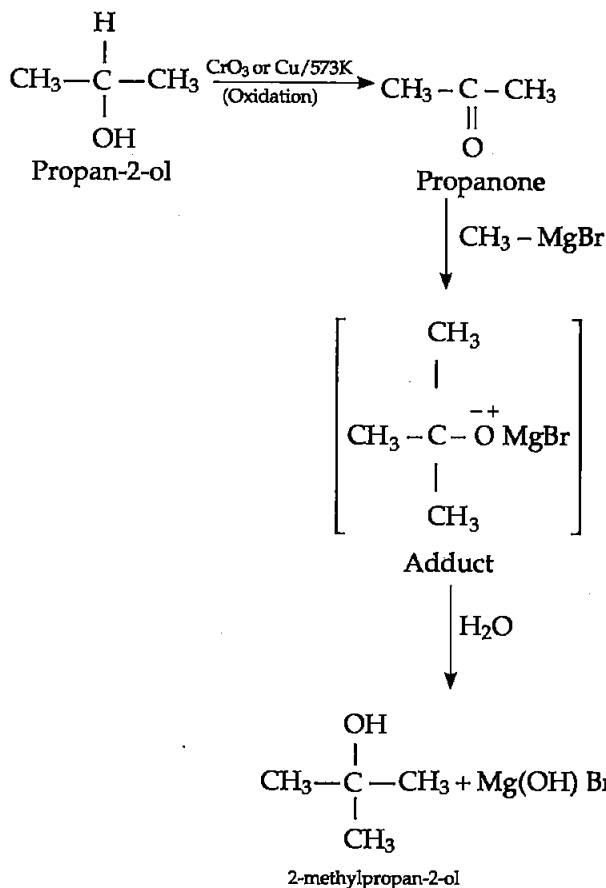


Answer :

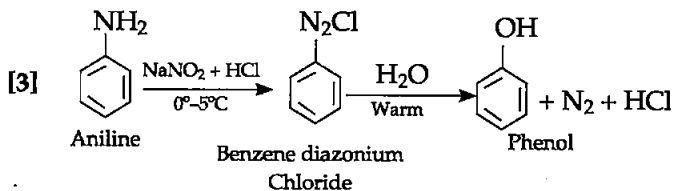
(i)



(ii)



(iii)



OR

20. How do you convert the following :

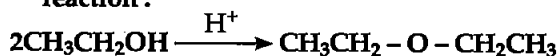
(i) Phenol to anisole

(ii) Propan-2-ol to 2-methylpropan-2-ol

(iii) Aniline to phenol

OR

(b) Write the mechanism of the following reaction :



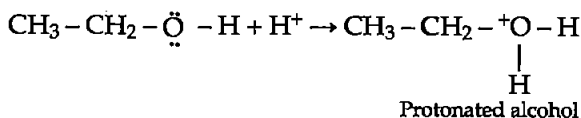
(b) Write the equation involved in the acetylation of Salicylic acid. [3]

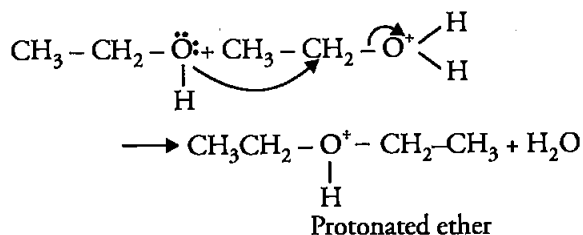
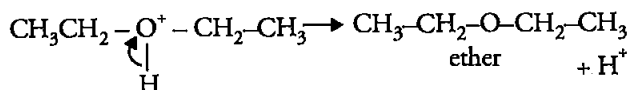
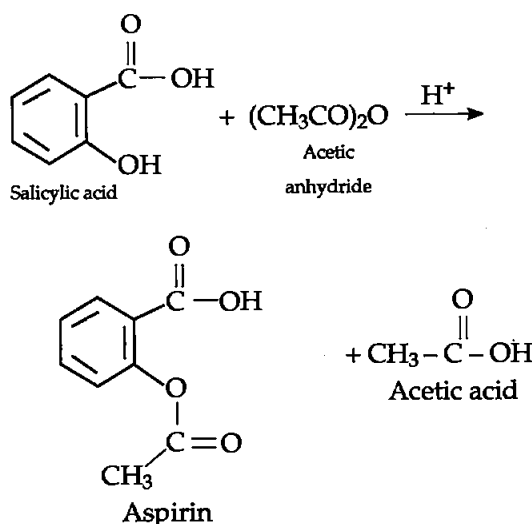
Answer :

(i)

(a) The given reaction follows $\text{S}_{\text{N}}2$ mechanism as shown below :

Step 1 : Protonation



Step 2 : Nucleophilic attack ($5N^2$)**Step 3 :****(b) Acetylation of Salicylic acids.**

21. (i) Which one of the following is a disaccharide :
Starch, Maltose, Fructose, Glucose ?
- (ii) What is the difference between fibrous protein and globular protein ?
- (iii) Write the name of vitamin whose deficiency causes bone deformities in children. [3]

Answer : (i) Maltose is a disaccharide, as it contains α -D-glucose units.

(ii) .

	Fibrous Proteins	Globular Proteins
1.	In fibrous proteins, the polypeptide chains, run parallel and are held together by strong hydrogen and disulphide bonds.	In globular proteins, the polypeptide chains are folded looped or tursted around themselves, giving these proteins a spherical structure.

2.	They are usually insoluble in water.	They are usually soluble in water.
3.	They are structural proteins. For example, keratin is present in nails and hair, collagen is present in tendons and myosin is present in muscles.	They are functional proteins. For example, most enzymes and some hormones like insulin.

(iii) Deficiency of Vitamin D causes the bone deformities in children.

22. Give reasons :

- (a) *n*-Butyl bromide has higher boiling point than *t*-butyl bromide.
- (b) Racemic mixture is optically inactive.
- (c) The presence of nitro group ($-\text{NO}_2$) at o/p positions increases the reactivity of haloarenes towards nucleophilic substitution reactions. [3]

Answer : (a) *n*-butyl bromide is a straight chain molecule having larger surface area and therefore, has stronger intermolecular forces. On the other hand, *t*-butyl bromide $(\text{CH}_3)_3\text{CBr}$ is branched molecule, so it has a smaller surface area. Hence, it has weaker intermolecular force.

(b) Racemic mixture is an equimolar solution of two enantiomers (*d* and *l* forms) and thus, the rotation due to one isomer is cancelled by the rotation due to another. Therefore, it has zero optical rotation and hence, it is optically inactive.

(c) This is because nitro group ($-\text{NO}_2$) at o/p positions withdraw the electrons from the benzene ring. The reduced electron density at o/p positions for haloarenes facilitate the attack of nucleophile. The negative charge in the Carbanion formed, at o/p positions with respect to halogen atom is stabilised through resonance and due to the presence of nitro groups (NO_2) respectively.

23. Mr. Roy, the principal of one reputed school organized a seminar in which he invited parents

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

and principals to discuss the serious issue of diabetes and depression in students. They all resolved this issue by strictly banning the junk food in school and to introduce healthy snacks and drinks like soup, lassi, milk etc. in school canteens. They also decided to make compulsory half an hour physical activities for the students in the morning assembly daily. After six months, Mr. Roy conducted the health survey in most of the schools and discovered a tremendous improvement in the health of students.

After reading the above passage, answer the following :

- (i) What are the values (at least two, displayed by Mr. Roy ?**
- (ii) As a student, how can you spread awareness about this issue ?
- (iii) What are tranquilizers ? Give an example.
- (iv) Why is use of aspartame limited to cold foods and drinks ? [4]

Answer :

(ii) As a student, I can spread awareness regarding diabetes and depression among students by conducting seminars, health camps, debates, distribution of pamphlets, and workshops by doctors. So as to highlight the needs to follow healthy eating.

(iii) Tranquilizers are neurologically active drugs that induce a sense of well being and are used to treat stress, anxiety and mild or severe mental disease. They perform their function by inhibiting the message transfer mechanism from nerve to receptor *e.g.*, equanil, meprobamate and iproniazid etc.

(iv) The use of aspartame is limited to foods and cold drinks because aspartame is unstable at cooking temperature.

24. (a) Account for the the following :

- (i) Acidic character increases from HF to HI.
- (ii) There is large difference between melting and boiling points of oxygen and sulphur.
- (iii) Nitrogen does not form pentahalide.

(b) Draw the structures of the following :

- (i) ClF_3
- (ii) XeF_4 [5]

OR

- (i) Which allotrope of phosphorus is more reactive and why ?
- (ii) How the supersonic jet aeroplanes are responsible for the depletion of ozone layers ?
- (iii) F_2 has lower bond dissociation enthalpy than Cl_2 . Why ?
- (iv) Which noble gas is used in filling balloons for meteorological observations ?
- (v) Complete the equation :

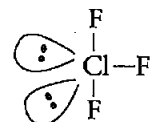


Answer : (a) (i) The acidic strength of the hydrohalic acids increases from HF to HI because the stability of the acids decreases from HF to HI on account of decrease in bond dissociation enthalpy of H - X bond from HF to HI.

(ii) The difference in melting point and boiling point of oxygen and sulphur is due to the difference in their atomicities oxygen exists as a diatomic (O_2) molecule, while sulphur exists as a polyatomic (S_8) molecule and also oxygen is small in size and have high electronegativities.

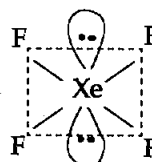
(iii) Being an element of second period, Nitrogen has no 'd' orbitals and its maximum covalency is restricted to four. Hence, due to the non-availability of d-orbitals, it can't form pentahalides.

(b) (i) Structure of ClF_3

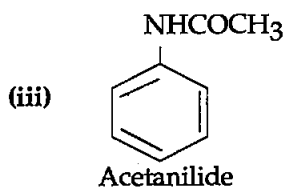
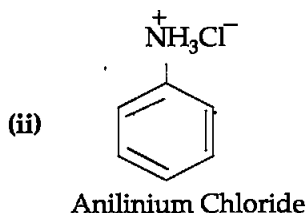
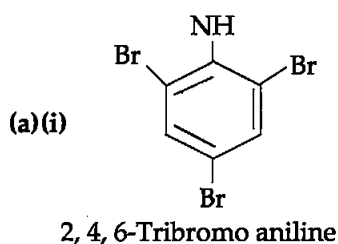


Bent-T-Shaped

(ii) Structure of XeF_4



Square planar

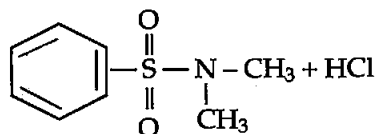
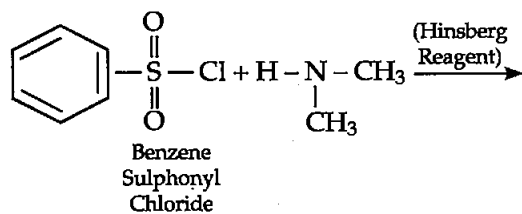


(b) Ethanol has high boiling point than ethylamine because oxygen, being more electronegative forms strong extensive hydrogen bond as compared to that of nitrogen. In trimethylamine there is no hydrogen and hence has the lowest boiling point.

Increasing order of boiling point.



(c) $(\text{CH}_3)_2\text{NH}$ reacts with benzene sulphonyl chloride (Hinsberg reagent) as follows :



$(\text{CH}_3)_3\text{N}$ does not react with benzene sulphonyl chloride.

26. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained :

t/s	0	30	60
$[\text{CH}_3\text{COOCH}_3]$ mol L^{-1}	/	0.60	0.15

(i) Show that it follows pseudo first order reaction, as the concentration of water remains constant.

(ii) Calculate the average rate of reaction between the time interval 30 to 60 seconds. (Given $\log 2 = 0.3010$, $\log 4 = 0.6021$) [5]

OR

(a) For a reaction $\text{A} + \text{B} \rightarrow \text{P}$, the rate is given by

$$\text{Rate} = k[\text{A}][\text{B}]^2$$

(i) How is the rate of reaction affected if the concentration of B is doubled ?

(ii) What is the overall order of reaction if A is present in large excess ?

(b) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction.

$$(\log 2 = 0.3010)$$

Answer :

For the hydrolysis of methyl acetate in aqueous solution :

$$(i) \quad K = \frac{2.303}{t} \log \frac{[\text{A}]_0}{[\text{A}]}$$

where $[\text{A}]_0$ = Initial concentration of reactant

$[\text{A}]$ = Final concentration of reactant.

At $t_1 = 30 \text{ sec}$,

$$K = \frac{2.303}{30} \log \frac{0.60}{0.30}$$

$$K = 0.07677 \log 2$$

$$K = 0.0231 \text{ s}^{-1}$$

for $t = 60 \text{ sec}$

$$K = \frac{2.303}{60} \log \frac{0.60}{0.15}$$

$$K = 0.07677 \log 2$$

$$K = 0.0231 \text{ s}^{-1}$$

∴ K is same for both the cases hence it is pseudo first order reaction.

(ii) Average rate of reaction between the time interval of 30 – 60 seconds is given by

$$K = \frac{-\Delta[\text{CH}_3\text{COOCH}_3]}{\Delta t}$$

$$K = -\left(\frac{0.15 - 0.30}{60 - 30}\right)$$

$$= \frac{0.15}{30} = 0.005 \text{ mol L}^{-1}\text{s}^{-1}$$

OR

(a) (i) Since the given reaction has order two with respect to reactant B, thus if the concentration of B is doubled in the given reaction, then the rate of reaction will become four times.

(ii) If the concentration of B is doubled *i.e.*; $[\text{B}]^2$ the overall reaction will be two, because if A is present in large excess, then the reaction will be independent of the concentration of A and will be dependent only on the concentration of B.

Order of reaction = 2.

(b) $t_{1/2} = 30 \text{ min}$

$$[\text{R}] = [\text{R}]_0 - 90\% \text{ of } [\text{R}]_0$$

$$= [\text{R}]_0 - \frac{90[\text{R}]_0}{100}$$

$$[\text{R}] = \frac{[\text{R}]_0}{10}$$

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{30} = 0.0231 \text{ min}^{-1}$$

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

$$t = \frac{2.303}{0.0231} \log \frac{[\text{R}]_0}{\frac{[\text{R}]_0}{10}}$$

$$= \frac{2.303}{0.0231} \log 10$$

$$t = 99.7 \text{ min}$$

Note : All questions of Delhi Set-II are from Delhi Set I and Delhi Set-III are from Set I and II.

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Chemistry 2014 (Outside Delhi)

SET I

Time allowed : 3 hours

Maximum marks : 70

1. What is the effect of temperature on chemisorption? [1]

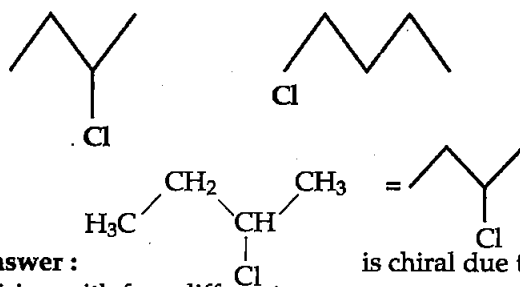
Answer : Chemisorption initially increases then decreases with rise in temperature. The initial increase is due to the high energy of activation and the decrease afterwards is due to the exothermic nature of adsorption equilibrium.

2. What is the role of zinc metal in the extraction of silver? [1]

Answer : Zinc is used as a reducing agent to recover silver from its cyanide complex. It reduces Ag^+ to Ag and itself get oxidised to Zn^{2+} .

3. What is the basicity of H_3PO_3 ? [1]

4. Identify the chiral molecule in the following pair: [1]



Answer : is chiral due to pairing with four different groups.

5. Which of the following is a natural polymer? [1]
Buna-S, Proteins, PVC Economics type

Answer : Protein, is a natural polymer having amino acid as a monomer.

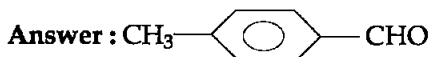
6. The conversion of primary aromatic amines into diazonium salts is known as _____. [1]

Answer : Diazotisation reaction.

7. What are the products of hydrolysis of sucrose? [1]

Answer : The products of Hydrolysis of sucrose are : Glucose and Fructose

8. Write the structure of *p*-methylbenzaldehyde. [1]



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

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