THE PREPARATORY PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS

Series 3

33rd – 37th IChOs
2001 – 2005

Edited by Anton Sirota

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33rd

International Chemistry Olympiad

PREPARATORY PROBLEMS

Edited by Anton Sirota

24 theoretical problems
6 practical problems

2001

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The Preparatory Problems from the 33rd IChO

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Preparatory Problems

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Notes:

- The symbol [X] denotes concentration of X. It may carry the unit mol dm^{-3} or, in some places, may denote concentration relative to the standard concentration of exactly 1 mol dm^{-3} in which case it is dimensionless. The particular usage should be obvious from the context. All equilibrium constants are dimensionless.
- The knowledge of mathematics required for the contest problems of the 33rd IChO will be no more than that indicated by the problems in this collection.

THE THIRTY THIRD INTERNATIONAL CHEMISTRY OLYMPIAD 6 – 15 JULY 2001, MUMBAI, INDIA

PREPARATORY PROBLEMS

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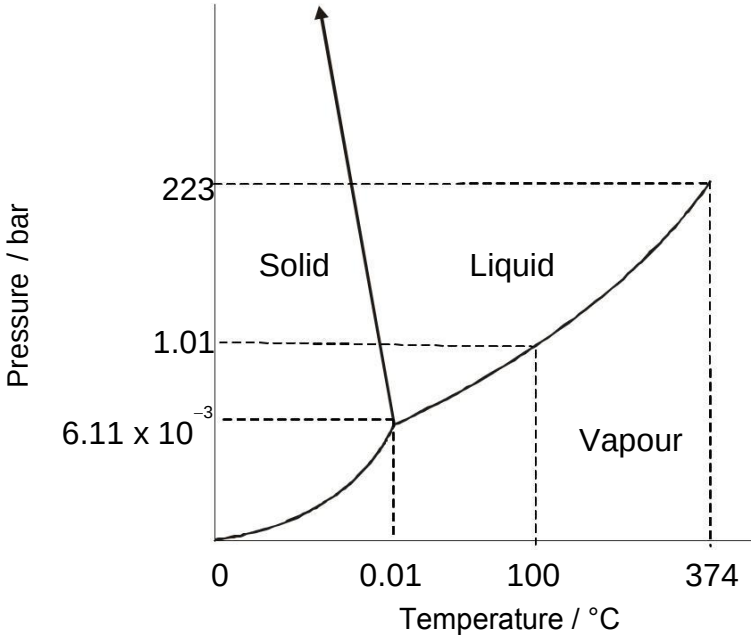
PREPARATORY THEORETICAL PROBLEMS

THEORETICAL PROBLEM 1

Water

Water, the commonest substance around us, is an excellent system to understand many concepts of thermodynamics. It exists in three different phases: solid (ice), liquid and vapour. [At high pressures, different solid phases of ice exist, but we do not consider them here.] The phase diagram for water, which gives the pressure versus temperature curves for its different phases in equilibrium, is shown below :

Phase diagram:



Phase diagram of water (not to scale)

1.1 At what temperature and pressure do all the three phases of water coexist in equilibrium?

1.2 What is the effect of decrease of pressure on boiling point of water and melting point of ice, as seen from the phase diagram?

1.3 The liquid-vapour coexistence curve ends at the point pc = 223 bar and Tc = 374 °C. What is the significance of this point?

1.4 What is the phase of water at T = 300 K, p = 12.0 bar; T = 270 K, p = 1.00 bar?

1.5 Below what value of pressure will ice, when heated isobarically, sublimate to vapour?

1.6 At a certain temperature and pressure on the liquid-vapour co-existence line, the molar volumes of water in the two phases are

$V_{liq} = 3.15\times10^{-5}$ m^3 $\quad$ $V_{vap} = 15.8\times10^{-5}$ m^3

Determine the volume fractions in liquid and vapour phases for 1.00 mol of water in a 0.100 dm^3 vessel at this temperature and pressure,

B Clausius – Clapeyron equation

1.7 Explain your answer to part **1.1 ii.** above on the basis of the Clapeyron equation.

1.8 Autoclaves used for medical sterilisation need to have a temperature of 120°C of boiling water to kill most bacteria. Estimate the pressure required for the purpose. The molar enthalpy change of vaporisation of water is 40.66 kJ mol^{-1} at the normal boiling point. Indicate the assumptions made in your estimate.

1.9 The molar enthalpy change of fusion at normal freezing point (273.15 K) is 6008 J mol^{-1}. Estimate the pressure at which water and ice are in equilibrium at –0.200 °C. Density of ice is equal to 917 kg m^{-3} and that of water is 1000 kg m^{-3}. Indicate the assumptions made in your estimate.

C Irreversible condensation

1.10 Consider 28.5 g of supercooled (liquid) water at –12.0 °C and 1.00 bar. Does this state lie on the p – T plane of the phase diagram?

1.11 This metastable state suddenly freezes to ice at the same temperature and pressure. Treat the metastable state as an equilibrium state and calculate the heat released in the process. Molar heat capacities, assumed constant, are :

$C_{p(\text{ice})} = 76.1$ J K^{-1}mol^{-1}

$C_{p(\text{liquid water})} = 37.15$ J K^{-1}mol^{-1}

$\Delta H_{(\text{fusion})} = -333.5$ J g^{-1}

1.12 Determine the total entropy change of the universe in the process and assure yourself that the answer is consistent with the Second Law of Thermodynamics. Take the surroundings to be at –12.0 °C.

_____

SOLUTION OF PREPARATORY PROBLEM 1

A. Phase diagram

1.1 The three phases of water coexist in equilibrium at a unique temperature and pressure (called the triple point):

T_{tr} = 273.16 K = 0.01 °C $p_{tr} = 6.11\times10^{-3}$ bar

1.2 If pressure decreases, boiling point decreases, but melting point increases (slightly).

1.3 Beyond this point, there is no distinction between liquid and vapour phases of water. Put alternatively, it is possible to have liquid to vapour transition by a continuous path going around the critical point. (In contrast, solid-liquid transition is discontinuous.)

1.4 T = 300 K, p = 12.0 bar: liquid phase

T = 270 K, p = 1.00 bar: solid phase

1.5 Below $p = 6.11\times10^{-3}$ bar, ice heated isobarically will sublimate to vapour.

1.6 If x_l and x_v are the mole fractions of water in liquid and vapour phases, respectively.

$$V = x_l \overline{V}_l + x_v \overline{V}_v = x_l \overline{V}_l + (1 - x_l)\overline{V}_v$$

$$x_l = \frac{\overline{V}_v - V}{\overline{V}_v - \overline{V}_l} = 4.6\times10^{-1}$$

$$\frac{V_l}{V} = \frac{x_l \overline{V}_l}{V} = 0.140$$

$$\frac{V_v}{V} = 1 - 0.140 = 0.860$$

B. Clausius – Clapeyron equation

1.7 $$\frac{dp}{dT} = \frac{\Delta\overline{H}}{T\,\Delta\overline{V}}$$

$\Delta\overline{H}$ = molar enthalpy change in phase transition

$\Delta\overline{V}$ = molar change in volume in phase transition

For ice – liquid water transition:

$\Delta\overline{H} > 0$ $\Delta\overline{V} < 0$ since ice is less dense than water.

$$\frac{dp}{dT} < 0$$

Since $\left|\Delta\overline{V}\right|$ is not large, the *p* – *T* curve for this transition is steep with a negative slope. Thus, decrease of pressure increases the melting point slightly.

For liquid water - vapour transition:

$\Delta\overline{H} > 0$ $\Delta\overline{V} < 0$

$$\frac{dp}{dT} > 0$$

Decrease of pressure decreases the boiling point.

1.8 *Clausius - Clapeyron equation for (solid) liquid – vapour transition is*

$$\frac{dp}{dT} = \frac{p\,\Delta\overline{H}_{vap}}{RT^2}$$

This equation follows from the Clapeyron equation under the assumptions:

1. Vapour follows ideal gas law.
2. Molar volume of the condensed phase is negligible compared to molar volume of vapour phase.
3. If further $\Delta\overline{H}_{vap}$ is assumed to be constant (no variation with *T*), the eq. is integrated to give

$$\ln\frac{p_2}{p_1} = \frac{\Delta\overline{H}_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Here p_1 = 1.01 bar , T_1 = 373.15 K

T_2 = 393.15 K $\Delta\overline{H}_{vap}$ = 40.66 kJ mol^{-1}

R = 8.31 J K^{-1} mol^{-1}

Then: p_2 = 2.01 bar

The estimate is based on the assumptions 1, 2 and 3.

1.9 *For ice - liquid water equilibrium, use Clapeyron equation*

At T_1 = 273.15 K, p_1 = 1.01 bar

Assume that for a small change in T, $\frac{\Delta\overline{H}}{\Delta\overline{V}}$ is constant.

Integrating the Clapeyron equation above

$$p_2 - p_1 = \frac{\Delta\overline{H}}{\Delta\overline{V}} \ln\left(\frac{T_2}{T_1}\right)$$

T_2 = 272.95 K $\quad \Delta\overline{H}_{fusion} = 6008\ \text{J mol}^{-1}$

$$\Delta\overline{V} = \left(\frac{1}{1.00} - \frac{1}{0.917}\right) \times 18.015 = -1.63 \times 10^{-6}\ \text{m}^3\,\text{mol}^{-1}$$

$p_2 - p_1$ = 27.0 bar

p_2 = 28.0 bar

The estimate is based on assumption 1.

C. Irreversible condensation

1.10 On the p -T plane, this equilibrium state is a solid phase (ice). Water in liquid phase at this temperature and pressure is not an equilibrium state - it is a supercooled state that does not lie on the given p -T plane.

1.11 Treating the metastable state as equilibrium state, we can go from the supercooled liquid state to the solid state at the same temperature and pressure by a sequence of 3 reversible steps.

1. *Supercooled liquid at -12.0 °C to liquid at 0 °C*

   q_1 = number of moles × $\overline{C_p}$ (liquid water) × change of temperature

2. *Liquid at* 0 °C *to ice at 0 °C*

   q_2 = 28.5 g × (–333.5) = 9505 J

3. *Ice at 0 °C to ice at* –12.0 *°C*

q_3 = number of moles × $\overline{C_p}$ (liquid water) × change of temperature

$$= \frac{28.5\ \text{g}}{18.015\ \text{g mol}^{-1}} \times 37.15\ \text{J K}^{-1}\text{mol}^{-1} \times (-12.0\ \text{K}) = -705.3\ \text{J}$$

$q = q_1 + q_2 + q_3 = -8765$ J

Since all the steps are at the constant pressure of 1.00 bar,

$q = \Delta H$

But ΔH is independent on the path, i. e. it depends only on the end points. Thus for the irreversible condensation of supercooled liquid to ice

$q = \Delta H = -8765$ J

1.12 The actual irreversible path between the two end states of the system is replaced by the sequence of three reversible steps, as above. ΔS can be calculated for each reversible step.

$$\Delta S_1 = n \int_{T_1}^{T_2} \frac{\overline{C_p}}{T}\, dT = n\, \overline{C_p} \ln \frac{T_2}{T_1}$$

$$\Delta S_1 = \frac{28.5\ \text{g}}{18.015\ \text{g mol}^{-1}} 76.1\ \text{J K}^{-1}\ \text{mol}^{-1} \times \ln \frac{273.15\ \text{K}}{261.15\ \text{K}} = 5.41\ \text{J K}^{-1}$$

$$\Delta S_2 = \frac{\Delta H_2}{T} = \frac{-9505}{273.15} = -34.79\ \text{J K}^{-1}$$

$$\Delta S_3 = \frac{28.5\ \text{g}}{18.015\ \text{g mol}^{-1}} 37.15\ \text{J K}^{-1}\ \text{mol}^{-1} \times \ln \frac{261.15\ \text{K}}{273.15\ \text{K}} = -2.64\ \text{J K}^{-1}$$

$\Delta S_{\text{system}} = \Delta S_1 + \Delta S_2 + \Delta S_3 = -32.02\ \text{J K}^{-1}$

$$\Delta S_{\text{sur}} = \frac{q_{sur}}{T_{sur}} = \frac{8765}{261.15} = 33.56\ \text{J K}^{-1}$$

$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{sur}} = 1.54\ \text{J K}^{-1}$

The entropy of the universe increases in the irreversible process, as expected by the Second Law of Thermodynamics.

THEORETICAL PROBLEM 2

Van der Waals gases

The ideal gas equation $p\,V = n\,R\,T$ implies that the compressibility factor

$$Z = \frac{p\,V}{n\,R\,T} = 1$$

However, the compressibility factor is known to deviate from 1 for real gases. In order to account for the behavior of real gases, van der Waals proposed the following equation of state :

$$\left(p + \frac{n^2\,a}{V^2}\right)(V - nb) = n\,R\,T$$

where *a* and *b* are constants, characteristic of the gas. The constant *a* is a measure of theintermolecular force and b that of the size of the molecules.

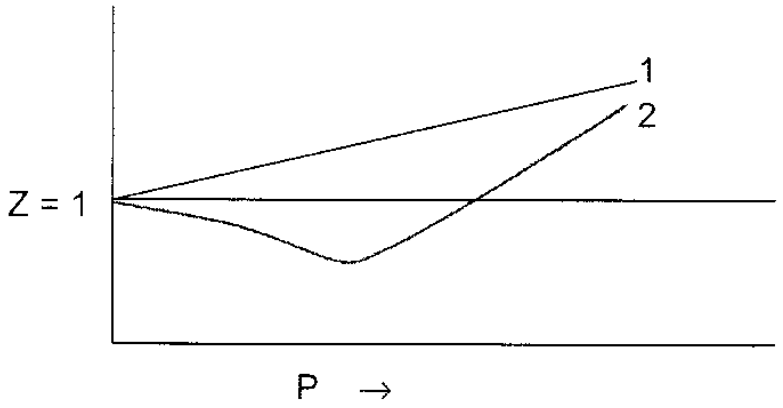
2.1 Show on the basis of van der Waals equation that

i. at sufficiently high temperatures Z is greater than unity for all pressures. At high temperatures and low pressures, Z approaches the value for an ideal gas.

ii. at lower temperatures, Z can be less than unity.

iii. for a = 0, Z increases linearly with pressure.

2.2 At a certain temperature, the variation of Z with P for He and N_2 is shown schematically in the following figure.



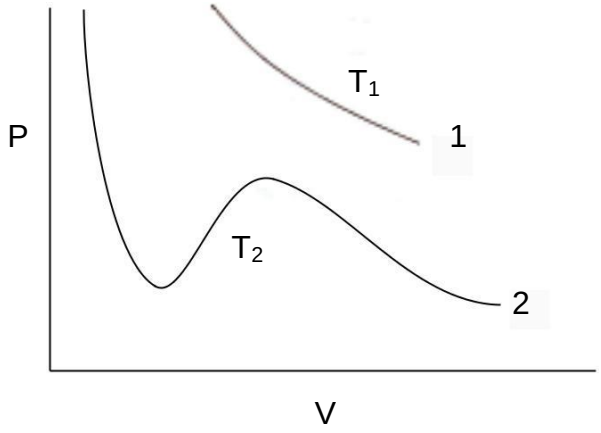
For He, $a = 3.46\times10^{-2}$ bar dm^6 mol^{-2} and $b = 2.38\times10^{-2}$ dm^3 mol^{-1}

For N_2, $a = 1.37\times10^{-2}$ bar dm^6 mol^{-2} and $b = 3.87\times10^{-2}$ dm^3 mol^{-1}

Identify the graph corresponding to He and N_2.

2.3 Two *p*-*V* isotherms of a van der Waals gas are shown below schematically.

Identify the one that corresponds to a temperature lower than the critical temperature (T_c) of the gas.



2.4 For a given *P*, the three roots of van der Waals equation in V coincide at a certain temperature $T = T_c$. Determine T_c in terms of a and b, and use the result to show that N_2 is liquefied more readily than He.

2.5 Determine the work done by 1 mol of N_2 gas when it expands reversibly and isothermally at 300 K from 1.00 dm^3 to 10.0 dm^3, treating it as a van der Waals gas.

SOLUTION OF PREPARATORY PROBLEM 2

2.1 For a van der Waals gas

$$Z = \frac{pV}{nRT} = 1 + \frac{\mathrm{b}p}{RT} - \frac{n\,\mathrm{a}}{V\,R\,T} + \frac{n^2\,a\,b}{V^2\,R\,T}$$

The ratio of the magnitudes of the second and third terms on the right side is:

$\frac{\mathrm{b}}{n\,\mathrm{a}}\,pV = \frac{\mathrm{b}}{\mathrm{a}}\,RT$, taking $p\,V = n\,R\,T$ up to zeroth order.

The ratio of the magnitudes of the fourth and third terms on the right side is :

$$\frac{n\,\mathrm{b}}{V} = \frac{\mathrm{b}\,p}{RT}$$

i. From the ratios above, it follows that at sufficiently high temperature for any given pressure, the second term dominates the third and fourth terms. Therefore,

$$Z = 1 + \frac{\mathrm{b}p}{RT} > 1$$

For small p, Z nearly equals to one.

ii. At lower temperatures, the third term can be greater (in magnitude) than the second term. It may be greater (in magnitude) than the fourth term also, provided p is not too large. Since the third term has a negative sign, this implies that Z can be less than unity.

Iii. For a = 0

$$Z = 1 + \frac{\mathrm{b}\,p}{RT}$$

which shows that Z increases linearly with p.

2.2 Helium has negligible value of a. Graph (1) corresponds to He and (2) corresponds to N_2.

2.3 Above $T > T_c$, only one phase (the gaseous phase) exists, that is the cubic equation in V has only one real root. Thus isotherm (2) corresponds to $T < T_c$.

2.4 At $T = T_c$ the three roots concide at $V = V_c$. This is an inflexion point.

$$\left.\frac{dp}{dV}\right/_{V_c} = \left.\frac{d^2p}{dV^2}\right/_{V_c} = 0$$

The first condition gives

$$\frac{RT_c}{(V_c - n\mathrm{b})^2} = \frac{2n\mathrm{a}}{V_c^{\,3}} \qquad (1)$$

The second condition gives

$$\frac{RT_c}{(V_c - n\mathrm{b})^2} = \frac{3\,n\,\mathrm{a}}{V_c^{\,4}} \qquad (2)$$

These equations give

$V_c = 3\,n\,\mathrm{b}$ and $T_c = \dfrac{8\,\mathrm{a}}{27\,\mathrm{b}\,R}$

For He, $T_c = 5.2$ K

For N_2, $T_c = 128$ K

Since T_c (N_2) is greater than T_c (He), N_2 is liquefied more readily than He.

2.5 $$W = \int_{V_1}^{V_2} p\,dV$$

$$= \int_{V_1}^{V_2} \left(\frac{RT}{V - \mathrm{b}} - \frac{\mathrm{a}}{V_2}\right) dV$$

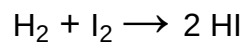
$$= RT \ln\left(\frac{V_2 - \mathrm{b}}{V_1 - \mathrm{b}}\right) + \mathrm{a}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$= 56.7 \text{ dm}^3 \text{ bar mol}^{-1}$$

THEORETICAL PROBLEM 3

Rates and reaction mechanisms

The observed rate law for a chemical reaction can arise from several different mechanisms. For the reaction



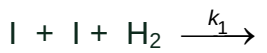
$$H_2 + I_2 \longrightarrow 2\,HI$$

the observed rate law is

$$-\frac{d[H_2]}{dt} = k\,[H_2][I_2]$$

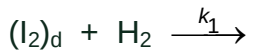
For a long time it was believed that the above reaction took place as it was written down; that is, it was a bimolecular elementary reaction. It is now considered that several mechanisms compete. Below a certain temperature, two alternative mechanisms have been proposed :

(1) $I_2 = 2\,I$ K : equilibrium constant



$$I + I + H_2 \xrightarrow{k_1} 2\,HI$$

(2) $I_2 = (I_2)_d$ K' : equilibrium constant



$$(I_2)_d + H_2 \xrightarrow{k_1} 2\,HI$$

where $(I_2)_d$ represents a dissociative state of I_2. The first step in each mechanism is fast and the second slow.

3.1 Show that both mechanisms are consistent with the observed rate law.

The values of the rate constant k for the reaction at two different temperatures are given in the table :

T (K)	k ($dm^3\ mol^{-1}\ s^{-1}$)
373.15	8.74×10^{-15}
473.15	9.53×10^{-10}

3.2 Determine the activation energy E_a.

3.3 The bond dissociation energy of I_2 is 151 kJ mol^{-1}. Justify why the second step in each mechanism is rate determining.

3.4 The change in internal energy (ΔU) for the reaction is –8.2 kJ mol^{-1}. Determine the activation energy for the reverse reaction.

The activation energy for a reaction can even be negative. An example is the gas phase recombination of iodine atoms in the presence of argon

$$I + I + Ar \rightarrow I_2 + Ar ,$$

whose activation energy is about –6 kJ mol^{-1}**.**

One of the proposed mechanisms of this reaction is :

$I + Ar + Ar = IAr + Ar$ $\quad K''$: equilibrium constant

$Ar + I \xrightarrow{k_3} I_2 + Ar$

where IAr is a very loosely bound species.

3.5 Assume that the second step is the rate determining and obtain the rate law for the reaction.

3.6 Give a possible explanation of why the activation energy for the iodine recombination is negative.

———————

SOLUTION OF PREPARATORY PROBLEM 3

3.1 Mechanism 1

$$\frac{1}{2}\frac{d[HI]}{dt} = k_1 [I]^2 [H_2]$$

Since the first step is fast, there is a pre – equilibrium:

$$K = \frac{[I]^2}{[I_2]}$$

$$\therefore \quad \frac{d[HI]}{dt} = 2\, k_1 K\, [I_2][H_2] = k\, [I_2][H_2]$$

Mechanism 2 :

$$\frac{1}{2}\frac{d[HI]}{dt} = k_2\, [I_2]_d [H_2]$$

$$K' = \frac{[I_2]_d}{[I_2]}$$

$$\frac{d[HI]}{dt} = 2\, k_2\, K'\, [I_2][H_2] = k\, [I_2][H_2]$$

Both mechanisms are consistent with the observed rate law.

3.2 **i.** $k = A\, e^{-E_a/RT}$

$$E_a \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = R \ln \frac{k_2}{k_1}$$

With the given numerical values,

E_a = 170 kJ mol^{-1}

ii. The activation energy is greater than the bond dissociation energy of I_2. Hence the second step is rate determining in both the mechanisms.

3.3 The activation energy $E_a^{'}$ for the reverse reaction is

$$E_p^{'} = E_p - \Delta U = 170 + 8.2 = 178.2 \text{ kJ mol}^{-1}$$

3.4 **i.** $\frac{d[I_2]}{dt} = k_3\,[Ar]_d[I]$

$$K'' = \frac{[I\,Ar]\,[Ar]}{[I]\,[Ar]^2}$$

$$\frac{d[I_2]}{dt} = K''\,k_3\,[I]^2[Ar] = k\,[I]^2[Ar]$$

ii. A possible reason why this is negative is that Ea_3 is positive and less in magnitude than $|H^0|$, while H^o is negative.

$k = k_3\,K''$

$$= A_3\,e^{-\frac{E_{a3}}{RT}}\,e^{-\frac{\Delta G^o}{RT}}$$

Since $\Delta G^o = \Delta H^o - T\,\Delta S^o$

$$k = A_3\,e^{\frac{\Delta S^o}{R}}\,e^{\frac{-(E_{a3} + \Delta H^o)}{RT}}$$

The activation energy for the overall reaction is $E_{a3} + \Delta H^0$.

THEORETICAL PROBLEM 4

Enzyme catalysis

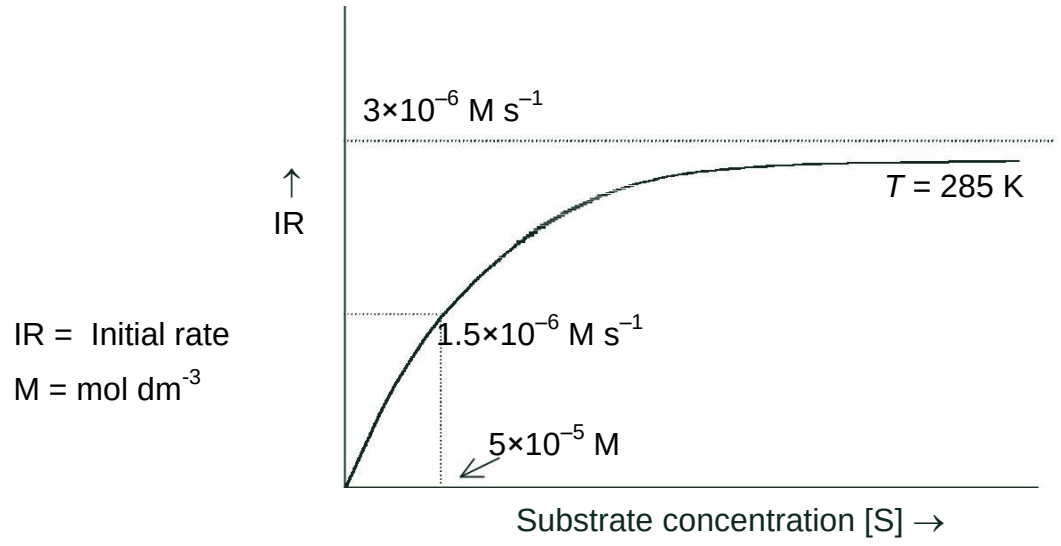
Enzymes play a key role in many chemical reactions in living systems. Some enzyme-catalysed reactions are described in a simple way by the Michaelis-Menten mechanism, as given below.

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + P$$

where E stands for the enzyme, S stands for the substrate on which it acts and P, the end product of the reaction. k_1 and k_1' are the forward and backward rate constants for the first step, respectively, and k_2 is the forward rate constant for the second step.

Ignore the backward rate for the second step and assume that the enzyme equilibrates with its substrate very quickly.

In an experiment, the initial rate (of formation of P) is determined for different concentrations of the substrate, keeping the total concentration of enzyme fixed at 1.5×10^{-9} mol dm^{-3}. The following graph is obtained.



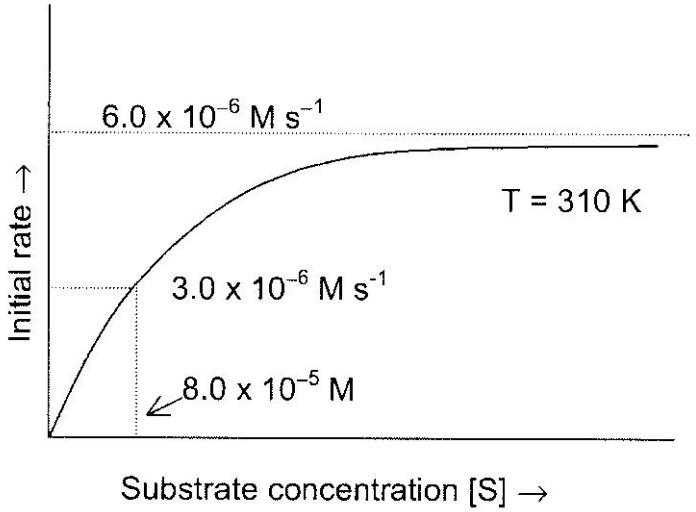
4.1 The graph is linear for small [S] and it approaches a constant value for large [S]. Show that these features are consistent with the Michaelis-Menten mechanism. (Use steady state approximation for the intermediate step.)

4.2 Determine the rate constant k_2 for the second step.

4.3 Predict the initial rate on the basis of the Michaelis-Menten mechanism for the substrate concentration [S] = 1.0×10^{-4} mol dm^{-3}.

4.4 Determine the equilibrium constant for the formation of the enzyme – substrate complex ES.

The experiment above studied at 285 K is repeated for the same total enzyme concentration at a different temperature (310 K), and a similar graph is obtained, as shown below.



4.5 Determine the activation energy for the conversion of ES to E and P.

One interesting application of the ideas above is the way enzyme catalysed reactions inactivate antibiotics. The antibiotic penicillin is, for example, inactivated by the enzyme penicillinase secreted by certain bacteria. This enzyme has a single active site. Suppose, for simplicity, that the rate constants obtained in a above apply to this reaction. Suppose further that a dose of 3.0 mol of the antibiotic triggers the release of 2.0×10^{-6} μmol of the enzyme in a 1.00 cm^3 bacterial suspension.

4.6 Determine the fraction of the enzyme that binds with the substrate (penicillin) in the early stage of the reaction.

4.7 Determine the time required to inactivate 50 % of the antibiotic dose.

In order to control the inactivation of penicillin a substance is introduced which has a similar structure to penicillin and is able to occupy the enzyme site but otherwise it is completely unreactive. This naturally inhibits the enzyme-catalysed reaction. The degree of inhibition, *i,* is defined by the relation:

$$i = 1 - \frac{r}{r_0}$$

where r and r_0 are the initial rates of reactions with and without the inhibitor, respectively.

Consider again the Michaelis-Menten type of mechanism to describe the situation:

$$E + S \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} ES$$

$$E + I \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} EI$$

$$ES \xrightarrow{k_2} E + P$$

4.8 Show that the degree of inhibition decreases with increase in concentration of the substrate (for constant concentration of the inhibitor), and the inhibitor ceases to be effective for large substrate concentrations. (This is known as competitive inhibition.)

4.9 For low substrate concentration of penicillin, determine the concentration of the inhibitor that reduces the rate of the inactivation of penicillin by a factor of 4. The dissociation constant of enzyme-inhibitor complex is given to be 5.0×10^{-5}.

SOLUTION OF PREPARATORY PROBLEM 4

4.1 **i.** The differential rate equations for the Michaelis-Menten mechanism are

$$\frac{d[\mathrm{ES}]}{dt} = k_1[\mathrm{E}][\mathrm{S}] - k'_1[\mathrm{ES}] - k_2[\mathrm{ES}] \quad (1)$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ES}] \quad (2)$$

In the steady-state approximation, $\frac{d[\mathrm{ES}]}{dt} = 0$ (3)

Eq. (1) then gives $[\mathrm{ES}] = \frac{k_1[E][S]}{k' + k_2}$ (4)

Now $[\mathrm{E}]_o = [\mathrm{E}] + [\mathrm{ES}]$ (5)

where $[\mathrm{E}]_o$ is the total enzyme concentration. Equations (4) and (5) give

$$[\mathrm{ES}] = \frac{[\mathrm{E}]_o[\mathrm{S}]}{K_m + [\mathrm{S}]} \quad (6)$$

where $K_m = \frac{k'_1 + k_2}{k_1}$ is the Michaelis-Menten constant.

From eq. 2: $\frac{d[\mathrm{P}]}{dt} = \frac{k_2[\mathrm{E}]_o[\mathrm{S}]}{K_m + [\mathrm{S}]}$ (7)

Since the backward rate is ignored, our analysis applies to the initial rate of formation of P and not close to equilibrium. Further, since the enzyme concentration is generally much smaller than the substrate concentration, [S] is nearly equal to $[\mathrm{S}]_0$ in the initial stage of the reaction.

Thus, according to the Michaelis-Menten mechanism, the initial rate versus substrate concentration is described by eq. (7), where [S] is replaced by $[\mathrm{S}]_0$.

For $[\mathrm{S}] << K_m$,

Initial rate = $\frac{k_2}{K_m}[E]_o[S]$ (8)

i.e., initial rate varies linearly with [S].

For [S] >> K_m,

Initial rate = $k_2\,[E]_0$ (9)

i.e. for a large substrate concentration, initial rate approaches a constant value k_2 $[E]_0$.

Thus the indicated features of the graph are consistent with Michaelis-Menten mechanism.

ii. The asymptotic value of initial rate is $k_2\,[E]_0$

From the graph,`

$k_2\,[E]_0 = 3.0\times10^{-6}$ mol dm^{-3} s^{-1}

With $[E]_0 = 1.5\times10^{-6}$ mol dm^{-3}

We get $k_2 = 2.0\times10^{3}$ s^{-1}

iii. From eq. (7), for [S] = K_m, the initial rate is half the asymptotic value. From the graph, therefore,

$K_m = 5.0\times10^{-5}$ M

For [S] = 1.0×10^{-4} mol dm^{-3} using eq. (7) again,

Initial rate $\frac{(2.0\times10^{3}\ \text{s}^{-1})\times(1.5\times10^{-9}\ \text{mol dm}^{-3})\times(1.0\times10^{-4}\ \text{mol dm}^{-3})}{(5.0\times10^{-5}\ \text{mol dm}^{-3})+(1.0\times10^{-4}\ \text{mol dm}^{-3})} =$

$= 2.0\times10^{-6}$ mol dm^{-3} s^{-1}

iv. We have $K_m = \frac{k_1^{'} + k_2}{k_1} = 5.0\times10^{-5}$ mol dm^{-3}

The enzyme equilibrates with the substrate quickly, that is the first step of equilibration between E, S and [ES] is very fast. This means that $k_1^{'}$ is much greater than k_2. Therefore, neglecting k_2 above,

$$\frac{k_1'}{k_1} = 5.0\times10^{-5}\ \text{mol dm}^{-3}$$

The equilibrium constant K for the formation of ES from E and S is

$$\frac{K}{1\text{M}} = \frac{k_1}{k_1'} = 2.0\times10^{-5}$$

4.2 From the graph at the new temperature, $k_2\,[\text{E}]_0 = 6.0\times10^{-6}$ mol dm^{-3} s^{-1}

i. e. $$k_2 = \frac{6.0\times10^{-6}\ \text{mol dm}^{-3}\,\text{s}^{-1}}{1.5\times10^{-9}\ \text{mol dm}^{-3}} = 4.0\times10^{3}\ \text{s}^{-1}$$

Using Arrhenius relation for temperature dependence of rate constant:

$$k = A\,e^{-\frac{E_a}{RT}} \qquad (10)$$

where E_a is the molar activation energy.

$$\frac{k(T_1)}{k(T_2)} = e^{-\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

i. e. $$E_a = R\,\frac{\ln\frac{k(T_1)}{k(T_2)}}{\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} \qquad (11)$$

Now $\frac{k(310)}{k(285)} = 2.0$ $\qquad R = 8.314$ J mol^{-1} K^{-1}

$E_a = 20.4$ kJ mol^{-1}

4.3 **i.** The fraction of the enzyme that binds with the substrate is, from eq. (6):

$$\frac{[\text{ES}]}{[\text{E}]_o} = \frac{[\text{S}]}{K_m + [\text{S}]} \qquad (12)$$

where [S] is nearly equal to $[S]_o$ in the initial stage of the reaction.

Now $[S]_o = \frac{3.0\times10^{-6}\ \text{mol}}{1\times10^{-3}\ \text{dm}^3} = 3.0\times10^{-3}\ \text{mol dm}^{-3}$

and $K_m = 5.0\times10^{-5}\ \text{mol dm}^{-3}$

$$\frac{[ES]}{[E]_o} = \frac{3.0\times10^{-5}}{(5.0\times10^{-5} + 3.0\times10^{-5})} = 0.98$$

Nearly the whole of the enzyme is bound with the substrate.

ii. From Eq. 7, integrating the equation gives:

$$\frac{d[S]}{dt} = -\frac{k_2\,[E]_o[S]}{K_m + [S]}$$

$$K_m \ln\frac{[S]}{[S]_o} + [S] - [S]_o = -k_2\,[E]_o\,t \qquad (13)$$

If at $t = T$, $[S] = 1/2\,[S]_o$

$$T\,k_2\,[E]_o = K_m \ln 2 + \frac{1}{2}[S]_o \qquad (14)$$

Here $[E]_o = \frac{2.0\times10^{-12}\ \text{mol dm}^{-3}}{1.0\times10^{-3}\ \text{dm}^3} = 2.0\ \text{mol dm}^{-9}$

$k_2 = 2.0\times10^3\ \text{s}^{-1}$ $K_m = 5.0\times10^{-5}\ \text{mol dm}^{-3}$

$[S]_o = 3.0\times10^{-3}\ \text{mol dm}^{-3}$

Substituting these values in eq. (14) gives

T = 384 s

Thus 50 % of the antibiotic dose is inactivated in 384 s.

4.4 i. The differential rate equations for the situation are:

$$\frac{d[ES]}{dt} = k_1[E]\,[S] - k_1'[ES] - k_2[ES] \quad (15)$$

$$\frac{d[EI]}{dt} = k_3[E]\,[I] - k_3'[EI] \quad (16)$$

$$\frac{d[P]}{dt} = k_2[ES] \quad (17)$$

where k_3 and k^{I}_3 are the forward and backward rate constants for the enzyme-inhibitor reaction.

Applying steady-state approximation to [ES] and [EI],

$$[ES] = \frac{k_1\,[E]\,[S]}{k_1' + k_2} \quad (18)$$

And $$[EI] = \frac{k_3\,[E]\,[I]}{k_3'} \quad (19)$$

Now $$[E]_0 = [E] + [ES] + [EI] \quad (20)$$

$$[ES] = \frac{[E]_o[S]}{[S] + K_m\left(1 + \frac{[I]}{K_I(1M)}\right)} \quad (21)$$

$$\frac{d[P]}{dt} = \frac{k_2\,[E]_o[S]}{[S] + K_m\left(1 + \frac{[I]}{K_I(1M)}\right)} \quad (22)$$

Here, $K_I = \frac{k_3^{I}}{k_3}$ is the equilibrium constant for the dissociation of EI to E and I.

The degree of dissociation is $i = 1 - \frac{r}{r_o}$

Using eq. 22

$$i = \frac{\frac{K_m}{K_I}[I]}{[S] + K_m\left(1 + \frac{[I]}{K_I}\right)} \quad (23)$$

For fixed [I], *i* decreases with increase in [S] *(competitive inhibition,* and for large [S], $I \rightarrow 0$, i.e. the inhibitor ceases to play any role.

ii. For small [S]

$$i = \frac{[I]}{K_I + [I]}$$

If $r = \frac{1}{4} r_o$ $i = \frac{3}{4}$

i. e. $[I] = 3\ K_I \text{ x } = 1.5 \times 10^{-4}$

The inhibitor concentration required to reduce the rate of inactivation by a factor of 4 is 1.5×10^{-4} mol dm^{-3}; i.e., 0.15 mol in a volume of 1.00 cm^3.

THEORETICAL PROBLEM 5

Schrödinger equation

The simplest Schrödinger equation, describing a free particle confined to move in a one-dimensional 'rigid box' brings out a most basic fact: quantization arises due to boundary conditions on the wave function.

An electron of mass *m* is confined to move in a line along the x-axis from x = 0 to x = L. Between the two ends it experiences no force.

5.1 Write down the (time-independent) Schrödinger equation for the wave function of an electron.

5.2 Which of the following are possible wave functions of an electron in one-dimensional rigid box:

e^{-kx}, $\cos\frac{n\pi x}{L}$, $\sin kx$, $\sin\frac{n\pi x}{L}$

where k is any real number and n is a positive integer ?

5.3 For the acceptable wave functions of the electron in (ii) above, show that the energies are given by

$$E_n = \frac{h^2 n^2}{8mL^2}$$

5.4 Plot schematically the wave function of the electron in the ground and the first two excited states. What is the number of nodes (in the region between x = 0 to L) of the wave function with energy En?

5.5 Normalize the ground state wave function of the electron.
(The integral of the square of the modulus of a normalized wave function over all space is unity.)

An interesting example of this one-dimensional model in chemistry is the motion of an electron in a conjugated system of single and double bonds. The molecule 1,3-butadiene has four electrons assumed to move freely in a line consisting of three carbon-carbon bonds, each of approximately the same length (1.4×10^{-10} m), with an additional length of 1.4×10^{-10} m at each end.

5.6 Using the aufbau principle, determine a scheme to fill the electrons in the available energy levels. Calculate the lowest excitation energy of the system.

Boundary conditions on wave functions result in quantization of not only energy but also other physical quantities, such as angular momentum. The wave function corresponding to the value $h\lambda / 2\pi$ for the z-component of angular momentum (L_z) is:

$$\psi(\phi) = e^{i\lambda\phi},$$

where ϕ is the (azimuthal) angle in the x-y plane measured relative to the x-axis.

5.7 Use the condition that this function is single valued at every point in space and show that this implies that λ is quantized. Give the quantized values of angular momentum projection along the z-axis.

_____

SOLUTION OF PREPARATORY PROBLEM 5

5.1 One-dimensional Schrödinger equation for a free particle of mass *m*:

$$-\frac{\mathbf{h}^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \qquad \mathbf{h} = \frac{h}{2\pi}$$

where *E* stands for the energy of the particle and ψ its wave function.

5.2 The boundary conditions are:

$\psi(0) = \psi(L) = 0$

Only $\psi_n(x) = \sin\frac{n\pi x}{L}$ satisfies the required boundary conditions.

Other functions are not possible wave functions of the electron in a one-dimensional rigid box.

5.3 $$-\frac{\mathbf{h}^2}{2m}\frac{d^2}{dx^2}\sin\frac{n\pi x}{L} = \frac{\mathbf{h}^2\pi^2}{2mL^2}n^2\sin\frac{n\pi x}{L}$$

$$E_n = \frac{\mathbf{h}^2\pi^2}{2mL^2}n^2 = \frac{h^2n^2}{8mL^2}$$

5.4

Ground state (n = 1)

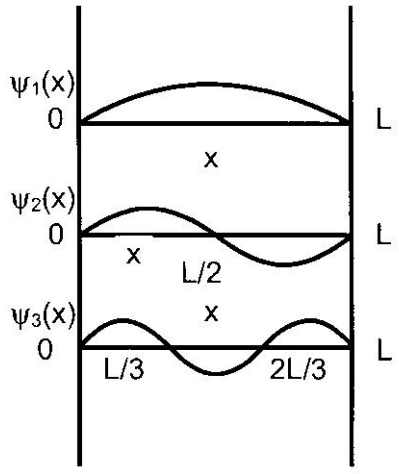
$\psi_1(x) = \sin\frac{\pi x}{L}$

First excited state (n = 2)

$\psi_2(x) = \sin\frac{2\pi x}{L}$

Second excited state (n = 3)

$\psi_3(x) = \sin\frac{3\pi x}{L}$



Number of nodes in $\psi_n = n - 1$, apart from the nodes at the end points.

5.5 $\psi_1^N(x) = N \sin\frac{\pi x}{L}$

$$1 = \int_{-\infty}^{\infty} \left|\psi_1^N(x)\right|^2 dx = N^2 \int_0^L \sin^2\frac{\pi x}{L}\, dx = \frac{N^2}{2}\int_0^L \left(1 - \cos\frac{2\pi x}{L}\right) dx = N^2\,\frac{L}{2}$$

$N = \sqrt{\frac{2}{L}}$ (N is chosen to be real)

$\psi_1^N(x) = \sqrt{\frac{2}{L}} \sin\frac{\pi x}{L}$

5.6 In the example

$L = 5 \times 1.4\times10^{-10}$ m $= 7.0\times10^{-10}$ m

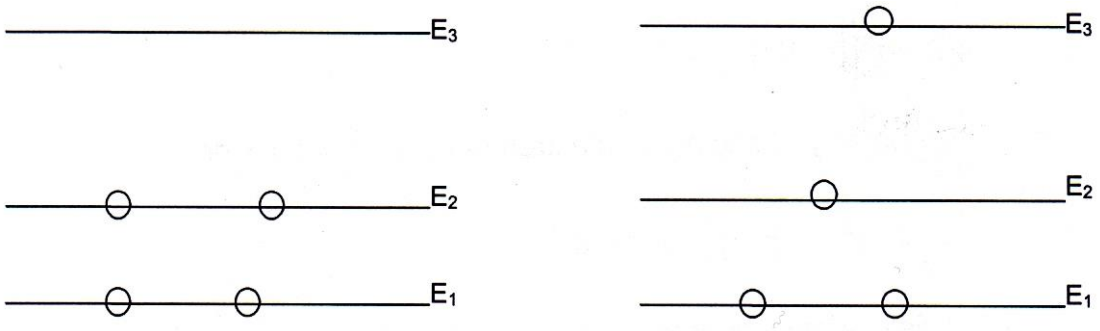
The first three energy levels are:

$$E_1 = \frac{h^2}{8mL^2} = 1.22\times10^{-19} \text{ J}$$

$E_2 = 4\ E_1 = 4.88\times10^{-19}$ J

$E_3 = 9\ E_1 = 10.98\times10^{-19}$ J

In the ground state, the four electrons will occupy the levels E_1 and E_2, each with two electrons.



Ground state Lowest excited state

The lowest excitation energy

$E_3 - E_2 = 6.10\times10^{-19}$ J

5.7 The condition that $\psi(\phi)$ is single valued demands that

$\psi(\phi) = \psi(\phi + 2\pi)$

$e^{i\lambda\phi} = e^{i\lambda(\phi + 2\pi)}$

$e^{i2\pi\lambda} = 1$

i.e. $\lambda = m$, where m = 0, ±1, ±2, ±3,…….

This shows that angular momentum projection (Lz) cannot be an arbitrary real number but can have only discrete values: m, where m is a positive or negative integer (including zero).

THEORETICAL PROBLEM 6

Atomic and molecular orbitals

Orbitals are one-electron wave functions, whether they refer to electronic motion in an atom (atomic orbitals) or in a molecule (molecular orbitals) or a solid. Each orbital corresponds to a certain probability distribution of finding an electron in different regions of space.

Atomic orbitals

The 1s orbital of hydrogen atom is given by

$$\Psi_{1s} = e^{-r/a_0}$$

where a_o is the Bohr radius ($a_o = 5.3\times10^{-11}$ m) and r is the radial co-ordinate (distance of a point in space from the centre).

6.1 Normalize the given wave function.

6.2 At what distance from the nucleus is the electron most likely to be found?

The wave functions for 2s, $2p_z$ and $3d_{z2}$ states are given below:

$$\Psi_{2s} = \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}}$$

$$\Psi_{2p_z} = \left(\frac{r}{a_0}\right) \cos\Theta\, e^{-\frac{r}{2a_0}}$$

$$\Psi_{3d_{z^2}} = \left(\frac{r^2}{a_0^2}\right) (3\cos^2\Theta - 1)\, e^{-\frac{r}{3a_0}}$$

6.3 What are the nodal surfaces of these orbitals?

It turns out that the solution of Schrödinger equation for a one-electron atom yields exactly the ‘good old’ formula of Bohr for quantized energies:

$$E_n = -\frac{(13.6\ \text{eV})\, Z^2}{n^2}$$

where, for convenience, the numerical value of the combination of constants appearing in the formula has been put in units of eV .

It is fun using this formula for a neutral helium atom, but we must exercise some care. In a helium atom, each electron 'sees' the nucleus screened by the other electron. That is, the effective charge of the nucleus 'seen' by each electron decreases from its bare value Z = 2 to some other value, say, Z_{eff} .

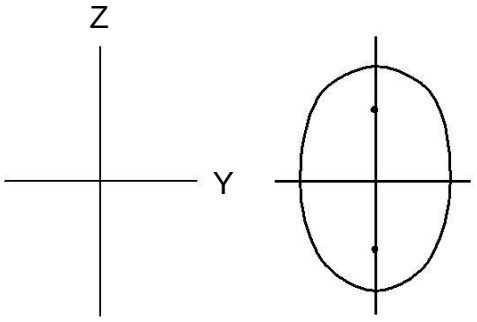
6.4 The ionization energy for a helium atom in its ground state is known experimentally to be 24.46 eV. Estimate Z_{eff} .

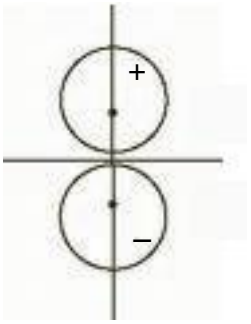
Molecular orbitals

Molecular orbitals of a hydrogen molecule ion (H_2^+) can be approximately written as linear combinations of atomic orbitals centered around the two nuclei of the molecule. Consider the (unnormalized) molecular orbitals constructed in this manner from the 1s and 2s orbitals of two hydrogen atoms, say, A and B:

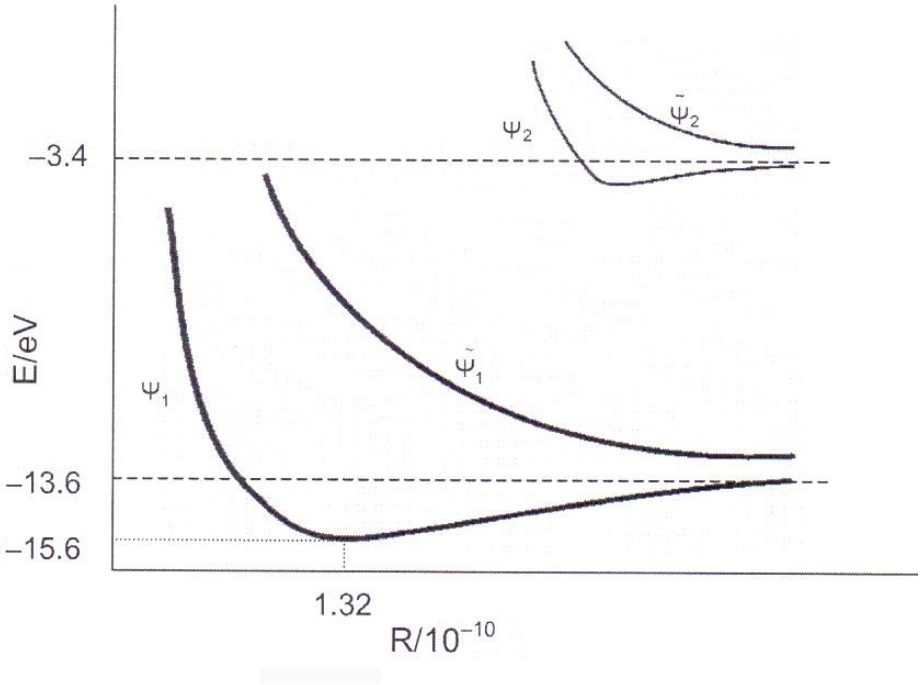
$$\Psi_1 = \psi_{1s}^A + \psi_{1s}^B$$
$$\tilde{\Psi}_1 = \psi_{1s}^A - \psi_{1s}^B$$
$$\Psi_2 = \psi_{2s}^A + \psi_{2s}^B$$
$$\tilde{\Psi}_2 = \psi_{2s}^A - \psi_{2s}^B$$

Taking the z-axis along the line joining the two nuclei, the orbital contours of ψ_1 and $\overline{\Psi}_1$ are shown schematically below :





Similar orbital contours (curves on which the value of ψ is constant) can be drawn for ψ_2 and $\overline{\Psi}_2$. The energies of these wave functions as a function of internuclear distance are shown below schematically:



6.5 Identify the bonding and antibonding orbitals. State qualitatively what makes one orbital bonding and another antibonding.

6.6 Determine the values of the equilibrium internuclear distance Re and the dissociation energy D of the ground state of H_2^+.

6.7 If the molecular ion H_2^+ is excited to the state ψ_2, to what atomic states will it dissociate?

In the following questions, assume that the energy versus internuclear distance graphs for the orbitals of H_2 and He_2 are similar to the one shown for H_2^+.

6.8 Explain why the ground state total electron spin of the neutral H_2 molecule is zero.

6.9 Write down the electronic configuration of the first excited state of H_2 molecule. Predict if it will stay bound or dissociate.

6.10 It is difficult to obtain He_2 in its ground state, but it has been observed in its excited states. Explain how this is possible.

SOLUTION OF PREPARATORY PROBLEM 6

6.1 $\psi_{1s}^{N} = N\, e^{-\frac{r}{a_0}}$

$$1 = \int \left|\psi_{1s}^{N}\right|^2 dv = 4\,\pi\, a_0^3\, N^2 = 4\,\pi\, N^2 \times \frac{a_0^3}{4} = \pi\, a_0^3\, N^2 \qquad \text{(N is chosen to be real)}$$

$$N = \left[\pi\, a_0^3\right]^{-\frac{1}{2}}$$

$$\psi_{1s}^{N} = \left[\pi\, a_0^3\right]^{-\frac{1}{2}} e^{-\frac{r}{a_0}}$$

6.2 Probability of finding an electron between r and r+dr =

$$= 4\pi r^2 \times \left[\pi\, a_0^3\right]^{-1} e^{\frac{2r}{a_0}}\, dr$$

This is a maximum at $r = r_{max}$, given by

$$\frac{d}{dr}\left(r_2\, e^{-\frac{2r}{a_0}} \right)_{r = r_{max}} = 0$$

This gives

$r_{max} = a_0$

The 1s electron is most likely to be found in the neighborhood of $r = a_0$.

6.3 $\Psi_{2p_z} = 0$ at $r = 2a_0$

Nodal surface is a sphere of radius $2a_0$.

$$\Psi_{3d_{z^2}} = 0 \quad \text{at} \quad 3\cos^2\theta - 1 = 0 \quad \text{i.e.} \quad \theta = \cos^{-1}\left(\pm\frac{1}{\sqrt{3}}\right)$$

Nodal surfaces are cones with these values of half-angle, one above the xy plane and the other below it.

(Note: all three wave functions vanish as $r \to \infty$. At $r = 0$ Ψ_{1s} does not vanish, but the other two wave functions vanish.)

6.4 Each electron in n = 1 shell of helium atom has energy $-Z_{eff}^2 \times 13.6\ \text{eV}$.

Helium ground state energy = $-Z_{eff}^2 \times 27.2\ \text{eV}$

Energy of He^+ ground state = $-4 \times 13.6 = -54.4$ eV

Ionization energy = $(-54.4 + Z_{eff}^2 \times 27.2)$ eV = 24.46 eV

This gives $Z_{eff} = 1.70$

6.5 ψ_1 and ψ_2 are bonding orbitals

$\overline{\Psi}_1$ and $\overline{\Psi}_2$ are antibonding orbitals

Bonding orbital:

No nodal surface between the nuclei. Electronic energy has a minimum at a certain internuclear distance. Qualitative reason: electron has considerable probability of being between the nuclei and thus has attractive potential energy due to both the nuclei.

Antibonding orbita:l

Nodal surface between the nuclei. Electronic energy decreases monotonically with internuclear distance. Hence bound state is not possible.

6.6 $R_e = 1.32 \times 10^{-10}$ m

D = –13.6 – (–15.36) = 1.76 eV

6.7 It will dissociate to a hydrogen atom in 2s state and a bare hydrogen nucleus (proton).

6.8 The two electrons occupy the same molecular orbital with the lowest energy. By Pauli's principle, their spins must be antiparallel. Hence the total electronic spin is zero.

6.9 In the first excited state of H_2, one electron is in ψ_1 (bonding orbital) and the other in ψ_1 (antibonding orbital). It will dissociate into two hydrogen atoms.

Using the aufbau principle, in the ground state two electrons of He_2 are in ψ_1 (bonding orbital) and two in $\overline{\Psi}_1$ (antibonding orbital). The bond order is ½ (2 – 2) = 0

Therefore, bond in He_2 is unstable and difficult to detect.

6.10 However, if one or more electrons are elevated from the antibonding orbital to (higher energy) bonding orbitals, the bond order becomes greater than zero. This is why it is possible to observe He_2 in excited states.

THEORETICAL PROBLEM 7

Fission

7.1 Consider the following fission reactions of 235U by thermal neutrons:

$^{235}_{92}U + n \rightarrow {}^{94}_{38}Sr + {}^{141}_{(...)}Xe + (.....)$

$^{235}_{92}U + n \rightarrow {}^{141}_{56}Ba + (.....) + 3\,n$

Identify the missing species and numbers.

7.2 Consider the first of the above reactions. The unstable fission fragments undergo successive β-decays giving Zr and Ce. Write down the net nuclear reaction and calculate the total energy released in MeV. You are given the following data on atomic masses :

$m(^{235}U) = 235.0493\ u$

$m(^{94}Zr) = 93.9063\ u$

$m(^{140}Ce) = 139.9054\ u$

$m_n = 1.00866\ u$

$1u = 931.5\ \text{Me V/c}^2$

7.3 A sample of natural uranium metal with a mass of 1 kg was put in a nuclear research reactor. When the total energy released reached 1 Mega Watt Day (MWd), it was removed from the reactor. What would be the percentage abundance of ^{235}U in the uranium metal at that time, if it is 0.72 % in natural uranium. Your result in 7.2 above may be taken to be the average energy released per fission. Assume that all the energy is due to fission of ^{235}U only.

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SOLUTION OF PREPARATORY PROBLEM 7

7.1 $^{235}_{92}U + n \rightarrow {}^{94}_{38}Sr + {}^{141}_{54}Xe + 2\,n$

$^{235}_{92}U + n \rightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3\,n$

The net nuclear reaction is

7.2 $^{235}_{92}U + n \rightarrow {}^{94}_{40}Zr + {}^{140}_{58}Ce + 2\,n + 6\,e^- + (Q)$

The energy released is

$Q = [m_N(^{235}U) - m_N(^{94}Zr) - m_N(^{140}Ce) - m_n - 6\,m_e]\,c^2$

where the small energy of the initial thermal neutron has been ignored. (m_N denotes the nuclear mass.) Now

$m_N(^{235}U) = m(^{235}U) - 92\,m_e$

ignoring the small electronic binding energies compared to rest mass energies.

Similarly for other nuclear masses.

$Q = [m_N(^{235}U) - m(^{94}Zr) - m(^{140}Ce) - m_n]\,c^2$

Using the given data,

Q = 213.3 MeV

7.3 1 MWd = 10^6 J s^{-1} × 24 × 3600 s = 8.64×10^{10} J

Number of atoms of ^{235}U fissioned = $\dfrac{8.64\times10^{10}}{213.3 \times 1.60\times10^{13}} = 2.53\times10^{21}$

Mass of ^{235}U fissioned = $\dfrac{2.53\times10^{21}\times235}{6.02\times10^{23}} = 0.99$

Mass of ^{235}U in 1 kg uranium removed from the reactor = 7.2 – 0.99 = 6.2 g

Abundance of ^{235}U is 0.62 %

THEORETICAL PROBLEM 8

Radioactive decay

The radioactive isotope ^{210}Bi is the daughter product of ^{210}Pb and decays by β-emission to ^{210}Po, which is also radioactive. ^{210}Po decays by α-emission to the stable ^{206}Pb.

$$^{210}\text{Pb} \xrightarrow{\beta,\ T_{1/2} = 22.3\ \text{y}} {}^{210}\text{Bi} \xrightarrow{\beta,\ T_{1/2} = 5.01\ \text{d}} {}^{210}\text{Po} \xrightarrow{\alpha,\ T_{1/2} = 138.4\ \text{d}} {}^{206}\text{Pb}$$

A sample of radiochemically pure ^{210}Bi was freshly isolated from ^{210}Pb and was allowed to stand for the growth of ^{210}Po. The radioactivity of the freshly purified ^{210}Bi sample was 100 μCi. (1 Ci = 3.7×10^{10} disintegration per second.)

8.1 What is the initial mass of the sample (^{210}Bi)?

8.2 Calculate the time it takes for the amount of ^{210}Po in the sample to grow to its maximum value. How much is the maximum amount of ^{210}Po?

8.3 Determine the α-disintegration rate of ^{210}Po and β-disintegration rate of ^{210}Bi at that time.

SOLUTION OF PREPARATORY PROBLEM 8

8.1 1 μCi = 3.7×10^{4} disintegrations per second (dps).

Initial β-activity = 3.7×10^{6} dps

$$\frac{-\mathrm{d}N_1}{\mathrm{d}t} = N_1^0\ \lambda_1 = 3.7\times10^{6}\ \text{dps}$$

where N_1^0 is the number of atoms of ^{210}Bi at t = 0 and λ_1 is its decay constant .

$$\frac{0.693}{5.01\times 24\times 3600} N_1^0 = 3.7\times10^{6}$$

$N_1^0 = 2.31 \times 10^{12}$

Intial mass of ^{210}Bi = $2.31 \times 10^{12} \frac{210}{6.02 \times 10^{23}}$ g = 8.06×10^{-10} g □

8.2 Number of atoms of ^{210}Bi at time *t* is given by

$N_1 = N_1^0 e^{-\lambda_1 t}$

The number of atoms of ^{210}Po, N_2, is given by equation

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2$$

where λ_2 is the decay constant of ^{210}Po.

$$\frac{dN_2}{dt} = \lambda_1 N_1^0 e^{-\lambda_1 t} - \lambda_2 N_2$$

Using the integrating factor $e^{\lambda_2 t}$

$$e^{\lambda_1 t} \frac{dN_2}{dt} + \lambda_2 N_2 e^{\lambda_2 t} = \lambda_1 N_1^0 e^{(\lambda_2 - \lambda_1)t}$$

$$\frac{d}{dt}(N_2 e^{\lambda_2 t}) = \lambda_1 N_1^0 e^{(\lambda_2 - \lambda_1)t}$$

Integrating

$$N_2 e^{\lambda_2 t} = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 e^{(\lambda_2 - \lambda_1)t} + C$$

To calculate C, use the condition that at $t = 0$, $N_2 = 0$

$$C = \frac{\lambda_1 N_1^0}{\lambda_2 - \lambda_1}$$

This gives

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t})$$

The time t = T when N_2 is maximum is given by the condition

$$\left.\frac{dN_2}{dt}\right|_{t=T} = 0$$

which gives

$$T = \frac{\ln \frac{\lambda_1}{\lambda_2}}{\lambda_1 - \lambda_2} = 24.9\, d$$

At $t = T$, N_2 can be calculated from above.

$N_2 = 2.04 \times 10^{12}$

Mass of ^{210}Po at $t = T$,

$m(^{210}\text{Po}) = 7.11 \times 10^{-10}$ g

8.3 At $t = T$

α-disintegration rate of ^{210}Po $= 1.18 \times 10^5$ dps

β-disintegration rate of ^{210}Bi = α-disintegration rate of ^{210}Po $= 1.18 \times 10^5$ dps

THEORETICAL PROBLEM 9

Redox reactions

A solution containing Sn^{2+} ions is titrated potentiometrically with Fe^{3+}. The standard reduction potentials for $Sn^{4+/2+}$ and $Fe^{3+/2+}$ are given below.

$Sn^{4+} + 2\,e^- = Sn^{2+}$ $\quad E^o = 0.154$ V

$Fe^{3+} + e^- = Fe^{2+}$ $\quad E^o = 0.771$ V

9.1 Write down the overall reaction and calculate the standard free energy change of the overall reaction.

9.2 Determine the equilibrium constant of the reaction.

9.3 A volume of 20 cm^3 of Sn^{2+} solution (c = 0.10 mol dm^{-3}) is titrated with Fe^{3+} solution (c = 0.20 mol dm^{-3}). Calculate the voltage of the cell:

i) when 5 cm^3 of Fe^{3+} solution is added,

ii) at the equivalence point,

iii) when 30 cm^3 Fe^{3+} of the solution is added.

The saturated calomel electrode ($E^o_{SCE.}$ = 0.242 V) is used as the reference electrode in the titration.

One of the important analytical methods for estimation of Cu^{2+} is iodometric titration. In this reaction Cu^{2+} is reduced to Cu^+ by I^- and the liberated I_2 is then titrated with standard $Na_2S_2O_3$ solution. The redox reaction is as follows:

$2\,Cu^{2+} + 4\,I^- \rightarrow 2\,CuI_{(s)} + I_{2\,(aq)}$

Electrode potentials of the relevant half-cells are:

$Cu^{2+} + e^- = Cu^+$ $\quad E^o = 0.153$ V

$I_2 + 2\,e^- = 2\,I^-$ $\quad E^o = 0.535$ V

A consideration of the electrode potentials would indicate that reduction of Cu^{2+} by I^- is not a spontaneous reaction. However, in the iodometric titration this reaction does take place. Let us try to understand the anomaly:

9.4 Cu^+ has low solubility in water with $K_{sp} = 1.1\times10^{-12}$. Calculate the effective E^o value for the equilibrium $CuI_{(s)} = Cu^+ + I^-$.

9.5 Using the result in 9.4 calculate the effective E^o value for the reduction of Cu^{2+} by I^-. What does this value suggest about the spontaneity of the reaction?

9.6 Calculate the equilibrium constant of the reduction reaction in **9.5**.

SOLUTION OF PREPARATORY PROBLEM 9

9.1 $Sn^{2+} + 2\ Fe^{3+} \rightarrow Sn^{4+} + 2\ Fe^{2+}$ $\qquad E^o = 0.617$ V

9.2 $\Delta G^o = -n\,F\,E^o = -2\,F\,E^o = -2 \times 96485 \times 0.617 = -119$ kJ

$$E^o = \frac{0.0592}{n} \log K$$

$$\log K = \frac{(2 \times 0.617)}{0.0592} \cong 20.84$$

$K = 6.92 \times 10^{20}$

9.3 Before the equivalence point**,** E of the cell is given by the following equation:

$$E_{cell} = {}_{ox}E^o_{SCE} + {}_{red}E^o_{Sn^{4+}/Sn^{2+}} = -\frac{0.0592}{2} \log \frac{[Sn^{2+}]}{[Sn^{4+}]}$$

i. The addition of 5.00 cm^3 of Fe^{3+} solution converts 5.00 / 20.00 of the Sn^{2+} to Sn^{4+}, thus

$$\frac{[Sn^{2+}]}{[Sn^{4+}]} = \frac{15.0 / 20.0}{5.0 / 20.0} = 3.00$$

$E_{cell} = -0.102$ V

ii. At the equivalence point, add the two expressions corresponding to Sn^{4+}/ Sn^{2+} and Fe^{3+}/ Fe^{2+}.

$$2\,E_{cell} = 2\,{}_{ox}E^{o}_{\mathrm{SCE}} + 2\,{}_{red}E^{o}_{\mathrm{Sn^{4+}/Sn^{2+}}} = -\,0.0592 \log \frac{[\mathrm{Sn^{2+}}]}{[\mathrm{Sn^{4+}}]}$$

$$E_{cell} = {}_{ox}E^{o}_{\mathrm{SCE}} + {}_{red}E^{o}_{\mathrm{Fe^{3+}/Fe^{2+}}} = -\,0.0592 \log \frac{[\mathrm{Fe^{2+}}]}{[\mathrm{Fe^{3+}}]}$$

to get

$$3\,E_{cell} = 3\,{}_{ox}E^{o}_{\mathrm{SCE}} + 2\,{}_{red}E^{o}_{\mathrm{Sn^{4+}/Sn^{2+}}} + {}_{red}E^{o}_{\mathrm{Fe^{3+}/Fe^{2+}}} = -\,0.0592 \log \frac{[\mathrm{Sn^{2+}}][\mathrm{Fe^{2+}}]}{[\mathrm{Sn^{4+}}][\mathrm{Fe^{3+}}]}$$

At the equivalence point, $[Fe^{3+}] = 2\,[Sn^{2+}]$ and $[Fe^{2+}] = 2\,[Sn^{4+}]$

Thus

$$E_{cell} = {}_{ox}E^{o}_{\mathrm{SCE}} + \frac{2\,{}_{red}E^{o}_{\mathrm{Sn^{4+}/Sn^{2+}}} + {}_{red}E^{o}_{\mathrm{Fe^{3+}/Fe^{2+}}}}{3} =$$

$$= -\,0.242 + \frac{2 \times 0.154 + 0.771}{3} = 0.118 \text{ V}$$

iii. Beyond the equivalence point, E of the cell is given by the following equation:

$$E_{cell} = {}_{ox}E^{o}_{\mathrm{SCE}} + {}_{red}E^{o}_{\mathrm{Fe^{3+}/Fe^{2+}}} = -\,0.0592 \log \frac{[\mathrm{Fe^{2+}}]}{[\mathrm{Fe^{3+}}]}$$

When 30 cm^3 of Fe^{3+} solution is added, 10 cm^3 of thesolution is in excess, e. i.

$$\frac{[\mathrm{Fe^{2+}}]}{[\mathrm{Fe^{3+}}]} = \frac{20.0}{10.0} = 2.00$$

$E_{\mathrm{cell}} = 0.551$ V

9.4 $\Delta G^{o} = -\,R\,T \ln K_{sp} = 68.27$ J mol^{-1}

$\Delta G^{o} = -\,n\,F\,E^{o}$ $\quad n = 1$

$E^{o} = -\,0.707$ V

9.5 $Cu^{+} + I^{-} \rightarrow CuI_{(s)}$ $\qquad E^{o} = 0.707$ V

$Cu^{2+} + e^{-} \rightarrow Cu^{+}$ $\qquad E^{o} = 0.153$ V

The overall reaction for reduction of Cu^{2+} by I^{-} is

$Cu^{2+} + I^{-} + e^{-} \rightarrow CuI_{(s)}$ $\qquad E^{o} = 0.86$ V

The E^{o} value for the reduction of Cu^{2+} by I^{-} can now be calculated

$2 \times (Cu^{2+} + I^- + e^- \rightarrow CuI_{(s)})$ $\quad E^o = 0.86$ V

$I_2 + 2\ e^- \rightarrow 2\ I^-$ $\quad E^o = 0.535$ V

The overall reaction is

$2\ Cu^{2+} + 4\ I^- \rightarrow 2\ CuI_{(s)} + I_2$ $\quad E^o = 0.325$ V

The positive value of effective E indicates that the reduction reaction is spontaneous. This has come about since in this reaction, I^- is not only a reducing agent, but is also a precipitating agent. Precipitation of Cu^+ as CuI is the key step of the reaction, as it practically removes the product Cu^+ from the solution, driving the reaction in the forward direction.

9.6 $\Delta G^o = -n F E^o$

Here $n = 1$, $\quad E^o = 0.325$V

$\Delta G^o = -31.3$ kJ

$\Delta G^o = -RT \ln K$

$K = 2.9 \times 10^5$

THEORETICAL PROBLEM 10

Solubility of sparingly soluble salts

Two important factors that affect the solubility of a sparingly soluble salt are pH and the presence of a complexing agent. Silver oxalate is one such salt, which has low solubility in water (2.06×10^{-4} at pH = 7.0). Its solubility is affected by pH as the anion oxalate reacts with hydronium ions, and also by a complexing agent such as ammonia as the cation silver forms complexes with ammonia.

10.1 Calculate the solubility of silver oxalate in acidified water with pH = 5.0. The first and second dissociation constants for oxalic acid are 5.6×10^{-2} and 6.2×10^{-5}, respectively.

10.2 In the presence of ammonia in aqueous solution, silver ion forms two complexes $Ag(NH_3)^+$ and $Ag(NH_3)_2^+$. The values of the stepwise stability constants for the formation of these complexes are 1.59×10^3 and 6.76×10^3. What is the solubility of silver oxalate in an aqueous solution in which the concentration of NH_3 is 0.02 mol dm^{-3} and its pH = 10.8 ?

SOLUTION OF PREPARATORY PROBLEM 10

10.1 $Ag_2C_2O_4(s) = 2\ Ag^+ + C_2O_4^{2-}$

The solubility product K_{sp} is given by

$K_{sp} = [Ag^+]^2\ [C_2O_4^{2-}]$

If S is the solubility of $Ag_2C_2O_4$

$[Ag^+] = 2S$ (1)

The total oxalate concentration, denoted by c_{ox}, is

$c_{ox} = S = [C_2O_4^{2-}] + [HC_2O_4^-] + [H_2C_2O_4]$ (2)

The dissociation reactions are:

$H_2C_2O_4 \leftrightarrow H^+ + HC_2O_4^-$ $K_1 = 5.6\times10^{-2}$ (3)

$HC_2O_4^- \leftrightarrows H^+ + C_2O_4^{2-}$ $K_2 = 6.2\times10^{-5}$ (4)

Eqs. (2), (3) and (4) give

$$c_{ox} = S = [C_2O_4^{2-}] + \frac{[C_2O_4^{2-}]\,[H^+]}{K_2} + \frac{[C_2O_4^{2-}]\,[H^+]^2}{K_1 K_2}$$

$[C_2O_4^{2-}]\,[H^+]$

$\therefore \quad [C_2O_4^{2-}] = \alpha\, c_{OX} = \alpha\, S$

where

$$\alpha = \frac{K_1 K_2}{[H^+]^2 + K_1[H^+] + K_1 K_2} \qquad (5)$$

At pH = 7, $[H^+] = 10^7$ and $\alpha \cong 1$

$K_{sp} = 4\ S^3 = 3.5\times10^{-11}$

At pH = 5.0, $[H+] = 1\times10^{-5}$

From the values of K_1, K_2 and $[H^+]$ we get

$\alpha = 0.861$ (6)

$K_{sp} = [2S]^2\ [\alpha S]$

$$\therefore \quad S = \left(\frac{K_{sp}}{4\,\alpha}\right)^{\frac{1}{3}} = 2.17 \times 10^{-4}$$

10.2 Eq. (5) implies

$\alpha = 1$

i. e. $c_{Ox} = S = [C_2O_4^{-2}]$ (7)

The total silver ion in the solution is given by

$c_{Ag} = 2\,S = [Ag^+] + [AgNH_3^+] + [Ag(NH_3)_2^+]$ (8)

The complex formation reactions are:

$Ag^+ + NH_3 = AgNH_3^+$ $K_3 = 1.59 \times 10^3$ (9)

$AgNH_3^+ + NH_3 = Ag(NH_3)_2^+$ $K_4 = 6.76 \times 10^3$ (10)

From eqs. (8), (9) and (10)

$c_{Ag} = 2\,S = [Ag^+]\,\{1 + K_3[NH_3] + K_3K_4[NH_3]^2\}$

$\therefore \quad [Ag+] = \beta \times c_{Ag} = \beta \times 2S$

where $\beta = \dfrac{1}{1 + K_3[NH_3] + K_3\,K_4\,[NH_3]^2}$

Using the values of K_3, K_4 and $[NH_3]$,

$\beta = 2.31 \times 10^{-4}$

$K_{sp} = [Ag^+]^2\,[C_2O_4^{2-}] = [\beta \times 2\,S]^2\,[S]$

$S = \left(\dfrac{K_{sp}}{4\,\beta}\right)^{\frac{1}{3}} = 5.47 \times 10^{-2}$

THEORETICAL PROBLEM 11

Spectrophotometry

Manganese and chromium in steel can be determined simultaneously by absorption spectral method. Dichromate and permanganate ions ($Cr_2O_7^{2-}$ and MnO_4^-) in the solution of H_2SO_4 (c = 1 mol dm^{-3}) absorb light at 440 nm and 545 nm. At these wavelengths, molar absorptivity of MnO_4^- solution is 95 $dm^3\ mol^{-1}\ cm^1$ and 2350 $dm^3\ mol^{-1}\ cm^1$, respectively and that of $Cr_2O_7^{2-}$ is 370 $dm^3\ mol^{-1}cm^1$ and 11 $dm^3\ mol^{-1}cm^1$, respectively.

A steel sample, weighing 1.374 g, was dissolved and Mn and Cr in the resulting solution oxidised to MnO_4^- and $Cr_2O_7^{2-}$. The solution was diluted with a H_2SO_4 solution (c = 1 mol dm^{-3}) to 100.0 cm^3 in a volumetric flask. The transmittances of this solution were measured with a cell of 1.0 cm path length and with the solution of H_2SO_4 as blank. The observed transmittances at 440 nm and 545 nm were 35.5 % and 16.6 %, respectively.

11.1 Calculate from these data the percentage of Mn and Cr in the steel sample. Assume that Beer's law is valid for each ion and that the absorption due to one ion is unaffected by the presence of the other ion.

Cobalt (II) forms a single complex CoL_3^{2+} with an organic ligand L and the complex absorbs strongly at 560 nm. Neither Co(II) nor ligand L absorbs at this wavelength. Two solutions with the following compositions were prepared:

Solution 1 $[Co(II)] = 8\times10^{-5}$ and $[L] = 2\times10^{-5}$

Solution 2 $[Co(II)] = 3\times10^{-5}$ and $[L] = 7\times10^{-5}$

The absorbances of solution 1 and solution 2 at 560 nm, measured with a cell of 1.0 cm path length, were 0.203 and 0.680, respectively. It may be assumed that all the ligand in solution 1 is consumed in the formation of the complex.

11.2 From these data calculate:

i. molar absorptivity of the complex CoL_3^{2+}

ii. stability constant for the formation of the complex CoL_3^{2+}.

SOLUTION OF PREPARATORY PROBLEM 11

11.1 Denote the molar absorptivity of MnO_4^- at 440 nm and 545 nm by ε_1 and ε_2 and that of $Cr_2O_7^{2-}$ by ε_3 and ε_4:

ε_1 = 95 dm^3 mol^{-1}cm^{-1}, ε_2 = 2350 dm^3 mol^{-1}cm^{-1}

ε_3 = 370 dm^3 mol^{-1}cm^{-1}, ε_4 = 11 dm^3 mol^{-1}cm^{-1}

The absorbance A is related to % transmittance T by

$A = 2 - \log T$

From the values given for the sample solution

$A_{440} = 2 - \log 35.5 = 0.45$

$A_{545} = 2 - \log 16.6 = 0.78$

Now if one denotes the molar concentrations of MnO_4^- and $Cr_2O_7^{2-}$ in the steel sample solution by c_1 and c_2 respectively, we have

$A_{440} = \varepsilon_1 c_1 + \varepsilon_3 c_2$

$A_{545} = \varepsilon_2 c_1 + \varepsilon_4 c_2$

Using the given data, we get

c_1 = 0.0003266 mol dm^{-3}

c_2 = 0.001132 mol dm^{-3}

The amount of Mn in 100 cm^3 of the solution:

0.0003266 mol dm^{-3} × 54.94 g mol^{-1} × 0.1 dm^3 = 0.001794 g

$$\% \text{ Mn in steel sample } = \frac{0.001794 \times 100}{1.374} = 0.13\,\%$$

The amount of Cr present in 100 cm^3 of the solution:

0.001132 mol dm^{-3} × 2 × 52.00 g mol^{-1} × 0.1 dm^3 = 0.0118 g

$$\% \text{ Cr in steel sample } = \frac{0.0118 \times 100}{1.374} = 0.86\,\%$$

11.2 In solution 1 all the ligand is consumed in the formation of the complex, thus:

$$[CoL_3^{2+}] = \frac{2\times10^{-5}}{3} = 0.667\times10^{-5}$$

Absorptivity of the complex CoL_3^{2+} is

$$\varepsilon = \frac{0.203}{0.667\times10^{-5}\ \text{mol dm}^{-3}\times1.0\ \text{cm}} = 3.045\times10^{4}\ \text{dm}^{-3}\,\text{mol}^{-1}\,\text{cm}^{-1}$$

If the concentration of the complex CoL_3^{2+} in solution 2 is *c*

$$c = \frac{0.68}{3.045\times10^{4}\ \text{dm}^{3}\,\text{mol}^{-1}\text{cm}^{-1}\times1\,\text{cm}} = 2.233\times10^{-5}\ \text{mol dm}^{-3}$$

$[Co^{2+}] = [Co^{2+}]_{total} - [CoL_3^{2+}] = 3\times10^{-5} - 2.233\times10^{-5} = 0.767\times10^{-5}$

Similarly,

$[L] = [L]_{total} - 3\,[CoL_3^{2+}] = 7\times10^{-5} - 3\times 2.233\times10^{-5} = 0.300\times10^{-5}$

The reaction of complex formation is

$Co^{2+} + 3\ L = [CoL_3^{2+}]$

The stability constant *K* is given by

$$\frac{[CoL_3^{2+}]}{[Co^{2+}][L]^3} = 1.08\times10^{17}$$

THEORETICAL PROBLEM 12

Reactions in buffer medium

An organic nitro-compound (RNO_2) is electrolytically reduced in an aqueous acetate buffer solution having total acetate concentration (HOAc + OAc^-) 0.500 and pH = 5.0. The buffered solution with the volume of 300 cm^3 in which the concentration of RNO_2 was 0.01 mol dm^{-3}, was reduced completely. The dissociation constant for acetic acid is 1.75×10^{-5} at 25 °C. The reduction reaction is

$$RNO_2 + 4\,H^+ + 4\,e^- \rightarrow RNHOH + H_2O$$

12.1 Calculate the pH of the solution after completion of the reduction of RNO_2.

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SOLUTION OF PREPARATORY PROBLEM 12

12.1 $RNO_2 + 4\,H^+ + 4\,e \rightarrow RNHOH + H_2O$

$$HOAc = H^+ + OAc^-$$

$$K_a = \frac{[H^+]\,[OAc^-]}{[HOAc]}$$

i. e.

$$pK_a = pH + \log\frac{[HOAc]}{[OAc^-]}$$

$$4.76 = 5.0 + \log\frac{[HOAc]}{[OAc^-]}$$

$$\frac{[HOAc]}{[OAc^-]} = 0.5715$$

$$[HOAc] + [OAc^-] = 0.500$$

$[OAc^-] = 0.3182$

$[HOAc] = 0.5 - 0.3182 = 0.1818$

mmoles of acetate (OAc^-) present initially in 300 cm^3 = 0.3182 × 300 = 95.45

mmoles of acetic acid (HOAc) present initially in 300 cm^3 = 0.1818 × 300 = 54.55

mmoles of RNO_2 reduced = 300 × 0.0100 = 3

From the stoichiometry of the equation:

3 mmoles of RNO_2 will consume 12 moles of H^+ for the reduction. The H^+ is obtained from dissociation of HOAc.

On complete electrolytic reduction of RNO_2,

mmoles of HOAc = 54.55 – 12.00 = 42.55

mmoles of OAc^- = 95.45 + 12.00 = 107.45

$$4.76 = pH + \log\frac{42.55}{107.45}$$

pH = 5.16

THEORETICAL PROBLEM 13

Identification of an inorganic compound

Some observations related to an unknown inorganic substance **A** are presented below.

- **A** is a yellowish – white deliquescent solid and it sublimes on heating. It has a molecular weight of 266.
- **A** reacts violently with water, forming solution **B**.
- When a solution of NH_4Cl and NH_3 is added to solution **B**, a white gelatinous precipitate is obtained.
- A sample of **B** also gives a curdy white precipitate **C** on addition of dilute nitric acid and silver nitrate solution. This white precipitate **C** readily dissolves when dilute aqueous NH_3 solution is added, though a gelatinous white precipitate **D** is formed in its place with excess of NH_3 .
- Precipitate **D** is filtered off and is dissolved in excess NaOH to give a clear solution **E**.
- When CO_2 is passed through solution **E**, compound **D** is reprecipitated.
- Substance **A** dissolves unchanged in dry ether. When this solution is reacted with LiH, a product **F** is formed. If LiH is used in excess, **F** transforms to **G**.

13.1 Identify the unknown compound **A**.

13.2 Write down the appropriate chemical equations for the given reactions and identify the different products from **B** to **G**.

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SOLUTION OF PREPARATORY PROBLEM 13

13.1 The white gelatinous precipitate in group (III) obtained by qualitative analysis of solution B indicates the presence of Al^{3+} ions. The white precipitate with $AgNO_3$ indicates the presence of Cl^- ions.

From the above data the compound **A** must be a dimer of aluminium chloride Al_2Cl_6.

13.2 The equations of the reactions in ionic form are as follows:

$Al_2Cl_6 \xrightarrow{H_2O} 2\,[Al(H_2O)_6]^{3+} + 6\,Cl^-$ $\quad Al_2Cl_6$ = **A** $\quad [Al(H_2O)_6]^{3+}$ = **B**

$Cl^- + Ag^+ \rightarrow AgCl(s)$ $\quad AgCl$ = **C**

$AgCl(s) + 2\,NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-$

$Al^{3+}(aq) + 3\,NH_3 + 3\,H_2O \rightarrow Al(OH)_3(s) + 3\,NH_4^+$ $\quad Al(OH)_3$ = **D**

$Al(OH)_3(s) + OH^-(aq) \rightarrow [Al(OH)_4]^-(aq)$ $\quad [Al(OH)_4]^-$ = **E**

$[Al(OH)_4]^- + CO_2 \rightarrow Al(OH)_3(s) + HCO_3^-$

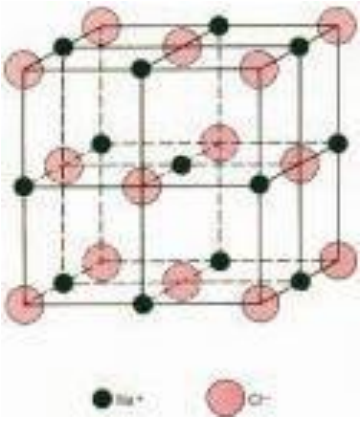
$Al_2Cl_6 + 8\,LiH \xrightarrow{\text{excess of LiH}} 2\,Li[AlH_4] + 6\,LiCl$ $\quad AlH_3$ = **F** $\quad Li[AlH_4]$ = **G**

THEORETICAL PROBLEM 14

Ionic and metallic structures

Modern methods of structural analysis using X-rays provide valuable information about the three dimensional arrangement of atoms, molecules or ions in a given crystal structure.

14.1 Crystal structure of rock salt (NaCl) is given below.



i. What is the type of crystal lattice presented in the diagram?

ii. What is the coordination number of a sodium ion in this structure?

iii. What is the number of formula units of NaCl per unit cell?

iv. Calculate the r_{Na^+} / r_{Cl^-} limiting radius ratio for this structure.

Why is the array of chloride ions slightly expanded, with the nearest Cl-Cl distance being 400 pm, compared to the close packed value of 362 pm?

v. What happens when the cation radius in the structure shown above is progressively increased till the cation/anion radius ratio reaches a value of 0.732?

vi. What is the range of cation/anion radius ratio for which the structure like that of NaCl is stable?

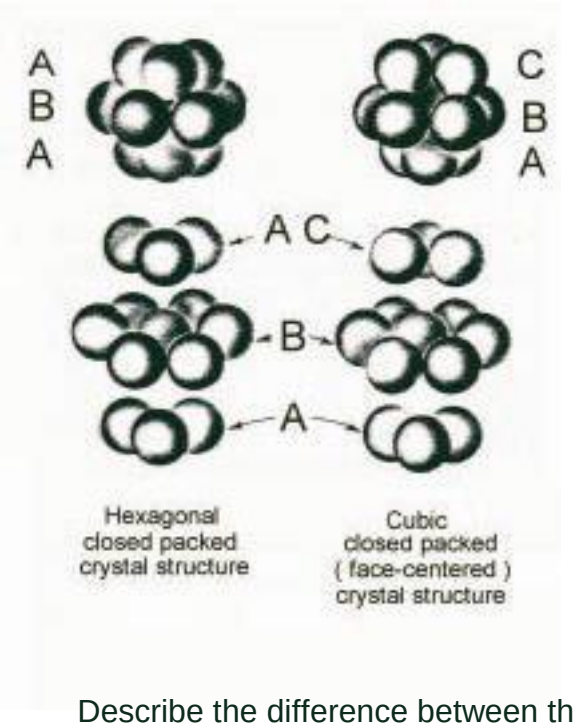
14.2 The Cu-Kα X-ray (λ = 154pm) reflection from (200) planes of sodium chloride crystal is observed at 15.8. Given that the radius of the chloride ion is 181 pm, calculate:

i. the separation between adjacent 200 planes of NaCl.

ii. the length of the unit cell edge (lattice constant) of NaCl.

iii. the radius of the sodium ion.

14.3 The diagram of a cubic close packing (*ccp*) and a hexagonal close packing (*hcp*) lattice arrangement (assuming rigid sphere model) is given below.



i. Describe the difference between the *ccp* and *hcp* lattice arrangements.

ii. Calculate the packing fraction for a *ccp* arrangement.

iii. Will the coordination number, and the packing fraction in a *hcp* arrangement be the same as that in a *ccp* arrangement?

14.4 Nickel (at.wt. 58.69) crystallizes in the *ccp* structure. X-ray diffraction studies indicate that its unit cell edge length is 352.4 pm. Given that the density of Nickel is 8.902 g cm^{-3}, calculate

i. the radius of the nickel atom.

ii. the volume of the unit cell.

iii. the Avogadro number.

SOLUTION OF PREPARATORY PROBLEM 14

14,1 i. The lattice of NaCl consist of interpenetrating fcc lattices of Na^+ and Cl^-.

ii. The co-ordination number of sodium is six since, it is surrounded by six nearest chloride ions.

iii. For NaCl, the number of Na^+ ions is: twelve at the edge centres shared equally by four unit cells thereby effectively contributing 12 × 1/4 = 3 Na^+ ions per unit cell and one at body center. Thus, a total of 3 + 1 = 4 Na^+ ions per unit cell.

Number of Cl^- ions is: six at the center of the faces shared equally by two unit cells, thereby effectively contributing 6 × 1/2 = 3 Cl^- ions per unit cell and eight at the corners of the unit cell shared equally by eight unit cells thereby effectively contributing 8 × 1/8 = 1 Cl^- ion per unit cell. Thus, a total of 3 + 1 = 4 Cl^- ions per unit cell. Hence, the number of formula units of NaCl per unit cell = 4 Na^+ + 4 Cl^- = 4 NaCl

iv. The face diagonal of the cube is equal to $\sqrt{2}$ times 'a' the lattice constant for NaCl. The anions/anions touch each other along the face diagonal. The anion/cations touch each other along the cell edge.

Thus, $a = 2\,(r_{Na^+} + r_{Cl^-})$ ……..(1)

Face diagonal $\sqrt{2}\ a = 4\ r_{Cl^-}$ ……..(2)

Substituting for 'a' from (1) into (2) we get :

$\sqrt{2} \times 2\,(r_{Na^+} + r_{Cl^-}) = 4\ r_{Cl^-}$ from which,

the limiting radius ratio $r_{Na^+} / r_{Cl^-} = 0.414$

v. The chloride ion array is expanded to make the octahedral holes large enough to accommodate the sodium ions since, the r_{Na^+} / r_{Cl^-} ratio of 0.564 is larger than the ideal limiting value of 0.414 for octahedral six coordination number.

vi. As the cation radius is progressively increased, the anions will no longer touch each other and the structure becomes progressively less stable. There is insufficient room for more anions till the cation / anion radius ratio equals 0.732

when, eight anions can just be grouped around the cation resulting in a cubic eight coordination number as in CsCl.

vii. Generally, the fcc structure with a six coordination number is stable in the cation/anion radius ratio range 0.414 to 0.732. That is, if 0.414 < r+/r- < 0.732 then, the resulting ionic structure will generally be NaCl type fcc.

14.2 i. Bragg's law states $\lambda = 2\, d_{hkl} \sin\theta$

154 pm = 2 × d_{200} sin(15.8°)

$$d_{200} = \frac{154\text{ pm}}{2\sin(15.8^{o})} = \frac{154\text{ pm}}{2 \times 0.272} = 283\text{ pm}$$

Thus, the separation between the (200) planes of NaCl is 283 pm.

ii. Length of the unit cell edge, a = d_{100} = 2 × d_{200}

a = 2 × 283 pm = 566 pm.

iii. Since it is an fcc lattice,

cell edge, a = 2 ($r_{Na^+} + r_{Cl^-}$)

radius of sodium ion $r_{Na+} = \frac{a - 2}{2}\ r_{Cl^-}$ = 566 – 362 = 102 pm

14.3 i. The difference in an hcp and a ccp arrangement is as follows:

The two 'A' layers in a hcp arrangement are oriented in the same direction making the packing of successive layers ABAB.. and the pattern repeats after the second layer whereas, they are oriented in the opposite direction in a ccp arrangement resulting in a ABCABC… packing pattern which repeats after the third layer.

The unit cell in a ccp arrangement is based on a cubic lattice whereas in a hcp arrangement it is based on a hexagonal lattice.

ii. Packing fraction $= \frac{\text{volume occupied by 4 atoms}}{\text{volume of unit cell}}$

Let 'a' be the length of the unit cell edge.

Since it is an fcc lattice, face diagonal = $\sqrt{2a}$ = 4 r (1)

Volume of the unit cell = a3

$$\text{Packing fraction} = \frac{4 \times 4\pi r^3}{3\,a^3} \qquad (2)$$

Substituting for 'a' from (1) into (2), we get

$$\text{Packing fraction} = \frac{4 \times 4 \times 22 \times (\sqrt{2})^3 \times r^3}{3 \times 7 \times (4r)^3} = 0.74$$

Thus, the packing fraction in a ccp arrangement = 0.74

iii. The coordination number(12) and the packing fraction (0.74) remain the same in a hcp as in a ccp arrangement.

14.4 **i.** For an fcc, face diagonal = $\sqrt{2}a$ = 4 r_{Ni} where a = lattice constant

r_{Ni} = radius of the nickel atom

$$r_{Ni} = \frac{\sqrt{2} \times a}{4} = \frac{\sqrt{2} \times 352.4\ \text{pm}}{4} = 124.6\ \text{pm}$$

ii. Volume of unit cell = a^3 = $(3.524\ \text{Å})^3$ = 43.76 Å^3

iii. Density of nickel $\rho_{Ni} = \frac{Z \times M / N_A}{V}$

No. of Ni atoms, Z = 4 for an fcc lattice

Avogadro constant

$$N_A = \frac{Z \times M}{\rho_{Ni} \times V} = \frac{4 \times 58.69\ \text{g mol}^{-1}}{8.902\ \text{g cm}^{-3} \times 43.76 \times 10^{-24}} = 6.02 \times 10^{23}\ \text{mol}^{-1}$$

THEORETICAL PROBLEM 15

Compounds of nitrogen

Nitrogen forms a number of oxides. One of the important oxides of nitrogen is NO_2, a red-brown colored reactive gas.

15.1 Draw the Lewis structure of NO_2 and predict its shape using valence shell electron pair repulsion theory.

15.2 Using VSEPR, predict the shapes of the NO_2^- and NO_2^+ ions. Compare the shapes of these two ions with that of NO_2 .

15.3 Consider two other compounds of nitrogen, trimethylamine (Me_3N) and trisilylamine $(H_3Si)_3N$. The observed bond angles at nitrogen in these compounds are 108° and 120° respectively. Explain the difference in the bond angles.

15.4 Both nitrogen and boron form trifluorides. The bond energy in BF_3 is 646 kJ mol^{-1} and that in NF_3 is only 280 kJ mol^{-1}. Account for the difference in bond energies.

The boiling point of NF_3 is –129 °C while that of NH_3 is –33 °C. Ammonia acts as a Lewis base whereas NF_3 does not. The observed dipole moment of NF_3 (0.24 D) is much less than that of NH_3 (1.46 D), even though fluorine is much more electronegative than hydrogen.

15.5 Explain the differences between boiling points and basicities of NF_3 and NH_3. Account for the low dipole moment of NF_3.

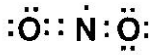
The reaction of aqueous sodium nitrate with sodium amalgam as well as that of ethyl nitrite with hydroxylamine in presence of sodium ethoxide give the same product. This product is the salt of a weak unstable acid of nitrogen. Identify the acid and write down its structure. This acid isomerises into a product, which finds use in propellant formulations.

15.6 Write the structure of the isomer.

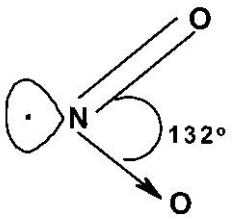
SOLUTION OF PREPARATORY PROBLEM 15

15.1 **NO_2**: The number of electrons in the valence shell around the nitrogen atom = = 5 + 0 + 2 = 7

The Lewis structure for NO_2 is as shown below.

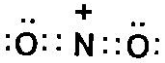


According to VSEPR, the molecule ideally should have linear geometry. However, this molecule has one single unpaired electron present on nitrogen. Due to the repulsion between the unpaired electron and the other two bonded pairs of electrons, the observed bond angle is less than 180° (132°). Thus, the shape of the molecule is angular as shown below.

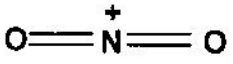


15.2 **NO_2^+**: The number of electrons in the valence shell around nitrogen atom = = (5 + 2 + 2 –1) = 8

The Lewis structure is as shown below

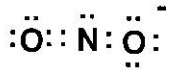


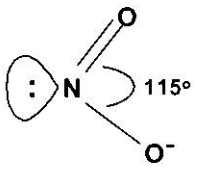
Thus, there are no non-bonded electrons present on nitrogen. The two σ-bonds will prefer to stay at 180° to minimize repulsion between bonded electron pairs giving a linear geometry (180°). The π-bonds do not influence the shape.



NO_2: The number of electrons in the valence shell around the nitrogen atom = = 5 + 2 + 1 = 8

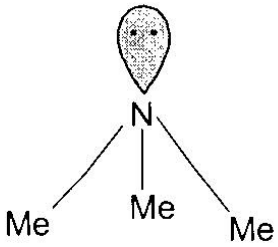
The Lewis structure is as shown below.

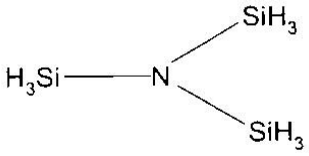




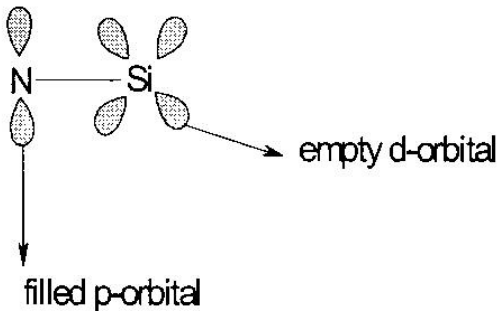
In case of anion NO_2^-, there is a lone pair of electrons present on the nitrogen atom. Due to strong repulsion between the lone pair of electrons and the bonded pairs of electrons the angle between the two bond pairs shrinks from the ideal 120° to 115°.

15.3 In case of trimethylamine, the shape of the molecule is pyramidal with a lone pair present on nitrogen. Due to the lone pair Me-N-Me angle is reduced from 109°4' to 108°.

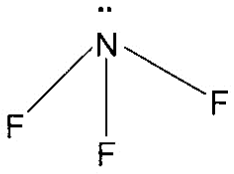


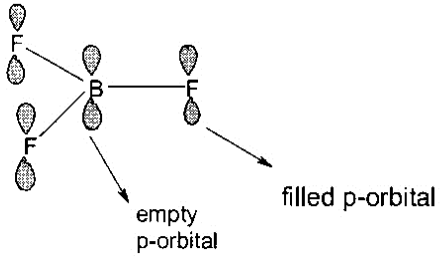


However, in case of trisilylamine, d orbital of silicon and p orbital of nitrogen overlaps giving double bond character to the N-Si bond. Thus, delocalisation of the lone electron pair of the nitrogen atom takes place and the resultant molecule is planar with 120° bond angle.



15.4 Both N and B are tricovalent. However, NF_3 is pyramidal in shape. In case of BF_3, the B-F bond gets double bond character due to the overlapping of p čorbitals present on boron and fluorine. The observed bond energy is, therefore, much greater in BF_3.

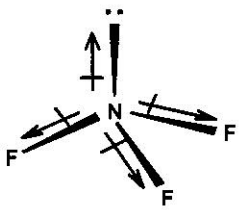




The difference in boiling points of NF_3 and NH_3 is due to hydrogen bonding which is present in ammonia.

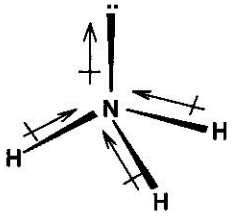
15.5 High electronegativity of fluorine decreases the basicity of nitrogen in NF_3. Thus, NF_3 does not act as a Lewis base.

In NF_3, the unshared pair of electrons contributes to a dipole moment in the direction opposite to that of the net dipole moment of the of the N-F bonds. See figure (a).



NF_3

(a)



NH_3

(b)

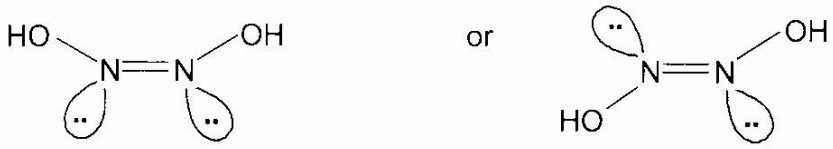
In NH_3, the net dipole moment of the N-H bonds and the dipole moment due to the unshared pair of electrons are in the same direction. See figure (b).

15.6 $NaNO_3 + 8\ Na(Hg) + 4\ H_2O \rightarrow Na_2N_2O_2 + 8\ NaOH + 8\ Hg$

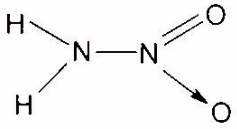
$NH_2OH + EtNO_2 + 2\ NaOEt \rightarrow Na_2N_2O_2 + 3\ EtOH$

$Na_2N_2O_2$ is the salt of $H_2N_2O_2$ (Hyponitrous acid).

Structure :



Isomer is: $H_2N—NO_2$ (Nitramide)



THEORETICAL PROBLEM 16

Structure elucidation with stereochemistry

Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) is the primary acid of citrus fruits, which contributes to their sour taste. Commercial manufacturing of citric acid involves fermentation of molasses or starch using the fungus Aspergillus niger at pH 3.5. It is widely used in food, soft drinks and as a mordant in dyeing. It is also an important biochemical intermediate.

16.1 What transformation will citric acid undergo when warmed with concentrated sulfuric acid at 45 – 50 °C? Give the structure and IUPAC name of the product obtained. Which type of organic acids would undergo a similar reaction?

After warming citric acid with sulfuric acid, anisole (methoxybenzene) is added to the reaction mixture and product **A** ($C_{12}H_{12}O_5$) is obtained. On heating with acetic anhydride, **A** forms an anhydride. 118 mg of **A** requires 20 cm^3 of KOH solution (c = 0.05 mol dm^{-3}) for neutralisation.

Reaction with bromine indicates that the same amount of compound **A** requires 80 mg of bromine to give an addition product.

16.2 Deduce the structure of **A**.

16.3 Identify the possible isomers of **A** in this reaction and give their structures, absolute configurations and the IUPAC names.

16.4 How many stereoisomers of **A** will be obtained in the bromination reaction? Draw their Fischer projections.

16.5 Assign absolute configurations to the stereocentres in all the stereoisomers formed in 16.4.

If phenol and resorcinol are separately added to the reaction mixture instead of anisole, compounds **B** and **C** are obtained, respectively. **B** does not give any coloration with

neutral $FeCl_3$ solution, but **C** does. Under identical reaction conditions, the yield of compound **C** is much higher than that of **B**.

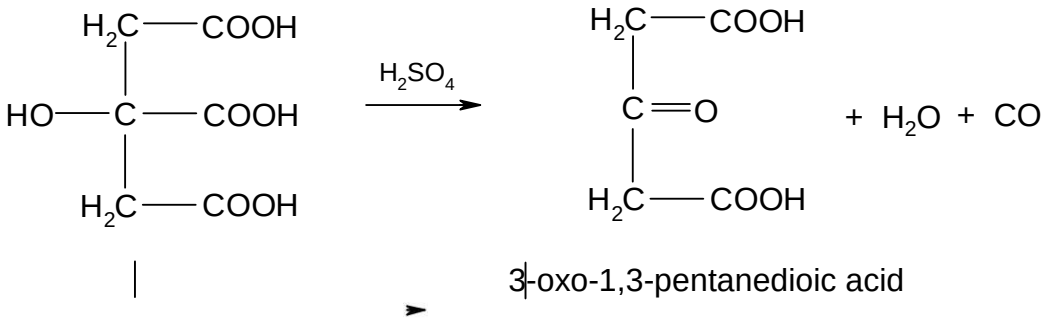
16.6 Give appropriate structures for **B** and **C**.

16.7 What is the difference between the reactions leading to the formations of **A** and **B,** respectively?

16.8 Why is the yield of **C** higher than that of **B**?

SOLUTION OF PREPARATORY PROBLEM 16

16.1



3-oxo-1,3-pentanedioic acid

α-Hydroxy carboxylic acids undergo similar reaction.

16.2 Molar mass of **A** = 236 g mol^{-1}.

20 cm^3 of KOH solution (c = 0.05 mol dm^{-3}) Α 118 mg **A**

1000 cm^3 of KOH solution (c = 1 mol dm^{-3}) Α 118 g **A**

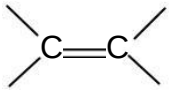
Thus, the acid is dibasic.

Molar mass of **A** = 236 g mol^{-1}

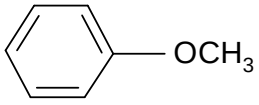
80 mg Br_2 Α 118 mg **A**

160 mg Br_2 Α 236 g **A**

A contains one double bond



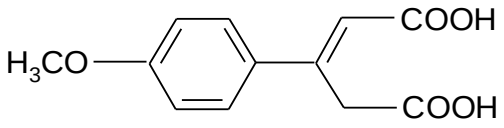
It has anisole ring in the molecule



It is formed from HOOC–CH_2–CO–CH_2–COOH

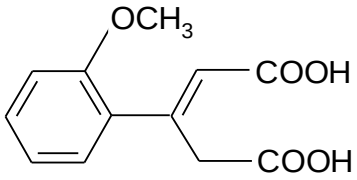
It has molecular formula $C_{12}H_{12}O_5$.

Due to steric hindrance the attachment of the aliphatic portion on the anisole ring will be para with respect to -OCH_3. Hence the structure will be

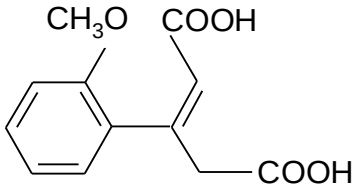


As **A** forms anhydride the two COOH groups should be on the same side of the double bond.

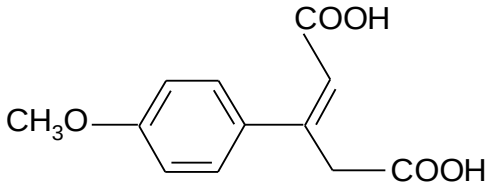
16.2 Isomers of **A**



(E) 3-(2-methoxyphenyl)-2-pentenedioic acid

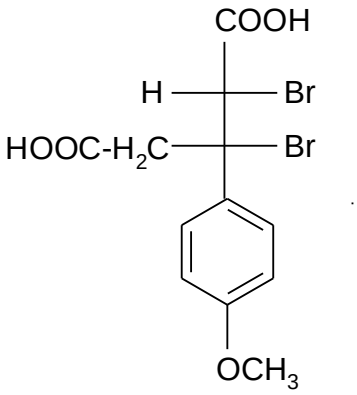


(Z) 3-(2-methoxyphenyl)-2-pentenedioic acid

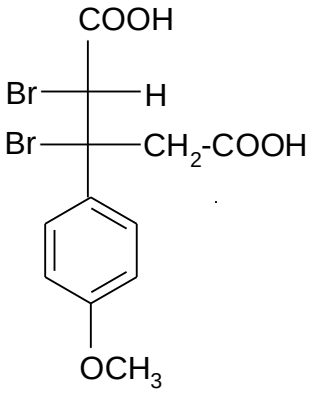


(Z) 3-(4-methoxyphenyl)-2-pentenedioic acid

16.4 Two products are possible when compound **A** reacts with bromine.



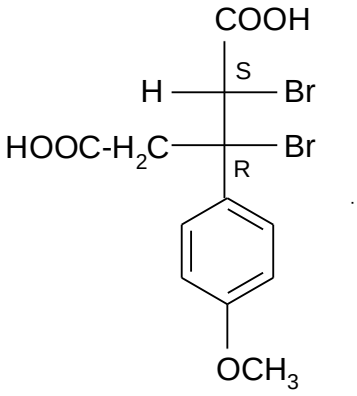
[1]



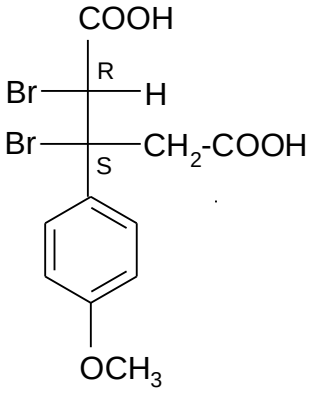
[2]

Structures 1 and 2 are enantiomers.

16.5

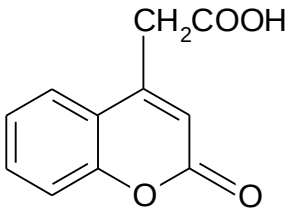


[1]



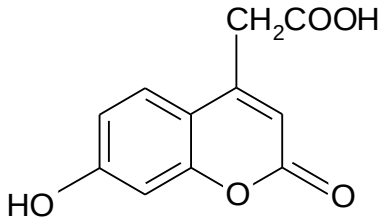
[2]

16.6



B

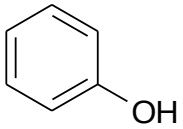
Product obtained by reaction with phenol



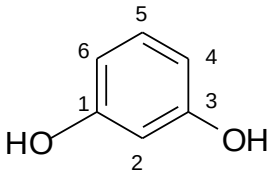
C Product obtained by reaction with resorcinol

16.7 In the formation of compound **A** from anisole, the attack takes place at the *p*-position of the OCH_3 group. However, when compound **B** is formed from phenol, the attack takes place at the *o*-position of the OH group. Steric hindrance of OCH_3 group favours the attack at the *para* position. Steric hindrance of the OH group is comparatively less. Thus, the attack is possible at the *ortho* or *para* positions. However, addition at *ortho* position is favoured as it leads to cyclization of the intermediate acid to stable **B**.

16.8 Phenol has only one OH group on the phenyl ring whereas resorcinol has two OH groups on the phenyl ring at the m-positions. Hence, position 4 is considerably more activated (i.e, electron rich) in the case of resorcinol.



Phenol



Resorcinol

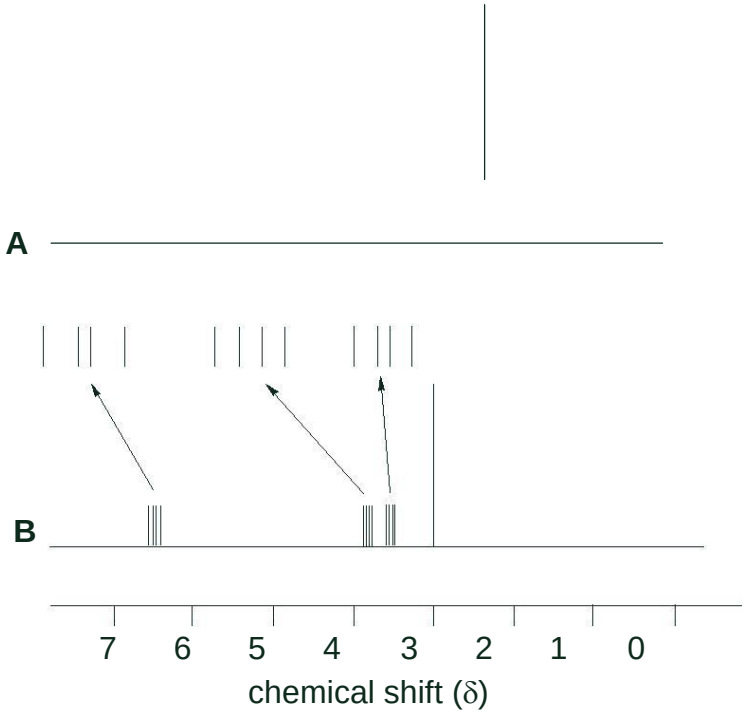
Therefore, under identical reaction conditions, the yield of compound **C** is much higher than that of **B.**

THEORETICAL PROBLEM 17

Organic spectroscopy and structure determination

When identifying two compounds **A** and **B** the following observations were recorded: Both have the molecular formula C_3H_6O. Schematic ^{1}H-NMR spectra of these compounds at 400 MHz are presented in the following figure. The peak positions and the relative intensities of the different lines in the ^{1}H-NMR spectrum of **B** are given in the accompanying Table (Note: the values have been altered slightly from the experimental values to facilitate analysis.)

One of these compounds reacts with malonic acid to form a compound known as Meldrum's acid with a molecular formula of $C_6H_8O_4$ which gives peaks between 0 and 7.0 δ in its ^{1}H-NMR spectrum. The IR spectrum shows a peak in the region 1700 – 1800 cm^{-1}. It condenses with an aromatic aldehyde in the presence of a base.



^{1}H-NMR schematic spectra of A and B at 400 MHz

Table 17.1.

Peak positions and relative intensities of individual lines in the ^{1}H NMR spectrum (400 MHz) of **B**

Line	(ppm)	Relative intensity	Line	(ppm)	Relative intensity
1	6.535	1	8	3.870	1
2	6.505	1	9	3.525	1
3	6.495	1	10	3.505	1
4	6.465	1	11	3.495	1
5	3.930	1	12	3.475	1
6	3.910	1	13	3.000	12
7	3.890	1			

17.1 Label the unknown compounds in the bottles with IUPAC names, using the NMR spectra given in the figure.

17.2 In the ^{1}H-NMR spectrum of **B**, assign the peak positions to specific protons.
Calculate the spin-spin coupling constants for protons of compound **B**.

17.3 Convert the peak positions of the first four lines into Hz (refer to the Table). What will be the peak positions of these lines in Hz, if the spectrum is recorded on a 600 MHz instrument?

17.4 Draw the possible structure of Meldrum's acid.

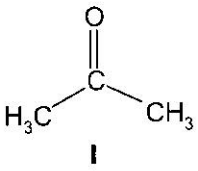
17.5 Meldrum's acid has pK_a = 4.83. Explain the acidity of Meldrum's acid.

17.6 Give the structure of the condensation product of Meldrum's acid with an aromatic aldehyde.

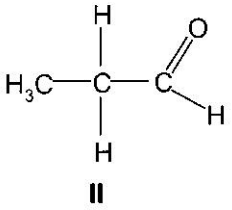
———————

SOLUTION OF PREPARATORY PROBLEM 17

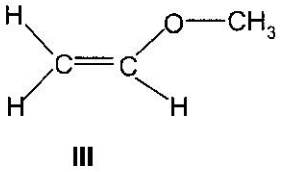
17.1 The given molecular formula is C_3H_6O. Therefore, the possible structures are:



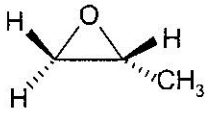
I



II

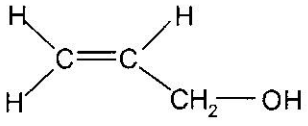


III



IV

V

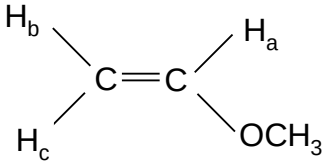


VI

The NMR spectrum of compound **A** shows a single peak which indicates that all the protons in **A** are equivalent. This holds true only for structure **I**. The IUPAC name of this compound is 2-propanone.

The NMR spectrum of compound **B** shows four sets of peaks, which indicate the presence of four non-equivalent protons. This holds true for structures **III** and **IV**. However, for structure **IV**, no singlet peak (see peak at $\delta = 3$) will be observed. So, compound B must have structure III. The IUPAC name is 1-methoxyethene.

17.2



Three doublets of doublets centred at 6.5 ppm, 3.9 ppm, 3.5 ppm are seen in the spectrum. The assignments in the spectrum are

H_a: 6.5 ppm

H_b: 3.5 ppm

H_c: 3.9 ppm

Due to the presence of electron donating OCH_3, the trans proton Hb has higher electron density and thus more shielded than H_c. Thus, Hb appears upfield as compared to H_c. There is also a singlet line at δ = 3. This corresponds to the H in OCH_3.

17.3 Coupling constants

H_a : 12, 16 Hz $J(H_a, H_b)$ = 12 Hz $J(H_a, H_c)$ = 16 Hz

H_b : 8, 12 Hz $J(H_a, H_b)$ = 12 Hz $J(H_b, H_c)$ = 8 Hz

H_c : 8, 16 Hz $J(H_b, H_c)$ = 8 Hz $J(H_c, H_a)$ = 16 Hz

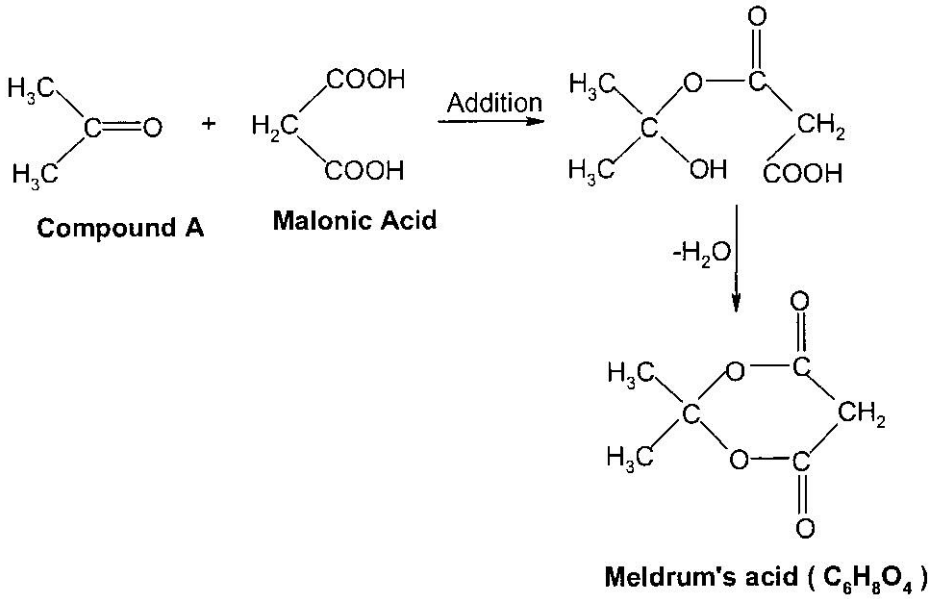
Note: J = (difference in two lines in ppm) $\times$ (instrument frequency)

Geminal coupling < cis-vicinal coupling < trans-vicinal coupling

17.4

Peak positions in Hz (for 400 MHz instrument)	Peak positions in Hz (for 600 MHz instrument)
2614	3921
2602	3903
2598	3897
2586	3879

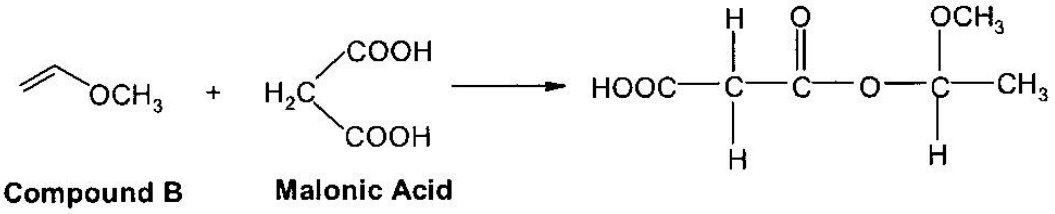
17.5 Compound A will react with malonic acid in the following manner



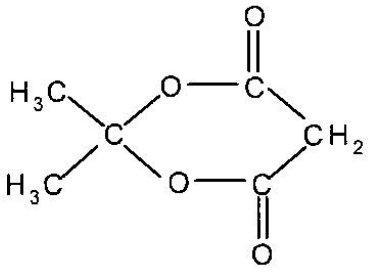
The structure of Meldrum's acid is consistent with the ^{1}H-NMR and IR data.

The peak in the IR spectrum at 1700 – 1800 cm^{-1} is because of the C=O stretching. The presence of peaks only between 0 – 7 δ in the ^{1}H-NMR spectrum indicates that the compound doesn't have any acidic group like COOH or OH.

If compound **B** reacts, the only possibility is that it will add across the double bond giving a product with molecular formula equal to $C_6H_{10}O_5$. This molecular formula does not match with the one stated in the problem. C

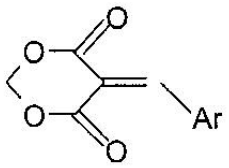


17.6 The increased acidity is due to active $–CH_2$ group of Meldrum's acid flanked by two –CO groups. The carbanion formed at $–CH_2$ will be stabilised by these –CO groups, which are coplanar.



Meldrum's acid ($C_6H_8O_4$)

17.7 The condensation product of Meldrum's acid with an aromatic aldehyde has the structure



THEORETICAL PROBLEM 18

Polymer synthesis

Ethylene finds extensive application in the manufacture of polymers and bulk chemicals. It is produced on a large scale by thermal and catalytic cracking of alkanes obtained from natural gas and petroleum.

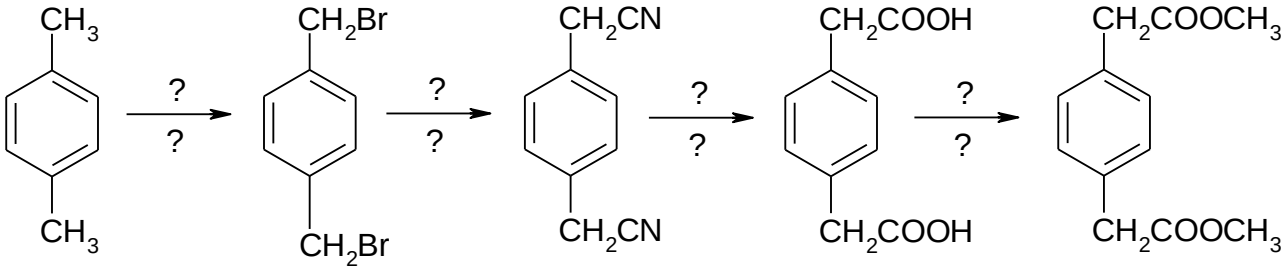
In the presence of silver catalyst, ethylene reacts with oxygen to give **P**. Compound **P** on heating with acidified water forms **Q**. 1H-NMR spectrum of **P** has only one signal while that of **Q** contains two signals.

18.1 Identify and draw the structures for compounds **P** and **Q**.

Compound **R** is obtained when **P** and **Q** react with each other. **R** reacts with $SOCl_2$ to give **S**. On heating with alcoholic KOH, **S** gives **T**, an anaesthetic under the name "vinethene".

18.2 Identify compounds **R**, **S** and **T**.

Another compound dimethyl benzene-1,4-bis(acetate) can be synthesised from p-xylene. Such a synthesis requires use of proper reagents so that desired intermediate compounds and the final product are obtained. Various intermediate compounds obtained in the synthesis of dimethyl benzene-1,4-bis(acetate) along with their structures are shown below.



p-xylen

benzene-1-4-biacetate

18.3 Identify the reagents used in this synthesis of dimethyl benzene –1,4-bis(acetate).

18.4 How many peaks would you expect in the 1H-NMR spectrum of dimethyl benzene – 1,4-bis(acetate)?

When dimethyl benzene-1,4-bis(acetate) (synthesised from p-xylene) and compound (obtained from ethylene) are heated together a polymer is formed.

18.5 Draw the structure of the polymer.

18.6 What happens when this polymer is treated

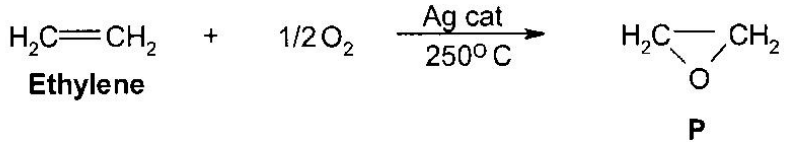
- with aqueous solution of KOH (heat), then with H^+/ H_2O,
- with $LiAlH_4$?

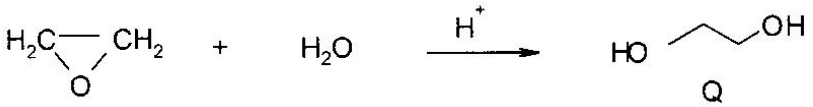
18.7 Inadvertently, an excess of dimethyl benzene-1,4-bis(acetate) was heated with glycerol and a different polymer was obtained. What is the probable structure of this polymer? Will it be suitable for drawing fibres?

———————

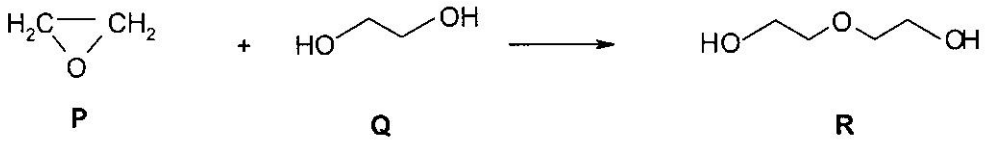
SOLUTION OF PREPARATORY PROBLEM 18

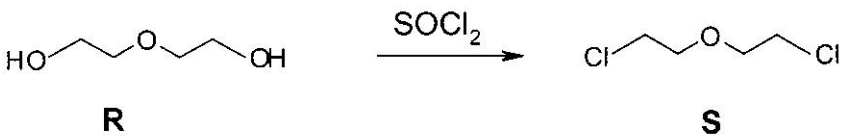
18.1

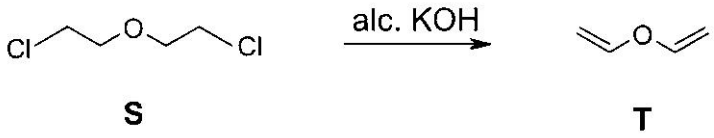




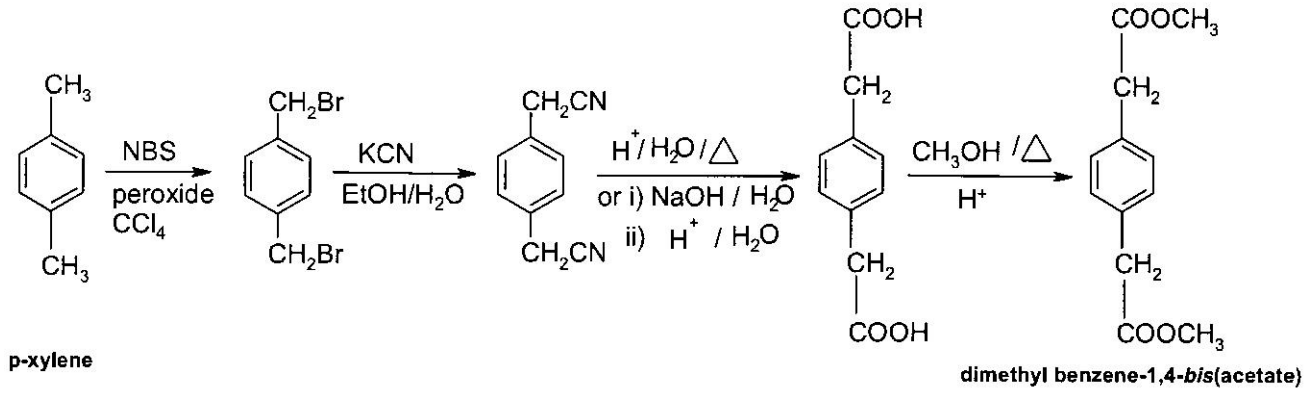
18.2





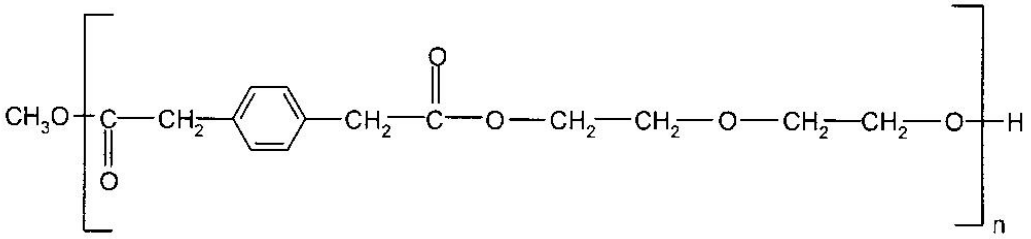


18.3

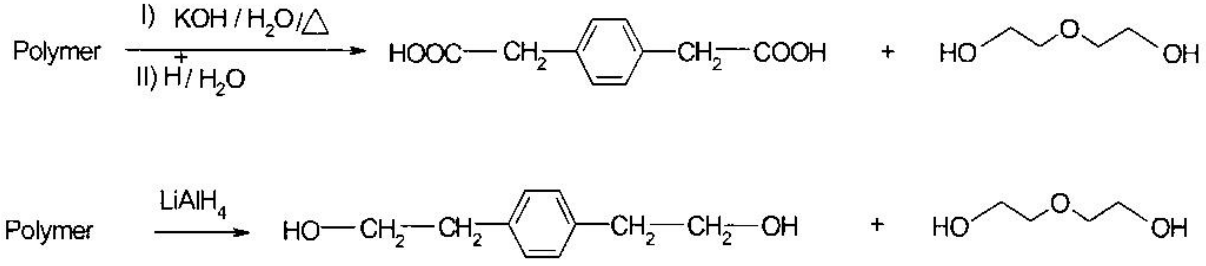


18.4 Three signals (three singlets for $-CH_3$, $-CH_2$ and aromatic protons)

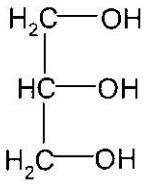
18.5 Structure of polymer



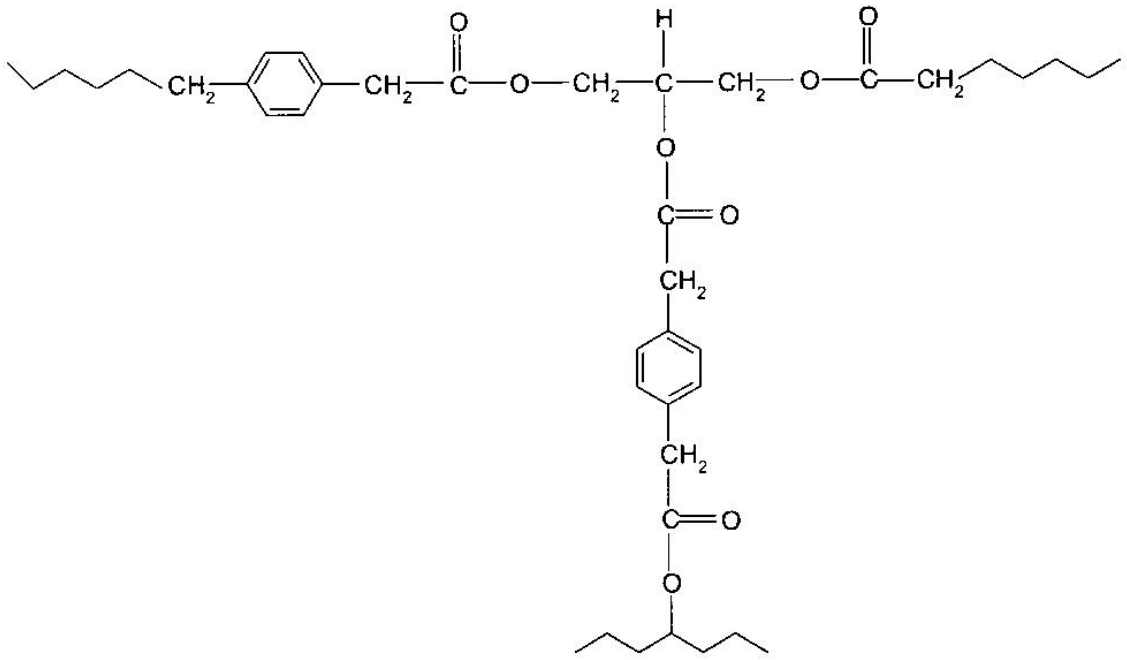
18.6



18.6 With Glycerol (being a triol), cross-links between the polymer chains involving the secondary hydroxyl group will form giving a three-dimensional network polymer is possible.



Glycerol

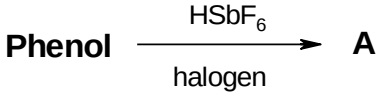


The polymer is unsuitable for drawing fibers because of its cross-linked, resin-like property.

THEORETICAL PROBLEM 19

Organic synthesis involving regioselection

One crucial problems in organic synthesis concerns the synthesis of a specific disubstituted benzene through an electrophilic substitution reaction on a monosubstituted benzene. This problem is elegantly tackled in a synthesis of Tramadol, an analgesic drug **($C_{16}H_{25}NO_2$)**, described below. The first step in this synthesis invovles:



A gives two equal intensity peaks at 172 and 174 in the highest m/z region of its mass spectrum. It gives a mixture of three isomeric mononitro derivatives on nitration under mild conditions.

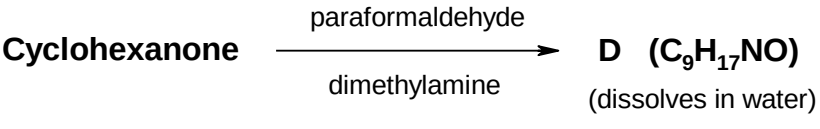
19.1 Draw the structure for compound **A**. What is the regioselection observed in the reaction of phenol to form **A**? State the significance of this reaction.

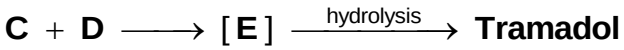
Consider the following reaction

Mass spectrum of **B** shows equal intensity peaks at 186 and 188 in the highest m/z region.

19.2 Give structures of compounds **B** and **C**. How does the reactivity of **B** change on its conversion to **C**?

Another intermediate compound **D** required for the synthesis of Tramadol is obtained as follows:





19.3 Show the structures of compound **D** and the final product Tramadol.

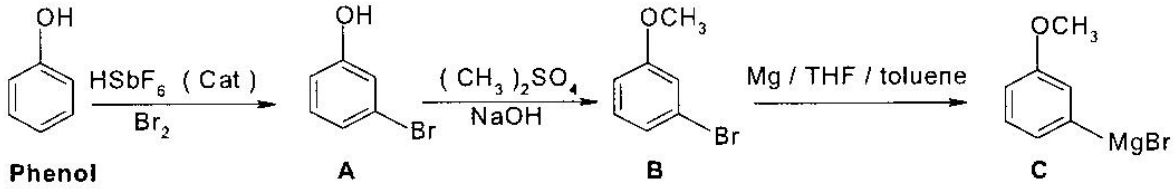
19.4 Give the structures of the possible stereoisomers of Tramadol.

_____

SOLUTION OF PREPARATORY PROBLEM 19

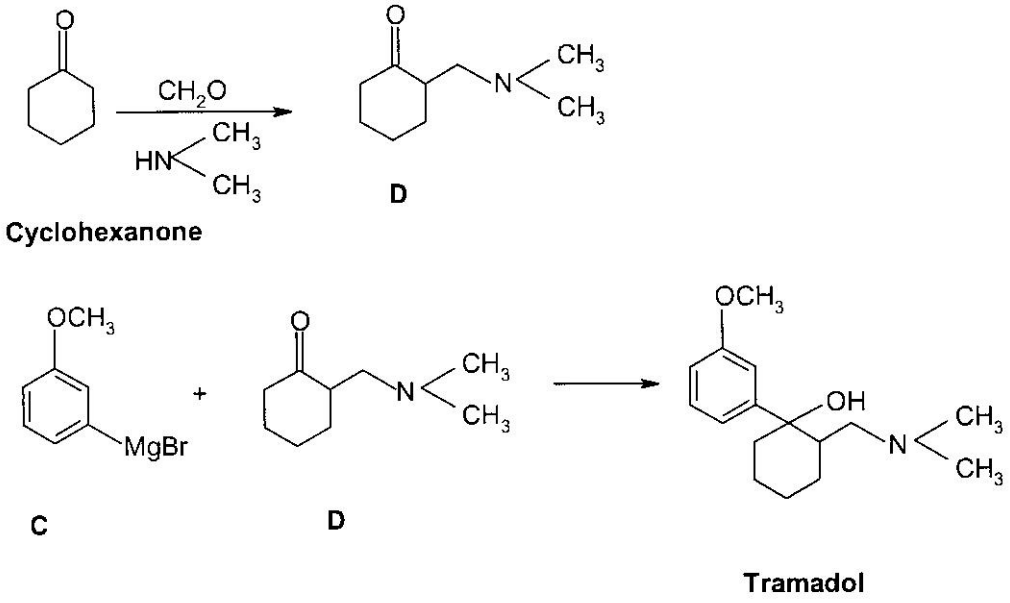
19.1 The product obtained in the presence of catalyst $HSbF_6$ is *m*-bromophenol. From the mass spectra given in the problem, direct bromination of phenol gives o/p–bromo derivatives as OH group present in phenol is *o*/*p*- directing.

19.2

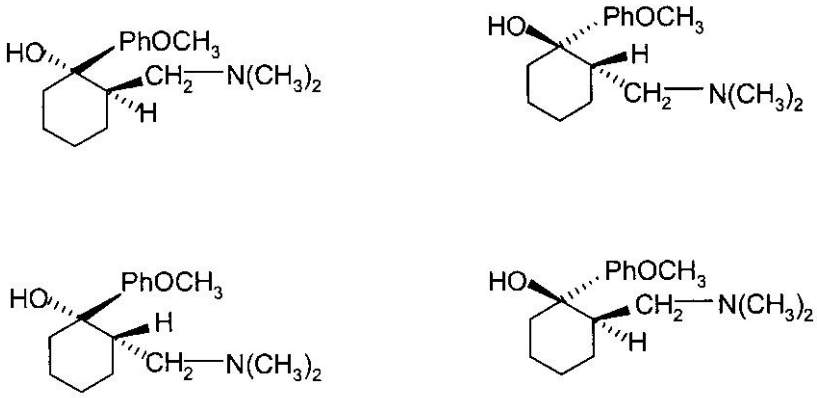


Compound **B** may undergo nucleophilic reaction at the carbon bearing bromine. Compound **C** contains a carbanion and hence functions as a nucleophile and will attack an electrophile. Thus, reactivity of **B** is reversed on its conversion to **C** (umpolung).

19.3



19.4



Tramadol has two asymmetric carbon atoms. It has two pairs of enantiomers.

THEORETICAL PROBLEM 20

Carbon acids

Keto esters are bifunctional reactive molecules and are important synthons for the synthesis of aliphatic and heterocyclic compounds.

20.1 Two isomeric keto esters X and Y have the same molecular formula $C_5H_8O_3$. Deduce their possible structures

Each ester is first reacted with benzyl bromide in the presence of CH_3ONa, and the resulting products are treated with 1 or 2 equivalent of a strong base (such as lithium diisopropyl amide, LDA) followed by 1 equivalent of CH_3I. Then the products are at the end of the second step hydrolysed by aqueous solution of HCl.

20.2 Write down the reaction sequences involved.

20.3 Explain why the final product of the reaction of keto ester **X** is a neutral compound (molecular formula $C_{11}H_{14}O$) whereas keto ester **Y** gives a keto acid with a molecular formula of $C_{12}H_{14}O_3$.

Keto ester X gives different products depending upon the amount of LDA used.

20.4 Explain what happens when

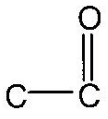
i. 1 equivalent of LDA is used.

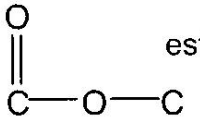
ii. 2 equivalents of LDA are used.

———————

SOLUTION OF PREPARATORY PROBLEM 20

20.1 The molecular formula of the keto ester is $C_5H_8O_3$. Since **X** and **Y** are keto esters, they must have the following units-


keto group

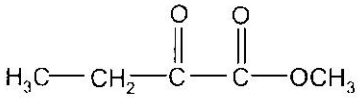

ester group

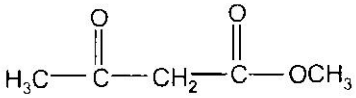
This accounts for C_4O_3 .The remaining part comprises of CH_8. Thus, only two types of ester groups are possible, methyl or ethyl.

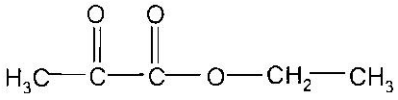
For a methyl ester: CH_3 will be a part of the ester moiety. This leaves CH_5 to be attached.

For an ethyl ester: CH_2CH_3 will be a part of the ester group. Therefore H_3 unit needs to be accounted for.

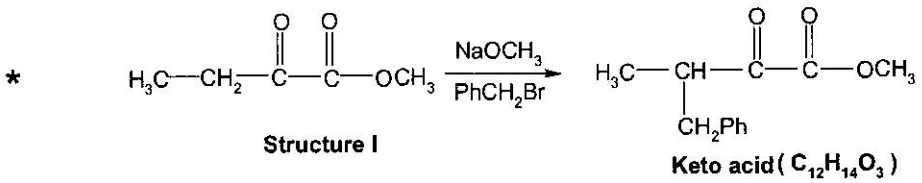
Therefore, possible structures of the keto esters are:


Structure I


Structure II

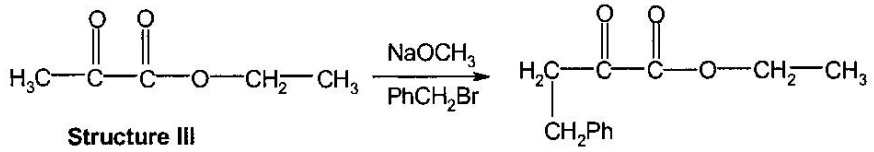

Structure III

20.2 Reaction sequence for keto esters

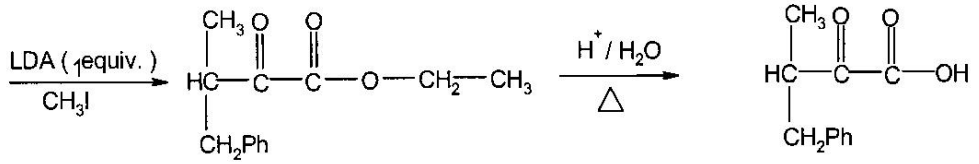


Structure I **Keto acid ($C_{12}H_{14}O_3$)**

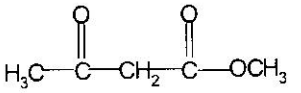
*



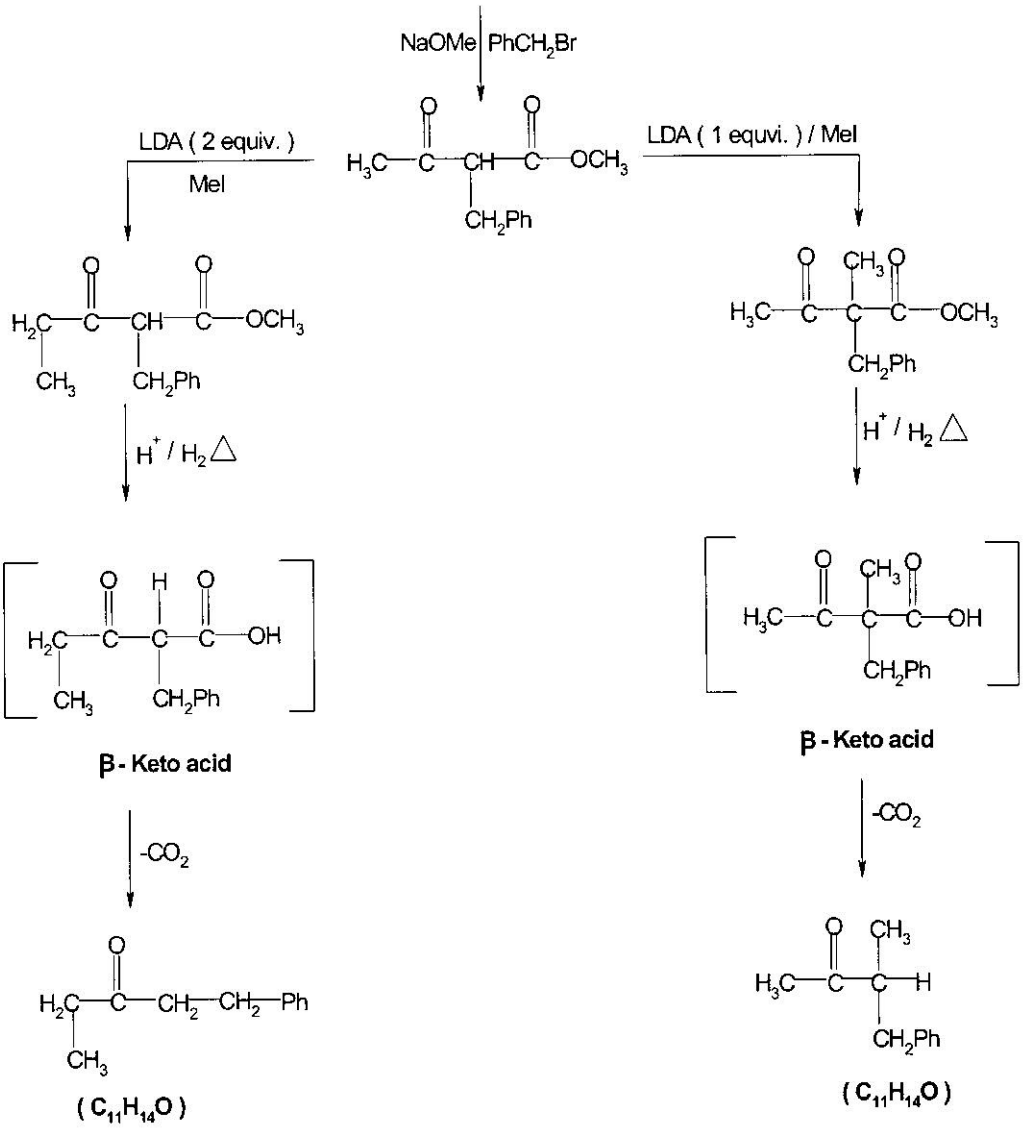
Structure III



Keto acid ($C_{11}H_{12}O_3$)



Structure II



β - Keto acid

β - Keto acid

($C_{11}H_{14}O$)

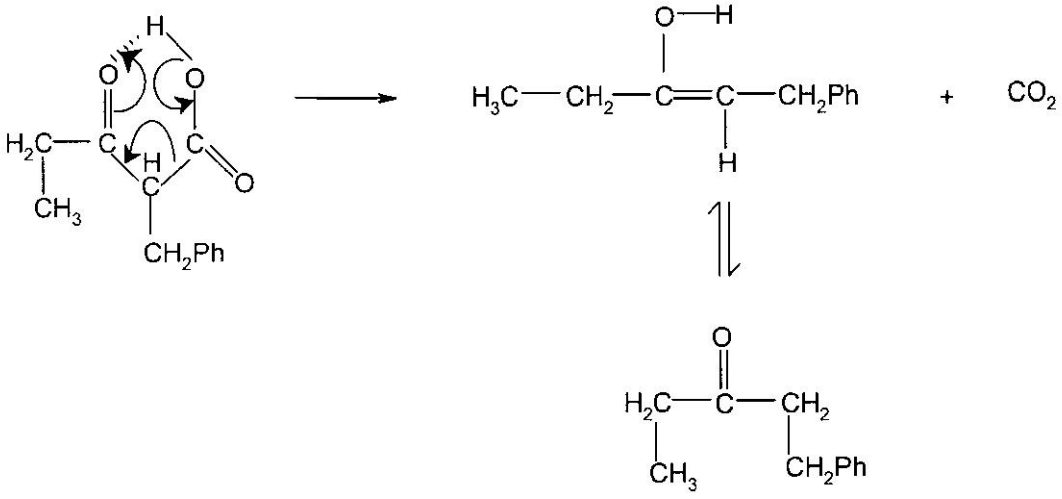
($C_{11}H_{14}O$)

- Structure I gives a keto acid with molecular formula $C_{12}H_{14}O_3$ which matches with the formula of the keto acid obtained from **Y.** Structure I is **Y**.
- Structure II gives a neutral compound with molecular formula $C_{11}H_{14}O$ that matches with the molecular formula of the neutral acid stated for **X**. Structure II is **X**.
- Structure III gives a keto acid with molecular formula $C_{11}H_{12}O_3$ that also does not match with any given molecular formula.

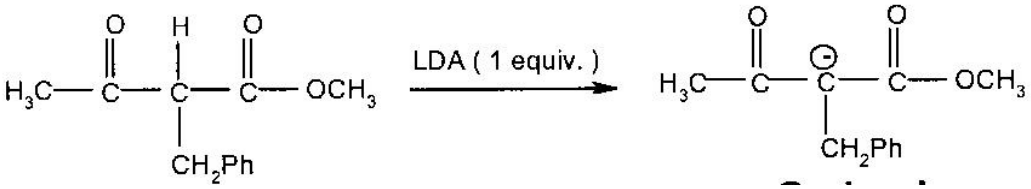
Hence the two keto esters are:

$CH_3–CH_2–CO–CO–OCH_3$	$CH_3–CO–CH_2–CO–OCH_3$
Compound **Y**	Compound **X**
(Structure I)	(Structure II)
α-keto ester	β-keto ester

20.3 The β-keto ester gives on hydrolysis a β-keto acid. This acid readily undergoes decarboxylation involving a 6-membered transition state, giving a neutral product (Ketone).

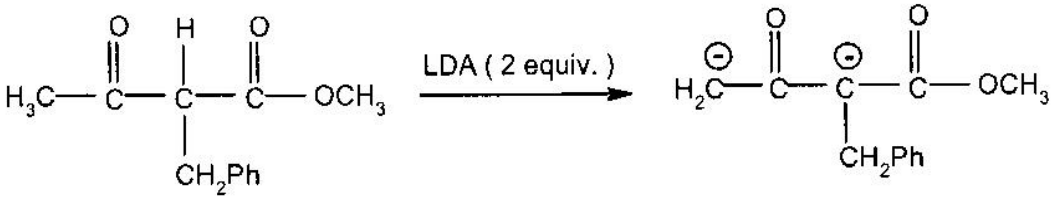


20.4 **i.** When 1 equivalent of LDA is used compound **X** produces a carbanion (monoanion) as shown below.



Compound X **Carbanion (monoanion)**

ii. Use of 2 equivalents of LDA leads to the formation of a dianion .

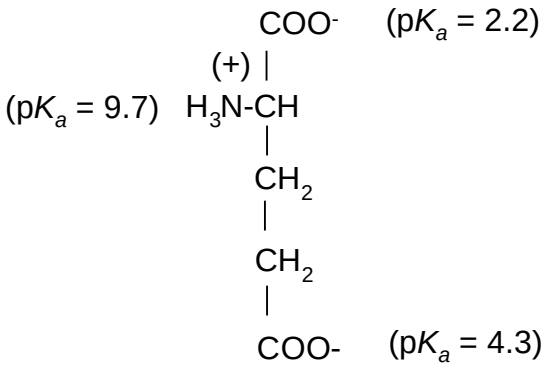


Compound X **Dianion**

THEORETICAL PROBLEM 21

Amino acids and enzymes

Amino acids are the building blocks of proteins. The presence of $–NH_2$ and –COOH groups makes amino acids amphoteric in nature. Certain amino acid side chains in proteins are critically important for their reactivity and catalytic role. Glutamic acid is one such amino acid, whose structure is shown below.

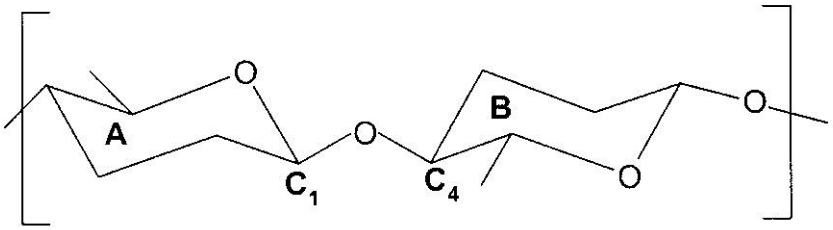


21.1 Why is the pK_a of the α-COOH group lower than that of the γ-COOH ?

21.2 Calculate the percent of γ-COOH group that remains unionized at pH = 6.3.

21.3 Glutamic acid is subjected to paper electrophoresis at pH = 3.25. Will it move towards the anode (+) or cathode (-)? Why ?

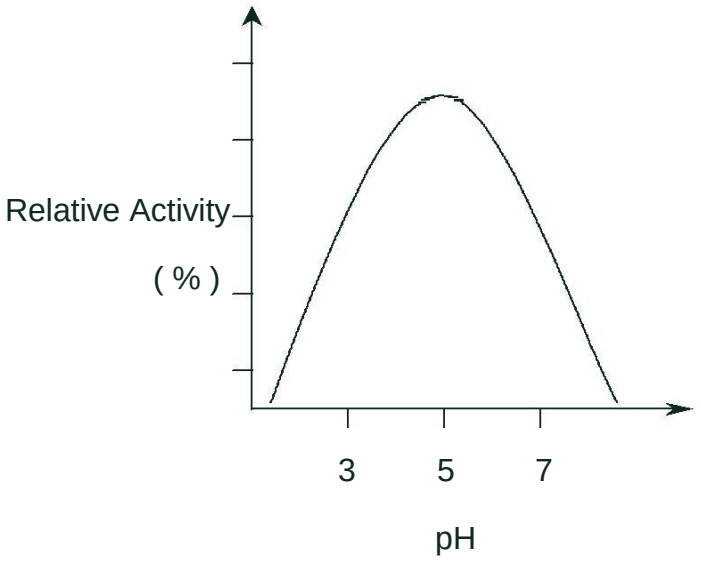
Hydrolysis of polysaccharides like chitin, cellulose and peptidoglycan is a common biochemical process. This involves the hydrolysis of a glycosidic bond like the γ-1,4 linkage shown below.



One such hydrolysis reaction is catalysed by lysozyme.

21.4 Suppose the lysozyme catalyzed reaction is performed in ^{18}O enriched water, do you expect the ^{18}O to be incorporated into the product? If yes, where?

The pH-activity profile of lysozyme is shown in the figure

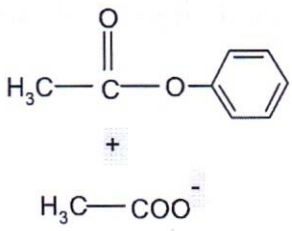


21.5 Explain this pH behavior in terms of two carboxylates (Asp-52 and Glu-35) present at the lysozyme active site (note : ionizable groups on the substrate are not involved). Write the ideal state of ionization at the lysozyme active site at pH 5.0.

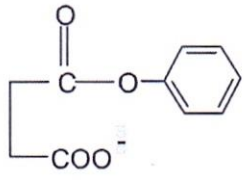
21.6 The pK_a of Glu-35 in lysozyme active site is 6.0 and not 4.3 as found in the free amino acid. Which of the following local effects is likely to be involved?

1. Enhanced negative charge
2. Enhanced positive charge
3. Enhanced polarity
4. Diminished polarity

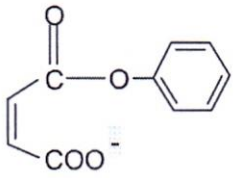
Organic model reactions have helped to understand many features of enzyme catalytic mechanisms. When a reaction is made intramolecular (like the enzyme catalysts do!), rate acceleration takes place as if the apparent reactant concentration felt at the site is enormously raised. The carboxylate group assisted hydrolysis of three phenylacetates and their rate constants (k) are shown below.

(1) 

$k_1 = 0.002\ s^{-1}$
(when $[CH_3COO^-] = 1\ M$)
(pseudo first order)

(2) 

$k_2 = 0.4\ s^{-1}$
(first order)

(3) 

$k_3 = 20\ s^{-1}$
(first order)

21.7 Calculate the effective local concentration of the COO- group felt in (2) and (3) above.

21.8 Why do you see a higher rate in (3) than in (2) ?

_____

SOLUTION OF PREPARATORY PROBLEM 21

21.1 The protonated amino group has an electron withdrawing effect. This enhances the release of proton from the neighbouring –COOH, by stabilizing the conjugate base – COO^-. This effect is greater when the $–COO^-$ is physically closer to NH_3^+. As NH_3^+ group is present on the α-carbon, the effect is greater on α-COOH than that on the γ-COOH. So the pK_a value of α-COOH is lower than that of γ-COOH.

21.2 The ratio of ionized to unionized -COOH group is obtained by using Henderson-Hasselbach equation,

$$\text{pH} = \text{p}K_a + \log \frac{[\text{COO-}]}{[\text{COOH}]}$$

The pH = 6.3 and pK_a of γ-COOH group is 4.3. Substituting these values in the above equation we get,

$$6.3 = 4.3 + \log \frac{[\text{COO-}]}{[\text{COOH}]}$$

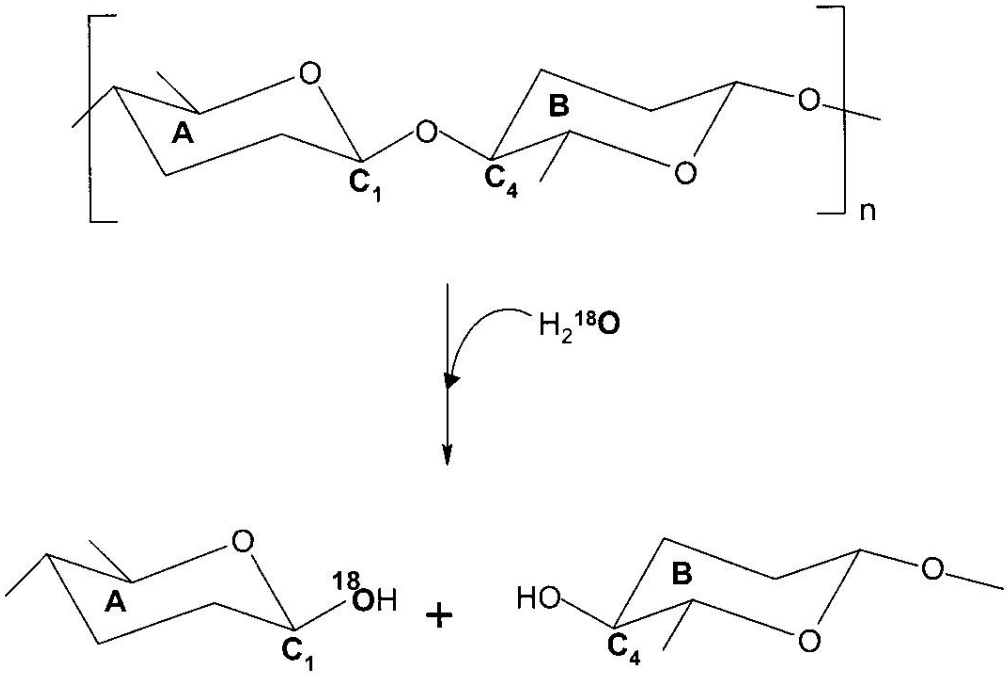
$$\text{Thus, } [\text{COOH}] = \frac{100}{101} = 0.99\,\% \text{ at pH} = 6.3$$

21.3 Glutamic acid has two pK_a values lower than 7.0 and one pK_a value higher than 7.0. Thus, the isoelectric point (pI) for glutamic acid will lie between the two acidic pK_a values.

pI = (2.2 + 4.3) / 2 = 3.25

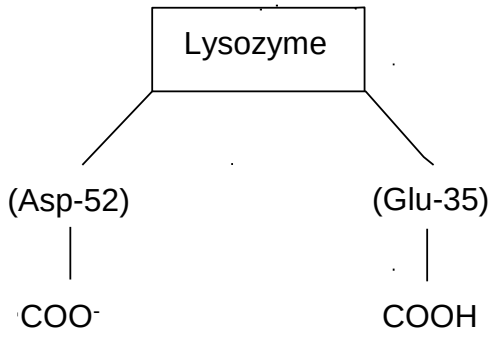
At pH = 3.25, net charge on glutamic acid will be zero since this pH coincides with pI of glutamic acid. Hence, glutamic acid will be stationary at pH 3.25.

21.4 In the hydrolysis of the glycosidic bond, the glycosidic bridge oxygen goes with C_4 of the sugar **B**. On cleavage, ^{18}O from water will be found on C_1 of sugar **A**.



NOTE: The reaction proceeds with a carbonium ion stabilized on the C_1 of sugar **A**.

21.5 Most glycosidases contain two carboxylates at the active site that are catalytically important. Lysozyme is active only when one carboxylate is protonated and the other is deprotonated. A descending limb on the alkaline side of the pH profile is due to ionization of –COOH. An ascending limb on the acidic side is due to protonation of $–COO^–$. Thus the enzyme activity drops sharply on either side of the optimum pH. The ideal state of ionization at pH = 5 will be,



NOTE: It is desirable to study the amino acid side chains (R-groups) and their ionization properties. The pK_a values of these groups significantly determine the pH dependence of enzyme activity.

21.6 Answers 2 and 4 are correct. Ionization of □COOH leads to generation of a negatively charged species, $COO^–$. This charged species is poorly stabilized by diminished

polarity and enhanced negative charge. Hence ionization of COOH group is suppressed and the pK_a is elevated.

21.7 The ratios of pseudo-first order rate constant (at $c(CH_3COO^-)$ = 1 mol dm^{-3}) in (a) to the first order rate constants in (b) and (c) provide the effective local concentrations.

For example, (2) (0.4) / (0.002) = 200

i. e. the effective concentration = 200 mol dm^{-3}

(3) (20) / (0.002) = 10,000

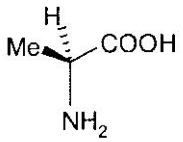
i. e. the effective concentration = 10,000 mol dm^{-3}

21.8 In addition to the enhanced local concentration effect, the COO^- group in (3) is better oriented to act in catalysis. The double bond restricts the motion of COO^- and thus reduces the number of unsuitable orientation of □COO^-, thereby enhancing the reaction rate.

THEORETICAL PROBLEM 22

Coenzyme chemistry

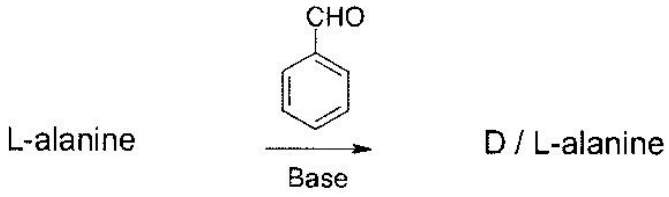
The protective outer cell wall in bacteria has D-alanine as one of the building blocks. However, metabolically only L-amino acids are available. Bacteria make D-alanine by inverting the L-alanine. The structure of L-alanine is given below:



L-alanine

The abstraction of α-proton from L-alanine and reprotonation of the resultant carbanion from the opposite side appears to be a simple process. However, it is not easy to deprotonate alanine unless its NH_2 group is masked and C_α-H is activated as an acid. Both these steps are brought about by the coenzyme pyridoxal phosphate (PLP) in the presence of the enzyme alanine racemase. The following observations made in certain model reactions will help you appreciate the role of PLP as the coenzyme.

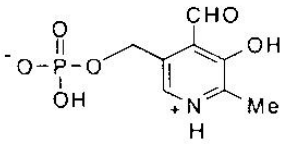
Under favorable experimental conditions, benzaldehyde can be used as a reagent to racemize alanine. In other words, it can mask the amine group and activate the C_α-H of alanine making it more acidic.



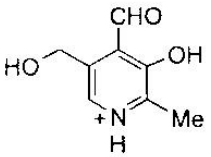
22.1 Propose a stepwise mechanism for this base catalyzed racemisation of L-alanine involving benzaldehyde as the reagent.

Compared to benzaldehyde, PLP is a somewhat complex molecule. With the help of a few carefully designed aromatic aldehydes, good insight about the role of PLP as a coenzyme can be obtained.

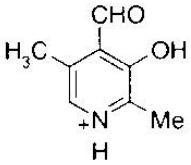
A few relevant structures are presented below. Underneath each, there is an indication about its activity.



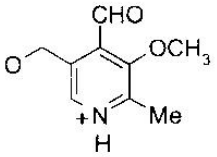
PLP (1)
Active



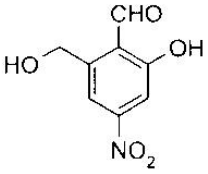
Pyridoxal (2)
Active



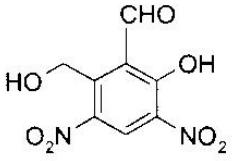
(3)
Active



(4)
Inactive



(5)
Active



(6)
Inactive

22.2 Based on this information, what inferences can you draw about the structural requirements for PLP to act as a coenzyme?

22.3 A trivalent metal ion is actually critically needed for any of the above shown compounds to display PLP-like activity without the involvement of the enzyme. Suggest a plausible explanation for the role of the metal ion.

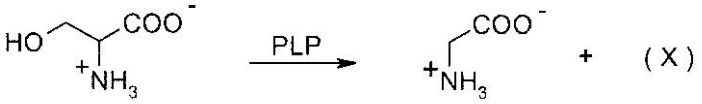
22.4 PLP is quite a versatile coenzyme. It participates in a variety of biologically important reactions. The activity of PLP is due to its functioning as an electron sink that stabilizes carbanions.

An important illustration of catalytic versatility of PLP is in the biosynthesis of the neurotransmitter gamma amino butyric acid (GABA). As shown below, GABA is made in a single step from L-glutamic acid. Suggest a mechanism explaining the role of PLP as the coenzyme in this particular reaction.

Glutamic Acid GABA

In yet another PLP mediated reaction, L-serine serves as a one-carbon donor in a complex process of nucleotide biosynthesis. The enzyme serine hydroxymethyltransferase degrades L-serine with the help of PLP into the simpler amino acid glycine. An important metabolic intermediate (X) is obtained as the side product in this reaction.

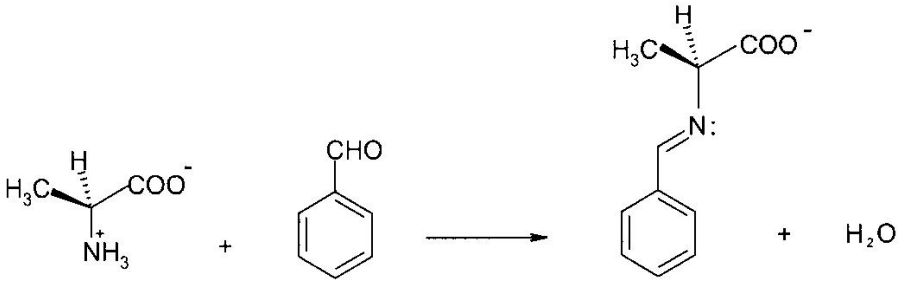
22.5 Identify the one carbon metabolic intermediate formed by analyzing its PLP based mechanism.



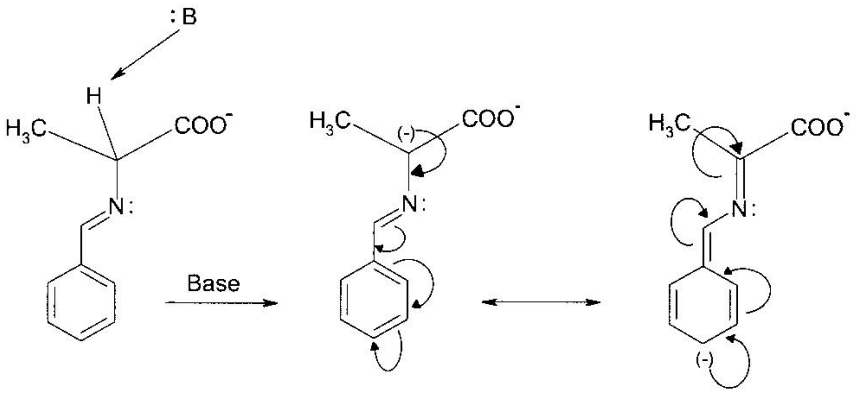
L-Serine Glycine

SOLUTION OF PREPARATORY PROBLEM 22

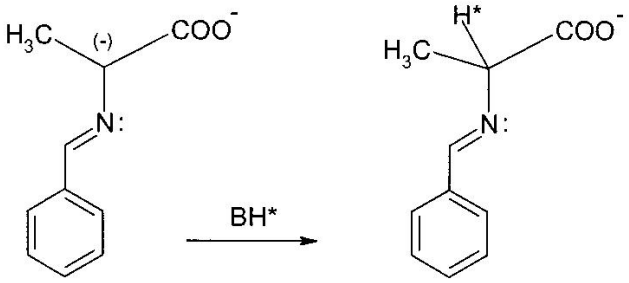
22.1 Step 1: Schiff base formation



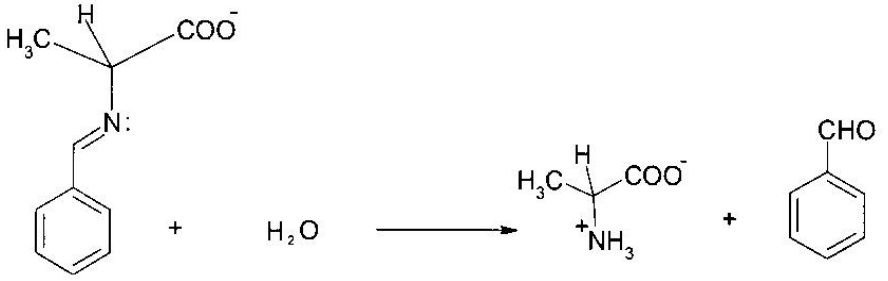
Step 2: Proton abstraction



Step 3: Reprotonation



Step 4: Hydrolysis



22.2 From the information stated in the problem, the following conclusions can be drawn:

Structure 2: Removal of the phosphate group does not hamper the activity.
This indicates that the phosphate is not critical for the activity of PLP.

Similarly,

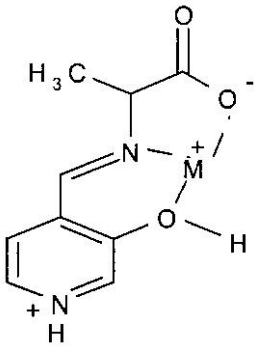
Structure 3: CH_2 -OH is not critical.

Structure 4: Phenolic OH is needed in the free form.

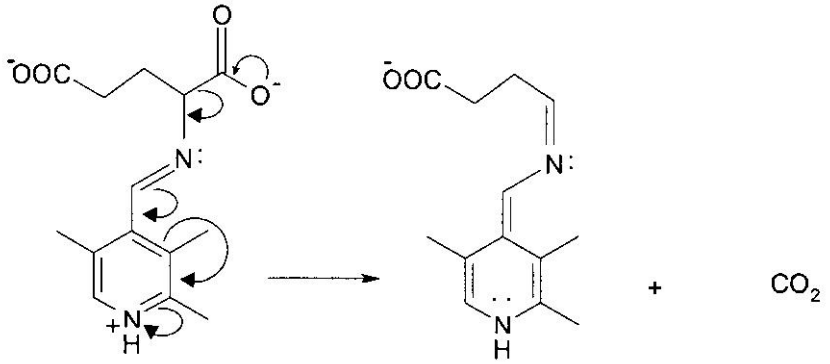
Structure 5: NO_2, a well-known electron withdrawing group, causes bnzaldehyde to become activated. Hence positively charged nitrogen in structure 3 must be also important for its electron withdrawing effect.

Structure 6: Electron withdrawing effect of NO_2 is only effective from the *para* position. Introduction of this group at *meta* position leads to an inactive analog.

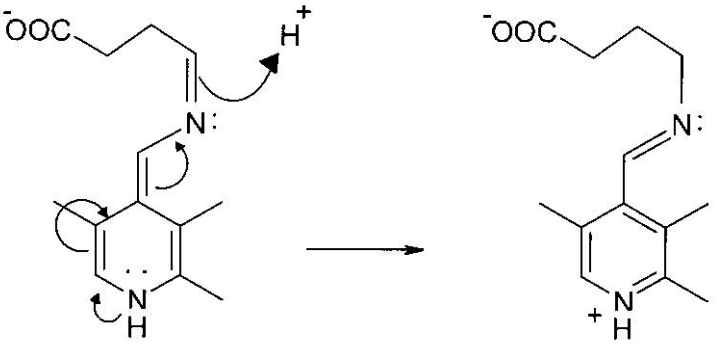
22.3 **Role of metal ion**: The metal ion is involved in a chelation, as shown below, and provides an explanation for the critical role of the phenolic OH. The planar structure formed due to chelation assists in the electron flow.



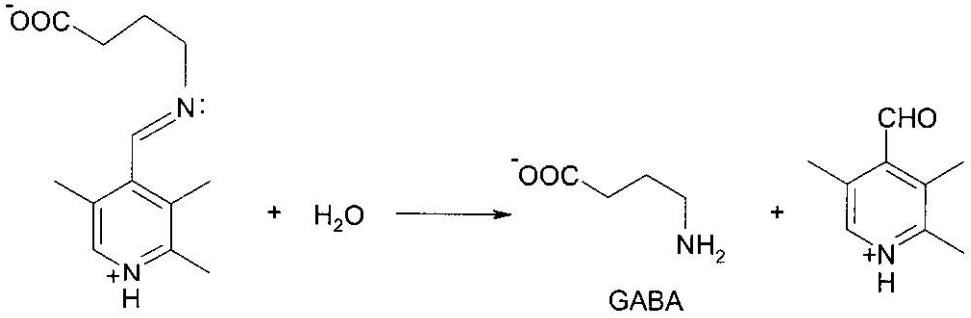
22.4 Step 1: Schiff base formation and decarboxlyation



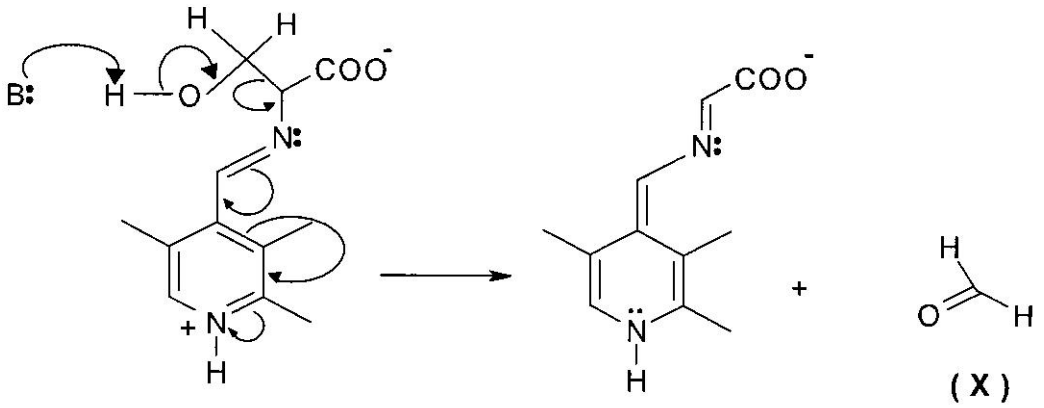
Step 2: Tautomerization



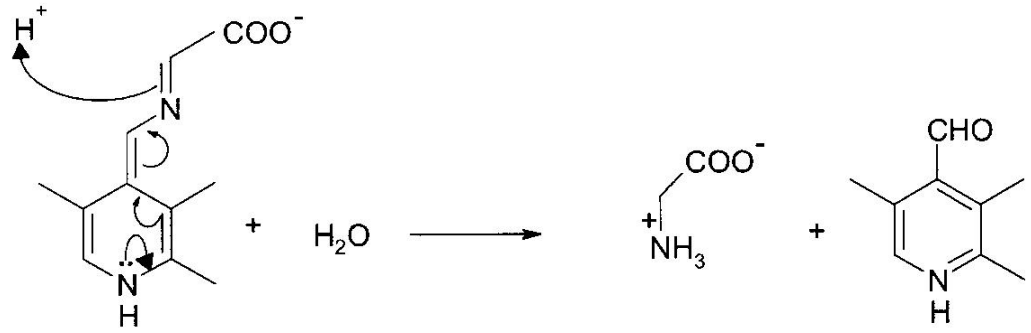
Step 3: Hydrolysis



22.5 Step 1: Schiff base formation followed by carbon- carbon bond scission.



Step 2: Tautomerization followed by hydrolysis

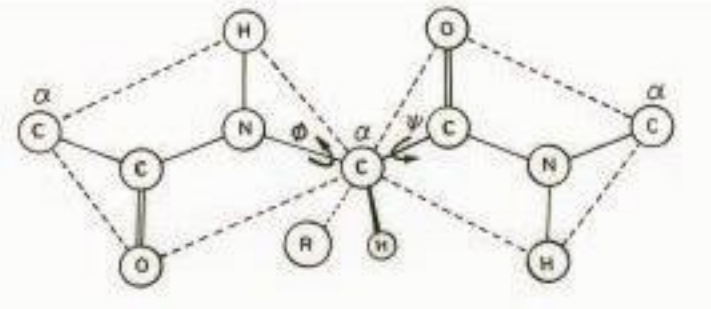


THEORETICAL PROBLEM 23

Protein folding

The link between amino acid sequence of a protein (the primary structure) and its precise three-dimensional fold (the tertiary structure) remains one of the most important unsolved mysteries of modern science.

All protein backbones are identical: planar amide units are linked via tetrahedral methylene bridges, the so called α-carbons. Each α-carbon carries an R group of a specific α-amino acid (see the following diagram).



A unique sequence of amino acids characterizes a particular protein, determining how it folds and functions.

23.1 Every amide group in the polypeptide backbone, including its flanking α-carbons, is a planar unit. Explain.

23.2 The α-carbons across each amide unit occur in a trans geometrical arrangement. However, in case of the amino acid proline, both cis and trans amide arrangements are almost equally favored. Why?

23.3 The conformational choices of amino acid residues in a polypeptide chain are stereochemically controlled. For nineteen of the genetically coded amino acids, the conformational choice is largely restricted to the α (folded) and β(extended) regions of the Ramachandran diagram. For the amino acid glycine, however, the conformational choices are much wider. Explain.

23.4 When a linear polypeptide folds forming a globular protein, an amino acid residue may assume α or β conformation. However it is observed that consecutive residues generally assume α or β conformation, rather than a random combination of α and β. Explain.

23.5 In an aqueous environment polypeptides generally fold into compact globular protein structures. The reason is (select one)

i. The R groups in polypeptides are largely polar.

ii. The R groups in polypeptides are largely nonpolar.

iii. Both polar and nonpolar R groups occur in comparable proportion.

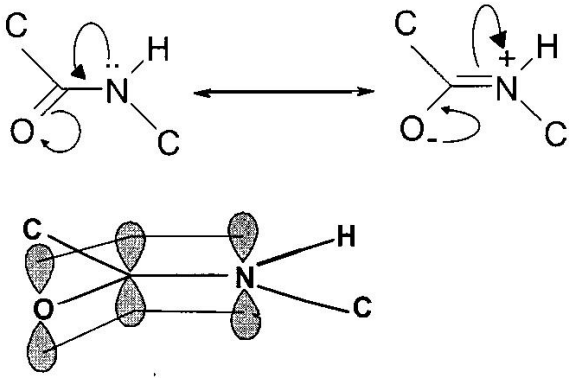
Justify your answer.

23.6 The pattern of R group polarities has an important role in determining whether α-helix or β-sheet will form when a polypeptide folds in water at an apolar surface. Explain the role of R group polarities.

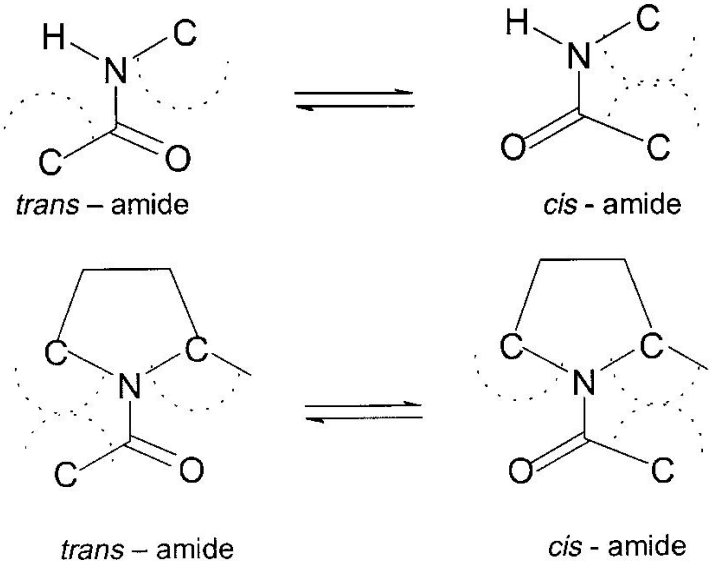
_____

SOLUTION OF PREPARATORY PROBLEM 23

23.1 The planar amide group, that is, C_α, O, H and the next C_α are in a single plane - is stabilized by resonance. The C-N bond of the amide assumes partial double bond character and the overlap between p orbitals of O, C and N is maximized. The C_α's across this partial double bond can assume *cis* or *trans* arrangement.



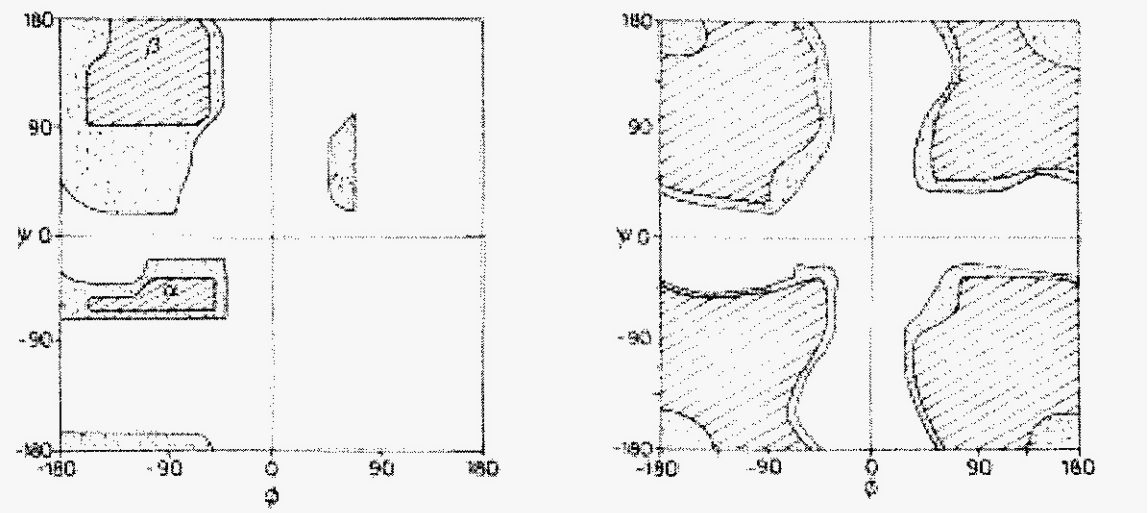
23.2 With nineteen of the amino acids, the *trans* arrangement is sterically favoured (i. e. it is comparatively less crowded). In the case of <u>proline</u>, *cis* and *trans* arrangements are almost equally crowded.



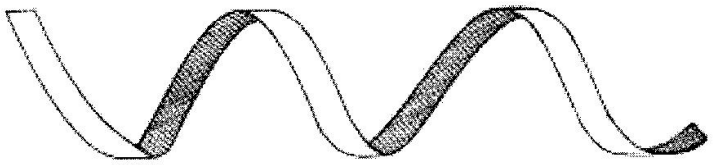
23.3 **Note about Ramchandran diagram**: In a polypeptide, the amide units are planar (partial double bond character across the N-C bond) but the bonds connecting N and

C_α, and the carbonyl carbon and C_α are free to rotate. These rotational angles are defined as ϕ and ψ, respectively. The conformation of the main chain is completely defined by these angles. Only some combinations of these angles are allowed while others are disallowed due to steric hindrance. The allowed range of ϕ and ψ angles are visualised as a steric contour diagram, shown below, known as the Ramachandran diagram.

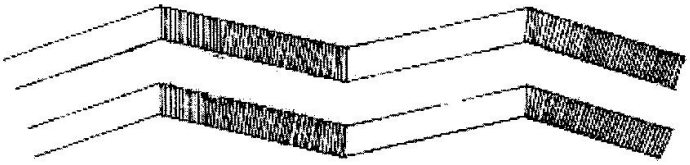
For nineteen amino acids, the conformational choice is largely restricted to the so-called α and β regions on left half of the Ramachandran diagram (Panel A). This is due to the L - chiral nature of amino acids and the steric effects of their R groups. Glycine is an achiral residue with H as the R group. Therefore, much larger conformational regions on both left and right halves of Ramachandran diagram are accessible to this residue (Panel B).



23.4 Consecutive residues in α conformation form the α-helix. Similarly, consecutive residues in β conformation form the β-sheet. Both α-helix and β-sheet structures feature extensive networks of hydrogen bonds which stabilise them. Thus random combinations of α and β conformations are rarely found.



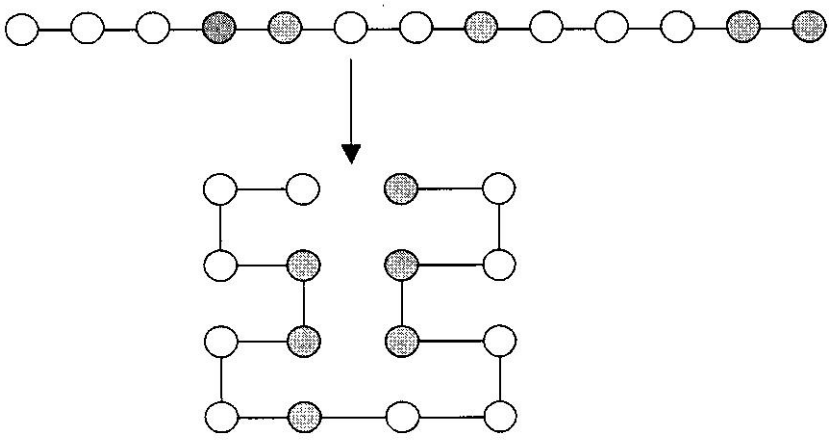
α - helix



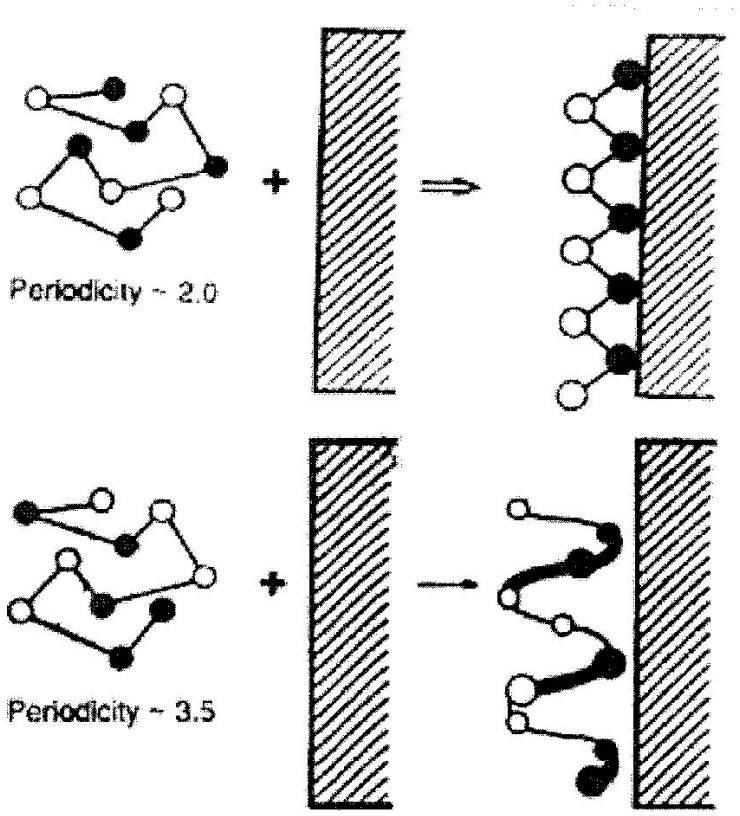
β - sheet

23.5 For a polypeptide to fold in an aqueous environment, nearly half the R groups should be non-polar (water hating) and the other half polar (water loving).

Upon folding to form a globular protein, the non-polar R groups are packed inside (away from water) while the polar groups are positioned on the surface (in contact with water). The phenomenon is similar to the hydrophobic aggregation of a micellar structure in water. If all the R groups are either polar or non-polar, no hydrophobic segregation is possible, and no folding will occur.



23.6 Alternating polar/nonpolar periodicity of R groups favours β-sheets. All the non-polar groups will face the apolar surface while the polar groups will be exposed to water. So the net folding will be like a β-sheet. On the other hand, a complex periodic pattern of R group polarities is needed in forming the α-helix.



Hydrophobic Periodicity (primary sequence)	+	Apolar surface (interface)	⇒	Induced (secondary structure)

THEORETICAL PROBLEM 24

Protein sequencing

Sequencing of a protein (polypeptide) involves the following steps: a) purification, (b) determination of N-terminal amino acid, (c) cleavage of the polypeptide chain by chemical or enzymatic methods, (d) isolation of the peptide fragments and (e) determination of their sequence by an automated sequencing machine (sequenator). It is also possible to sequence the mixture of peptide fragments without resolving it. The final sequence could be determined by constructing overlapping sequences after analyzing the information on the positional data on amino acids in different fragments.

A small protein, made up of 40 amino acid residues was sequenced as follows:

- Edman degradation involves treatment with phenyl isothiocyanate, subsequent hydrolysis and spectrophotometric identification of the modified amino acid. This procedure identified aspartic acid (Asp) as the N-terminal residue.
- The protein was cleaved with CNBr (cyanogen bromide) which cleaves the peptide bond between methionine and any other amino acid on its C-terminal side. The resulting peptide fragments were not separated. This mixture of peptides was analyzed on the protein sequenator. Therefore, the sequenator would detect as many amino acids in the given position as the number of fragments. The results are shown in Table 1(a).
- The protein was digested with a proteolytic enzyme trypsin. This enzyme cleaves the peptide bond between a basic amino acid (Arg or Lys) and the next C-terminal residue. The resulting mixture of peptides was also analyzed as above. The results are shown in Table 1(b).

Based on this information:

24.1 Deduce the amino acid sequence common to the first fragment (N-terminal) obtained by CNBr and trypsin treatments.

24.2 Deduce the sequence of the first fragment generated by CNBr treatment.

24.3 Deduce the entire sequence in the original polypeptide. Indicate the CNBr-labile and trypsin-labile sites in this sequence.

24.4 What percentage of the total residues are basic amino acids?

24.5 If the polypeptide were exist as an α helix, what will be the length of this α helical structure?

Table 1. Data from protein sequenator .

Treatment	Position on number							
	1	2	3	4	5	6	7	8
a) CNBr: (Met)	Arg Asp Glu Gly	Gln Pro Thr Tyr	Asn Pro Ser Tyr	Arg His Ilu Val	Asn Ilu Leu Phe	Arg His Trp Val	Ala Gly Phe Thr	Ala Lys Met Tyr
b) Trypsin: (Arg or Lys)	Asp Gly Gly Phe Tyr	Cys His Pro Pro Tyr	His Met Thr Tyr	Ala Asn Glu Val	Ilu Leu Thr Trp	Arg Phe Ser Ser	Cys Lys Ilu	Glu Leu

24.6 What will be the size of the DNA segment (exon) coding for this polypeptide of 40 amino acids? Give the size in base pairs as well as in daltons. (consider average molecular weight of a nucleotide in DNA = 330).

24.7 Assuming that the DNA corresponding to the exon contains equal numbers of Adenine and Cytosine, calculate the number of H-bonds which will hold this double helix.

_____

SOLUTION OF PREPARATORY PROBLEM 24

The sequence of amino acids in a protein or polypeptide is expressed starting from the N-terminal amino acid. From Edman degradation method the N-terminal amino acid is Asp. In the N-terminal fragment generated by trypsin or CNBr this amino acid should, therefore, be in position1. All other peptides generated by CNBr cleavage will be preceded by Met on their N-terminal side. Likewise, all peptides generated by trypsin should be preceded by Arg or Lys. As we proceed from N-terminal amino acid to C-terminal amino acid, we carefully examine the different amino acids in each position shown in Table1(a) and 1(b).

For the first fragment starting from N-terminal Asp in position 1, we look for residues common in each position to CNBr and trypsin cleaved peptides. This gives

Position	1		2		3		4		5		6	
Residue	Asp	–	Pro/Tyr	–	Tyr	–	Val	–	Ile/Leu	–	Arg	(1)

At position 6 Arg will render the polypeptide susceptible to trypsin. Therefore, The 7th residue of this CNBr fragment (Table1a) should be the same as residue1 in another peptide generated by trypsin and the 8th residue of this CNBr fragment will be the same as residue 2 in Table 1(b). Therefore we get

7		8	
Gly/Phe	–	Tyr	(2)

Since 8 will be Tyr, Pro will be assigned to position 2 of the polypeptide (3)

Residue 9 in the polypeptide should be at position 3 in the Table1(b) and residues 10,11,12,13 and 14 should be at positions 4,5,6,7 and 8 respectively in Table1(b). The same residues should be in positions 1 onwards in Table1(a).

None of the residues in position 3 (Table1b) is same as in position 1 in Table 1(a). However, positions 4 to 8 in Table 1(b) have residues common with positions 1 to 5 in Table 1(a). Further Glu in position 1 (Table 1a) will be preceded by Met (since it is a part of CNBr cleaved peptide). And position 3 in Table 1(b) has Met. Therefore, we get

9 10 11 12 13 14

Met – Glu – Thr – Ser – Ilu – Leu (4)

Position 5 in the polypeptide can now be firmly assigned to Ilu (5)

Positions 15 and 16 in the polypeptide will be beyond residue 8 in the trypsin cleaved peptide (not shown here). We now attempt to construct the remaining trypsin or CNBr fragments.

Table 1 (a) shows Arg in position 1. This will be preceded by a Met. Matching of the unassigned residues in position 2 in Table 1(a) with those in position 1 in Table 1(b) and for subsequent positions by the procedure demonstrated earlier that will give.

Met – Arg – Tyr – Pro – His – Asn – Trp – Phe – Lys – Gly – Cys (6)

position 7 on

(The last two residues are the unassigned residues in position 1 and 2 in Table 1b) Considering (2), (5) and (6) together it is now possible to firmly assign the polypeptide to Gly (7)

24.1 The amino acid sequence common to the first fragments (N-terminal) obtained by CNBr and trypsin treatments is

1 2 3 4 5

Asp – Pro – Tyr – Val – Ile

24.2 The sequence of the first fragment generated by CNBr treatment is

1 2 3 4 5 6 7 8

Asp – Pro – Tyr – Val – Ile – Arg – Gly –Tyr

To complete the sequence of the polypeptide we need to construct the sequence of another trypsin fragment. Starting from position 4-(Arg) in Table 1(a) we get the sequence,

Arg–Phe–His–Thr–Ala (8)

At this stage, we again examine the unassigned residues. The Arg in (8) will have to be serially preceded by Asn, Gln, Gly and Met (these are the unassigned residues in respective positions in Table 1(a). We then get the sequence,

Met–Gly–Gln–Asn–Arg–Phe–His–Thr–Ala (9)

And following the Ala in (9)

Leu–Ser–Cys–Glu (10)

From (9) and (10), we get the sequence

Met–Gly–Gln–Asn–Arg–Phe–His–Thr–Ala–Leu–Ser–Cys–Glu (11)

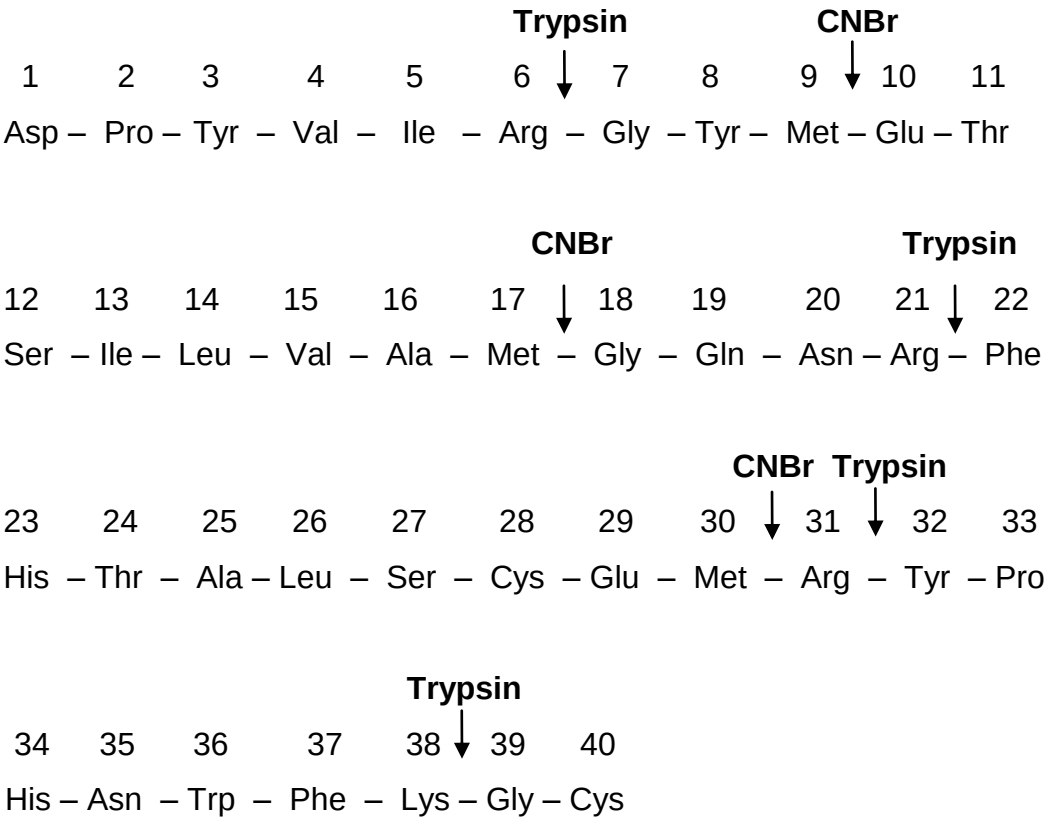
Since the smallest fragment is a dipeptide (Table 1b) and (6) shows that it follows Lys, it follows that this will be at the C-terminal end. Therefore, the partial sequence shown in (6) will follow the partial sequence shown in (11).Thus, we get Met-Gly-Gln-Asn-Arg-Phe-His-Thr-Ala-Leu-Ser-Cys-Glu-Met-Arg-Tyr-Pro-His-Asn-

Trp–Phe–Lys–Gly–Cys (12)

There is already a Met in position 9 of the polypeptide. The next Met can only come earliest at position 17 since CNBr fragment have at least 8 amino acids. Therefore, the starting residues of (12) can be assigned position 17.

This leaves positions 15 and 16 which will be filled by the unassigned residues Val and Ala in the CNBr fragment at positions 6 and 7 (Table 1a).

24.3 The final sequence, therefore, will be



Arrows (↓) indicate the CNBr and trypsin-labile sites.

24.4 There are 6 basic amino acid residues in the polypeptide. 6/40 = 15%

24.5 An α- helix has 3.6 amino acid residues per turn of 5.4 Å.

Thus, the length of the polypeptide in α-helical conformation will be :

$40/3.6 \times 5.4 = 59.4$ Å.

24.6 The polypeptide has 40 amino acids. Since each amino acid is coded for by a triplet of nucleotides, the total number of nucleotide pairs in the double stranded DNA of the exon will be

$40 \times 3 = 120$ base pairs.

The molecular weight of the DNA making the exon = $330 \times 2 \times 120 = 79200$ Da

24.7 If the exon contains 120 base pairs and A and C are in equal numbers, there will be 60 A-T pairs and 60 G-C pairs. Each A-T pair is held by two H-bonds and each G-C pair is held by three H-bonds. Hence the total number of H-bonds holding this double helix is :

$(60 \times 2) + (60 \times 3) = 300$

PRACTICAL PROBLEMS

PREPARATORY PROBLEM 25 (PRACTICAL)

Determination of aspirin in the given sample

Acetyl salicylic acid ($CH_3COO.C_6H_4.COOH$) undergoes hydrolysis when boiled gently with aqueous NaOH, which forms a basis for its estimation.

Chemicals and solutions

- Plain aspirin tablets
- Hydrochloric acid, c = 0.1 mol dm^{-3}
- Sodium hydroxide, aqueous solution, c = 1 mol dm^{-3}
- Borax (AR Grade)
- Phenol red, indicator

Preparation of HCl aqueous solution (c = 0.1 mol dm^{-3})

A volume of 9 cm^3 of concentrated HCl is diluted to 1000 cm^3 using freshly prepared distilled water in a standard volumetric flask.

Preparation of NaOH aqueous solution (c = 0.1 mol dm^{-3})

Weigh rapidly approximately 10.5 g of NaOH in a small beaker. Dissolve it in minimum amount of distilled water. Transfer the solution in a 250 cm^3 flask and dilute the solution using boiled out distilled water.

Procedure

Standardisation of HCl solution

Weigh 0.15 g of borax accurately and transfer it quantitatively in a clean 250 cm^3 conical flask. Add 50 cm^3 of distilled water to the flask. Titrate the resulting solution with HCl solution using methyl red indicator until the colour changes from yellow to red.

25.1 Calculate the concentration of the HCl solution.

Blank titration

Dilute the 25 cm^3 of NaOH solution (c = 1 mol dm^{-3}) in a 250 cm^3 standard flask using freshly boiled distilled water. Pipette out 25 cm^3 of the diluted NaOH solution and titrate it against the HCl solution using phenol red as indicator until the colour changes from red to yellow.

Titration of sample aliquot

Weigh accurately about 1.5 g of the crushed tablet sample and transfer it quantitatively in a 250 cm^3 beaker. Add 25 cm^3 of NaOH solution (c = 1 mol dm^{-3}) using pipette and swirl the content. Boil the mixture gently on water bath for 15 min and then cool the solution. Transfer the solution to a 250 cm^3 standard flask. Dilute the solution up to the mark with distilled water and mix well. Titrate 25 cm^3 of the diluted solution against the standardised HCl solution using phenol red indicator until the colour changes from red to yellow.

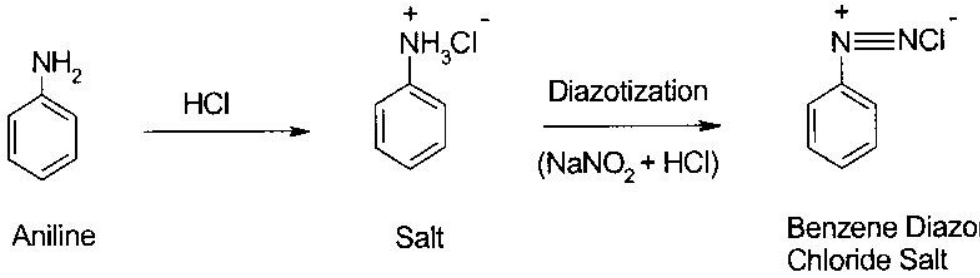
25.2 Write down the appropriate chemical reaction for hydrolysis of acetyl salicylic acid.

25.3 Calculate the percentage of aspirin in the sample.

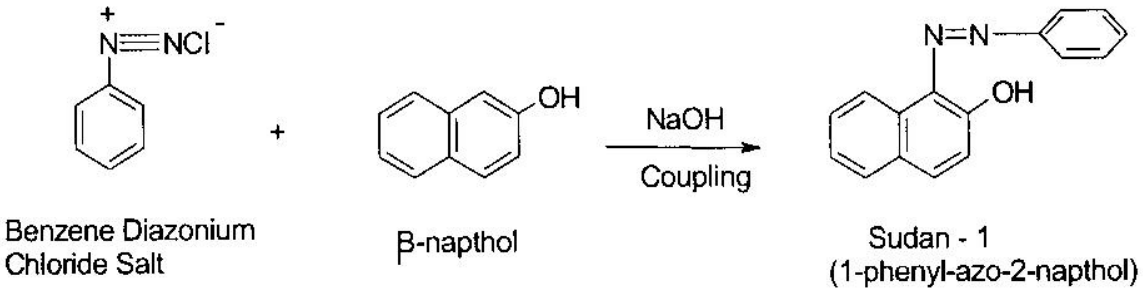
PREPARATORY PROBLEM 26 (PRACTICAL)

Synthesis of 1-phenyl-azo-2-naphthol ($C_{16}H_{12}ON_2$)

Reactions:



Aniline — Salt — Benzene Diazonium Chloride Salt



Benzene Diazonium Chloride Salt + β-napthol → Sudan - 1 (1-phenyl-azo-2-napthol)

Chemicals and solutions

- Aniline
- Concentrated hydrochloric acid
- Solid sodium nitrite
- β-naphthol
- Ethyl alcohol
- Urea
- Sodium hydroxide

Preparation of diazonium salt

Take 1 cm^3 of aniline in a clean 50 cm^3 beaker. Add approximately 5 cm^3 of distilled water to aniline. Place the beaker in an ice-bath. Slowly add 2.5 cm^3 of conc. HCl. Stir the solution with a glass rod to obtain a clear solution. Cool this solution in the ice-bath.

Weigh accurately 0.5 g of sodium nitrite ($NaNO_2$) and transfer it quantitatively in a 15 (or 25) cm^3 test tube. Add 5 cm^3 of distilled water (to the test tube) to dissolve $NaNO_2$. Cool the resulting $NaNO_2$ solution in an ice-bath.

Allow both the solutions to attain 0 °C temperature. Add sodium nitrite solution in a dropwise manner to the aniline solution with continuous stirring. (During addition, the temperature of the reaction mixture should not rise above 10 °C.)

The presence of excess nitrous acid in the reaction mixture is checked using starch iodide paper.

To decompose the excess nitrous acid formed, add a small portion of solid urea. The solution is then filtered. The filtrate contains the diazonium salt.

Coupling reaction

Weigh 0.75 g of powdered β-naphthol in a 50 cm^3 beaker. Add 5 cm^3 of 10% NaOH solution and 5 cm^3 of distilled water to the beaker. Stir well with glass rod to obtain a clear solution. This solution is also cooled in an ice-bath to 0 °C.

The ice cooled filtrate containing diazotised salt is added dropwise to the ice cooled solution of β-naphthol with constant stirring. At this stage, an orange-red dye will start precipitating. After the addition of the solution is complete, filter the dye using Büchner funnel. Cold water is used for washing the precipitate. Dry the product and record the yield.

Determination of melting point

Recrystallise a small portion of the organic dye prepared using ethyl alcohol. Gently heat the solution in a water bath (careful!) to dissolve the dye. Filter the hot solution. Cool the filtrate and filter the recrystallised product using Büchner funnel and suction.

26.1 Record the mass of the crude product.

26.2 Record the melting point of the recrystallised product.

PREPARATORY PROBLEM 27 (PRACTICAL)

Determination of calcium in a sample solution

Reaction: $Ca^{2+} + H_2Y^{2-} \longrightarrow CaY^{2-} + 2\,H^{+}$

Chemicals and solutions

- Sample solution containing calcium (prepared from A.R. grade $CaCl_2$)
- Patton and Reeders indicator
- KOH solution.
- EDTA disodium salt

Preparation of EDTA solution (c = 0.01 mol dm^{-3})

Weigh 1.861 g of Na_2EDTA (AR grade) and quantitatively transfer it to 500 cm^3 volumetric flask. Add distilled water to the flask to dissolve Na_2EDTA and make up the solution to 500 cm^3 mark with distilled water.

Procedure

Dilute the given sample solution to 100 cm^3 in a 100 cm^3 volumetric flask using distilled water. Pipette out 25 cm^3 of the diluted sample solution in a clean conical flask. Add 25 cm^3 of distilled water and adjust the pH using freshly prepared KOH solution to 12. Check the pH with pH paper. Add a pinch of solid indicator and titrate with Na_2EDTA solution till the colour changes from wine red to blue.

27.1 Calculate the amount of calcium in mmoles in 100 cm^3 of the diluted sample solution.

PREPARATORY PROBLEM 28 (PRACTICAL)

Estimation of methyl ketone by back titration

Methyl ketones like acetone can be estimated by iodinating with excess of standard iodine in an alkaline medium. The unreacted iodine is then back titrated with standard sodium thiosulphate solution.

Chemicals and solutions

- Iodine, aqueous solution, c = 0.05 mol dm^{-3}
- NaOH, aqueous solution, c = 0.1 mol dm^{-3}
- HCl, conc. aqueous solution
- H_2SO_4. aqueous solution, c = 0.5 mol dm^{-3}
- $Na_2S_2O_3$, aqueous solution, c = 0.1 mol dm^{-3}

Preparation of $Na_2S_2O_3$ solution

Weigh 25 g of $Na_2S_2O_3$ (AR grade) and quantitatively transfer it to a 1 dm^3 volumetric flask. Prepare the solution using freshly boiled distilled water. Add 3 drops of chloroform while preparing the solution. Avoid exposure to light.

Preparation of iodine solution, c = 0.05 mol dm^{-3}

Dissolve 20 g of iodate-free potassium iodide in 30 - 40 cm^3 of distilled water in a 1 dm^3 volumetric flask. Weigh 12.7 g iodine and quantitatively transfer it to the concentrated potassium iodide solution. Shake the flask well until all the iodine dissolves and then dilute up to the mark with distilled water.

P r o c e d u r e

Standardisation of $Na_2S_2O_3$ solution

Weigh out accurately 0.14 to 0.15 g of dry potassium iodate. Dissolve it in 25 cm^3 of distilled and freshly boiled water and add 2 g of iodate free potassium iodide. Add 5 cm^3 of sulphuric acid (c = 0.5 mol dm^{-3}). Titrate the liberated iodine with thiosulphate solution with constant shaking. When the colour of the solution is pale yellow add 200 cm^3 of distilled water

and 2 cm^3 of starch indicator. Continue the titration until the colour changes from blue to colourless.

Determination of ketone

Weigh accurately 0.2 g of the given acetone sample in a clean 50 cm^3 beaker and add minimum amount of distilled water. Transfer the acetone solution to a 250 cm^3 standard volumetric flask. Add distilled water to the flask to prepare acetone solution in water and make up the solution to 250 cm^3 mark with distilled water. Pipette out 10 cm^3 of the acetone solution in a clean conical flask. Add 10 cm^3 of 10% aqueous sodium hydroxide, and stopper the flask. Shake the flask for 10 min. Then add 35 cm^3 of iodine solution (c = 0.05 mol dm^{-3}) from the burette. Swirl the content, preferably using magnetic stirrer for 5 minutes, and keep it standing for 15 minutes.

Yellow crystals of iodoform will appear. Acidify the solution with H_2SO_4 (check the pH with pH paper).

Titrate the solution against the standardised sodium thiosulphate using starch indicator.

28.1 Write down the appropriate chemical reactions for iodination of acetone.

28.2 Calculate the amount of acetone in the given sample solution.

PREPARATORY PROBLEM 29 (PRACTICAL)

Determination of phenol in the given sample

Reactions:

$KBrO_3 + 5\ KBr + 6\ HCl \rightarrow 6\ KCl + 3\ H_2O + 3\ Br_2$

$C_6H_5OH + 3\ Br_2 \rightarrow C_6H_2OHBr_3 + 3\ HBr$

$3\ Br_2 + 6\ KI \rightarrow 6\ KBr + 3\ I_2$

$6\ Na_2S_2O_3 + 3\ I_2 \rightarrow 3\ Na_2S_2O_3 + 6\ NaI$

Chemicals and solutions:

- Phenol, solid, 0.3 g
- $KBrO_3$, aqueous solution, c = 0.02 mol dm^{-3}
- H_2SO_4, aq., c = 3 mol dm^{-3}
- KBr, solid
- KI, solid
- $Na_2S_2O_3$, aqueous solution, c = 1 mol dm^{-3}
- Starch indicator.

Preparation of $Na_2S_2O_3$ aqueous solution, c = 0.1 mol dm^{-3}

Weigh 25 g of $Na_2S_2O_3$ (AR grade) in a small beaker. Quantitatively transfer it to a 1 dm^3 volumetric flask. Prepare the solution using freshly boiled distilled water. Add 3 drops of chloroform while preparing the solution. Avoid exposure to light.

Standardisation of $Na_2S_2O_3$ solution

Weigh out accurately 0.14 to 0.15 g of dry potassium iodate. Dissolve it in 25 cm^3 of fresh, boiled distilled water and add 2 g of iodate free potassium iodide. Add 5 cm^3 of sulphuric acid solution (c = 0.5 mol dm^{-3}). Titrate the liberated iodine with thiosulphate solution with constant shaking. When the colour of the solution is pale yellow add 200 cm^3 of distilled water and 2 cm^3 of starch indicator. Continue the titration until the colour changes from blue to colourless.

P r o c e d u r e

Dissolve the given sample of phenol to 250 cm^3 with distilled water. Take 25 cm^3 of the phenol solution into 250 cm^3 stoppered conical flask. Add 25 cm^3 of standard potassium bromate solution and 0.5 g of potassium bromide. Add 5 cm^3 of aqueous solution of sulphuric acid (c = 3 mol dm^{-3}). Stopper the flask immediately. Mix the reagents and let them stand for 15 min (avoid exposure to light). Then, add 2.5 g of potassium iodide rapidly. Re-stopper the flask immediately and swirl the contents of the flask to dissolve the solid.

Titrate the liberated iodine with standard $Na_2S_2O_3$ solution (c = 0.1 mol dm^{-3} using starch indicator.

29.1 Calculate the amount of phenol per 250 cm^3 of the solution.

PREPARATORY PROBLEM 30 (PRACTICAL)

Determination of amount of Fe (III) present in the given sample

Fe (III) in the sample solution is first reduced to Fe (II) in HCl medium using stannous chloride. Excess of stannous chloride is oxidized by addition of mercury (II) chloride. The Fe(II) is then titrated with standard potassium dichromate solution.

Chemicals and solutions

- Sample solution
- $K_2Cr_2O_7$ aqueous solution, c = 0.0167 mol dm^{-3}
- Equimolar H_2SO_4 and H_3PO_4 acid mixture
- Conc. HCl
- 5% $HgCl_2$ solution
- 3% $SnCl_2$ solution
- Diphenylamine indicator

Note : $NH_4Fe(SO_4)_2.12\ H_2O$ is used for the preparation of the sample solution

Preparation of $K_2Cr_2O_7$ aqueous solution, c = 0.0167 mol dm^{-3}

Weigh accurately 1.226 g of pure $K_2Cr_2O_7$ and transfer it to a 250 cm^3 volumetric flask. Prepare the solution using distilled water.

P r o c e d u r e

Dilute the given Fe(III) sample solution to 100 cm^3 using the standard volumetric flask. Take 10 cm^3 of the diluted sample solution in a clean conical flask. Add 2 cm^3 of concentrated HCl and boil the solution. To the hot solution, add $SnCl_2$ solution dropwise till the reaction mixture becomes colourless. Add 2 - 3 drops of $SnCl_2$ solution in excess.

Cool the solution under tap water. Add 2 to 3 cm^3 of $HgCl_2$ solution at once. A white precipitate is obtained at this stage. (If a grey precipitate is obtained, reject the sample and start again.)

Add 2 to 3 cm^3 of the acid mixture and 1 drop of the diphenylamine indicator and titrate it against $K_2Cr_2O_7$ solution. Continue the titration until a colour change from colourless to permanent blue or violet is observed.

30.1 Write down the appropriate chemical reactions.

30.2 Calculate the amounts of Fe(III) and $NH_4Fe(SO_4)_2 \times 12\ H_2O$ per 100 cm^3 of the sample solution.