

CHEMISTRY

Paper – 1

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

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

PART I

Answer **all** questions

Question 1

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

(electron, proton, neutron, decreases, increasing, lowering, one, two, acidic, basic, anion, cation, paramagnetic, Lewis acid, Lewis base, carbonic acid, sulphurous acid, sulphuric acid, ammonium carbonate, sodium bicarbonate, six, increases)

- (i) A positive catalyst _____ the rate of a reaction by _____ the activation energy.
 - (ii) Human blood is a buffer solution of _____ and _____.
 - (iii) BF_3 is a _____ since it is an _____ deficient molecule.
 - (iv) Oxygen is _____ due to the presence of _____ unpaired electrons.
 - (v) A solution of FeCl_3 is _____ due to _____ hydrolysis.
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(b) Complete the following statements by selecting the correct alternative from the choices given:

[5]

- (i) $[\text{Co}(\text{NH}_3)_5\text{Br}] \text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4] \text{Br}$ exhibit
1. Coordination isomerism.
 2. Ionisation isomerism.
 3. Hydrate isomerism.
 4. Geometrical isomerism.
- (ii) Cannizzaro's reaction is given by:
1. Formaldehyde.
 2. Acetaldehyde.
 3. Acetone.
 4. Ethanol.
- (iii) Out of the following solutions, the one having the highest boiling point will be:
1. 0.01 M Na_2SO_4 .
 2. 0.01 M KNO_3 .
 3. 0.01 M Urea.
 4. 0.01 M Glucose.
- (iv) The bond angle of water is:
1. 90°
 2. 105°
 3. 107.3°
 4. 120°
- (v) The co-ordination number of each ion in copper crystals is:
1. 4
 2. 12
 3. 14
 4. 8

(c) Answer the following questions:

[5]

- (i) The depression of freezing point caused by a 1M NaCl solution is 0.0123°C . What will be the depression of freezing point caused by a 1 M glucose solution?
- (ii) What happens to the pH of a solution containing equimolar amount of acetic acid and sodium acetate when a few drops of dilute HCl is added? Give reason.
- (iii) Express the relationship between molar conductivity and specific conductivity of a solution. What is the unit of molar conductivity?
- (iv) Give the electrode reactions of the galvanic cell in which the reaction $\text{Zn}(\text{s}) + 2 \text{Ag}^+(\text{aq}) \rightarrow \text{Zn}^{+2}(\text{aq}) + 2 \text{Ag}(\text{s})$ takes place.
- (v) How is the free energy change related to the enthalpy and entropy change of a substance?

(d) Match the following: [5]

- | | |
|------------------------------|--------------------------|
| (i) Buffer solution | (a) Co-ordinate bond |
| (ii) Co-ordination compounds | (b) Raoult's Law |
| (iii) Dilute solution | (c) Warner's Theory |
| (iv) Ammonium ion | (d) Faraday's Law |
| (v) Electrolysis | (e) Henderson's equation |

PART II

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

SECTION A

Answer any **two** questions

Question 2

- (a) (i) The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. When a non-volatile and non-electrolyte solid weighing 2.175 g is added to 39.0 g of benzene, the vapour pressure of the solution is 600 mm Hg. What is the molecular mass of the solid substance? [3]
- (ii) Calculate the standard enthalpy change for a reaction $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$. Given that ΔH_f° for $\text{CO}_2(\text{g})$, $\text{CO}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are -393.5 , -110.5 , and $-244.8 \text{ KJ mol}^{-1}$ respectively. [3]
- (b) Give reasons for the following:
- (i) A solution of copper sulphate is acidic in nature. [2]
- (ii) The boiling point of p-nitrophenol is more than that of o - nitrophenol. [2]

Question 3

- (a) (i) An element crystallizes in a structure having F.C.C. unit cell of an edge 200 pm. Calculate its density if 200g of this element contains 24×10^{23} atoms. [3]
- (ii) Draw the electron dot structure of perchloric acid clearly distinguishing between the electrons of each atom. [1]
- (b) (i) What is the activation energy of a reaction? How is the rate constant of a reaction related to the activation energy? How can activation energy be calculated from this relationship? [3]

- (ii) Consider the following data for the reaction $A + B \rightarrow \text{Products}$. [3]

Conc. of A (mol l ⁻¹)	Conc. of B (mol l ⁻¹)	Initial rate (mol l ⁻¹ s ⁻¹)
0.1	0.1	4.0×10^{-4}
0.2	0.2	1.6×10^{-3}
0.5	0.1	1.0×10^{-2}
0.5	0.5	1.0×10^{-2}

Calculate:

- The order with respect to A and B for the reaction.
- The rate constant of the reaction.

Question 4

- (a) (i) What is the type of hybridization in PCl_5 molecule? Explain why PCl_5 is very reactive in nature. [2]
- (ii) If 100 ml. of 0.1 M CH_3COOH is mixed with 200 ml of 0.5 M CH_3COONa , what will be the pH of the resulting mixture? [3]
- (b) Give reasons why: [5]
- Aluminium trichloride exists as a dimer.
 - When H_2S is passed through a solution of acidified copper nitrate and zinc nitrate, only copper is precipitated as sulphide.

SECTION B

Answer any **two** questions

Question 5

- (a) Explain how fluorine is prepared by the electrolysis of potassium hydrogen fluoride. [3]
- (b) Give balanced equations for each of the following reactions:
- Fluorine and dilute NaOH.
 - Ozone and aqueous potassium oxide. [2]

Question 6

- (a) Name the following compounds according to I.U.P.A.C. rules:
- $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$
 - $\text{K}[\text{Pt} \text{Cl}_3(\text{NH}_3)]$ [2]
- (b) Explain why an aqueous solution of potassium hexacyanoferrate(II) does not give a test for ferrous ion. [1]

- (c) Draw the geometrical isomers of the compound $[\text{Co}(\text{NH}_3)_2\text{Cl}_2]$ [1]
- (d) Write the formula of potassium trioxalatoferrate (III). [1]

Question 7

- (a) Write the steps involved in the preparation of potassium dichromate from chromite ore. [3]
- (b) Explain why transition metals form many co-ordination complexes. [2]

SECTION C

Answer any **two** questions

Question 8

- (a) How can the following conversions be brought about?
- Methyl amine to ethylamine. [2]
 - Propanol to isopropyl alcohol. [2]
 - Acetaldehyde to Acetone. [2]
- (b) Name the organic compounds which have the same molecular formula $\text{C}_2\text{H}_6\text{O}$. [3]
Write the reactions of these two compounds with PCl_5 .
- (c) An alkyl halide having the molecular formula $\text{C}_4\text{H}_9\text{Cl}$ is optically active. What is its structural formula? [1]

Question 9

- (a) Identify the compounds A, B, C and D. [2]

$$\text{CH}_3\text{COOH} \xrightarrow{\text{LiAlH}_4} \text{A} \xrightarrow{\text{red P, I}_2} \text{B} \xrightarrow{\text{Alc. KCN}} \text{C} \xrightarrow{\text{H}^+, \text{H}_2\text{O}} \text{D}$$
- (b) Give one good chemical test to distinguish between the following pairs of compounds: [2]
- Benzoic acid and phenol.
 - Formaldehyde and Acetaldehyde.
- (c) Fill in the blanks and name the following reactions. [3]
- $\text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH}_{(\text{alc.})} \xrightarrow{\Delta} \text{_____} + \text{KCl} + 3\text{H}_2\text{O}$
 - $\text{C}_6\text{H}_5\text{COCl} + \text{H}_2 \xrightarrow{\text{Pd/BaSO}_4} \text{_____} + \text{HCl}$
 - $$\text{C}_6\text{H}_5\text{OH} + \text{C}_6\text{H}_5\text{COCl} \xrightarrow{\text{OH}^-} \text{_____} + \text{HCl}$$

- (d) Give reasons for the following: [3]
- Phenol is acidic but ethanol is not.
 - Acetaldehyde does not give Cannizzaro's reaction but formaldehyde and benzaldehyde give the reaction.

Question 10

- (a) What are proteins? How are they formed? What is the primary structure of proteins? [3]
- (b) Give the monomers of: [2]
- Bakelite.
 - Nylon – 66.
- (c) An organic compound (A) on treatment with acetic acid in the presence of Sulphuric acid produces an ester (B). (A) on mild oxidation gives (C). (C) reduces Tollen's reagent to give silver mirror and (D). (D) on reacting with Phosphorous pentachloride followed by ammonia gives (E). (E) on dehydration produces methyl cyanide. Identify (A), (B), (C), (D) and (E) and write the relevant reactions. [5]