33rd

International Chemistry Olympiad

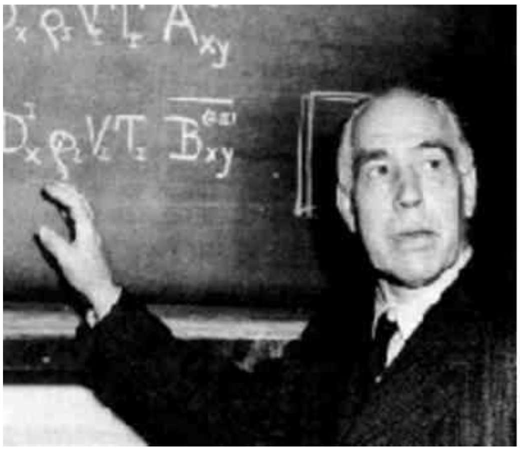
7 theoretical problems
3 practical problems

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

THEORETICAL PROBLEMS

PROBLEM 1

Hydrogen Atom and Hydrogen Molecule



Niels Bohr (1885-1962)

The observed wavelengths in the line spectrum of hydrogen atom were first expressed in terms of a series by Johann Jakob Balmer, a Swiss teacher. Balmer's empirical formula is

$$\frac{1}{\lambda} = R_\text{H}\left(\frac{1}{2^2} - \frac{1}{n^2}\right); \qquad n = 3, 4, 5, ...$$

Here, $$R_\text{H} = \frac{m_e\, e^4}{8\, \varepsilon_0^2\, h^3\, c} = 109\,678\ \text{cm}^{-1}$$

is the Rydberg konstant, m_e is the mass of an electron. Niels Bohr derived this expression theoretically in 1913. The formula is easily generalized to any one electron atom/ion.

1.1 Calculate the longest wavelength in Å (1 Å = 10^{-10} m) in the 'Balmer series' of singly ionized helium (He^+). Ignore nuclear motion in your calculation.

1.2 A formula analogous to Balmer's formula applies to the series of spectral lines which arise from transitions from higher energy levels to the lowest energy level of hydrogen atom. Write this formula and use it to determine the ground state energy of a hydrogen atom in eV.

A 'muonic hydrogen atom' is like a hydrogen atom in which the electron is replaced by a heavier particle, the muon. The mass of a muon is about 207 times the mass of an electron, while its charge is the same as that of an electron. A muon has a very short lifetime, but we ignore its unstable nature here.

1.3 Determine the lowest energy and the radius of the first Bohr orbit of the muonic hydrogen atom. Ignore the motion of the nucleus in your calculation. The radius of the first Bohr orbit of a hydrogen atom

(called the Bohr radius, $a_0 = \dfrac{\varepsilon_0\, h^2}{m_e\, e^2\, \pi}$) is 0.53 Å.

The classical picture of an "orbit" in Bohr's theory has now been replaced by the quantum mechanical notion of an 'orbital'. The orbital $\psi 1\sigma_{1s}$ (r) for the ground state of a hydrogen atom is given by

$$\Psi_{1s}(r) = \frac{1}{\sqrt{\pi\, a_0^3}}\, e^{-\frac{r}{a_0}}$$

where r is the distance of the electron from the nucleus and a_0 is the Bohr radius.

1.4 Consider a spherical shell of radius a_0 and thickness $0.001a_0$. Estimate the probability of finding the electron in this shell. Volume of a spherical shell of inner radius r and small thickness Δr equals $4\pi r^2\,\Delta r$.

The H_2 molecule can dissociate through two different channels:

(i) $H_2 \rightarrow H + H$ (two separate hydrogen atoms)

(ii) $H_2 \rightarrow H^+ + H^-$ (a proton and a hydride ion)

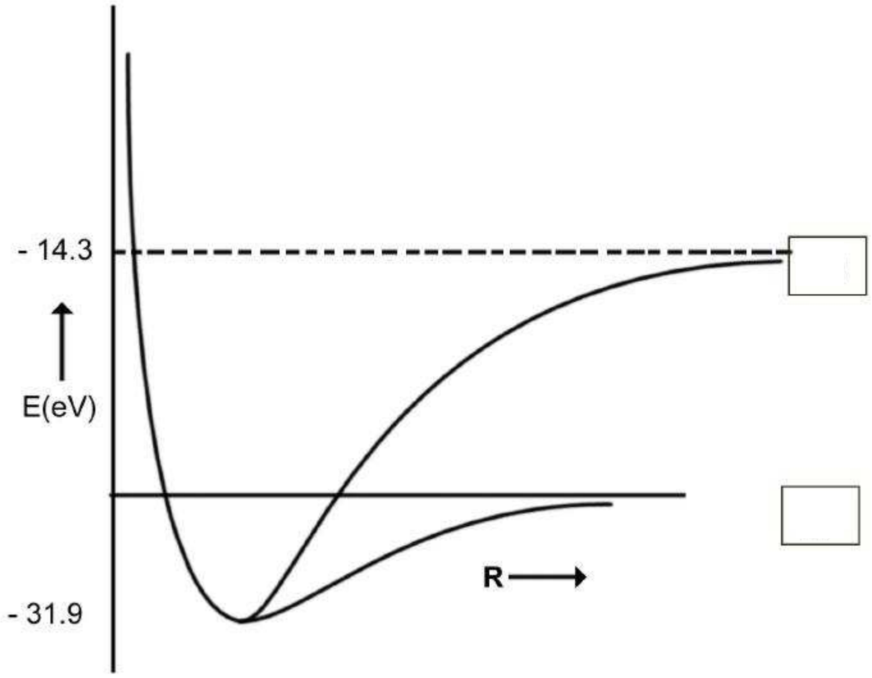
The graph of energy (E) vs internuclear distance (R) for H_2 is shown schematically in the figure. The atomic and molecular energies are given in the same scale.

1.5 Put appropriate channel labels (i) or (ii) in the boxes below.

1.6 Determine the values of the dissociation energies (D_e in eV) of the H_2 molecule corresponding to

channel (i) ☐

channel (ii) ☐



1.7 From the given data, calculate the energy change for the process

$H^- \rightarrow H + e^-$

1.8 H^- is a two-electron atomic system. Assuming that the Bohr energy formula is valid for each electron with nuclear charge Z replaced by Z_{eff}, calculate Z_{eff} for H^-.

SOLUTION

1.1 Longest wavelength A_L corresponds to n = 3

For He^+

$$\frac{1}{\lambda} = 4R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

λ_L = 1641.1 Å

1.2 $\frac{1}{\lambda} = 4R_H\left(\frac{1}{1^2} - \frac{1}{n^2}\right) \qquad n = 2, 3, 4, ...$

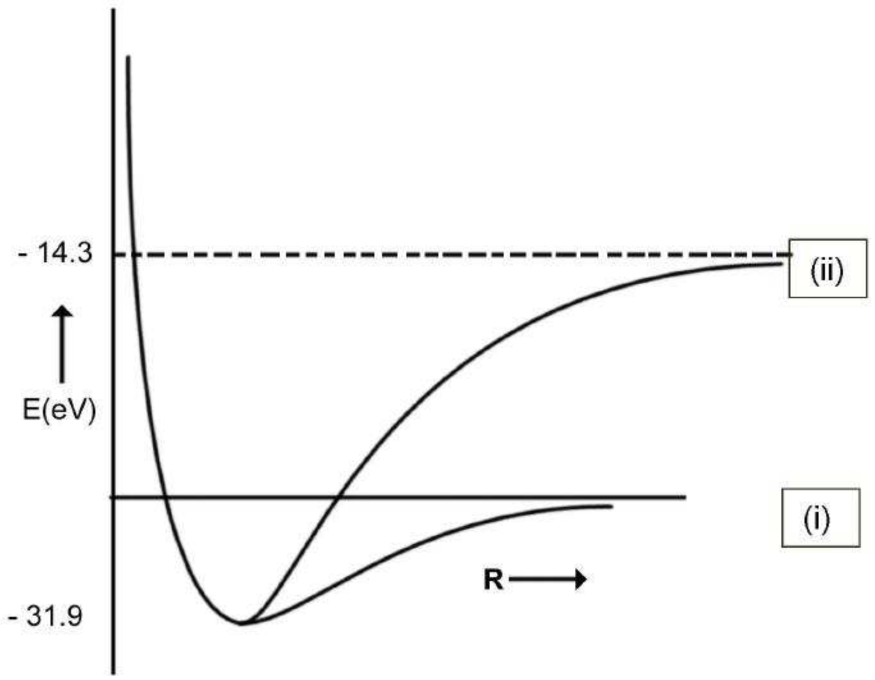
$E = -hcR_H = -13.6$ eV

1.3 Lowest energy = – 207 × 13.6 = –2.82 keV

Radius of the first Bohr orbit = 0.53 / 207 = 2.6×10^{-3} Å

1.4 Probability = $|\psi(a_0)|^2\, 4\pi a_0^2 \times 0.001a_o = 0.004\, e^{-2} = 5.41\times10^{-4}$

1.5



1.6 Channel (i): 4.7 eV

Channel (ii): 17.6 eV

1.7 Electron affinity = – 13.6 – (– 14.3) = 0.7 eV

1.8 $Z_{eff} = -13.6 + 27.2\, Z^2_{eff} = 0.7$

PROBLEM 2

Phosphoric Acid

Phosphoric acid is of a great importance in fertilizer industry. Besides, phosphoric acid and its various salts have a n umber of applications in metal treatment, food, detergent and toothpaste industries.

2.1 The pK values of the three successive dissociations of phosphoric acid at 25 °C are:

pK_{1a} = 2.12

pK_{2a} = 7.21

pK_{3a} = 12.32

Write down the conjugate base of dihydrogen phosphate ion and determine its pK_b value.

Small quantities of phosphoric acid are extensively used to impart the sour or tart taste to many soft drinks such as colas and root beers. A cola having a density of 1.00 g cm^{-3} contains 0.05 % by weight of phosphoric acid.

2.2 Determine the *pH* of the cola (ignoring the second and the third dissociation steps for phosphoric acid). Assume that the acidity of the cola arises only from phosphoric acid.

2.3 Phosphoric acid is used as a fertiliser for agriculture. 1.00×10^{-3} M phosphoric acid is added to an aqueous soil suspension and the *pH* is found to be 7.00.

Determine the fractional concentrations of all the different phosphate species present in the solution. Assume that no component of the soil interacts with any phosphate species.

2.4 Zinc is an essential micronutrient for plant growth. Plant can absorb zinc in water soluble form only. In a given soil water with *pH* = 7.0, zinc phosphate was found to be the only source of zinc and phosphate. Calculate the concentration of [Zn^{2+}] and [PO_4^{3-}] ions in the solution. Ksp for zinc phosphate is 9.1×10^{-33}.

SOLUTION

2.1 The conjugate base of dihydrogen phosphate ($H_2PO_4^-$) is monohydrogen phosphate (HPO_4^{2-}) :

$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$ K_{2a}

$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$ K_{2b}

$2\ H_2O \rightleftharpoons H_3O^+ + OH^-$ K_w

$pK_{2a} + pK_{2b} = pK_w = 14$

$pK_{2b} = 6.79$

2.2 Concentration of $H_3PO_4 = \frac{0.5}{98} = 0.0051$ M

$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$

0.0051-x x + x

$pK_{1a} = 2.12$ gives $K_{1a} = 7.59\times10^{-3}$

$$7.59\times10^{-3} = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]} = \frac{x^2}{0.0051 - x}$$

$x = [H_3O^+] = 3.49\times10^{-3}$

$pH = 2.46$

2.3 Let $f_0 = \frac{[H_3X]}{C}$, $f_1 = \frac{[H_2X^-]}{C}$,

$f_2 = \frac{[HX^{2-}]}{C}$ and $f_3 = \frac{[X^{3-}]}{C}$

denote the fractional concentrations of different phosphate species. C is the total initial concentration of H_3X. (X = PO_4)

$f_0 + f_1 + f_2 + f_3 = 1$

$$K_{1a} = \frac{[H_2X^-][H_3O^+]}{[H_3X]} = \frac{f_1}{f_0}[H_3O^+]$$

$$K_{2a} = \frac{[HX^{2-}][H_3O^+]}{[H_2X^-]} = \frac{f_2}{f_1}[H_3O^+]$$

$$K_{3a} = \frac{[X^{3-}][H_3O^+]}{[HX^{2-}]} = \frac{f_3}{f_2}[H_3O^+]$$

These equations lead to

$$f_0 = \frac{[H_3O^+]^3}{D}, \quad f_1 = \frac{K_{1a}[H_3O^+]^2}{D}, \quad f_2 = \frac{K_{1a}K_{2a}[H_3O^+]}{D}, \quad f_3 = \frac{K_{1a}K_{2a}K_{3a}}{D}$$

where D = $K_{1a}\ K_{2a}\ K_{3a} + K_{1a}\ K_{2a}\ [H_3O^+] + K_{1a}\ [H_3O^+]^2 + [H_3O^+]^3$

From the values of pK_{1a}, pK_{2a}, pK_{3a} and pH one gets

$K_{1a} = 7.59\times10^{-3}$; $K_{2a} = 6.17\times10^{-8}$; $K_{3a} = 4.79\times10^{-13}$; $[H_3O^+] = 1\times10^{-7}$

The fractional concentrations of different phosphate species are:

H_3PO_4 $(f_0) = 8.10\times10^{-6}$

$H_2PO_4^-$ $(f_1) = 0.618$

HPO_4^{2-} $(f_2) = 0.382$

PO_4^{3-} $(f_3) = 1.83\times10^{-6}$

2.4 Let S (mol dm^{-3}) be the solubility of $Zn_3(PO_4)_2$ in soil water.

$[Zn^{2+}] = 3\,S$

Total concentration of different phosphate species = $2\,S$

$[PO_4^{3-}] = f_3 \times 2\,S$

f_3 can be determined from the relation derived in **2.3**

For $pH = 7$, $f_3 = 1.83\times10^{-6}$

$K_{sp} = [Zn^{2+}]^3\,[PO_4^{3-}]^2$

$9.1\times10^{-33} = (3\,S)^3\,(f_3 \times 2\,S)^2$

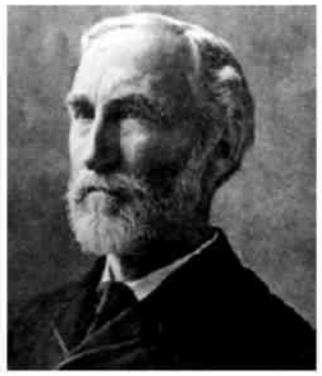
$[Zn^{2+}] = 9\times10^{-5}$

$[PO_4^{3-}] = 1.1\times10^{-10}$

Solubility of $Zn_3(PO_4)_2 = 3.0\times10^{-5}$ mol dm^{-3}

PROBLEM 3

Second Law of Thermodynamics



J.W.Gibbs (1839 –1903)

The second law of thermodynamics is a fundamental law of science. In this problem we consider the thermodynamics of an ideal gas, phase transitions and chemical equilibrium.

3.00 mol of CO_2 gas expands isothermically (in thermal contact with the surroundings; temperature = 15 °C) against a fixed external pressure of 1.00 bar. The initial and final volumes of the gas are 10.0 dm^3 and 30.0 dm^3, respectively.

3.1 Choose the correct option for change in the entropy of the system (ΔS_{sys}) and of the surroundings (ΔS_{sur}):

(a) $\Delta S_{sys} > 0$ $\Delta S_{sur} = 0$ ☐
(b) $\Delta S_{sys} < 0$ $\Delta S_{sur} > 0$ ☐
(c) $\Delta S_{sys} > 0$ $\Delta S_{sur} < 0$ ☐
d) $\Delta S_{sys} = 0$ $\Delta S_{sur} = 0$ ☐

(Mark X in the correct box.)

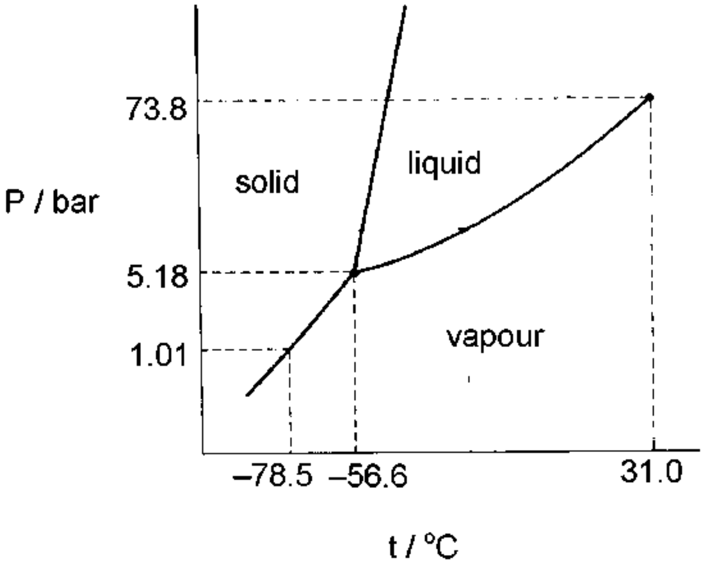
3.2 Calculate ΔS_{sys} assuming CO_2 to be an ideal gas.

3.3 Calculate ΔS_{sur}.

3.4 Calculate the change in entropy of the universe.

Does your answer agree with the Second Law of Thermodynamics? ☐ ☐
(Mark X in the correct box.) Yes No

The pressure – temperature phase diagram of CO_2 is given below schematically. The diagram is not to scale.



Phase diagram of CO_2

3.5 CO_2 gas, initially at a pressure of 4.0 bar and temperature of 10.0 °C is cooled at constant pressure. In this process,

(a) it goes first to the liquid phase and then to the solid phase. ☐

(b) it goes to the solid phase without going through the liquid phase. ☐

3.6 Starting with the same pressure and temperature as above (in 3.5), CO_2 is compressed isothermatically. In this process,

(a) it goes first to the liquid phase and then to the solid phase. ☐

(b) it goes to the solid phase without going through the liquid phase. ☐

3.7 From the data given in the phase diagram, calculate the molar enthalpy change of sublimation of CO_2. Write down the formula used.

3.8 CO gas, used extensively in organic synthesis, can be obtained by reacting CO_2 gas with graphite. Use the data given below to show that the equilibrium constant at 298.15 K is less than unity.

At 298.15 K

CO_2(g):	ΔH_f^0 = –393.51 kJ mol^{-1};	S^0 = 213.79 J K^{-1} mol^{-1}
CO(g):	ΔH_f^0 = –110.53 kJ mol^{-1};	S^0 = 197.66 J K^{-1} mol^{-1}
C(graphite)	S^0 = 5.74 J K^{-1} mol^{-1}	

3.9 Estimate the temperature at which the reaction would have an equilibrium constant equal to 1. Ignore slight variations in the thermodynamic data with temperature.

3.10 The reaction above (in 3.8) is carried out between CO_2 and excess hot graphite in a reactor maintained at about 800 °C and a total pressure of 5.0 bar. The equilibrium constant K_p under these conditions is 10.0. Calculate the partial pressure of CO at equilibrium.

SOLUTION

3.1 Correct solution: (c) $\Delta S_{sys} > 0$ $\Delta S_{sur} < 0$

3.2 Since ΔS_{sys} is independent of path, it is the same as for isothermal reversible expansion of an ideal gas.

$$\Delta S_{sys} = nR\ \ln\frac{V_f}{V_i} = 27.4\ \text{J K}^{-1}$$

3.3 $q = p_{ext}\,\Delta V$

$$\Delta S_{sur} = -\frac{q}{T} = -\,6.94\ \text{J K}^{-1}$$

3.4 $\Delta S_{uni} = \Delta S_{sys} + \Delta S_{sur} = 20.5\ \text{J K}^{-1}$

The answer agrees with the second law of thermidynamics (correct is YES)

3.5 Correct answer:

(b) it goes to the solid phase without going through the liquid phase.

3.6 Correct answer:

(a) it goes first to the liquid phase and then to the solid phase.

3.7 $$\ln\frac{p_2}{p_1} = -\frac{\Delta H_{sub}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$\Delta H_{sub} = 26.1\ \text{kJ mol}^{-1}$

3.8 $\Delta H^0 = 172.45\ \text{kJ mol}^{-1}$

$\Delta S^0 = 176\ \text{J K}^{-1}\text{mol}^{-1}$

$\Delta G^0 = \Delta \text{H}^0 - T\Delta \text{S}^0 = 120\ \text{kJ mol}^{-1}$

$\Delta G^0 > \text{O}$ implies $K < 1$

3.9 $\Delta G^0 = 0$ when $\Delta \text{H}^0 = T\Delta \text{S}^0$

$T = 980\ \text{K}$

3.10

$$CO_2\,(g) + C(s) \rightleftharpoons 2\,CO\,(g)$$

$$1 - \alpha \qquad\qquad 2\,\alpha$$

Partial pressure: $\frac{1-\alpha}{1-\alpha}\times 5 \qquad \frac{2\,\alpha}{1-\alpha}\times 5$

$$K_p = \frac{p^2(\text{CO})}{\text{p}(\text{CO}_2)}$$

$p(\text{CO}) = 3.7\ \text{bar}$

PROBLEM 4

Beach Sand Mineral in Kerala

Beach sand mineral, monazite, is a rich source of thorium, available in large quantities in the state of Kerala in India. A typical monazite sample contains about 9 % ThO_2 and 0.35 % U_3O_8. ^{208}Pb a ^{206}Pb are the stable end-products in the radioactive decay series of ^{232}Th and ^{238}U, respectively. All the lead (Pb) found in monazite is of radiogenic origin.

The isotopic atom ratio $^{208}Pb/^{232}Th$, measured mass spectrometrically, in a monazite sample was found to be 0.104. The half-lives of ^{232}Th and ^{238}U 1.41×10^{10} years and 4.47×10^{9} years, respectively. Assume that ^{208}Pb, ^{206}Pb, ^{232}Th and ^{238}U remained entirely in the monazite sample since the formation of monazite mineral.

4.1 Calculate the age (time elapsed since its formation) of the monazite sample.

4.2 Estimate the isotopic atom ratio $^{206}Pb/^{238}U$ in the monazite sample.

4.3 Thorium-232 is a fertile material for nuclear energy. In thermal neutron irradiation, it absorbs a neutron and the resulting isotope forms ^{233}U by successive β^- decays. Write the nuclear reactions for the formation of ^{233}U from ^{232}Th.

In nuclear fission of ^{233}U a complex mixture of radioactive fission products is formed. The fission product ^{101}Mo initially undergoes radioactive decay as shown below:

$$^{101}_{42}Mo \xrightarrow[t_{1/2}\,=14.6\,\text{min}]{} {}^{101}_{43}Tc \xrightarrow[t_{1/2}\,=14.3\,\text{min}]{} {}^{101}_{44}Ru$$

4.4 A freshly prepared radiochemically pure sample of ^{101}Mo contains 5000 atoms of ^{101}Mo initially. How many atoms of

i) ^{101}Mo

ii) ^{101}Tc

iii) ^{101}Ru

will be present in the sample after 14.6 min?

SOLUTION

4.1 $N = N_0\ \mathrm{e}^{-\frac{0.6931\ t}{t_{1/2}}}$

$$\frac{N_0 - N}{N} = \mathrm{e}^{\frac{+0.6931\ t}{t_{1/2}}} - 1$$

(N_0 - N) = Total number of ^{232}Th atoms decayed. = Total number of ^{208}Pb atoms formed.

$$\frac{N_0 - N}{N} = 0.104$$

$$\mathrm{e}^{\frac{0.6931\ t}{1.41\times10^{10}}} = 1.104$$

t = 2.01×10^9 years.

4.2 Let x be the required ratio.

$$\mathrm{x} = \mathrm{e}^{\frac{+0.6931\ t}{t_{1/2}}} - 1$$

where $t = 2.01\times10^9$ years, and $t_{1/2} = 4.47\times10^9$ years.

x = 0.366

4.3 $^{232}\mathrm{Th} \xrightarrow{(\mathrm{n},\gamma)} {}^{233}\mathrm{Th} \xrightarrow{\beta^-} {}^{233}\mathrm{Pa} \xrightarrow{\beta^-} {}^{233}\mathrm{U}$

4.4 (i) The number of atoms of ^{101}Mo (N_1) in the sample after one half-life is :

N_1 = 2500

(ii) The number of atoms of ^{101}Tc (N_2) is given by

$$N_2 = \frac{\lambda_1 N_0}{\lambda_2 - \lambda_1}(\mathrm{e}^{-\lambda_1 t} - e^{-\lambda_2 t})$$

where N_0 (= 5000) is the initial number of atoms of ^{101}Mo.

$$\lambda_1 = \frac{0.693}{14.6}\ \mathrm{min}^{-1}$$

$$\lambda_2 = \frac{0.693}{14.3}\ \mathrm{min}^{-1}$$

At t = 14.6 min

N_2 = 1710

(iii) Number of atoms of ^{101}Ru (N_3) at t = 14.6 min is :

$N_3 = N_0 - N_1 - N_2$ = 790 atoms

PROBLEM 5

Halogen Chemistry

Halogens in their reactions among themselves and with a variety of other elements give rise to a large number of compounds with diverse structure, bonding and chemical behaviour. Metal halides, halogen derivatives and interhalogens represent major types of halogen compounds.

(A) Photography

A "black and white" photographic film contains a coating of silver bromide on a support such as cellulose acetate.

5.1 Write the photochemical reaction that occurs when light falls on AgBr(s) coated on a film.

5.2 During the developing process, unexposed AgBr is washed away by complexation of Ag(I) by sodium thiosulphate solution. Write down this chemical reaction.

5.3 These washings are often disposed of as waste. However, metallic silver can be recovered from them by adding cyanide, followed by zinc. Write down the reactions involved.

(B) Shapes, spectra and reactivity

The most reactive halogen, fluorine, reacts with other halogens Cl_2, Br_2 and I_2 under controlled conditions giving a tetra-atomic, hexa-atomic and an octa-atomic molecule, respectively.

5.4 Write the formulae and 3-dimensional structures of these interhalogen molecules on the basis of VSEPR theory. Show the disposition of the lone pairs on the central atom, where appropriate.

A mixture of iodine vapour and chlorine gas when fed into a mass spectrometer gave two sets (A and B) of mass spectral peaks corresponding to molecular ions of two chemical species at *m*/*z*:

A: 162, 164

B: 464, 466, 468, 470, 472, 474, 476

5.5 Identify the molecular species corresponding to *m*/*z* = 162, 164, 466 and 476. Draw the structure of the heaviest species (*m*/*z* = 476) indicating clearly the lone pairs on atom(s) of I (iodine). Show the isotopic composition of each species.

In aqueous medium chlorine gas oxidises sodium thiosulphate to an ion containing the highest oxidation state of sulphur.

5.6 Write down the chemical equation for this reaction.

5.7 Write down the Lewis dot structure of the thiosulphate ion. Circle the sulphur atom that has the lower oxidation state.

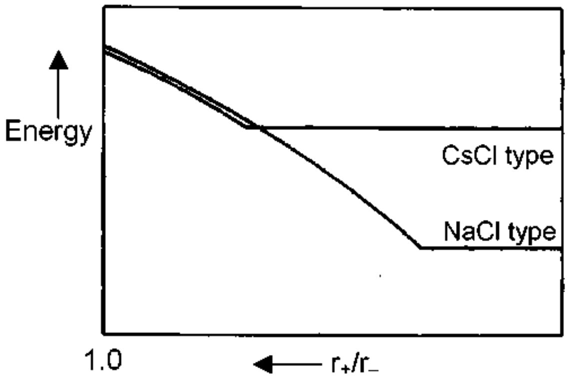
5.8 Chlorine dioxide reacts with sodium hydroxide as shown below. Identify the products X and Y (both containing chlorine) and balance the equation.

5.9 Reaction of chlorine an alkali is used by manufacturing bleach. Write the chemical reaction for its formation.

5.10 Write the oxidation state(s) of chlorine in bleach.

(C) Alkali metal halides and X-ray crystallography

X-ray crystallography reveals many aspects of the structure of metal halides. The radius ratio (r_+/r_-) is a useful parameter to rationalise their structure and stability. A table of radius ratio (r_+/r_-) for some alkali halides with radius ratio (r_- kept constant) is shown schematically for NaCl-type and CsCl-type crystal structures.



	Li^+	Na^+	K^+	Rb^+	Cs^+
Cl^-	0.33	0.52	0.74	0.82	0.93
Br^-	0.31	0.49	0.68	0.76	0.87
I^-	0.28	0.44	0.62	0.69	0.78

5.11 For a given anion, the graph for NaCl-type structure levels off at low r_+/r_- values because of

(a) cation-cation contact along the face diagonal. ☐

(b) anion-anion contact along the face diagonal. ☐

(c) cation-anion contact along the cell edge. ☐

(Mark X in the correct box.)

5.12 Which among the halides LiBr, NaBr and RbBr is likely to undergo phase transition from NaCl-type to CsCl-type structure with change of temperature and / or pressure?

5.13 Show by calculation the radius ratio (r_+/r_-) at which the energy of CsCl-type structure levels off.

5.14 Using CuKα X-rays (λ = 154 nm), diffraction by a KCl crystal (fcc structure) is observed at an angle (θ) of 14.2 °. Given that (i) diffraction takes place from the planes with $h^2 + k^2 + l^2 = 4$, (ii) in a cubic crystal $d_{hkl} = a / (h^2 + k^2 + l^2)^{1/2}$, where "d" is the distance between adjacent hkl planes and "a" is a lattice parameter, and (iii) reflections in an fcc structure can occur only from planes with "all odd" or "all even" hkl (Miller) indices, calculate the lattice parameter "a" for KCl.

5.15 Indicate in the table given below the required information for the 2nd and 3rd nearest neighbours of a K^+ ion in the KCl lattice.

2nd nearest neighbours			3rd nearest neighbours		
number	sign of the charge	distance (pm)	number	sign of the charge	distance (pm)

5.16 Determine the lowest value of diffraction angle θ possible for the KCl structure.

SOLUTION

5.1 $2\ AgBr\ (s) \xrightarrow{h\nu} 2\ Ag\ (s) + Br_2\ /2\ Br\ \bullet$

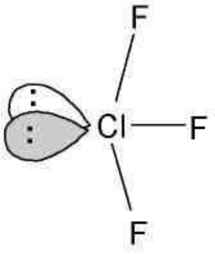
5.2 $AgBr(s) + 2\ Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

5.3 $[Ag(S_2O_3)_2]^{3-} + 2\ CN^- \rightarrow [Ag(CN)_2]^- + 2\ S_2O_3^{2-}$

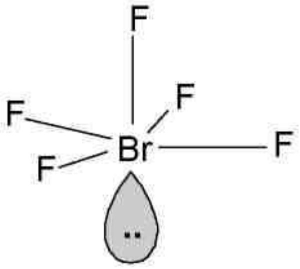
$2\ [Ag(CN)_2]^- + Zn \rightarrow [Zn\ (CN)_4]^{2-} + 2\ Ag \downarrow$

5.4

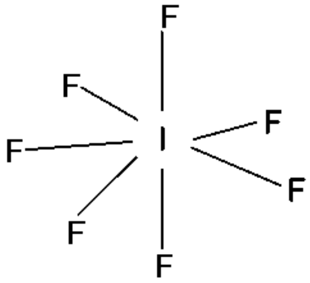
ClF_3



BrF_5



IF_7

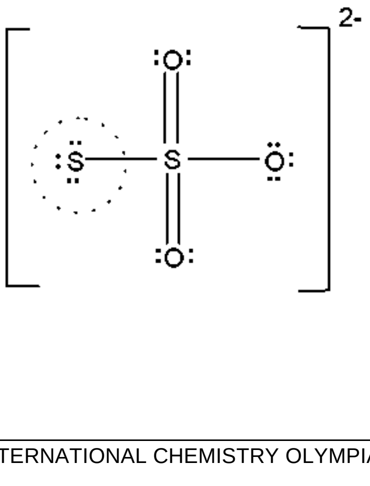


5.5.

Mass:	162	164	466	476
Species:	I ^{35}Cl	I ^{37}Cl	$I_2{}^{35}Cl_5{}^{37}Cl$	$I_2{}^{37}Cl_6$

5.6 $4\ Cl_2 + S_2O_3^{2-} + 5\ H_2O \rightarrow 8\ Cl^- + 2\ SO_4^{2-} + 10\ H^+$

5.7



5.8 $2\ ClO_2 + 2\ NaOH \rightarrow \underset{X}{NaClO_2} + \underset{Y}{NaClO_3} + H_2O$

5.9 $Cl_2 + Ca(OH)_2 \rightarrow Ca(Cl)(OCl) + H_2O$

or

$Cl_2 + CaO \rightarrow Ca(Cl)(OCl)$

or

$2\ OH^- + Cl_2 \rightarrow Cl^- + OCl^- + H_2O$

5.10 The oxidation state(s) of chlorine in bleach is (are): -I and I

5.11 Correct answer: (b) anion–anion contact along the face diagonal.

5.12 RbBr

5.13 In CsCl-type structure,

Cell edge, a = 2 r

Body diagonál: $\sqrt{3}\,a = 2(r_+ + r_-)$

$$\frac{r_+}{r_-} = \sqrt{3} - 1 = 0.732$$

5.14 $\lambda = 2d \sin\theta$

$$d_{200} = \frac{\lambda}{2\sin\theta} = 314 \text{ pm}$$

$$d_{200} = \frac{a}{(h^2+k^2+l^2)^{1/2}} = \frac{a}{(2^2+0^2+0^2)^{1/2}} = \frac{a}{2}$$

a = 628 pm

5.15 The 2nd and 3rd nearest neighbours of a K^+ ion in the KCl lattice.

2nd nearest neighbours			3rd nearest neighbours		
number	sign of the charge	distance (pm)	number	sign of the charge	distance (pm)
12	+	444	8	-	544

5.16 Lowest θ value is for the plane with hkl = (111)

$$d = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{628}{\sqrt{3}} = 363\ \text{pm}$$

$$\sin\theta_{111} = \frac{\lambda}{2\,d_{111}} = \frac{154\ \text{pm}}{2 \times 363\ \text{pm}} = 0.212$$

$$\theta_{111} = 12.2\,^\circ$$

PROBLEM 6

Organic Chemistry of Indian Spices

The rhizomes of ginger (*Zingiber officinale*) are well known for their medicinal and flavouring properties. In Ayurveda (the traditional system of medicine in India) different formulations of ginger are used for the treatment of gastrointestinal problems, common cold and other aliments. Several compounds are responsible for the pungency of ginger. Many are simple substituted aromatic compounds with different side chains. Three of them, Zingerone, (+)[6] Gingerol (to be referred hereafter as Gingerol only), and Shogaol are particularly important.

Zingerone: $C_{11}H_{14}O_3$
Gingerol: $C_{17}H_{14}O_4$
Shogaol: $C_{17}H_{24}O_3$

6.1 Zingerone gives positive FeCl3 and 2,4-DNP (2,4-dinitrophenylhydrazine) tests. It does not react with Tollen's reagent. Therefore, Zingerone contains the following functional groups: (Mark X in the correct boxes.)

(a) alcoholic hydroxyl ☐
(b) aldehydic carbonyl ☐
(c) ketonic carbonyl ☐
(d) phenolic hydroxyl ☐
(e) ester ☐
(f) alkoxyl ☐
(g) unsaturation ☐

The data obtained from the ^{1}H NMR spectrum of Zingerone are shown in Table 1. Some other relevant information is given in Table 2.

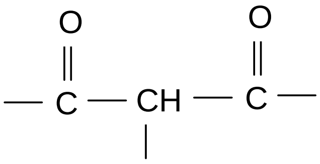
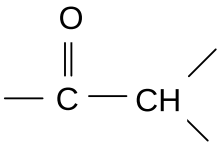
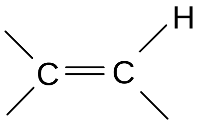
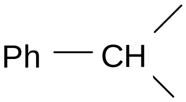
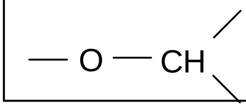
Table 1: ^{1}H NMR spectral data on Zingerone

Chemical shifts (δ)	Multiplicity	Relative intensity
2.04	singlet	3
2.69, 2.71	two (closely spaced) triplets of equal intensity	4
3.81	singlet	3
5.90	broad singlet (D_2O exchangeable)	1
6.4 – 6.8	two doublets with similar chemical shifts and one singlet	3

*) For clarity, some of the data have been altered slightly.)

Table 2: Approximate 1H chemical shifts (δ) and spin-spin coupling constants (J) of some protons

^{1}H Chemical shifts

alkyl - H	0.9 - 1.5		3.4 - 3.6
	2.0 - 2.7		4.0 - 7.0
	2.3 - 2.9	Ph — H	6.0 - 8.0
	3.3 - 3.9	Ar — OH	4.0 - 11.0

Spin–spin coupling constants (J)

Alkenes *cis* 5 – 14 Hz (commonly around 6 – 8 Hz)

trans 11 – 19 Hz (commonly around 14 – 16 Hz)

Zingerone on bromination with bromine water gives only one nuclear mono brominated product. The IR spectrum of Zingerone indicates the presence of a week *intramolecular* hydrogen bond. The same is present even after Clemmensen reduction (Zn – Hg/HCl) of Zingerone.

6.2 From the information above deduce the following:

i) side chain in Zingerone ☐

ii) substituent on the aromatic ring ☐

iii) relative positions of the substituents on the ring ☐

6.3 Draw a possible structure of Zingerone based on the above inferences.

6.4 Complete the following reaction sequence for the synthesis of Zingerone.

$$\boxed{} + \boxed{} \xrightarrow{\text{aq. NaOH}} \mathbf{C}$$

A + **B** (C_3H_6O)

$$\boxed{} \xrightarrow{H_2\text{/ Catalyst}} \text{Zingerone } (C_{11}H_{14}O_3)$$

C

6.5 Zingerone can be easily converted into Gingerol by the following reaction sequence:

$$\underset{(C_{11}H_{14}O_3)}{\text{Zingerone}} \xrightarrow[\text{(ii) LDA, 78 ℃}]{\text{(i) } Me_3SiCl\ /\ (Me_3Si)_2NH} \mathbf{D} \xrightarrow[\text{(ii) } H_2O/\ H+]{\text{(i) hexanal}} \underset{(C_{17}H_{28}O_4)}{\text{Cingerol}}$$

Notes: (1) Me_3SiCl / $(Me_3Si)_2NH$ is used to convert OH into $–OSiMe_3$; the group $–SiMe_3$ can be removed by acid hydrolysis.

(2) LDA is lithium disopropylamine, a strong, very hindered, non.nucleophilic base.

i) Draw the structure of **D.**

ii) Draw the structure of Gingerol.

iii) Complete the Fischer projection of the *R*-enantiomer of Gingerol.

iv) In the above reaction sequence (6.5), about 2 – 3 % another constitutional isomer (**E**) of Gingerol is obtained. Draw the likely structure of **E**.

v) Will the compound **E** be formed as

(a) a pair of enatiomers? ☐
(b) a mixture of diastereomers? ☐
(c) a mixture of an enantiomeric pair and a meso isomer? ☐
(Mark X in the correct box.)

vi) Gingerol ($C_{17}H_{26}O_4$) when heated with a mild acid (such as $KHSO_4$) gives Shogaol ($C_{17}H_{24}O_3$). Draw the structure of Shogaol.

6.6 Turmeric (*Curcuma longa*) is a commonly used spice in Indian food. It is also used in Ayurvedic medicinal formulations. Curmunin ($C_{21}H_{20}O_6$), an active ingredient of turmeric, is structurally related to Gingerol. It exhibits keto-enol tautomerism. Curcumin is responsible for the yellow colour of turmeric and probably also for the pungent taste.

The ^1H NMR spectrum of the keto form of Curcumin shows aromatic signal similar to that of Gingerol. It also shows a singlet around δ 3.5 (2H) and two doublets (2H each) in the region δ 6 – 7 with J = 16 Hz. It can be synthesized by condensing TWO moles of **A** (refer to **6.4**) with one mole of pentan-2,4-dione.

i) Draw the stereochemical structure of Curcumin.

ii) Draw the structure of the enol form of Curcumin.

iii) Curcumin is yellow in colour because it has

(a) a phenyl ring ☐
(b) a carbonyl group ☐
(c) an extended conjugation ☐
(d) a hydroxyl group ☐
(Mark X in the correct box.)

SOLUTION

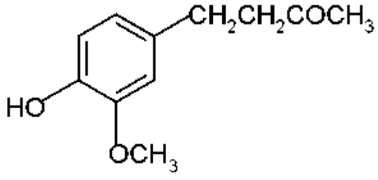
6.1 Zingerone contains the following functional groups:

(c) ketonic carbonyl

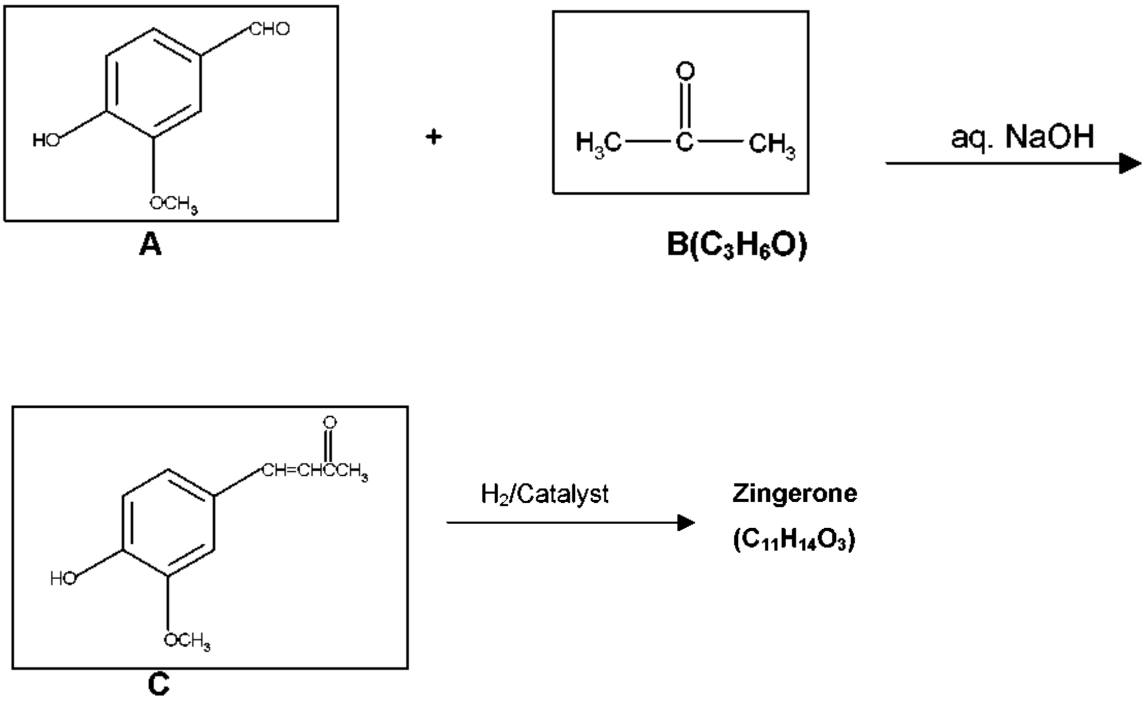
(d) phenolic hydroxyl

6.2	i)	side chain in Zingerone:	$CH_2CH_2COCH_3$
	ii)	substituents on the aromatic ring:	OH, OCH_3
	iii)	relative positions of the substituents on the ring:	1, 2, 4

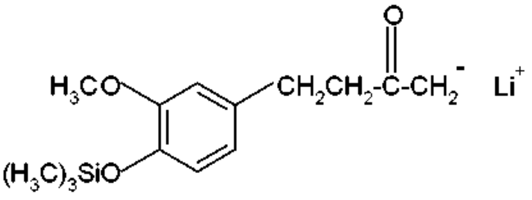
6.3



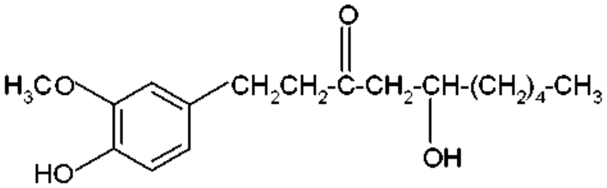
6.4



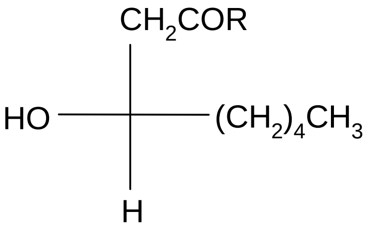
6.5 i)



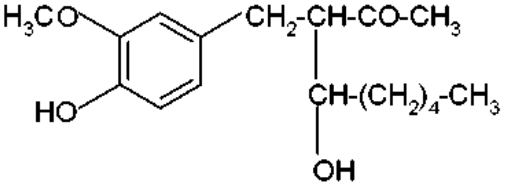
ii)



iii)

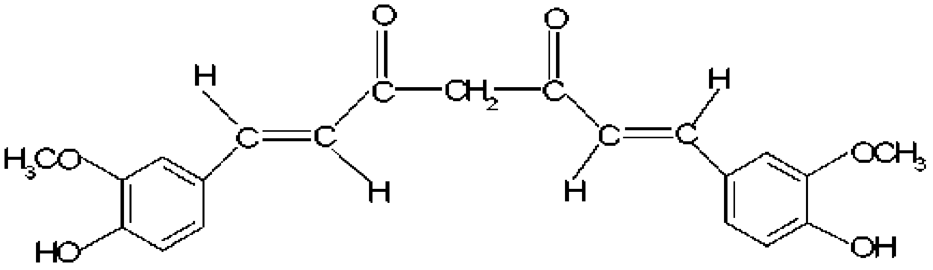


iv)

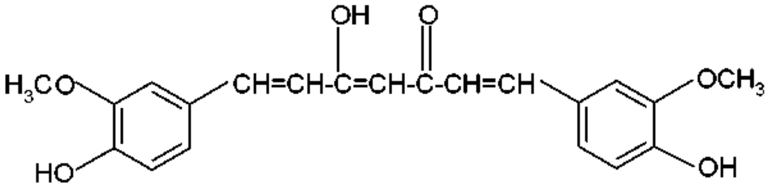


v) Compound **E** will be formed as: (b) a mixture of diastereomers

6.6 i)



ii)

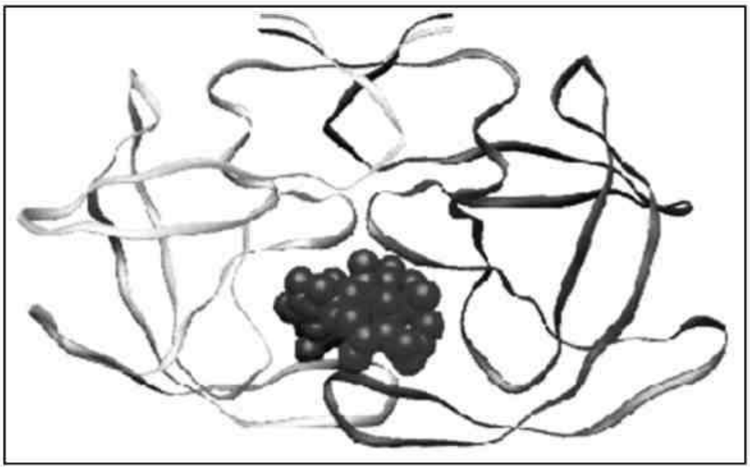


iii) Curcumin is yellow in coulour because it has:

(c) an extended conjugation.

PROBLEM 7

Peptides and Proteins



Protein folding

Proteins (polypeptides) are known to assume a variety of backbone conformations. In one conformation, the backbone is almost fully extended arrangement (as in a parallel or anti-parallel β-sheet), and in another conformation it is in a fully folded arrangement (as in an α-helix).

7.1 The end-to-end distance in a hexapeptide when it is in a fully extended conformation is approximately:

(a) 10 Å ☐
(b) 15 Å ☐
(c) 20 Å ☐
(d) 25 Å ☐

(Mark X in the correct box.)

7.2 Assuming that the following hexapeptide is a α-helix conformation, draw a connecting arrow between an oxygen atom and an amide NH with which it is hydrogen bonded.

7.3 The following hexapeptides (**A** and **B**) display contrasting conformations in water at *pH* 7.0, especially when their serine hydroxyls are phosphorylated. **A** is moderately helical and it becomes a stronger helix on serine phosphorylation. **B** is weakly helical and it is completely disorded on serine phosphorylation. Draw connecting arrows to indicate the interactions between the residues that are responsible for this differing behaviour.

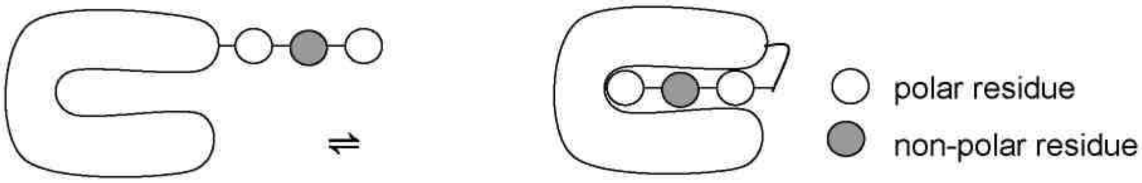
Consider the following process of folding/unfolding of a tripeptide segment in a large protein. The free energy change (AG) will depend on the interaction of the unfolded tripeptide with the solvent (water) and with the rest of the protein in the folded state (see below). Assume that the tripeptide is made up of one non-polar (hydrophobic; shaded) and two polar (hydrophilic; unshaded) residues. Assume the following approximate changes in the interaction free energies :

(a) a non-polar residue and the solvent (water): ΔG = +8 kJ mol^{-1}

(b) a non-polar residue and the rest of the protein: ΔG = – 4 kJ mol^{-1}

(c) a polar residue and the solvent (water): ΔG = – 16 kJ mol^{-1}

(d) a polar residue and the rest of the protein: ΔG = – 14 kJ mol^{-1}



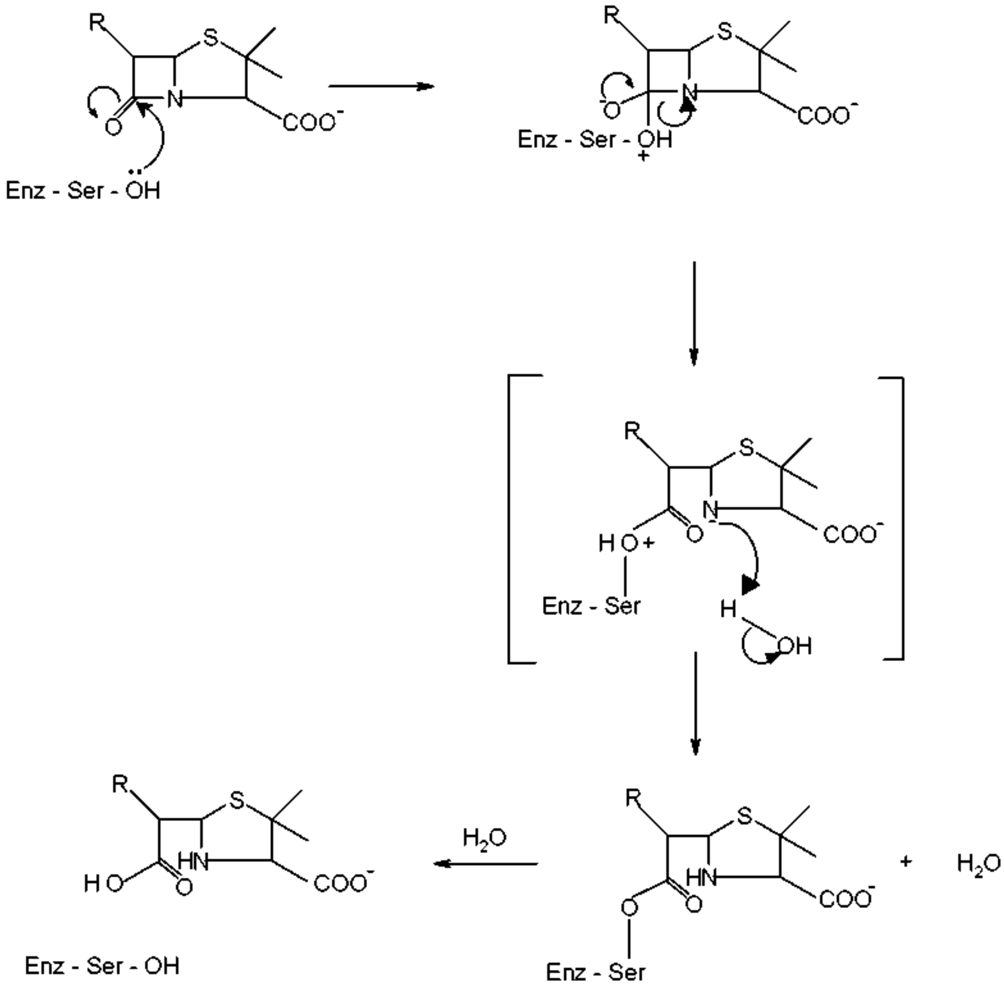
Tripeptide segment in unfolded form   Tripeptide segment in folded form

7.4 Calculate ΔG for the foldinq of the tripeptide segment.

7.5 Calculate ΔG for the folding of the tripeptide segment if all the three residues are polar.

β - lactamase and drug resistance

Penicillins are effective drugs in combating bacterial infections. An alarming development over the years has, however, been the emergence of drug resistant bacteria. Penicillin resistance arises due to the secretion of an enzýme called (3-lactamase (also known as penicillinase), which inactivates penicillin by opening its (3-lactam ring. The mechanism for this (3-lactam ring opening involves the nucleophilic attack by serine-OH at the active site of the enzýme as shown below.



An attempt was made to characterize the b–lactamase from *Staphylococcus aureus*. When the pure enzyme was treated with a radiolabelled [^{32}P] phosphorylating agent, only the active site serine got labelled. On analysis, this serine {molecular mass = 105 mass units (Da)} constituted 0.35% by weight of the b–lactamase.

7.6 Estimate the minimal molecular mass of this b–lactamase.

7.7 The approximate number of amino acid residues present in a protein of this size is :

(a) 100 ☐

(b) 150 ☐

(c) 275 ☐

(d) 375 ☐

[Mark X in the correct box.]

To map its active site, the b–lactamase was hydrolysed using trypsin, a specific enzyme. This resulted in a hexapeptide P1 containing the active site serine. Amino acid analysis revealed the following in equimolar proportion : Glu, Leu, Lys, Met, Phe and Ser. Treatment of P1 with Edman's reagent (phenyl isothiocyanate) yielded phenyl thiohydantoin (PTH) derivative of phenyalanine and a peptide P2.

Treatment of P1 with cyanogen bromide (CNBr) gave an acidic tetrapeptide P3 and a dipeptide P4.

Treatment of P2 with 1–fluoro–2,4–dinitrobenzene, followed by complete hydrolysis, yielded N–2,4–dinitrophenyl–Glu. P1, P2, and P3 contain the active site serine.

7.8 From the above information, deduce the amino acid sequence of P1, P2, P3 and P4.

7.9 Calculate the molecular mass of P3 in mass units (Da) from the information given in the attached Table.

The β–lactamase active site provides a unique microenvironment that makes the catalytic serine**–**OH an unusually reactive nucleophile. The first order rate constant for β–lactamase catalysed reaction is 350 s^{-1}. For penicillin hydrolysis by free serine**–**OH (at 1 M) in solution, the pseudo first order rate constant is 0.5 s^{-1}.

7.10 From the information above, calculate the effective concentration of this nucleophile at the enzyme active site?

A molecule competing with penicillin for binding to the b–lactamase active site can inhibit the enzyme. Dissociation constants (K_D) for the inhibitor–lactamase complex for three different inhibitors are given below :

Inhibitor	Dissociation constant (K_D)
A	2.0×10^{-3}
B	1.0×10^{-6}
C	5.0×10^{-9}

7.11 Indicate which of these inhibitors is most effective in protecting penicillin against β–lactamase. [Mark X in the correct box]

A ☐

B ☐

C ☐

A β–lactamase inhibitor was designed rationally. On binding to the enzyme active site, a nucleophilic attack by the OH group of serine resulted in the opening of the β–lactam moiety of the inhibitor and elimination of Br^-. A reactive electrophile is generated as a result and it captures an active site residue X, inactivating the enzyme.

7.12 Based on the above information, identify the electrophile (A) generated and the final product (B) formed in the enzyme inactivation by the inhibitor shown.

Table

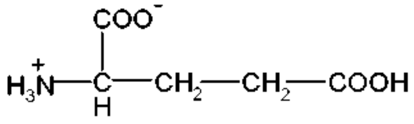
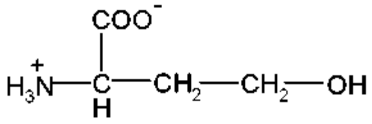
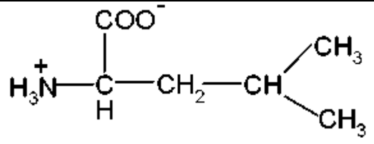
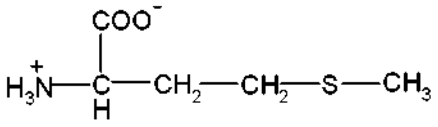
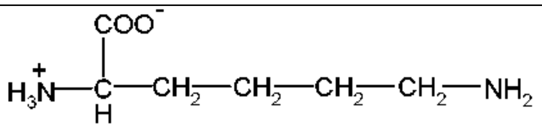
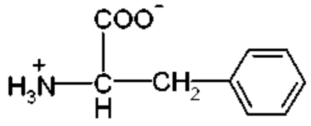
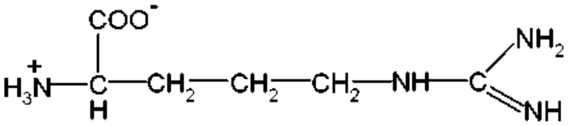
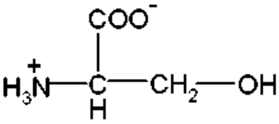
Amino Acid	Structure	Molecular mass (Da)
Glu – Glutamic acid	 $H_3\overset{+}{N}-\underset{H}{\overset{COO^-}{C}}-CH_2-CH_2-COOH$	147
Hms – Homoserine	 $H_3\overset{+}{N}-\underset{H}{\overset{COO^-}{C}}-CH_2-CH_2-OH$	119
Leu – Leucine		131
Met – Methionine	 $H_3\overset{+}{N}-\underset{H}{\overset{COO^-}{C}}-CH_2-CH_2-S-CH_3$	149
Lys – Lysine	 $H_3\overset{+}{N}-\underset{H}{\overset{COO^-}{C}}-CH_2-CH_2-CH_2-CH_2-NH_2$	146
Phe – Phenylalanine		165

Table (continued)

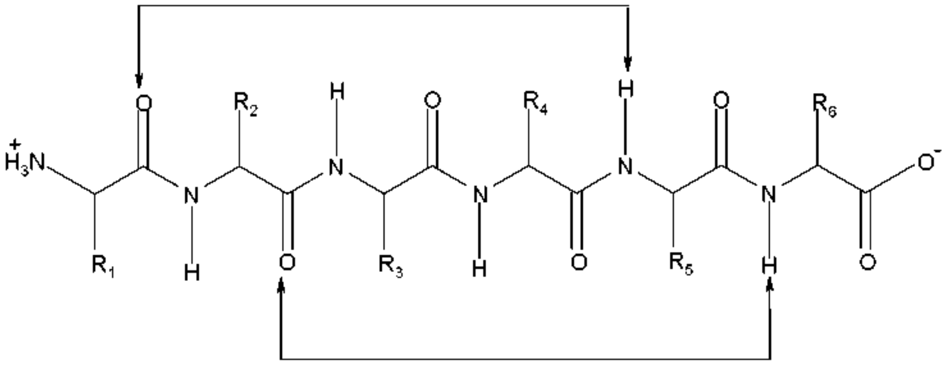
Arg – Arginine		174
Ser – Serine		105

SOLUTION

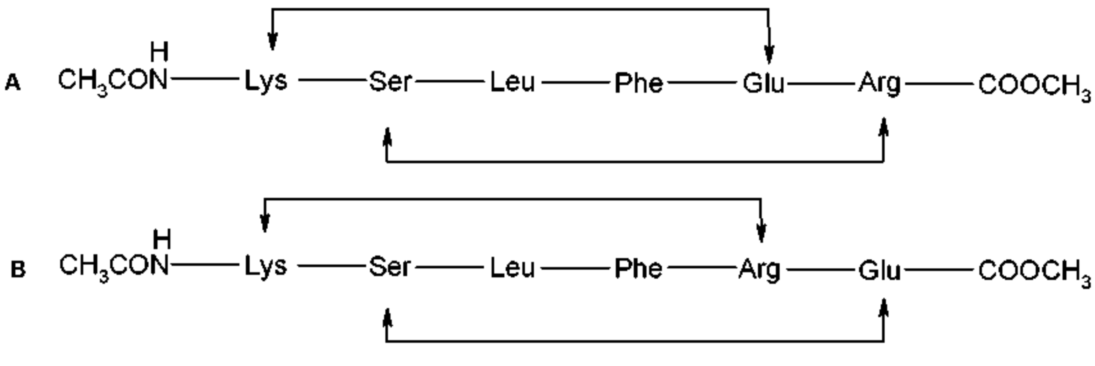
7.1 The end-to-end distance in a hexapeptide when it is in a fully extended conformation is approximately :

(c) 20 Å

7.2



7.3



7.4 $\Delta G = -8 - (-16 \times 2) + (-4 \times 1) + (-14 \times 2) = -8$ kJ mol^{-1}

7.5 $\Delta G = -(14 \times 3) - (-16 \times 3) = +6$ kJ mol^{-1}

7.6 $\frac{105 \times 100}{0.35} = 30000 \text{ Da}$

7.7 The approximate number of amino acid residues present in a protein of this size is:

(c) 275

7.8 P1: Phe – Glu – Ser – Met – Leu – Lys

P2: Glu – Ser – Met – Leu – Lys

P3: Phe – Glu – Ser – Hms/Met

P4: Leu – Lys

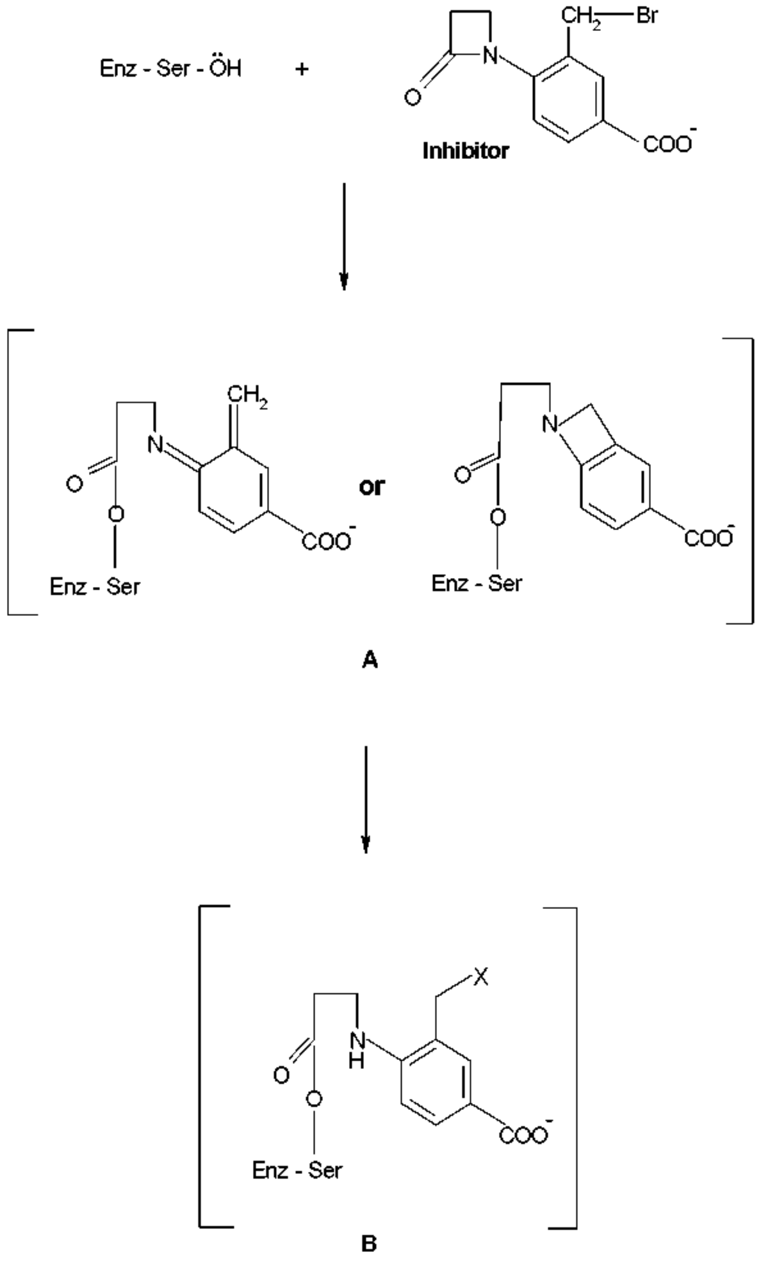
7.9 Phe - Glu - Ser - Hms

$(165 + 147 + 105 + 119) - 3\ H_2O = 536 - 54 = 482$ Da

7.10 700 M

7.11 The most effective inhibitor is C.

7.12


Enz - Ser - ÖH
+
CH2—Br
N
O
COO-
Inhibitor
CH2
N
O
O
Enz - Ser
COO-
or
N
O
O
Enz - Ser
COO-
A
X
NH
O
O
Enz - Ser
COO-
B

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Preparation of 2-Iodobenzoic Acid

This laboratory task involves preparation of 2-iodobenzoic acid from 2-aminobenzoic acid. The procedure consists of diazotization of 2-aminobenzoic acid followed by reaction with KI (in H_2SO_4).

Procedure

1) Quantitatively transfer the given sample of solid 2-aminobenzoic acid into a 100 cm^3 beaker placed in the ice-bath. Add 7.2 cm^3 of H_2SO_4 (2.6 M) (labelled H_2SO_4) and mix the contents thoroughly for 1 minute with the help of a glass rod. Cool the solution for 5 minutes.
2) Using a measuring cylinder, measure out 4.4 cm^3 of supplied cooled $NaNO_2$ solution from the vial placed in the ice-bath.
3) With the help of a dropper, slowly add the cooled $NaNO_2$ solution to the acid solution with constant gentle stirring using a glass rod to obtain an almost clear solution (3 – 5 minutes).
4) Remove the beaker from the ice bath and then slowly add 9.4 cm^3 of KI solution from the stoppered tube, with stirring.
5) Get hot water from the laboratory expert. Keep the beaker in hot water for 5 minutes.
6) Filter the crude product and wash it thoroughly with distilled water (10 cm^3). Collect the washings along with the main filtrate.
7) Neutralize the combined filtrate by gradually adding the given solid Na_2CO_3 until effervescence ceases. Dispose of the filtrate in the appropriate plastic bucket.

Purification of the crude product

Place the funnel containing the precipitate on a 100 cm^3 conical flask. Pour about 15 to 20 cm^3 of the supplied $NaHCO_3$ solution (using test tube) over the filter paper so as to dissolve the precipitate completely.

8) Add the supplied charcoal powder to the filtrate and mix it thoroughly. Filter the solution to remove charcoal.

9) Add dilute H_2SO_4 gradually to the filtrate till effervescence ceases. Filter the purified product. Use 10 -15 cm^3 distilled water to wash the precipitate. Keep the filter paper with the product on a watch glass.

10) Cover the product with the same funnel and hand over the product to the laboratory expert for drying (for a minimum of one hour).

Towards the end of the practical session have the product weighed by the laboratory expert and record the same.

SOLUTION

The following values were required to be written on the Answer Sheet :

- Mass of the product.
- The calculated theoretical yield (based on 2 aminobenzoic acid) in g.
- The yield obtained as a percentage of the theoretical yield.
- Colour of the product obtained.

Tasks:

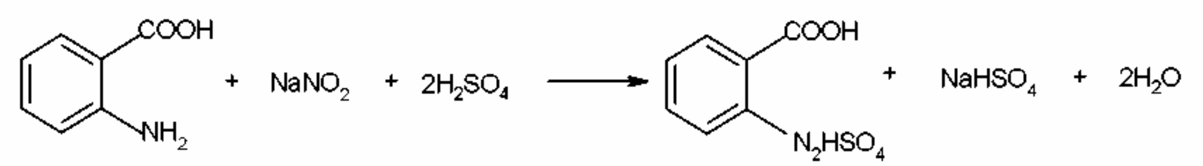
Write down the balanced chemical equations for:

(a) diazotization of 2-aminobenzoic acid using $NaNO_2$ and H_2SO_4.

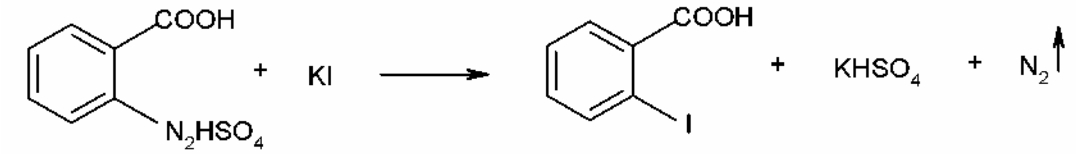
(b) the reaction of KI with the diazotized product.

Solutions of the tasks:

a)



b)



PROBLEM 2 (Practical)

Estimation of Mn(II) and Mg(II) Present in the Given Sample

In this experiment, estimation of the amounts of Mn (II) and Mg (II) present in the given sample is carried out by complexometric titration using standard Na_2EDTA solution. Total metal ion content is obtained from the first titration. At this stage, by using adequate solid NaF, selective and quantitative release of EDTA present in Mg-EDTA complex is achieved. The EDTA thus released is bound again by the addition of a known excess of standard Mn (II) solution. The unused Mn (II) is estimated by a back titration using the same standard Na_2EDTA solution. From these two different titre values, individual amounts of metal ions present can be obtained. Both the titrations are performed using a buffer (*pH* = 10) and Erichrome black T indicator.

The sample in duplicate is given in two 250 cm^3 conical flasks (labelled as Trial I and Trial II). Perform the titrations for both and record your readings on the answer sheet.

Procedure

Two burettes (25 cm^3) are supplied to you. Fill one with the given standard Na_2EDTA solution and the other with the given standard Mn (II) solution.

Titration 1

To the sample solution (supplied in the 250 cm^3 conical flask), add all of the solid hydroxylamine hydrochloride given in one vial followed by 50 cm^3 of distilled water. With the help of a measuring cylinder, add 10 cm^3 buffer solution (*pH* = 10) and one metal spatula full of the solid indicator. Shake the contents of the flask thoroughly and titrate the solution against the standard Na_2EDTA solution until the colour changes from wine red to blue. Record your burette reading (**A** cm^3). Ensure that you shake the contents of the flask thoroughly throughout the titration.

Titration 2

To the same flask, add all of the solid NaF given in one vial and shake the contents well for a minute. To this add 20 cm^3 of the given standard Mn (II) solution from the other burette. The addition of the Mn (II) solution should be done in small increments (2 – 3 cm^3) with thorough shaking. After addition of the total Mn (II) solution, shake the contents for two to three minutes. The colour of the solution will change from blue to wine red. Titrate the excess of Mn (II) in the solution against the standard Na_2EDTA solution till the colour changes from wine red to blue. Record your burette reading (**B** cm^3).

Repeat the same procedure for Trial II.

SOLUTION

The results of the titration (volumes) were required to be written on the Answer Sheet.

The other tasks to be solved:

2.2 Give the balanced chemical equation for the reactions of Mg(II) and Mn(II) with Na_2EDTA . (Use the symbol Na_2HY for Na_2EDTA.)

Answer: $Mg^{2+} + H_2Y^{2-} \rightarrow MgY^{2-} + 2\ H^+$

$Mn^{2+} + H_2Y^{2-} \rightarrow MnY^{2-} + 2\ H^+$

2.3 Give the equation for the release of EDTA by the addition of NaF to the MgEDTA complex.

Answer: $MgY^{2-} + 2\ F^{-} \rightarrow MgF_2 + Y^{4-}$

2.4 Calculate the amount of Mg (II) and Mn (II) in gram for any one of the two trials. (Show the main steps in your calculation.)

2.5 The colour change at the end point (wine red to blue) in Titration 1 is due to

a) the formation of metal-indicator complex, ☐

b) the release of free indicator from metal-indicator complex, ☐

c) the formation of metal-EDTA complex. ☐

[Mark X in the correct box.]

Correct answer is (b).

PROBLEM 3 (Practical)

Determination of the Rate Constant for the Redox Reaction between Ethanol and Chromium (VI)

The oxidation of alcohols by chromium (VI) forms the basis for analysis of breath samples for measuring alcohol content. A dilute solution of $K_2Cr_2O_7$ in the presence of a strong acid (3.6 M HCl here) is a source of $HCrO_4^-$ which is the oxidant involved in the reaction.

In this experiment, the rate of the reaction between $HCrO_4^-$ and CH_3CH_2OH is determined titrimetrically. Under the given experimental conditions, the rate law reduces to

rate = $k[HCrO_4^-]^x$

where **x** is the order of the reaction.

At any given time, $[HCrO_4^-]$ is obtained by iodometric titration.

Procedure

You are given 100 cm^3 of standard $K_2Cr_2O_7$ solution in HCl in a bottle. Transfer all the absolute ethanol given in a vial into this bottle and stopper it. Mix the contents thoroughly, start the stopwatch immediately and regard this as time *t* = 0. Fill the burette with this solution.

After every 10 minutes, start to draw 10 cm^3 of this solution to a clean conical flask containing 4 cm^3 of the given KI solution. The solution will turn brown. Titrate this solution with the given standard $Na_2S_2O_3$ solution until the colour changes to pale greenish yellow. Add 2 cm^3 of starch indicator and continue the titration until the colour changes from blue to pale green. Record the burette reading in the answer sheet. Repeat this procedure at 10 minutes intervals to obtain four readings.

SOLUTION

The results of the titration (volumes) were required to be written on the Answer Sheet.

The other tasks to be solved:

3.1 Write down the possible oxidation products in the reaction of $HCrO_4^-$ and CH_3CH_2OH.

Solution: Acetic acid, CH_3COOH
Acetaldehyde, CH_3CHO

3.2 Write the chemical equation for the reaction between $HCrO_4^-$ and KI:

Solution: $2\ HCrO_4^- + 6\ I^- + 14\ H^+ \rightarrow 3\ I_2 + 2\ Cr^{3+} + 8\ H_2O$

3.3 Write down the balanced chemical equation involved in the titration.

Solution: $I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

3.4 Give the main steps for the calculation of $HCrO_4^-$ concentration (mol dm^{-3}) for any one titration reading.

3.5 Give **c**oncentrations of $HCrO_4^-$ at different times (in a table attached).

3.6 Plot the graph of log $[HCrO_4^-]$ *vs.* time.

3.7 From the nature of the graph determine the order (**x**) of the reaction with respect to $HCrO_4^-$

3.8 Determine the rate constant for the reaction.