

INCHO 2004

Problem 1

19 marks

A. Crystal Structure

1.1

$$a = \sqrt{3} \cdot d = 687 \text{ pm}$$

1.2

$$\text{Number} = 8 \times \frac{1}{8} = 1$$

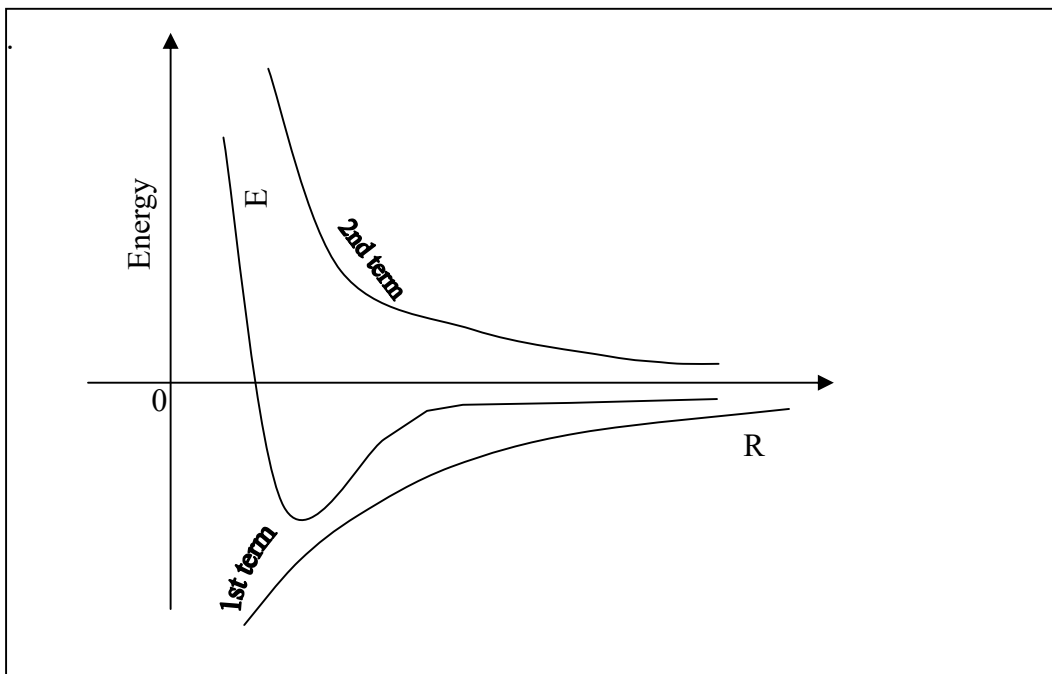
1.3

% of the occupied volume is 52

1.4

$$A = \frac{1}{n} \frac{q^2}{4\pi\epsilon_0} \cdot R_e^{n-1}$$

1.5



1.6

$$E_{\text{ion-ion}} = -432.4 \text{ kJ mol}^{-1}$$

1.7

$$\Delta E = 165.89 \text{ kJ mol}^{-1}$$

B. Spectroscopy

1.8

Reduction of intensity will be by a factor of f^2 .

1.9

Since $\Delta(n) = \pm 1$ corresponds to $\Delta E = h\nu$, only one line will be observed

1.10

No. Since the energy required to separate the atoms is infinite as is clear from the harmonic oscillator potential energy expression
 $V(R) = \frac{1}{2} k (R - R_e)^2$.

1.11

x_e is dimensionless

1.12

$$\Delta E_{(n)} = E_{(n+1)} - E_{(n)} = h\nu [1 - 2x_e(n+1)].$$

1.13

The total number of vibrational energy levels possible is $n_{\max} + 1 = 1/2x_e$, Since $n = 0$ is also one energy levels.

1.14

$$\bar{\nu} = 2897 \text{ Cm}^{-1}$$

1.15

$$\bar{\nu}_2 = 1488.9 \text{ Cm}^{-1}$$

Problem 2

12 marks

Thermodynamics of Solutions

2.1

- a) Freezing point of the solution = $-5\text{ }^{\circ}\text{C}$.
- b) molecular mass of **R** = $12/0.188 = 63.83\text{g}$
- c) $\Delta T_f = 1.612\text{ mol kg}^{-1}$
 $K_f = 5.73\text{ K kg mol}^{-1}$

2.2

The molecular mass of 300.15 g will be ruled out.

2.3

% of acetic acid dissociated = 4.83

2.4

The molecular mass of acetic acid in benzene = 118 g

Since the molecular mass of acetic acid in benzene is twice its molecular mass
 \Rightarrow acetic acid dimerizes in benzene

Problem 3

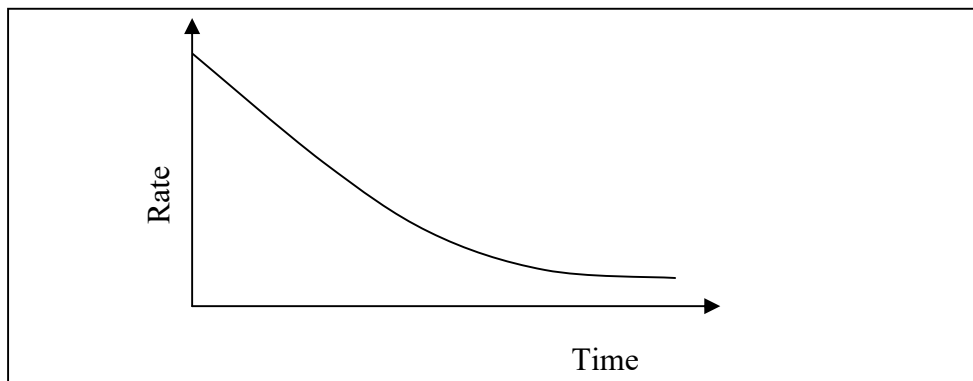
10 marks

Chemical Kinetics

3.1 iv) The reacting substances are present in less concentrated form.



3.2



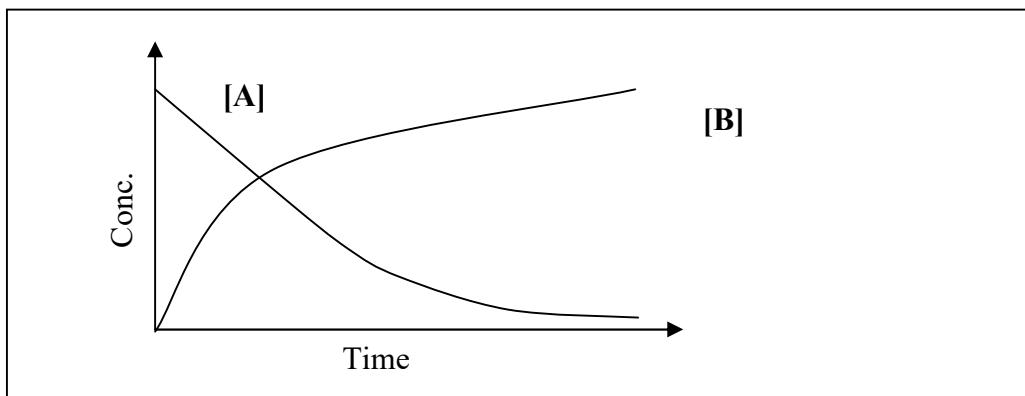
3.3

$$R_0 = k \cdot a_0$$

3.4

$$t = \frac{1}{k}$$

3.5



3.6

[A] + [B] is constant

3.7

$$\alpha = 0, \quad \beta = R_0, \quad \gamma = \frac{R_0 k}{2}$$

3.8

Plot of $\ln(V_\infty - V_t)$ vs t is linear. First order reaction.

$$k = 1.32 \times 10^{-4} \text{ s}^{-1}$$

Problem 4

15 marks

Chemistry of Iron

4.1

a) ii) oxygen/sulphur



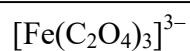
b) i) iron gets oxidized by aerial oxygen from iron(II) to iron(III)
which is hydrolyzed



c) ii) as a catalyst for Friedel-Craft reaction

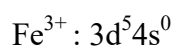
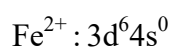
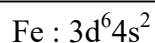


4.2

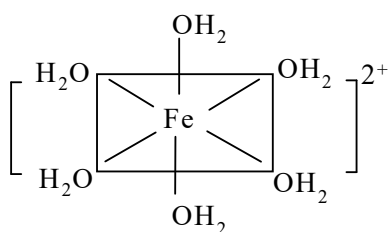


Name : tris oxalato ferrate(III)

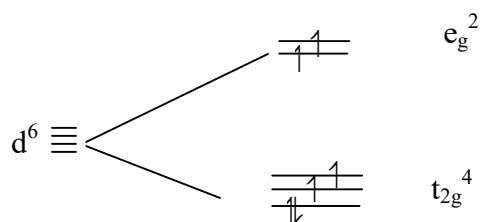
4.3



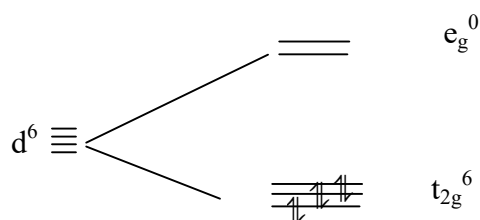
4.4



4.5



4.6

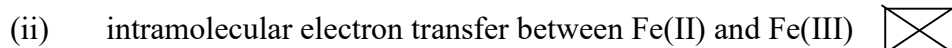
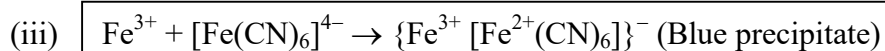
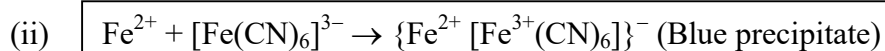
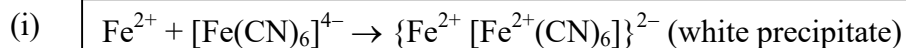


4.7

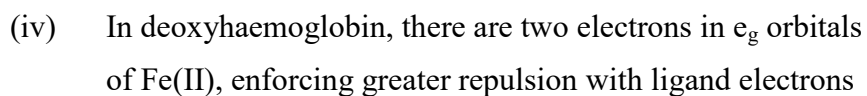
High Spin: $t_{2g}^4 e_g^2 = 4$ unpaired electrons: $\sqrt{24}$ BM (spin only)

Low Spin: $t_{2g}^6 e_g^0 =$ no unpaired electrons: 0 BM (spin only)

4.8



4.9

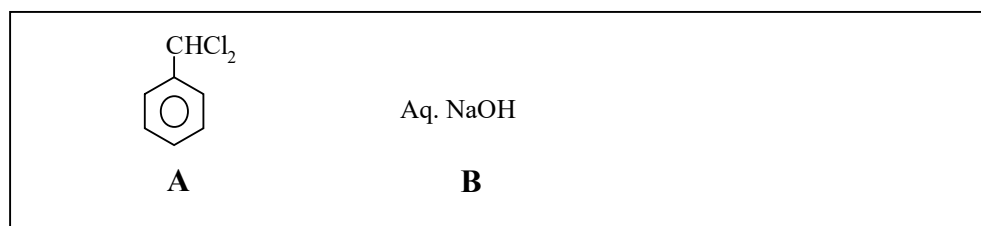


Problem 5

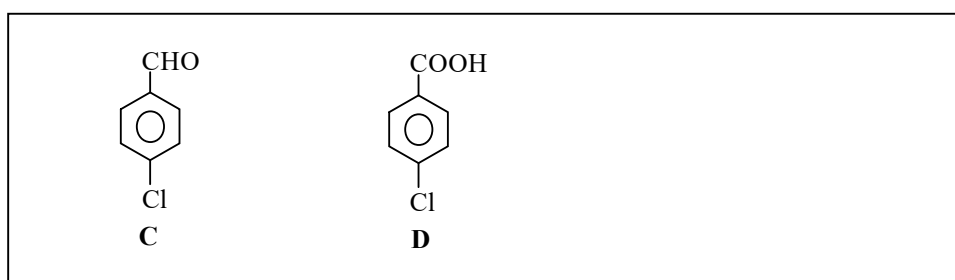
28 marks

Organic Chemistry of Perfumery Compounds

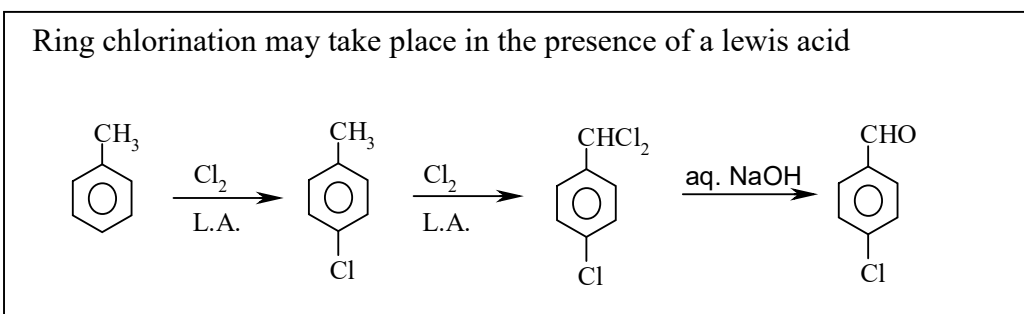
5.1



5.2

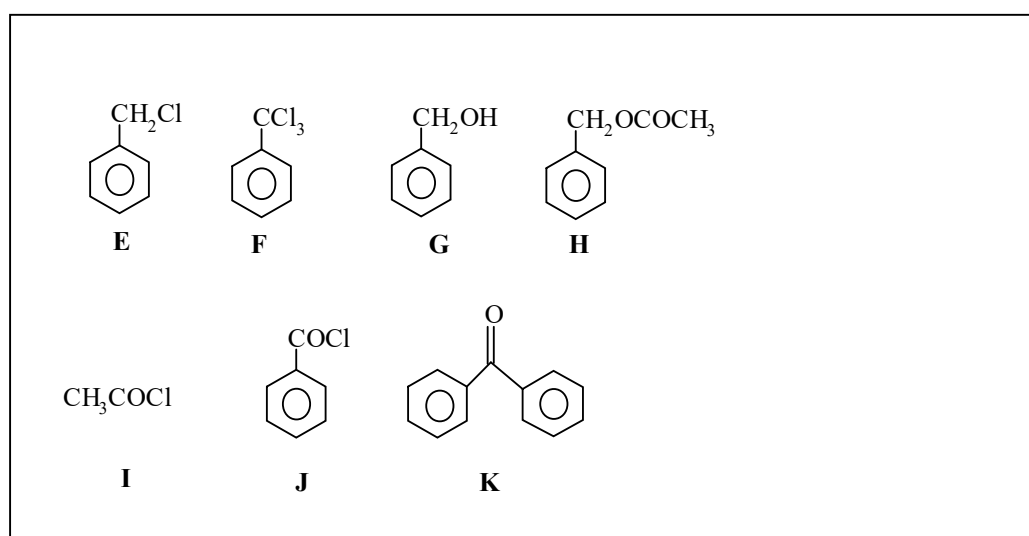


5.3



5.4

Identify E to K.



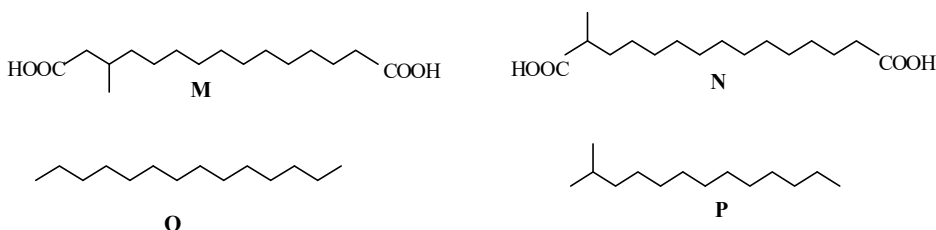
5.5

Saturated cyclic ketone.

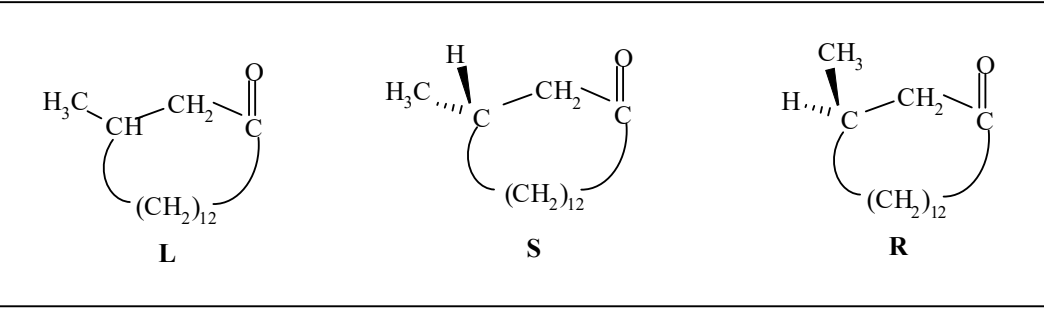
5.6

The acids are dicarboxylic acids.

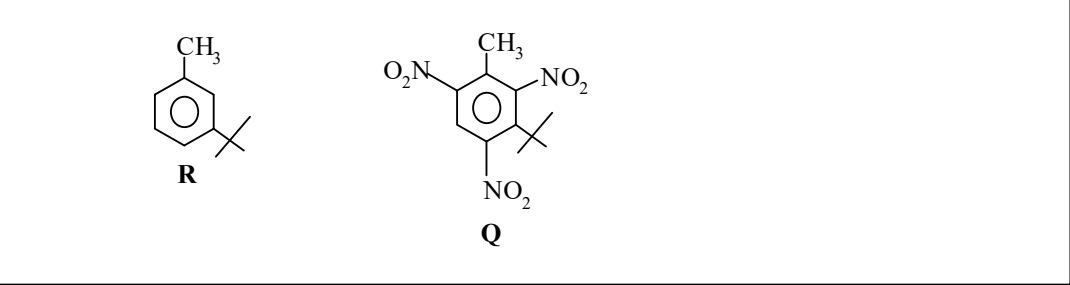
5.7



5.8



5.9



5.10

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



5.11

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



Problem 6

12 marks

6.1

$$[\text{H}^+] = 1.32 \times 10^{-3} \text{ mol L}^{-1}.$$

$$[\text{A}^-] = 1.32 \times 10^{-3} \text{ mol L}^{-1}.$$

$$[\text{HA}] = 0.1 - 1.32 \times 10^{-3} = 0.0987 \text{ mol L}^{-1}$$

6.2

(i) Change in pH = 3.94

(ii) Change in pH = 1.943

6.3

$$\Delta\text{pH} / \Delta V = 3.94/0.2 = 19.7$$

$$\Delta\text{pH} / \Delta V = 1.943/0.02 = 97.15$$

6.4

Both Phenol red and Phenolphthalein can be used as indicators. The pH range for change in colour for these indicators coincides with the pH change at the equivalence point

6.5

From Curve **B** buffer range for acid **HX** $\approx 8 - 10$, $\Rightarrow \text{pK}_a \approx 9$

From Curve **A** buffer range for acetic acid $\approx 4.5 - 5.3$, $\Rightarrow \text{pK}_a \approx 4.8$

So acid **HX** is a weak acid as compared to acetic acid.

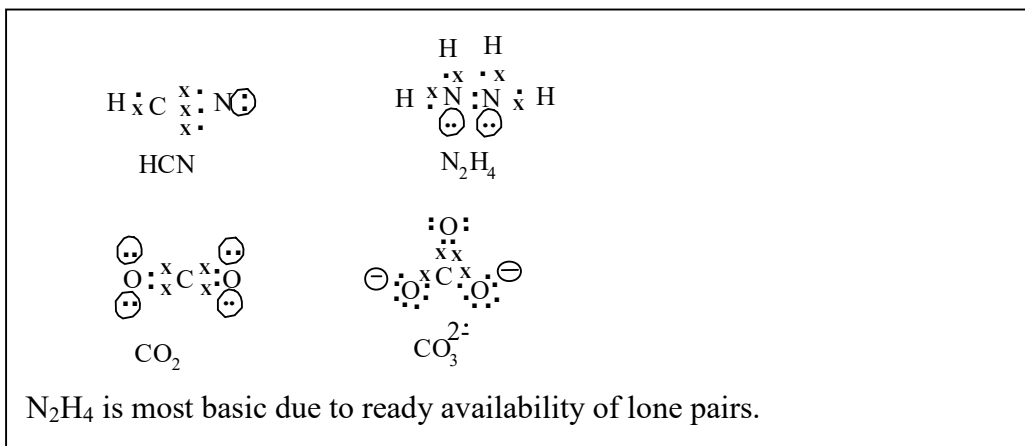
6.6

So, we need to mix 42.8 mL of 0.426 M NaOH and 57.2 mL of 0.5 M acetic acid to prepare 100 mL the desired buffer

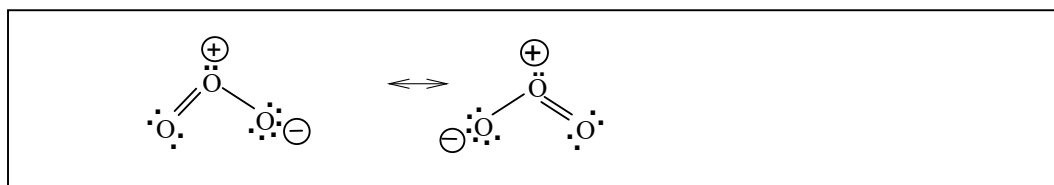
Problem 7

9 marks

7.1



7.2



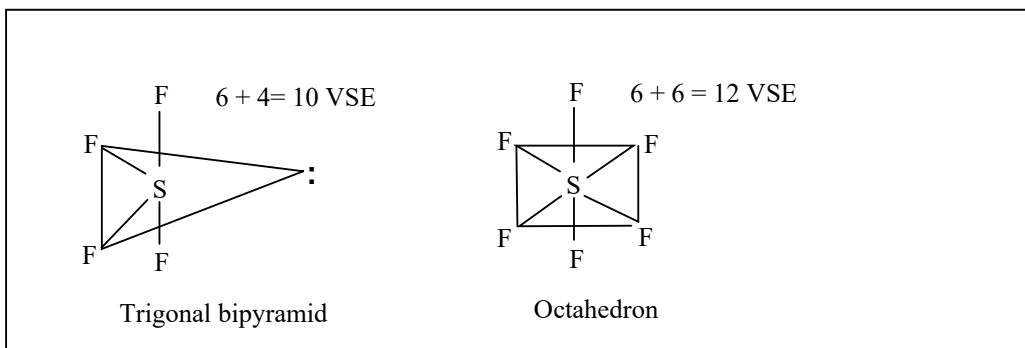
7.3

HCN and O_3 are expected to have a non-zero dipole moment.

7.4

A is energetically most favorable. Oxygen is more electronegative than nitrogen. The structure with negative charge on 'O' is more favorable than the one with negative charge on 'N'.

7.5

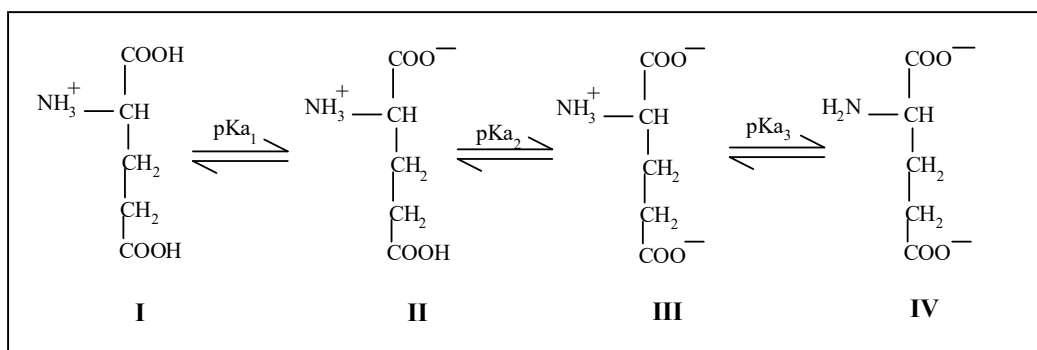


Problem 8

15 marks

Amino Acids and Proteins

8.1



8.2

Isoelectric point (pI) of glycine = $(2.34 + 9.60)/2 = 5.97$

pI of glutamic acid = $(2.19 + 4.25)/2 = 3.22$

pI of glutamic acid is less than glycine since glutamic acid contains an ionizable $-\text{COOH}$ group in the side chain.

8.3

(i) Negatively charged group

Justify your answer.

At pH 3.0, both the amino acids have positive charge. So, negatively charged resins should be used for their separation.

(ii)

The amino acid with lower pI elutes first, that is, glutamic acid in this case.

8.4

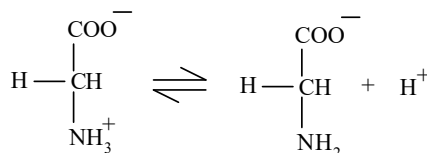
(i) Glycine : 2.34 and 9.60

(ii) Glutamic acid : 2.19, 4.25 and 9.67

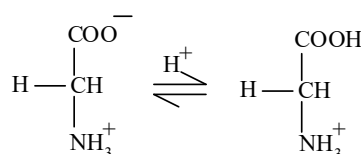
(iii) Neither of the amino acids can act as buffer at pH of 7.4. The buffering region varies by ≈ 1.2 units about the pK_a . For glycine, this region will be 9.6 ± 1.2 and similarly for glutamic acid = 9.67 ± 1.2 .

8.5

As proton donor (acid)



As proton acceptor (base)



- 8.6 (i) At alkaline pH, the side chain $-\text{COOH}$ group will be negatively charged.
- Hence repetitive sequence of glutamic acid will have repulsive force destabilizing the α -helical structure.
- Glycine has small side chain with only hydrogen that allows the peptides to have flexibility of assuming multiple conformations hence destabilizes the α -helical structure.
- (ii) Glutamic acid can contribute in formation of the H-bond due to the presence of $-\text{COOH}$ group in the side chain.