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Problem 1 **19 marks**

A. Crystal Structure

The structure of a crystal can be determined using the technique of X-ray diffraction. The English chemist William Bragg described this diffraction process in terms of an equation that now bears his name.

1.1 The minimum angle at which X-rays of wavelength 154 pm are reflected from the {111} planes of a simple cubic crystal of a metal is 11.2°. Find the dimension of the unit cell.

(2 marks)

1.2 What is the effective number of atoms in the above unit cell?

(0.5 mark)

1.3 Assuming the atoms to touch each other in the above cubic crystal lattice, what percentage of the space is occupied by the atoms?

(1.5 marks)

1.4 The interaction energy between two ions with charges q and –q placed at a distance R can be expressed as

$$E = -\frac{q^2}{4\pi\varepsilon_0 R} + \frac{A}{R^n}$$

where, the two terms represent purely electrostatic and repulsive contributions, respectively.

Find an expression for the positive constant A in terms of the equilibrium distance R_e for these two oppositely charged ions.

(2 marks)

1.5 Sketch qualitatively the variation of the individual terms as well as the total E (as given in **(1.4)**) as a function of R for the case n = 8.

.

(1.5 marks)

1.6 Obtain the expression for the interaction energy, when the two ions are at a distance of R_e. Hence, calculate the energy of interaction (kJ mol^{-1}) between the ions in NaCl molecule assuming it to be 100% ionic, the interionic distance being 281 pm. Assume n = 8 for these ions.

(1.5 marks)

1.7 Using the above result and the information given below, find the energy change associated with the process

$Na(g) + \frac{1}{2} Cl_2(g) \longrightarrow NaCl\ (g)$

ionization energy of Na (E_1) = 496 kJ mol^{-1}

electron affinity of Cl (E_2) = 350 kJ mol^{-1}

bond energy of Cl-Cl (E_3) = 241 kJ mol^{-1}

(2 marks)

B. Spectroscopy

1.8 An experiment on the measurement of the intensity of sunlight at various depths in the sea is being carried out at noon on a summer day. It is found that the intensity of sunlight reduces by a factor „f‟at a depth of 100 m. Assuming the intensity to fall off exponentially with depth, what will be the reduction of intensity at a depth of 200 m?

(2 marks)

1.9 The vibrational energy levels of a diatomic molecule corresponding to a harmonic oscillator model for its potential energy curve are characterized by the vibrational quantum number n (=0,1,2,…..etc) and are given by

$$E_n = \left(n + \frac{1}{2}\right)h\nu$$

where ν is the vibrational frequency.

Assuming Δn = ±1 as the condition to be satisfied for a transition between two energy levels, how many spectral lines would be observed in the vibrational spectrum of this model molecule and why?

(1 mark)

1.10 Does this model molecule in **1.9** dissociate into atoms? Explain your answer.

(0.5 mark)

1.11 A better representation of the potential energy curve for a diatomic molecule is given by the Morse potential, which incorporates anharmonicity correction with the quantized energy levels given as

$$E_n = \left(n+\frac{1}{2}\right)h\nu - \left(n+\frac{1}{2}\right)^2 x_e h\nu$$

where x_e is the anharmonicity constant.

What is the unit of x_e?

(0.5 mark)

1.12 Find the spacing between the two adjacent energy levels in **1.11** corresponding to the vibrational quantum numbers n and (n + 1).

(1 mark)

1.13 Hence, find the maximum number of vibrational energy levels possible for this diatomic molecule of **1.11**.

(1.5 marks)

1.14 For the HCl molecule with ^{35}Cl isotope, assume the potential energy to be given by $V(R) = \frac{1}{2} k(R - R_e)^2$ for small amplitude vibrations. Using k = 481 Nm^{-1}, calculate the wavenumber (cm^{-1}) for the transition from n = 0 to n = 1 vibrational levels of this molecule.

(1 mark)

1.15 Hence, find the value of the wavenumber for this transition of DCl molecule assuming the potential energy curve to be the same as that of HCl.

(0.5 mark)

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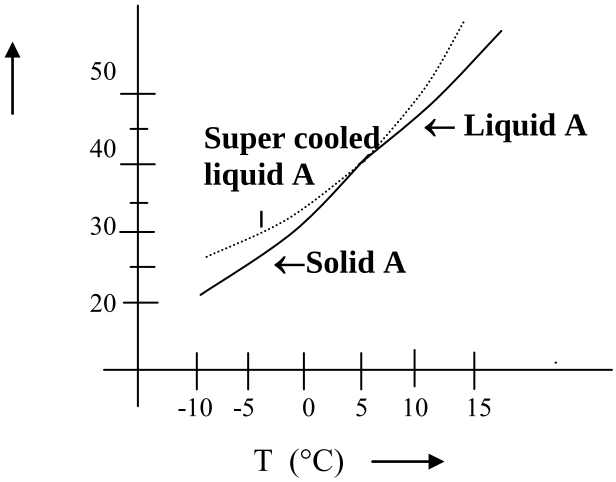
Problem 2 **12 marks**

Thermodynamics of Solutions

A research student is conducting her studies regarding depression of freezing point of solvents by dissolution of different salts. In one of her experiments, she prepares a 12.00% (w/w) solution of a nonvolatile substance **R** in solvent **A**. This solution is first cooled until solid **A** just begins to appear. At this temperature, the vapour pressure of the mixture (that is, of solvent A above the solution) is found to be 25 mm of Hg. The molecular mass of **A** is 78.11 g and its heat of fusion, $\Delta H_f = 9.95$ kJ mol^{-1}.

The following graph shows variation in vapour pressure with temperature for the solid and liquid phases of solvent **A**.



2.1 Answer the following questions from the above information and the graph.

a) Find out the freezing point of the solution.

b) Assuming the solution to be ideal, calculate the molecular mass of solute **R**.

c) Calculate the depression in freezing point ΔT_f for **A** and hence the cryoscopic constant K_f defined as $\Delta T_f = K_f.m$, where m is the molality of **R**.

(4 marks)

2.2 The same student receives another non-volatile solid sample, which is expected to have molecular mass = 278.35 or 285.21 or 300.15 g.

In order to estimate the molecular mass, she prepares the solution by dissolving 1.37 g of solid sample in 17.50 g of benzene. The freezing point of benzene is lowered by 1.44 ± 0.05 K. Which of the stated molecular masses she can rule out from the experimental data? (K_f for benzene = 5.12 K kg mol^{-1}).

(2 marks)

2.3 The same student prepares an aqueous solution of acetic acid by dissolving 0.60 g of acetic acid in 1000 g of water. Precise measurement in freezing point showed a depression of 19.5×10^{-3} K for this solution. Calculate the percentage of acetic acid that is ionized in water. ($K_{f \text{ for water}} = 1.86$ K kg mol^{-1}).

(3 marks)

2.4 While continuing her study with acetic acid, she dissolves 7g of acetic acid in 130 g of benzene. The vapor pressure of this solution was 13341 Pa at 25°C (vapour pressure of pure benzene at 25°C = 13816 Pa). Assuming acetic acid to be non-volatile, calculate the molecular mass of acetic acid in benzene. From this calculation, what can you say about the state of acetic acid in benzene? (Molecular mass of acetic acid = 60).

(3 marks)

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Problem 3 **10 marks**

Chemical Kinetics

3.1 The rate of a simple chemical reaction normally decreases with time as the reaction progresses. Which of the following statements explains this fact?

- i) The product acts as an inhibitor and suppresses the rate as it accumulates with time. ☐
- ii) Energy is taken away from the reaction mixture. The temperature of the mixture falls resulting into slower reaction rate. ☐
- iii) The reaction becomes reversible as time progresses. ☐
- iv) The reacting substances are present in less concentrated form. ☐

(0.5 mark)

3.2 Consider a first order reaction A$\rightarrow$ B with a rate constant k. There is no B present at t = 0. Make a qualitative sketch of the **Rate** of the reaction as time progresses.

(1 mark)

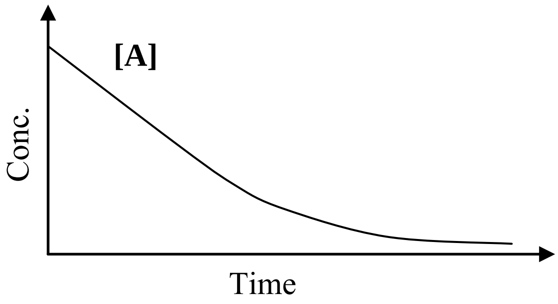
3.3 What is the value of the initial rate (R_0) in terms of k and the initial concentration (a_0) of **A**?

(0.5 mark)

3.4 For this reaction, calculate the time at which the rate becomes 0.368 times R_0.

(1 mark)

3.5 Make a qualitative sketch of concentration of **B** vs time on the following plot.



(1 mark)

3.6 How does the sum of concentrations [**A**] + [**B**] vary with time as the reaction progresses?

(1 mark)

3.7 For this first-order reaction, the concentration [**B**] of the product can be expressed as a series [**B**] = $\alpha + \beta t + \gamma t^2 + \ldots\ldots$..

Obtain the expressions for α, β, γ in terms of R_0 and k.

(2 marks)

3.8 Methyl acetate is hydrolyzed in approximately 1 mol L^{-1} HCl solution at 25 °C. Aliquots of equal volume are removed at intervals and titrated with a solution of NaOH. The titre values (V_t) at different times are given below.

t/s	339	1242	2745	4546	∞
V_t/mL	26.34	27.80	29.70	31.81	39.81

(i) Obtain the order of the reaction by plotting an appropriate graph? Explain your reason.

(ii) Calculate the rate constant.

(3 marks)

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Problem 4 15 marks

Chemistry of Iron

Iron belongs to a class of metals called transition metals that are generally hard, capable of forming alloys like steel and exhibit magnetic properties. Transition metal chemistry is dominated by coordination complexes and variable valence. Iron, its alloys, and its coordination complexes are of high industrial and biological importance.

4.1 Mark **X** in the correct box

a) The main ores of iron are compounds of iron with

(i) oxygen/nitrogen ☐

(ii) oxygen/sulphur ☐

(iii) nitrogen/sulphur ☐

(iv) nitrogen/chlorine ☐

b) Soluble iron present in ground water causes slow turbidity in water and "yellowing" of white cotton clothes washed with such water. This happens because

(i) iron gets oxidized by aerial oxygen from iron(II) to iron(III), which is hydrolyzed ☐

(ii) iron(II) present in ground water forms a complex with cellulose of white cotton clothes ☐

(iii) soluble iron salts get reduced by cellulose present in cotton clothes, causing coloration ☐

(iv) iron catalytically oxidizes cellulose to generate conjugated double bonds ☐

c) Anhydrous ferric chloride ($FeCl_3$) can be used

(i) as a desiccant for organic solvents ☐

(ii) as a catalyst for Friedel-Craft reaction ☐

(iii) as a primary standard for making solution with known iron ☐

(iv) for fortification of food to control iron deficiency anemia ☐

(3 marks)

4.2 Rust stains containing iron (III) can be removed by oxalic acids ($H_2C_2O_4$), as iron forms a soluble coordination complex with oxalic acid. Write appropriate chemical formula for the complex and give its IUPAC name.

(1 mark)

4.3 In iron compounds, iron is present in a bivalent or a trivalent state. Write the valence shell electronic configurations of Fe, Fe(II) and Fe(III).

(1 mark)

4.4 In an aqueous solution of $FeSO_4.7H_2O$, iron exists as an octahedral complex. Write the structure of this octahedral complex.

(1 mark)

4.5 In an octahedral ligand environment, the d orbitals of iron split. Show the splitting pattern of d orbitals of iron for the octahedral complex mentioned in **4.4**. Show the electronic configuration of the split d orbitals.

(1 mark)

4.6 Strong ligands like CN^- enforce pairing of spin, giving rise to a low-spin complex. What will be the electronic configuration of the split d-orbitals of iron in $[Fe(CN)_6]^{4-}$?

(1 mark)

4.7 What is the spin-only magnetic moments (in Bohr Magnetons) in high-spin and low-spin octahedral iron(II) complexes?

(1 mark)

4.8 Write balanced chemical equations with colors of the products for the reactions that takes place when

(i) an aqueous solution of Fe(II) is added to an aqueous solution of $[Fe(CN)_6]^{4-}$.

(ii) an aqueous solution of Fe(II) is added to an aqueous solution of $[Fe(CN)_6]^{3-}$.

☐

(iii) an aqueous solution of Fe(III) is added to an aqueous solution of $[Fe(CN)_6]^{4-}$.

☐

The species formed in reaction (ii) and (iii) are intensely colored. This is due to

(i) presence of unpaired electron/s in the species $[Fe(CN)_6]^{4-}$ ☐

(ii) intramolecular electron transfer between Fe(II) and Fe(III) ☐

(iii) intermolecular electron transfer between Fe(II) and Fe(III) ☐

(iv) formation of conjugate double bonds in the complex formed ☐

(4 marks)

4.9 Iron in haemoglobin can reversibly bind with oxygen, forming oxyhaemoglobin. In both oxyhaemoglobin and deoxyhaemoglobin, iron is essentially bivalent. However, oxyhaemoglobin is diamagnetic, whereas deoxyhaemoglobin is paramagnetic. Iron has a larger bonding radius in deoxyhaemoglobin than in oxyhemoglobin because

(i) in paramagnetic deoxyhaemoglobin, two adjacent Fe(II) units of similar magnetic polarity repel each other, leading to larger bonding radius ☐

(ii) in deoxyhaemoglobin, Fe(II) is high spin. The larger spinning speed of the Fe(II) ions keeps the ligands at a larger distance ☐

(iii) in deoxyhaemoglobin, the t_{2g} orbitals of Fe(II) are fully occupied with electrons, causing larger repulsion of the metal ion with ligands ☐

(iv) in deoxyhaemoglobin, there are two electrons in e_g orbitals of Fe(II), enforcing greater repulsion with ligand electrons ☐

(2 marks)

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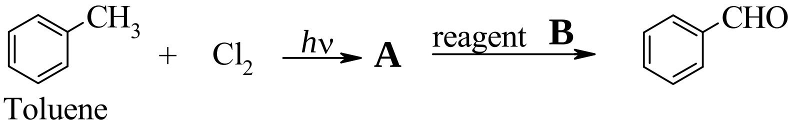
Problem 5 28 marks

Organic Chemistry of Perfumery Compounds

The compounds required in perfumery industry need high degree of purity. Benzaldehyde is one such perfumery compound. It can be prepared from toluene by the following route:



5.1 Identify compound **A** and reagent **B**.

(1.5 marks)

Benzaldehyde prepared by this route, quite often, does not have the desired odour demanded by the industry. The unacceptable odour is due to the presence of an impurity **C** (C_7H_5ClO). **C** on treatment with aqueous $KMnO_4$ gives **D**($C_7H_5ClO_2$), which on nitration can give only one mononitro derivative.

5.2 Identify the structures of **C** and **D**.

(2 marks)

5.3 Give an explanation for the formation of **C** in the above reaction and complete the sequence of reaction leading to **C** from toluene.

(3 marks)

In the reaction of Cl_2 with toluene, compounds **E** (C_7H_7Cl) and **F** ($C_7H_5Cl_3$) are also obtained along with **A**. **E** on warming with aqueous Na_2CO_3 forms **G** (C_7H_8O), which itself is a perfumery compound. **E** when heated with sodium acetate forms another perfumery compound **H**. **F** when heated with acetic acid, forms **two** compounds **I** (C_2H_3ClO) and **J** (C_7H_5ClO). **J** on reaction with C_6H_6 in the presence of $AlCl_3$ forms **K** ($C_{13}H_{10}O$), which is a perfumery compound.

5.4 Identify **E** to **K**.

(7 marks)

In a perfume, traces of foul odouring compounds are sometimes added. One such compound, which is rather expensive is **L** ($C_{16}H_{30}O$). It does not react with Br_2 and is optically active. It reacts with phenylhydrazine, but not with Tollen"s reagent.

5.5 Deduce the basic structural features of **L**.

(1.5 marks)

When **L** is oxidized with acidic $KMnO_4$, **two** isomeric acids **M** and **N** ($C_{16}H_{30}O_4$) are formed. One of these is optically active and can exist as a pair of enantiomers, while the other is optically inactive. 429 mg of **M/N** are neutralized by 30 mL of 0.1 N NaOH.

5.6 Draw the conclusion from this titration.

(1 mark)

Complete decarboxylation of the two acids gives two isomeric hydrocarbons **O** and **P** ($C_{14}H_{30}$). One of these has terminal isobranching, while the other is a linear hydrocarbon.

5.7 Identify the compounds **M** to **P**.

(3 marks)

5.8 Draw the structure of **L**. Draw its two stereoisomers and assign their absolute configurations.

(4 marks)

5.9 As a substitute to this costly compound **L**, compound **Q** ($C_{11}H_{13}N_3O_6$) has been developed. It is prepared by reacting toluene with *tert*-butyl chloride in the presence of $AlCl_3$ at an elevated temperature, resulting in compound **R**. **R** is reacted with a mix of conc. HNO_3 and conc. H_2SO_4 yielding **Q**. Write the structures of **R** and **Q**.

(3 marks)

5.10 To sense the odour of a substance, the sample is normally put on a piece of odour-free absorbing paper and waved in front of the nose. The same substance placed on the back of a clean hand smells quite different. This is because

(i) the compound reacts with the oily substance in the skin ☐

(ii) the compound spreads quickly on the skin, due to the low interfacial tension ☐

(iii) the warmth of the skin produces vapour of the compound in high concentration ☐

(iv) the compound produces different odour by interacting with some compounds present in the pores of the skin ☐

(1 mark)

5.11 It is an interesting fact that an ethanolic solution of a perfume ingredient smells like a perfume rather than ethanol. It is because

(i) the perfume ingredient vaporizes faster than ethanol ☐

(ii) the odour of ethanol is masked by the odour of the perfume ingredient ☐

(iii) the perfume ingredient suppresses the evaporation of ethanol ☐

(iv) the detectable concentration of ethanol is much higher than that of the perfume ingredient ☐

(1 mark)

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Problem 6 **12 marks**

6.1 K_a of acetic acid (HA) at 25°C is 1.75×10^{-5}. Calculate the concentrations of H^+, HA and A^- in a 0.1M solution of this acid.

(2 marks)

6.2 10 mL of 0.1M acetic acid is titrated with 0.1M solution of NaOH. A student titrated this solution using a burette with least count of 0.1 mL, whereas another titrated using a burette with least count 0.01 mL. Calculate the change in pH of the mixture when (i) volume of alkali added by the first student changes from 9.9 to 10.1 mL and (ii) volume of alkali added by the second student changes from 9.99 to 10.01 mL.

(3 marks)

6.3 Calculate ΔpH / ΔV for both the titrations in **6.2**, where ΔpH and ΔV denote the change in pH and volume, respectively. Comment on the result.

(1 mark)

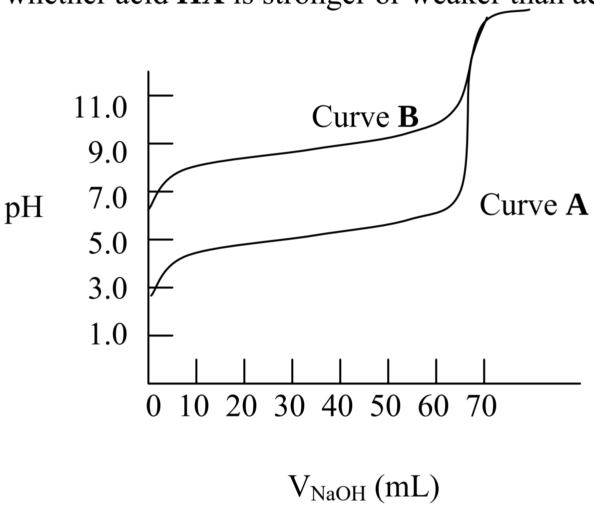
6.4 From the table given below, select the appropriate indicator/s for the titrations. Justify your answer.

Table 1: Some common acid/base indicators

Common name	**Transition range, pH**	**Color change**
Methyl orange	3.2 - 4.4	red-orange
Methyl red	4.2 - 6.2	red-yellow
Phenol red	6.8 - 8.2	yellow-red
Phenolphthalein	8.0 - 9.8	colorless-red

(1 mark)

6.5 In the following graph, curve **A** represents titration of acetic acid with 0.1 M NaOH. Curve **B** represents titration of another acid **HX** with 0.1 M NaOH. State, with reason, whether acid **HX** is stronger or weaker than acetic acid.



(1 mark)

6.6 A student of chemistry wants to prepare 100 mL of acetate buffer of pH = 5.0. She is given 0.5 M acetic acid and 0.426 M NaOH solutions. Calculate the volumes of acetic acid and NaOH to be mixed to prepare this buffer.

(4 marks)

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Problem 7 **9 marks**

7.1 Draw the electron-dot structures of the following molecules and highlight the lone pairs wherever they are present.

(i) HCN (ii) N_2H_4

(iii) CO_2 (iv) CO_3^{2-}

Identify with reasoning the most basic species of these.

(3 marks)

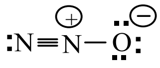
7.2 Draw the resonance structures of ozone molecule.

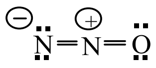
(1 mark)

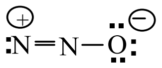
7.3 Which of the molecules in **7.1** and **7.2** may be expected to have a non-zero dipole moment?

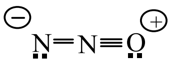
(2 marks)

7.4 The electronic structure of N_2O may be represented by the following Lewis structures. Which one is energetically most favorable and why?


A


B


C


D

(1 mark)

7.5 Using VSEPR theory, calculate the total valence shell electrons in SF_4 and SF_6 molecules. Draw structures with appropriate geometry of these molecules and indicate the location/s of lone pair/s wherever present.

(2 marks)

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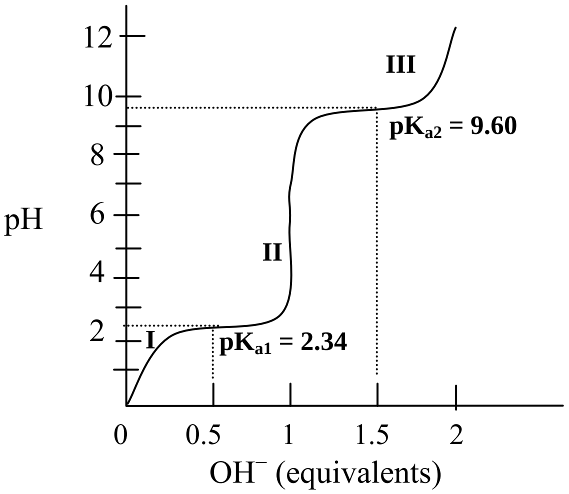
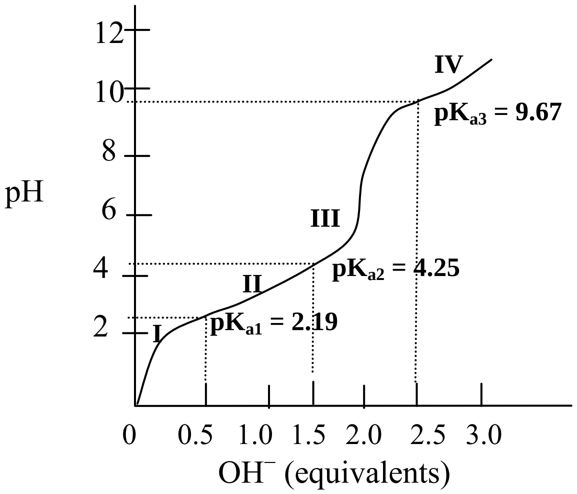
Problem 8 **15 marks**

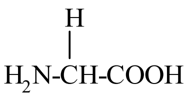
Amino Acids and Proteins

Amino acids are the building blocks of proteins. A mixture of amino acids was analyzed and the presence of two amino acids, glycine and glutamic acid, was confirmed. Separate titration curves of the individual amino acids (0.1M, 25°C) are shown below.



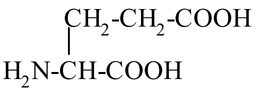


Glycine



$H_2N\text{-}CH(H)\text{-}COOH$

Glutamic acid



$H_2N\text{-}CH(CH_2\text{-}CH_2\text{-}COOH)\text{-}COOH$

During the course of the titration, the fully protonated amino acid loses its proton to neutralize the added base. This results in change of the pH, which in turn affects the structure of the amino acid at different stages of titration. The pH at which the amino acid remains fully ionized with no net electric charge is called isoelectric point (pI).

8.1 Write the structures of glutamic acid at different stages **I**, **II**, **III** and **IV** shown in the titration curve of glutamic acid.

(2 marks)

8.2 Calculate the isoelectric points (or isoelectric pH) for glycine and glutamic acid. Explain the difference in the pI values.

(3 marks)

8.3 Since amino acids exist in solution as charged molecules, they can be separated in a column containing suitable resins. The resins used for this purpose have charged groups that help in the separation of amino acid species.

(i) At pH = 3, to separate glycine and glutamic acid mixture, the resin should have

Negatively charged group ☐ Positively charged group ☐

Justify your answer.

(1.5 marks)

(ii) At this pH, which of the two amino acids will be eluted out (that is, will come out of the column) first and why?

(1.5 marks)

8.4 Amino acids can act as buffers. Specify the buffering pH/s for

(i) glycine and

(ii) glutamic acid

(iii) Give your opinion with reason, if either of the amino acids can act as buffer at physiological pH = 7.4

(3 marks)

8.5 Substances such as amino acids, that can act as either acids or bases in an aqueous solution are known as amphoteric. Explain by appropriate reactions how glycine behaves as an amphoteric substance in an aqueous solution.

(1 mark)

8.6 Proteins (polypeptides) take up specific three-dimensional structures in aqueous solutions. Secondary structure of protein refers to the regular, recurring arrangements of adjacent amino acids residues in space. α-helix is that secondary structure in which the polypeptide winds itself around a long axis forming a helix.

(i) At alkaline pH, how a repetitive sequence of glycine and glutamic acid will affect the α-helical structure of the protein?

(2 marks)

(ii) Name the amino acid that can form additional H-bond (other than the H-bond formed due to interaction between groups involved in peptide bond). Why?

(1 mark)