

CHEMISTRY

(THEORY)

(Three Hours)

(Candidates are allowed additional 15 minutes for **only** reading the paper.

They must NOT start writing during this time.)

Answer **all** questions in **Part I** and **six** questions from **Part II**, choosing **two** questions from Section A, **two** from Section B and **two** from Section C.

All working, including rough work, should be done on the same sheet as, and adjacent to, the rest of the answer.

The intended marks for questions or parts of questions are given in brackets [].

Balanced equations must be given wherever possible and diagrams where they are helpful.

When solving numerical problems, all essential working must be shown.

In working out problems use the following data:

Gas constant $R = 1.987 \text{ cal deg}^{-1} \text{ mol}^{-1} = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$

$1 \text{ l atm} = 1 \text{ dm}^3 \text{ atm} = 101.3 \text{ J}$. $1 \text{ Faraday} = 96500 \text{ Coulombs}$.

Avagadro's number $= 6.023 \times 10^{23}$.

PART I (20 Marks)

Answer **all** questions.

Question 1

- (a) Fill in the blanks by choosing the appropriate word/words from those given in the brackets: [5]

(hydrolysis, reduction, oxidation, vacant, osmotic, above, benzoic acid, phenol, aniline, below, can, decreases, increases, cannot, crystal, ionization, rate, rate constant.)

- (i) A catalyst _____ start a reaction but it can increase the _____ of the reaction.
- (ii) Electrons trapped in the _____ sites of the _____ lattice are called F-centres.
- (iii) An aqueous solution of sugar boils _____ 100°C and freezes _____ 0°C .

- (iv) Toluene on _____ with alkaline potassium permanganate gives _____.
- (v) The degree of _____ of ammonium hydroxide _____ on addition of ammonium chloride.
- (b) Complete the following statements by selecting the **correct alternative** from the choices given:- [5]
- (i) For reaction $2\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \text{O}_2$, the rate and rate constants are $1.02 \times 10^{-4} \text{ mole litre}^{-1} \text{ sec}^{-1}$ and $3.4 \times 10^{-5} \text{ sec}^{-1}$ respectively. The concentration of N_2O_5 at that time will be:
- (1) $1.732 \text{ mol lit}^{-1}$
 - (2) 3 mol lit^{-1}
 - (3) $1.02 \times 10^{-4} \text{ mol lit}^{-1}$
 - (4) $3.2 \times 10^5 \text{ mol lit}^{-1}$
- (ii) Ethanoic acid dimerises in solution. Its molecular mass determined from its depression of freezing point of the solution will be:
- (1) Same as the theoretical value
 - (2) Half its theoretical value
 - (3) Double its theoretical value
 - (4) One third of its theoretical value.
- (iii) Magnesium displaces hydrogen from dilute acid solution because:
- (1) The oxidation potential of magnesium is less than that of hydrogen.
 - (2) The reduction potential of magnesium is less than that of hydrogen.
 - (3) Both magnesium and hydrogen have same oxidation potential.
 - (4) Both magnesium and hydrogen have same reduction potential .
- (iv) In the series of reactions $\text{CH}_3\text{COOH} \xrightarrow{\text{NH}_3} \text{A} \xrightarrow{\text{heat}} \text{B} \xrightarrow{\text{P}_2\text{O}_5} \text{C}$, the product C is:
- (1) Acetyl chloride
 - (2) Ammonium acetate
 - (3) Acetic anhydride
 - (4) Methyl cyanide.

(v) In the reaction $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{PCl}_5(\text{g})$, the equilibrium will shift in the opposite direction, if:

- (1) Chlorine is added.
- (2) PCl_3 is added
- (3) Pressure is increased
- (4) Pressure is reduced.

(c) Answer the following questions:

[5]

(i) Among equimolar aqueous solutions of MgCl_2 , NaCl , FeCl_3 and $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, which will show minimum osmotic pressure? Why?

(ii) If K_c for the reaction $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ is $1.5 \times 10^{-5} (\text{mol /lit})^{-2}$, write the value of K_{c1} for the reaction $\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \rightarrow \text{NH}_3$

(iii) *The pH of acetic acid decreases on dilution.* State the Law governing this statement.

(iv) Xenon gives a series of fluorides, but Helium and Neon do not. Why?

(At. No: Xe = 54, Ne = 10, He = 2)

(v) Calculate the number of coulombs required to deposit 20.25 g of aluminium (at. mass = 27) from a solution containing Al^{+3} .

(d) Match the following:

[5]

(i) $\text{CHCl}_3 + \text{NaOH}$

(a) Fluorine

(ii) Proteins

(b) Starch

(iii) Carbohydrate

(c) Ammonia

(iv) Lewis base

(d) Peptide linkage

(v) KHF_2

(e) Isocyanide test

PART II (50 Marks)

Answer **six** questions choosing **two** from **Section A**, **two** from **Section B** and **two** from **Section C**.

SECTION A

Answer any **two** questions.

Question 2

- (a) (i) A certain aqueous solution boils at 100.303°C . What is its freezing point? K_b for water = 0.5 K mol^{-1} and $K_f = 1.87 \text{ K mol}^{-1}$. [2]
- (ii) A solution containing 1g of sodium chloride in 100g of water freezes at 0.604°C . Calculate the degree of dissociation of sodium chloride. ($\text{Na} = 23$, $\text{Cl} = 35.5$, K_f for water = 1.87 K mol^{-1}) [4]
- (b) (i) Explain graphically how the rate of a reaction changes with every 10°C rise in temperature. [2]
- (ii) How is the activation energy of a reaction related to its rate constant? [1]
- (iii) The half life period for the decomposition of a substance is 2.5 hours. If the initial weight of the substance is 160 g, how much of the substance will be left after 10 hours? [1]

Question 3

- (a) (i) Define Frenkel defects of an ionic crystal. [1]
- (ii) Iron has an edge length 288 pm. Its density is 7.86 gm cm^{-3} . Find the type of cubic lattice to which the crystal belongs. (at. mass of iron = 56) [3]
- (b) Explain giving reasons why:
- (i) $\text{Mg}(\text{OH})_2$ is sparingly soluble in water but highly soluble in ammonium chloride solution. [2]
- (ii) When H_2S is passed through acidified zinc sulphate solution, white precipitate of zinc sulphide is not formed. [2]
- (c) The equilibrium constant for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$ is 49.5 at 440°C . If 0.2 mole of H_2 and 0.2 mole of I_2 are allowed to react in a 10 litre flask at this temperature, calculate the concentration of each at equilibrium. [2]

Question 4

- (a) (i) What is specific conductance of a solution and what is its unit? How is it related to the equivalent conductance of the solution? [2]
- (ii) 2.5 amperes of current is passed through copper sulphate solution for 30 minutes. Calculate the number of copper atoms deposited at the cathode ($\text{Cu} = 63.54$). [2]
- (iii) Four metals W, X, Y and Z have the following values of E°_{red} : [2]
- E°_{red}
- W = -0.140 V
- X = - 2.93 V
- Y = +0.80 V
- Z = +1.50 V
- Arrange them in the increasing order of reducing power.
- (b) (i) On adding sodium acetate to aqueous solution of acetic acid, what happens to the pH of the solution? Give a reason for your answer. [2]
- (ii) Calculate the pH of an aqueous solution of ammonium formate assuming complete dissociation. $\text{p}K_a$ for formic acid = 3.8 and $\text{p}K_b$ of ammonia = 4.8 [1]
- (c) Explain auto catalysis with one example. [1]

SECTION B

Answer any two questions

Question 5

- (a) (i) State the geometry and magnetic property of tetracarbonyl nickel according to the valence bond theory. [1]
- (ii) What type of structural isomers are $[\text{Pt}(\text{OH})_2(\text{NH}_3)_4]\text{SO}_4$ and $[\text{Pt SO}_4(\text{NH}_3)_4](\text{OH})_2$? How will you identify the isomers with a chemical test? [2]
- (b) Name the co-ordination compound used for the following: [2]
- (i) Treatment of cancer.
- (ii) Treatment of lead poisoning.

Question 6

- (a) Explain giving reasons why:
- (i) The halogens are coloured and the colour deepens from fluorine to iodine. [2]
 - (ii) In a given transition series, the atomic radius does not change very much with increasing atomic number. [2]
- (b) Draw the resonating structures of ozone molecule. [1]

Question 7

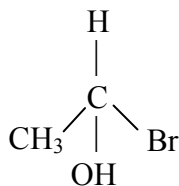
- (a) (i) Give equations to show the use of aqua regia in dissolving platinum. [1]
- (ii) Draw the structure of Xenon hexafluoride molecule and state the hybridisation of the central atom and the structure of the molecule. [2]
- (b) Write balanced equations for the following reactions: [2]
- (i) Ozone and alkaline potassium iodide.
 - (ii) Sodium sulphite and acidified potassium permanganate.

SECTION C

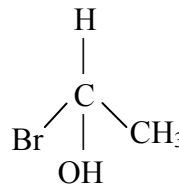
Answer any **two** questions.

Question 8

- (a) Write equations for the following reactions and name the reactions: [3]
- (i) Benzene diazonium chloride is treated with copper and hydrochloric acid.
 - (ii) Formaldehyde is treated with 50% caustic soda solution.
- (b) (i) Write the structures of the isomers of 3 phenyl prop-2-enoic acid. [1]
- (ii) What type of isomerism is exhibited by the following pairs of compounds: [2]
- (1) $\text{CH}(\text{CH}_2)_3\text{CH}_2\text{OH}$ and $(\text{C}_2\text{H}_5)_2\text{CHOH}$
 - (2)



and



- (c) Give one good chemical test to distinguish between the following pairs of compounds: [3]
- (i) Urea and acetamide
 - (ii) 1-propanol and 2-methyl 2-propanol.

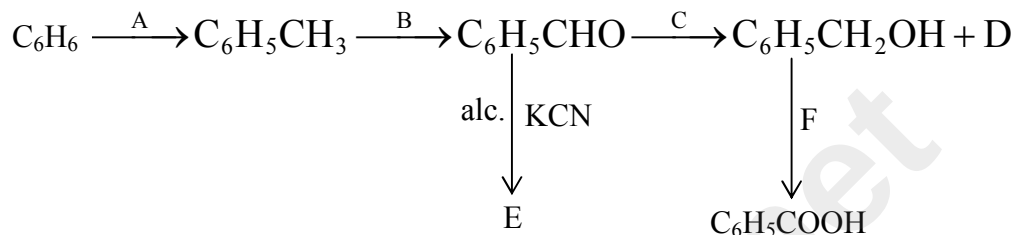
(d) Name the monomeric units of Nylon 66.

[1]

Question 9

(a) Identify the compounds A, B, C, D, E and F.

[3]



(b) How can the following conversions be brought about?

(i) Ethanoic acid to ethylamine.

[3]

(ii) Aniline to benzoic acid.

[3]

(c) What is a zwitter ion? Represent the zwitter ion of glycine.

[1]

Question 10

(a) An organic compound A on treatment with ethanol gives a carboxylic acid B and a compound C. Hydrolysis of C under acidic condition gives B and D. Oxidation of D with acidified potassium permanganate also gives B. B on heating with calcium hydroxide gives E with molecular formula $\text{C}_3\text{H}_6\text{O}$. E does not give Tollen's test but reacts with iodine and caustic potash to give a yellow precipitate.

[4]

(i) Identify A, B, C, D and E.

(ii) Write balanced equation of E with iodine and caustic potash and name the reaction.

(b) (i) Name the functional groups that distinguish glucose and fructose. How will you distinguish between the two compounds?

[2]

(ii) What are polyesters? Give one example of polyester and the monomers.

[2]

(c) Give balanced equations for the following reactions:

[2]

(i) Aniline and benzoyl chloride.

(ii) Diethyl ether and hydroiodic acid (cold).