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IChO

International Chemistry Olympiad

6 theoretical problems
2 practical problems

THE THIRTY-FIRST
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THEORETICAL PROBLEMS

PROBLEM 1

A compound **Q** (molar mass 122.0 g mol^{-1}) consists of carbon, hydrogen and oxygen.

PART A

The standard enthalpy of formation of CO_2(g) and H_2O(l) at 25.00 ℃ are –393.51 and –285.83 kJ mol^{-1}, respectively. The gas constant, R = 8.314 J K^{-1} mol^{-1}.
(Relative atomic masses : H = 1.0; C = 12.0; O = 16.0)

A sample of solid **Q** that weighs 0.6000 g, is combusted in an excess of oxygen in a bomb calorimeter, which initially contains 710.0 g of water at 25.000 ℃. After the reaction is completed, the temperature is observed to be 27.250 ℃, and 1.5144 g of CO_2 (g) and 0.2656 g of H_2O(l) are produced.

1.1 Determine the molecular formula and write a balanced equation with correct state of matters for the combustion of **Q**.

If the specific heat of water is 4.184 J g^{-1} K^{-1} and the internal energy change of the reaction (ΔU^0) –3079 kJ mol^{-1}.

1.2 Calculate the heat capacity of the calorimeter (excluding the water).

1.3 Calculate the standard enthalpy of formation ($\Delta H_f{}^0$) of **Q**.

PART B

The following data refer to the distribution of **Q** between benzene and water at 6 ℃, C_B and C_W being equilibrium concentrations of the species of **Q** in the benzene and water layers, respectively:

Assume that there is only one species of **Q** in benzene independent of concentration and temperature.

Concentration (mol dm^{-3})	
C_B	C_W
0.0118	0.00281
0.0478	0.00566
0.0981	0.00812
0.156	0.0102

1.4 Show by calculation whether **Q** is monomer or dimer in benzene. Assume that **Q** is a monomer in water.

The freezing point depression, for an ideal dilute solution, is given by

$$T_f^0 - T_f = \frac{R(T_f^0)^2 \, X_s}{\Delta H_f}$$

where T_f is the freezing point of the solution, T_f^0 the freezing point of solvent, ΔH_f the heat of fusion of the solvent, and X_s the mole fraction of solute. The molar mass of benzene is 78.0 g mol^{-1}. At 1 atm pure benzene freezes at 5.40 ℃. The heat of fusion of benzene is 9.89 kJ mol^{-1}.

1.5 Calculate the freezing point (T_f) of a solution containing 0.244 g of **Q** in 5.85 g of benzene at 1 atm.

SOLUTION

PART A

1.1 Mole C : H : O = $\frac{\frac{15144 \times 12.0}{44.0}}{12.0} : \frac{\frac{0.2656 \times 2.0}{18.0}}{1.0} : \frac{0.1575}{16.0}$

= 0.0344 : 0.0295 : 0.00984 = 7 : 6 : 2

The formula mass of $C_7H_6O_2$ = 122 which is the same as the molar mass given.

$C_7H_6O_2(s) + 15/2\ O_2(g) \rightarrow 7\ CO_2(g) + 3\ H_2O(l)$ or

$2\ C_7H_6O_2(s) + 15\ O_2(g) \rightarrow 14\ CO_2(g) + 6\ H_2O(l)$

1.2 $n(\text{Q}) = \dfrac{0.6000}{122.0} = 4.919\times10^{-3}$ mol

$q_v = n\,\Delta U^0 = \dfrac{0.6000}{122.0} \times (-3079) = -15.14$ kJ

Total heat capacity = $\dfrac{-q_v}{\Delta T} = \dfrac{15.14}{2.250} = 6.730$ kJ K^{-1}

Heat capacity of water = $710.0 \times 4.184 = 2971$ J K^{-1}

Heat capacity of calorimeter = $6730 - 2971 = 3759$ J K^{-1}

1.3 $\Delta n_g = 7 - 15/2 = -0.5$ mol

$\Delta H° = \Delta U° + RT\,\Delta n_g = -3079 + (8.314\times10^{-3}) \times (298) \times (-0.5) = -3079 - 1 = -3080$

$\Delta H° = (7\,\Delta_f H°, CO_2(g) + 3\,\Delta_f H°, H_2O(l)) - (\Delta_f H°, Q)$

$\Delta_f H°$ of Q = $7 \times (-393.51) + 3 \times (-285.83) - (-3080) = -532$ kJ mol^{-1}

PART B

1.4

c_B (mol dm^{-3})	0.0118	0.0478	0.0981	0.156
c_W (mol dm^{-3})	0.00281	0.00566	0.00812	0.0102
either c_B/c_W	4.20	8.44	12.1	15.3
or c_B/c_w^2	1.49×10^3	1.49×10^3	1.49×10^3	1.50×10^3
(or $\sqrt{c_B}\,/\,c_W$	38.6	38.6	38.6	38.7)

From the results show that the ratio c_B/c_W varies considerably, whereas the ratio c_B/c_w^2 or $\sqrt{c_B}\,/\,c_W$ is almost constant, showing that in benzene, Q is associated into double molecule. Q in benzene is dimer.

1.5 If Q is completely dimerized in benzene, the apparent molecular mass should be 244.

Mole fraction of $Q_2 = \dfrac{\dfrac{0.244}{244}}{\dfrac{0.244}{244} + \dfrac{5.85}{78.0}} = 1.32\times10^{-2}$ (0.01316)

$\Delta T_f = \dfrac{8.314 \times 278.55^2}{9.89\times10^3} \times 1.32\times10^{-2} = 0.861$

$T_f = 5.40 - 0.861 = 4.54$ ℃

PROBLEM 2

PART A

A diprotic acid , H_2A , undergoes the following dissociation reactions :

$$H_2A \rightleftharpoons HA^- + H^+; \qquad K_1 = 4.50\times10^{-7}$$

$$HA^- \rightleftharpoons A^{2-} + H^+; \qquad K_2 = 4.70\times10^{-11}$$

A 20.00 cm^3 aliquot of a solution containing a mixture of Na_2A and NaHA is titrated with 0.300 M hydrochloric acid. The progress of the titration is followed with a glass electrode *pH* meter. Two points on the titration curve are as follows :

cm^3 HCl added	*pH*
1.00	10.33
10.00	8.34

2.1 On adding 1.00 cm^3 of HCl, which species reacts first and what would be the product?

2.2 What is the amount (mmol) of the product formed in (2.1)?

2.3 Write down the main equilibrium of the product from (2.1) reacting with the solvent?

2.4 What are the amounts (mmol) of Na_2A and NaHA initially present?

2.5 Calculate the total volume of HCl required to reach the second equivalence point.

PART B

Solutions I, II and III contain a *pH* indicator HIn ($K_{In} = 4.19\times10^{-4}$) and other reagents as indicated in the table. The absorbance values at 400 nm of the solutions measured in the same cell, are also given in the table. K_a of CH_3COOH is 1.75×10^{-5}.

Table:

	Solution I	Solution II	Solution III
Total concentration of indicator HIn	1.00×10^{-5} M	1.00×10^{-5} M	1.00×10^{-5} M
Other reagents	1.00 M HCl	0.100 M NaOH	1.00 M CH_3COOH
Absorbance at 400	0.000	0.300	?

2.6 Calculate the absorbance at 400 nm of solution III.

2.7 Apart from H_2O, H^+ and OH^-, what are all the chemical species present in the solution resulting from mixing solution II and solution III at 1 : 1 volume ratio?

2.8 What is the absorbance at 400 nm of the solution in (2.7)?

2.9 What is the transmittance at 400 nm of the solution in (2.7)?

SOLUTION

PART A

2.1 Species which reacts first is A^{2-}.

The product is HA^-.

2.2 n(product) = 1.00×0.300 = 0.300 mmol

2.3 $HA^- + H_2O \rightleftharpoons H_2A + OH^-$

2.4 At *pH* 8.34 which is equal to $(pK_{a1} + pK_{a2}) / 2$ all A^- are protonated as HA^-.

Therefore $n(A^{2-})$ initially present in the solution = 0.300×10.00 = 3.00 mmol

At *pH* = 10.33, the system is a buffer in which the ratio of $[A^{2-}]$ and $[HA^-]$ is equal to 1.

Thus

$[HA^-]_{initial} + [HA^-]_{formed} = [A^{2-}]_{jnitial} - [HA^-]_{formed}$

$n(HA^-)_{initial}$ = 3.00 – 0.300 – 0.300 mmol = 2.40 mmol

$n(Na_2A)$ = <u>3.00 mmol</u>

n(NaHA) = <u>2.40 mmol</u>

2.5 Total volume of HCl required = $[(2 \times 3.00) + 2.40] / 0.300$ = 28.00 cm^3

PART B

2.6 Solution III is the indicator solution at 1×10^{-5} M in a solution containing 1.0 M CH_3COOH.

To obtain the absorbance of the solution, it is necessary to calculate the concentration of the basic form of the indicator which is dependent on the $[H^+]$ of the solution.

$[H^+]$ of solution III = $\sqrt{K_a c} = \sqrt{1.75\times10^{-5}\times1.0} = 4.18\times10^{-3}$

$$K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

$$\frac{[In^-]}{[HIn]} = \frac{K_{In}}{[H^+]} = \frac{1\times10^{-3.38}}{1\times10^{-2.38}} = 0.100$$

Since $[HIn] + [In^-] = 1\times10^{-5}$

$10\,[In^-] + [In^-] = 1\times10^{-5}$

$[In^-] = 0.091\times10^{-5}$

Absorbance of solution III = $\frac{0.091\times10^{-5}}{1.00\times10^{-5}}\times 0.300 = 0.027$

2.7 All the chemical species present in the solution resulting from mixing solution II and solution III at 1 : 1 volume ratio (apart from H^+, OH^- and H_2O) are the following: CH_3COOH , CH_3COO^-, Na^+ , HIn , In^-.

2.8 When solutions II and III are mixed at 1 : 1 volume ratio, a buffer solution of 0.05 M CH_3COO^- / 0.45 M CH_3COOH is obtained.

$[H^+]$ of the mixture solution = $K_a\frac{[CH_3COOH]}{[CH_3COO^-]} = 1.75\times10^{-5}\times\frac{0.45}{0.05} = 15.75\times10^{-5}$

$$\frac{[In^-]}{[HIn]} = \frac{K_{In}}{[H^+]} = \frac{1\times10^{-3.38}}{15.75\times10^{-5}} = 2.65$$

Since $[HIn] + [In^-] = 1\times10^{-5}$

$\frac{[In^-]}{2.65} + [In^-] = 1\times10^{-5}$

$[In^-] = 0.726\times10^{-5}$

Absorbance of solution = $\frac{0.726\times10^{-5}}{1.00\times10^{-5}}\times 0.300 = 0.218$

2-9 Transmittance of solution = $10^{-0.218} = 0.605 \Rightarrow 60.5\%$

PROBLEM 3

One of naturally occurring radioactive decay series begins with $^{232}_{90}Th$ and ends with a stable $^{208}_{82}Pb$.

3.1 How many beta (β^-) decays are there in this series? Show by calculation.

3.2 How much energy in MeV is released in the complete chain?

3.3 Calculate the rate of production of energy (power) in watts (1 W = J s^{-1}) produced by 1.00 kilogram of ^{232}Th ($t_{½} = 1.40\times10^{10}$ years).

3.4 ^{228}Th is a member of the thorium series. What volume in cm^3 of helium at 0 °C and 1 atm collected when 1.00 gram of ^{228}Th ($t_{1/2}$ = 1.91 years) is stored in a container for 20.0 years. The half-lives of all intermediate nuclides are short compared to the half-life of ^{228}Th.

3.5 One member of thorium series, after isolation, is found to contain 1.50×10^{10} atoms of the nuclide and decays at the rate of 3440 disintegrations per minute. What is the half-life in years?

The necessary atomic masses are :

$^{4}_{2}He$ = 4.00260 u, $^{208}_{82}Pb$ = 207.97664 u, $^{232}_{90}Th$ = 232.03805 u; and 1u = 931.5 MeV

1 MeV = 1.602×10^{-13} J

$N_A = 6.022\times10^{23}$ mol^{-1}

The molar volume of an ideal gas at 0 °C and 1 atm is 22.4 dm^3 mol^{-1}.

SOLUTION

3.1 A = 232 – 208 = 24; 24/4 = 6 alpha particles

The nuclear charge is therefore reduced by $2 \times 6 = 12$ units, however, the difference in nuclear charges is only 90 – 82 = 8 units. Therefore there must be

12 – 8 = 4 β^- emitted.

Number of beta decays = 4

3.2 $^{232}_{90}Th \rightarrow {}^{208}_{82}Pb + 6\,{}^{4}_{2}He + 4\beta^-$

Energy released is Q value

$Q = [m(^{232}\text{Th}) - m(^{208}\text{Pb}) - 6\, m(^{4}\text{He})]\, c^2$

(the mass of $4e^-$ are included in daughters)

$= [232.03805\ u - 207.97664\ u - 6 \times 4.00260\ u] \times 931.5\ \text{MeV u}^{-1} =$

$= (0.04581u) \times (931.5\ \text{MeV}) = 42.67\ \text{MeV}$

3.3 The rate of production of energy (power) in watts (1 W = J s^{-1}) produced by 1.00 kilogram of ^{232}Th ($t_{1/2} = 1.40\times10^{10}$ years).

1.00 kg contains = $\dfrac{1000\ \text{g} \times 6.022\times10^{23}\ \text{mol}^{-1}}{232\ \text{g mol}^{-1}} = 2.60\times10^{24}$ atoms

Decay constant for ^{232}Th:

$$\lambda = \frac{0.693}{1.40\times10^{10}\ \text{y} \times 3.154\times10^{7}\ \text{s y}^{-1}} = 1.57\times10^{-18}\ \text{s}^{-1}$$

For activity: $A = N\,\lambda = 2.60\times10^{24} \times 1.57\times10^{-18} = 4.08\times10^{6}$ dis s^{-1}

(disintegrations s^{-1})

Each decay liberates 42.67 MeV

Rate of production of energy (power):

4.08×10^{6} dis $s^{-1} \times 42.67$ MeV $dis^{-1} \times 1.602\times10^{-13}$ J MeV^{-1} =

$= 2.79\times10^{-5}$ J $s^{-1} = 2.79\times10^{-5}$ W

3.4 The volume in cm^3 of helium at 0 ℃ and 1 atm collected when 1.00 gram of ^{228}Th ($t_{1/2}$ = 1.91 years) is stored in a container for 20.0 years.

$^{228}\text{Th} \rightarrow {}^{208}\text{Pb} + 5\ {}^{4}\text{He}$

The half-lives of various intermediates are relatively short compared with that of ^{228}Th.

$$A = \lambda N = \frac{0.693}{1.91\,\text{y}} \times \frac{1.000\ \text{g} \times 6.022\times10^{23}\ \text{mol}^{-1}}{228\ \text{g mol}^{-1}} = 9.58\times10^{20}\ \text{y}^{-1}$$

Number of He collected:

$N_{He} = 9.58\times10^{20}\ \text{y}^{-1} \times 20.0\ \text{y} \times 5$ particles $= 9.58\times10^{22}$ particles of He

$$V_{He} = \frac{9.58\times10^{22} \times 22{,}4\ \text{dm}^3\,\text{mol}^{-1}}{6.022\times10^{23}\ \text{mol}^{-1}} = 3.56\ \text{dm}^3 = 3.56\times10^{3}\ \text{cm}^3$$

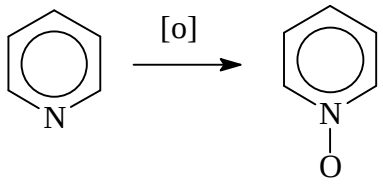
3.5 The half-life:

$A = \lambda N$

$$t_{½} = \frac{0.693}{\lambda} = \frac{0.693\,N}{A} = \frac{0.693 \times 510 \times 10^{10}\ \text{atoms}}{3440\ \text{atoms min}^{-1}} = 3.02 \times 10^{6}\ \text{min} = 5.75\ \text{years}$$

PROBLEM 4

Ligand **L** can form complexes with many transition metals. **L** is synthesized by heating a mixture of a bipyridine, glacial acetic acid and hydrogen peroxide to 70 – 80 °C for 3 hrs. The final product **L** crystallizes out as fine needles and its molecular mass is 188. An analogous reaction with pyridine is ;



Complexes of **L** with Fe and Cr have the formulae of $FeL_m(ClO_4)_n$. 3 H_2O (**A**) and $CrL_xCl_y(ClO_4)_z.H_2O$ (**B**), respectively. Their elemental analyses and physical properties are given in Tables 4a and 4b. The relationship of colour and wavelength is given in Table 4c.

Table 4a: Elemental analyses.

Complex	Elemental analyses , (wt. %)
A	Fe 5.740, C 37.030, H 3.090 , Cl 10.940, N 8.640
B	Cr 8.440, C 38.930, H 2.920, Cl 17.250, N 9.080

Use the following data:

Atomic number: Cr = 24, Fe = 26

Relative atomic mass: H = 1, C = 12, N = 14, O = 16, Cl = 35.45, Cr = 52, Fe = 55.8

Table 4b: Physical properties

Complex	Magnetic moment , μ B.M.	Colour
A	6.13	Yellow
B	Not measured	Purple

Table 4c Relationship of wavelength to colour.

Wavelength (nm) and colour absorbed	Complementary colour
400 (violet)	Yellow Green
450 (blue)	Yellow
490 (blue green)	Orange
500 (green)	Red
570 (yellow green)	Violet
580 (yellow)	Blue
600 (orange)	Blue green
650 (red)	Green

4.1 Write down the molecular formula of **L**.

4.2 If **L** is a bidentate chelating ligand, draw the structure of the bipyridine used. Also draw the structure of **L** .

4.3 Does the ligand **L** have any charge, i. e. net charge?

4.4 Draw the structure when one molecule of **L** binds to metal ion (M).

4.5 From the data in Table 4a, determine the empirical formula of **A**. What are the values of m and n in $FeL_m(ClO_4)_n$ .3 H_2O? Write the complete formula of **A** in the usual IUPAC notation. What is the ratio of cation to anion when **A** dissolves in water?

4.6 What is the oxidation number of Fe in **A**? How many d-electrons are present in Fe ion in the complex? Write the high spin and the low spin configurations that may exist for this complex. Which configuration, high or low spin, is the correct one? What is the best evidence to support your answer?

4.7 From Table 4c, estimate λ_{max} (nm) of **A**.

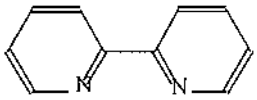
4.8 Detail analysis of **B** shows that it contains Cr^{3+} ion. Calculate the 'spin-only' magnetic moment of this compound.

4.9 Compound **B** is a 1 : 1 type electrolyte. Determine the empirical formula of **B** and the values of x, y, z in $CrL_xCl_y(ClO_4)_z$. H_2O.

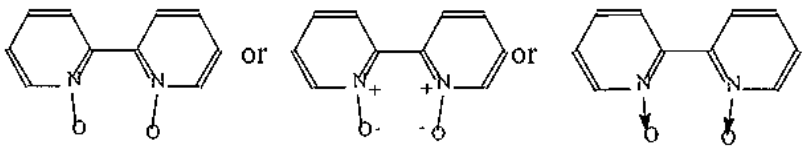
SOLUTION

4.1 Knowing that L was synthesized from bipyridine and during the reaction bipyridine was simply oxidized to bipyridine oxide. The molecular mass of bipyridine is 156 (for $C_{10}H_8N_2$) while the molecular mass of **L** is 188. The difference of 32 is due to 2 atoms of oxygen. Therefore, the molecular formula of **L** is $C_{10}H_8N_2O_2$.

4.2 The structures of bipyridine and **L**:



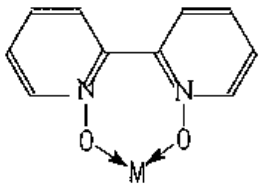
Structure of bipyridine



structure of **L**

4.3 The ligand **L** has no charge.

4.4 The structure when one molecule of **L** binds to metal ion (M):



4.5 The empirical formula of **A**. Calculation:

	Fe	C	H	Cl	N	O
%	5.740	37.030	3.090	10.940	8.640	34.560*
mol	0.103	3.085	3.090	0.309	0.617	2.160
mol ratio	1.000	29.959	30.00	2.996	5.992	20.971
atom ratio	1	30	30	3	6	21

*) Percentage of O is obtained by difference.)

The empirical formula of **A** is $FeC_{30}H_{30}Cl_3N_6C_{21}$

The values of m and n in $FeL_m(C104)_n$. 3 H_2O:

Since the molecular formula contains one atom of Fe, so in this case the empirical formula is equivalent to the molecular formula. The molecular formula of **L** has been

obtained previously in (4a) and (4b), therefore we can work to find m = 3. Having obtained the value of m , one can work out for n and find that n = 3.

The complete formula of **A** is $[FeL_3](ClO_4)_3 \cdot 3\ H_2O$

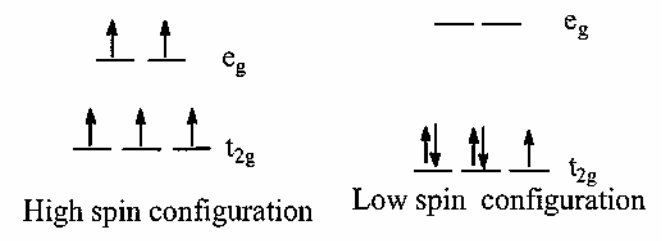
The ratio of cation to anion is equal to 1 : 3.

The three ClO_4^- groups will dissociate as free ion in solution. So the entire complex will be in the ion forms as $[FeL_3]^{3+}$ and 3 ClO_4^- in solution.

4.6 The oxidation number of Fe in complex **A** is +3 or III.

The number of *d*-electrons in Fe^{3+} ion in the complex = 5.

The high spin and the low spin configuration that may exist for this complex:



The correct answer is high spin configuration.

The best evidence to support your answer for this high/low spin selection is magnetic moment.

There exist a simple relation between number of unpaired electrons and the magnetic moment as follows:

$$\mu = \sqrt{n(n+2)}$$

where μ is the so-called 'spin-only' magnetic moment and n is the number of unpaired electrons. Thus, for high spin configuration in the given case,

$$\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92\ \text{B.M.}$$

For low spin case:

$$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73\ \text{B.M.}$$

The measured magnetic moment, for **A** is 6.13 B.M. (Table 4b) which is in the range for high spin configuration. Therefore, we can conclude that **A** can exist as a high spin complex.

4.7 From Table 4c, the color absorbed is complementary to the color seen. Thus, λ_{max} for complex A is 450 nm.

4.8 The 'spin-only' magnetic moment of complex **B**.

For Cr^{3+}: n = 3

Therefore, $\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87$ B.M.

4.9 The empirical formula of B is $Cr_{20}H_{18}N_4Cl_3O_9$, i.e. x = 2, y = 2, z = 1.

PROBLEM 5

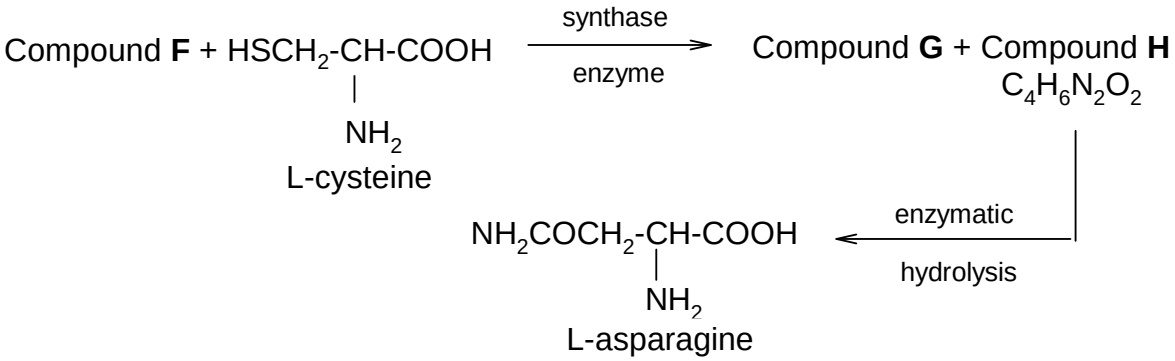
Glycoside **A** ($C_{20}H_{27}NO_{11}$), found in seeds of *Rosaceae* gives a negative test with Benedicts' or Fehling's solutions. Enzymatic hydrolysis of **A** yields (-) **B**, C_8H_7NO and **C**, $C_{12}H_{22}O_{11}$, but complete acid hydrolysis gives as organic products, (+) **D**, $C_6H_{12}O_6$ and (-) **E**, $C_8H_8O_3$.

C has a β-glycosidic linkage and gives positive test with Benedicts' or Fehling's solution. Methylation of **C** with MeI/Ag_2O gives $C_{20}H_{38}O_{11}$, which upon acidic hydrolysis gives 2,3,4-tri-*O*-methyl-D-glucopyranose and 2,3,4,6-tetra-*O*-methyl-D-glucopyranose.

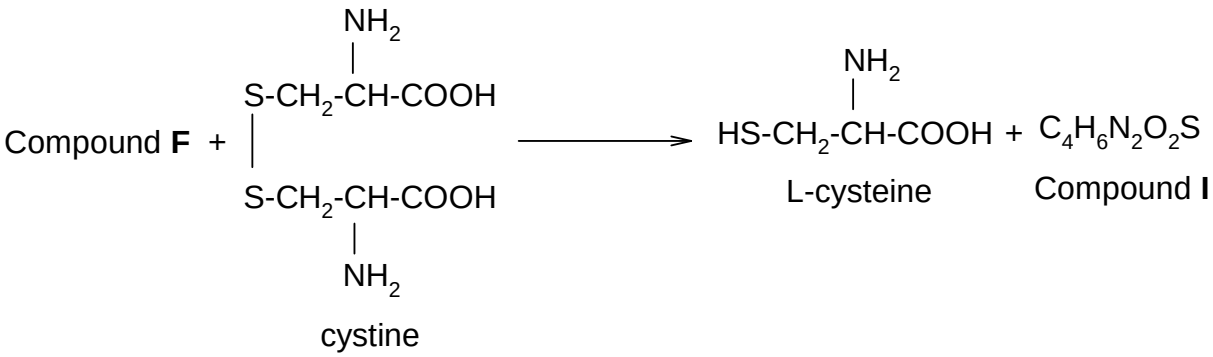
(±)**B** can be prepared from benzaldehyde and $NaHSO_3$ followed by NaCN. Acidic hydrolysis of (±)**B** gives (±)**E**, $C_8H_8O_3$.

5.1 Write structures of **A** – **D** with appropriate stereochemistry in Haworth projection, except for **B**.

Glycoside **A** is found to be toxic and believed to be due to extremely toxic compound **F**, liberated under the hydrolytic conditions. Detoxification of compound **F** in plant may be accompanied by the reactions (stereochemistry not shown).



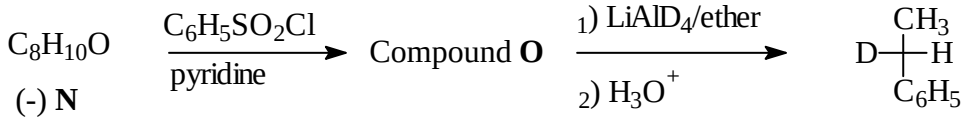
A small amount of compound **F** in human being is believed to be detoxified by a direct reaction with cystine giving L-cysteine and compound **I**, $C_4H_6N_2O_2S$ which is excreted in urine (stereochemistry not shown).



Compound **I** shows no absorption at 2150-2250 cm^{-1} in its IR spectrum but a band at 1640 cm^{-1} and the bands of carboxyl group are observed.

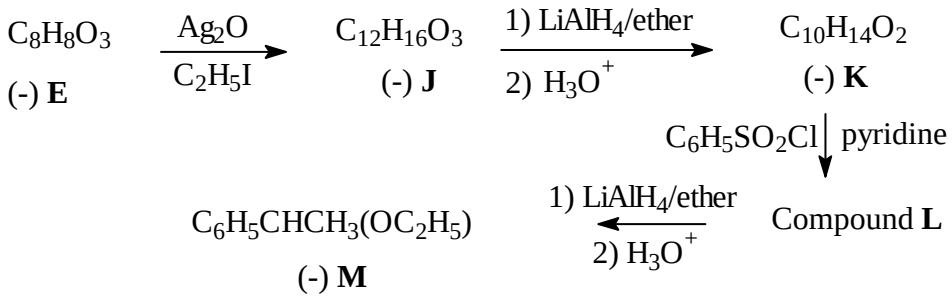
5.2 Write molecular formula for compounds **F** and **G,** and structural formula for compounds **H** and **I** and indicate stereochemistry of **H**. (Table 5.1 may be useful for structure identification.)

(-)1-Phenylethane-1-*d*, $C_6H_5CHDCH_3$ can be prepared in optically active form and the magnitude of its rotation has the relatively high value, $[\alpha]_D$ is equal to -0.6.

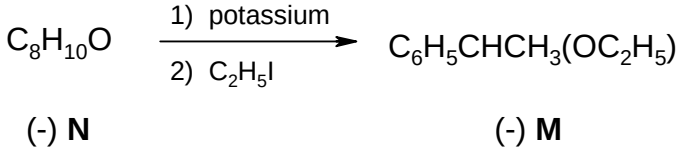


(-) 1-phenylethane-1-*d*

The absolute configuration of (-)1-phenylethane-1-*d* is related to (-) **E** according to the following reactions.



Compound (-) **M** can also be obtained from compound **N** as follows.



5.3 Deduce the absolute configuration of (-) **E** and the structure with configuration of each intermediate (**J – O**) in the sequence with the proper *R*,*S*-assignment as indicated in the answer sheet.

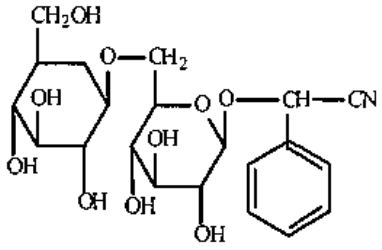
5.4 Choose the mechanism involved in the conversion of compound **O** to 1-phenylethane-*1-d*.

Table 5.1 Characteristic Infrared Absorption

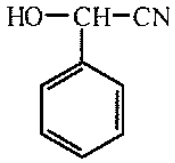
Stretching Vibration	Region (cm^{-1})	Stretching Vibration	Region (cm^{-1})
C-H (alkane)	2850-2960	O-H (free alcohol)	3400-3600
C-H (alkene)	3020-3100	O-H (H-bonded alcohol)	3300-3500
C=C	1650-1670	O-H (acid)	2500-3100
C-H (alkyne)	3300	C-O	1030-1150
C≡C	2100-2260	NH, NH_2	3310-3550
C-H (aromatics)	3030	C-N	1030, 1230
C=C (aromatics)	1500-1600	C=N	1600-1700
C-H (aldehyde)	2700-2775, 2820-2900	C≡N	2210-2260
C=O	1670-1780		

SOLUTION

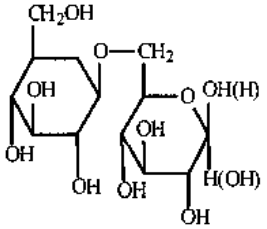
5.1



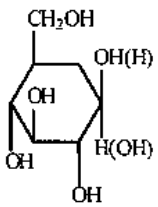
A



B



C

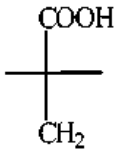


D

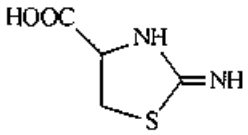
5.2

Molecular formula of compound **F** = HCN

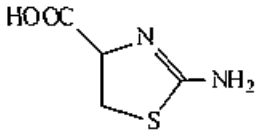
Molecular formula of compound **G** = H_2S



Compound **H**

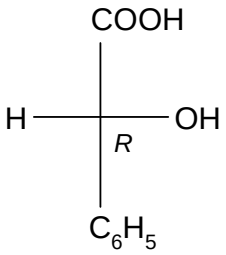


or

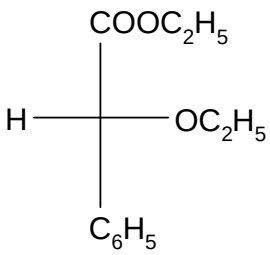


Compound **I**

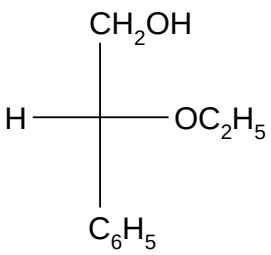
5.3



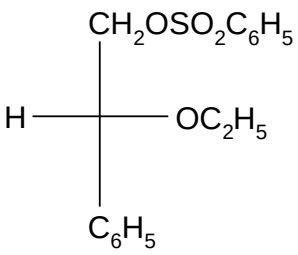
(-) **E**



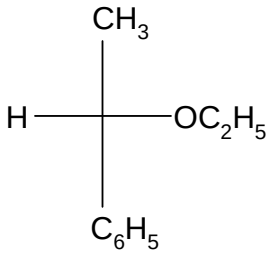
(-) **J**



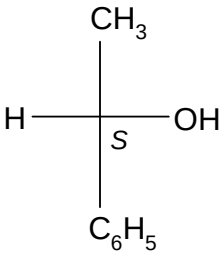
(-) **K**



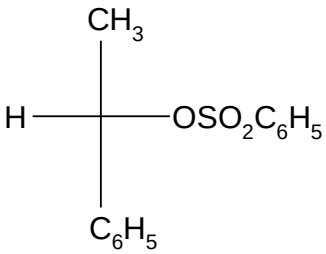
Compound **L**



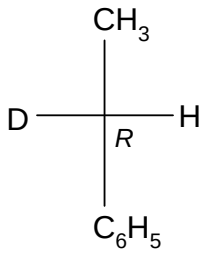
(-) **M**



(-) **N**



Compound **O**



(-) 1-phenylethane-*1-d*

5.4 The mechanism involved in the conversion of compound **O** to (-) 1-phenylethane-*1-d* is S_N2.

PROBLEM 6

Peptide **A** has a molecular weight of 1007. Complete acid hydrolysis gives the following amino acids in equimolar amounts: Asp, Cystine, Glu, Gly, Ile, Leu, Pro, and Tyr (see Table 1). Oxidation of **A** with HCO_2OH gives only **B** which carries two residues of cysteic acid (**Cya** which is a cysteine derivative with its thiol group oxidized to sulfonic acid).

6.1 How many sulphonic acid groups are formed from oxidation of a disulfide bond ?

Partial hydrolysis of **B** gives a number of di and tri-peptides (B1-B6). The sequence of each hydrolysis product is determined in the following ways.

The N-terminal amino acid is identified by treating the peptide with 2,4-dinitrofluorobenzene (DNFB) to give DNP-peptide. After complete acid hydrolysis of the DNP-peptide, a DNP-amino acid is obtained which can be identified readily by comparison with standard DNP-amino acids.

6.2 B1, on treatment with DNFB followed by acid hydrolysis gives a product, DNP-Asp. This suggests that B1 has aspartic acid at the N-terminus. Write down the <u>complete</u> structure of DNP-Asp at its isoelectric point (no stereochemistry required).

Next, the C-terminal amino acid is identified by heating the peptide at 100 °C with hydrazine, which cleave all the peptide bonds and convert all except C-terminal amino acids into amino acid hydrazides, leaving the C-terminal carboxyl group intact.

In this way N- and C-terminal amino acids are identified and the complete sequences of B1-B6 are as shown :

B1	Asp-Cya	B4	Ile-Glu
B2	Cya-Tyr	B5	Cya-Pro-Leu
B3	Leu-Gly	B6	Tyr-Ile-Glu

Hydrolysis of **B** with an enzyme from *Bacillus subtilis* gives B7-B9 with the following compositions:

B7 Gly-NH_2 (Glycinamide)

B8 Cya, Glu, Ile, Tyr

B9 Asp, Cya, Leu, Pro

6.3 Write down the sequence of B8, if DNP-Cya is obtained on treatment of B8 with DNFB followed by complete acid hydrolysis.

6.4 If the N- and C-terminal amino acids of B9 are identified as Asp and Leu respectively, write down the sequence of B9.

6.5 Write down the complete structure of **A** using abbreviation in Table 1, indicating the position of the disulfide bond.

However, the calculated molecular weight of **A** based on the above sequence is 2 mass units higher than the experimental value. On careful observation of the mixture from complete acid hydrolysis of **A**, 3 molar equivalents of ammonia are also produced in addition to the amino acids detected initially.

6.6 Suggest the revised structure of **A** and circle the site(s) of the structure to indicate all the possible source of ammonia.

6.7 Using the information in Table 2, calculate the isoelectric point of **A**.

Table 1**:** Formulae and symbols of common amino acids at isoelectric point

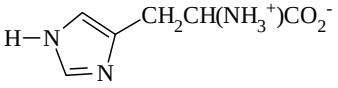
Name	Formula	Three-letter symbol
Alanine	$CH_3CH(NH_3^+)CO_2^-$	Ala
Arginine	$H_2NC(=NH)NH(CH_2)_3CH(NH_3^+)CO_2^-$	Arg
Asparagine	$H_2NCOCH_2CH(NH_3^+)CO_2^-$	Asn
Aspartic Acid	$HO_2CCH_2CH(NH_3^+)CO_2^-$	Asp
Cysteine	$HSCH_2CH(NH_3^+)CO_2^-$	Cys
Cystine	$[SCH_2CH(NH_3^+)CO_2^-]_2$	-
Glutamic Acid	$HO_2CCH_2CH_2CH(NH_3^+)CO_2^-$	Glu
Glutamine	$H_2NCOCH_2CH_2CH(NH_3^+)CO_2^-$	Gln
Glycine	$^+H_3NCH_2CO_2^-$	Gly
Histidine		His
Isoleucine	$CH_3CH_2CH(CH_3)CH(NH_3^+)CO_2^-$	Ile
Leucine	$(CH_3)_2CHCH_2CH(NH_3^+)CO_2^-$	Leu
Lysine	$H_2N(CH_2)_4CH(NH_3^+)CO_2^-$	Lys

Table 1 (continued)

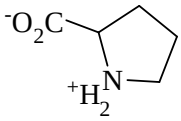
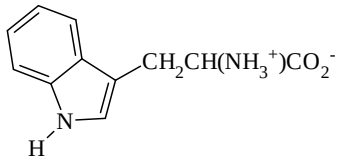
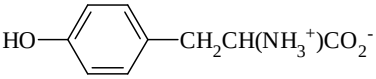
Methionine	$CH_3SCH_2CH_2CH(NH_3^+)CO_2^-$	Met
Phenylalanine	$PhCH_2CH(NH_3^+)CO_2^-$	Phe
Proline		Pro
Serine	$HOCH_2CH(NH_3^+)CO_2^-$	Ser
Threonine	$CH_3CH(OH)CH(NH_3^+)CO_2^-$	Thr
Tryptophan		Trp
Tyrosine		Tyr
Valine	$(CH_3)_2CHCH(NH_3^+)CO_2^-$	Val

Table 2: pK_a of some important groups in amino acids

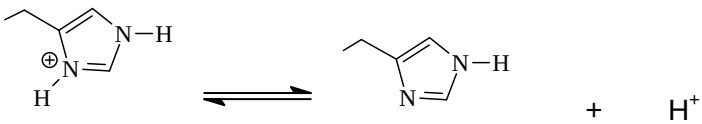
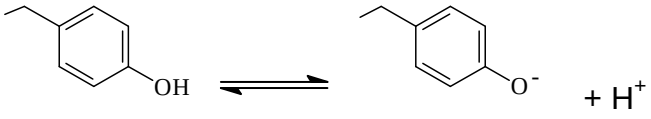
Groups	**Equilibrium**	**pK_a**
Terminal carboxyl	$-CO_2H \rightleftharpoons -CO_2^- + H^+$	3.1
Asp /or Glu side- chain carboxyl	$-CO_2H \rightleftharpoons -CO_2^- + H^+$	4.4
His side-chain		6.5
Terminal amino	$-NH_3^+ \rightleftharpoons -NH_2 + H^+$	8.0
Cys side-chain	$-SH \rightleftharpoons -S^- + H^+$	8.5

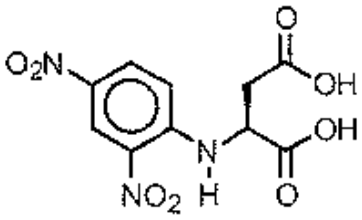
Table 2 (continued)

Tyr side-chain		10.0
Lys side-chain amino	$-NH_3^+ \rightleftharpoons -NH_2 + H^+$	10.0
Arg side-chain	$-NH(NH_2)C=NH_2^+ \rightleftharpoons -NH(NH_2)C=NH + H^+$	12.0

SOLUTION

6.1 Two sulphonic acid groups are formed from oxidation of a disulfide bond.

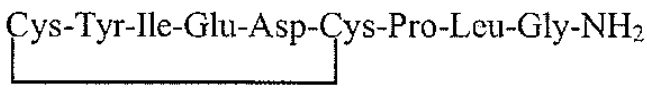
6.2 Complete structure of DNP-Asp at its isoelectric point is



6.3 The sequence of B8 is: Cya-Tyr-Ile-Glu

6.4 The sequence of B9 is: Asp-Cya-Pro-Leu

6.5 The *complete* structure of A is



6.6 Write the revised structure of A below and circle the site(s) to indicate all the possible source of ammonia

6.7 The isoelectric point of A is 9.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

A Kinetic Study of the Acid Catalyzed Reaction Between Acetone and Iodine in Aqueous Solution

The reaction between acetone and iodine in aqueous solution is catalyzed by H^+.

$$CH_3\text{-}CO\text{-}CH_3\ (aq) + I_2\ (aq) \xrightarrow{H^+} CH_3\text{-}CO\text{-}CH_2I\ (aq) + H^+(aq) + I^-(aq)$$

In this experiment, the kinetics of the iodination is measured to determine the rate law of the reaction. The rate equation for the loss of I_2(aq) has been shown to have the form

$$\text{Rate} = -\frac{d[I_2]}{dt} = k\,[CH_3COCH_3]^x\,[I_2]^y\,[H^+]^z$$

where H^+ ions are the catalyst.

In order to determine the rate constant k and the kinetic orders x, y and z, the initial rate of reaction is measured.

$$\text{Initial rate} = k\,[CH_3COCH_3]_0^x\,[I_2]_0^y\,[H^+]_0^z$$

where $[\ ]_0$ are the initial concentrations of acetone, I_2 and H^+, respectively.

If the initial rates are measured for various initial concentrations of the reactants then the order with respect to each reactant can be obtained.

The initial rate is obtained by measuring the decrease in the I_2(aq) concentration after a short time interval (7.0 min. in this experiment) after the start of the reaction. Aqueous sodium acetate solution is added to stop the reaction after 7 minutes. The acetate ion reacts immediately with the H^+ to produce acetic acid and so reducing the concentration of H^+. The reaction is thus stopped as there is no catalyst present.

Since the reaction does not come to a complete halt, the solution should be titrated immediately after the addition of the sodium acetate solution.

The remaining iodine I_2 (aq) is determined by titration with sodium thiosulphate, $Na_2S_2O_3$. As the end point of the titration is approached, starch indicator is added and the titration is continued until the blue colour disappears.

Chemicals

1. Aqueous iodine solution in 0.4 M KI 80 cm^3
2. 0.100 M aq. HCl 50 cm^3
3. 0.50 M aq. CH_3COONa 80 cm^3
4. Standard 0.02 M $Na_2S_2O_3$(aq) solution 200 cm^3
   (the exact concentration will be announced at the beginning of practical part)
5. Aqueous acetone (50% by volume) 50 cm^3
   (Density of pure acetone; 0.787 g cm^{-3}, MW. = 58.08)
6. Starch indicator 7 cm^3

Procedure

A. Standardization of Iodine Solution

1. Pipet 5.00 cm^3 of aqueous iodine into a clean 125 cm^3 Erlenmeyer flask.
2. Add 10 cm^3 of distilled water using graduated cylinder.
3. Titrate the iodine with the standard 0.02 M sodium thiosulphate solution until the colour of the solution is pale yellow.
4. Add 3 – 4 drops of starch indicator and continue the titration until the blue colour disappears.
5. Record the initial and the final volumes of the thiosulphate solution and the volume used in the answer sheet.
6. Repeat the titration as necessary (Steps 1 to 5).
7. Give the titre volume for calculation in the answer sheet.
8. Calculate the iodine concentration.

B. A kinetic study of acid catalyzed reaction between acetone and iodine in aqueous solution

1. Label the stoppered flasks as follows: Flask I, II, III and IV.
2. To each respective flask add the following volumes of distilled water, 0.100 M hydrochloric acid and 50 % acetone:

Flask No.	Volume (cm^3)		
	water	0.100 M HCl	50 % acetone
I	5.00	5.00	5.00
II	0.0	5.00	5.00
III	0.0	5.00	10.00
IV	0.0	10.00	5.00

Stopper each flask immediately after addition of the solutions.

3. Measure out 10 cm^3 of 0.50 M aq. CH_3COONa into the graduated cylinder.
4. Set the stop-watch to 0.0000 display.
5. Pipet 5.00 cm^3 of iodine solution into the stoppered Flask No. I.
   Start the stop-watch as soon as the first drop of iodine solution is added.
6. Stopper the flask and swirl continuously.
7. Just before 7.0 min, remove the stopper, at 7.0 min, immediately pour 10 cm^3 of sodium acetate solution (from step 3) into the reaction flask. Shake well.
8. Titrate the remaining iodine with standard thiosulphate solution.
9. Record the volume of the thiosulphate solution.
10. Repeat the above steps (Steps 3 to 9) for Flask II, III and IV but add in step 5 the I_2(aq) solution to each flask as indicated:

    Flask II: 10.00 cm^3 I_2 solution
    Flask III: 5.00 cm^3 I_2 solution
    Flask IV: 5.00 cm^3 I_2 solution

Calculations

B-1. Calculate the initial concentrations (M) of iodine, acetone and HCl solutions in Flasks I to IV, assuming volumes are additive.

B-2. Calculate concentrations of iodine (M) remaining in Flasks I to IV at 7.0 minutes.

B-3. Calculate the initial reaction rate for Flasks I to IV in M s^{-1}.

B-4. The rate of reaction has the form

$$\text{Rate} = -\frac{d[I_2]}{dt} = k\,[CH_3COCH_3]^x\,[I_2]^y\,[H^+]^z$$

Calculate the reaction orders x, y and z from the initial rates and the initial concentrations of acetone, iodine and HCl. The values of x, y and z should be rounded off to the nearest integer and fill in the answer sheet. Write rate equation or rate law.

B-5. Calculate the rate constant, k, for Flasks I to IV with proper unit.

B-6. Give the mean value of the rate constant.

SOLUTION

The competitors were required to perform the following tasks:

In part A: Using the concentration of standard $Na_2S_2O_3$ solution (in bottle) and titration results it was required to calculate the concentration of iodine in the solution. Results were expected to be shown in a table in the answer sheet.

In part B: The following calculations B1 – B5 were required to be shown in the answer sheet:

B-1. *Calculation for initial concentrations (M) in the solution mixtures.*

B-2. *Calculation of the concentration (M) of iodine remaining in flasks I to IV at 7 minutes.*

B-3. *Calculation of initial rate of disappearance of I_2 at 7 minutes in flasks I to IV*.

$$\text{Rate of disappearance of iodine (M s}^{-1}) = -\frac{d[I_2]}{dt} = \frac{c(I_2)_{\text{initial}} - c(I_2)_{7\,\text{min}}}{7 \times 60\ s}$$

B-4. *Calculation of x, y, and z in the rate equation*:

$$\text{rate} = -\frac{d[I_2]}{dt} = k\,[CH_3COCH_3]^x\,[I_2]^y\,[H^+]^z$$

In comparing the rates in solutions **II** : **I**, **III** : **I**, and **IV** : **I** one can calculate the following values:

x = 1; y = 0; z = 1

The rate equation has the form: rate = $k\,[CH_3COCH_3]\,[H^+]$

B-5. *Calculation of the rate constants for solution mixtures **I** to **IV** and the mean value of the rate constant.*

PROBLEM 2 (Practical)

Isolation and Identification of an Essential Oil from Natural Source

In this experiment, you will steam distil and determine the structures of the main essential oil (**S**) from a given natural source and a product from its chemical conversion (unknown **Y**).

To determine the structures, you have to use organic qualitative analysis to identify any functional groups present in the compounds by using the reagents at your station. NMR data will be given only after the functional group test is completed.

Chemicals Available:

Sample (1 g in a vial)

Unknown **Y** (in a vial)

Anhydrous Na_2SO_4 (in a plastic vial), dichloromethane, ceric ammonium nitrate solution, 2,4-Dinitrophenylhydrazine (labelled as 2,4-DNP), 2 % aq. NH_3, 5 % aq. $AgNO_3$, 5 % aq. HCl, 5 % aq. NaOH, 5 % aq. $NaHCO_3$, 1 % $FeCl_3$ in EtOH, 0.2 % aq. $KMnO_4$, decolourised with easily oxidised functional groups, acetone (for washing).

Procedure:

1. Apparatus: Assemble a distillation apparatus using a 25 cm^3 round bottomed flask for distillation and a 10 cm^3 round bottomed flask to collect the distillate. Heat the sand bath to approximately 150 °C before proceeding the next step.

Simplified Steam Distillation: Mix 1 g of ground sample with 15 cm^3 of water in the 25 cm^3 round bottomed flask and allow the sample to soak in the water for about 10 minutes before distillation. Do not forget to put in a magnetic bar, turn on the water in the condenser and stirring motor, heat the mixture (the temperature of the sand bath should not be below 170 °C) to provide a steady rate of distillation. At least 5 cm^3 of distillate must be collected. Hot plate must be turned off after distillation is finished. Disassemble the apparatus and rinse the condenser with acetone. Be sure that the condenser is dry before using in the next step

Extraction of the Essential Oil: Transfer the distillate to a 15 cm^3 capped centrifuge tube and add 1 cm^3 of dichloromethane to extract the distillate. Cap the tube securely and shake vigorously, cool in ice. Allow the layers to separate.

Using a Pasteur pipette, transfer the dichloromethane layer to a 10 cm^3 test tube. Repeat this extraction with fresh 1 cm^3 dichloromethane twice and combine with the first extract.

Drying: Dry the dichloromethane extract by adding anhydrous Na_2SO_4 and stir occasionally for 10 minutes.

Evaporation: With a clean, dry cotton plugged Pasteur pipette transfer the organic layer to a dry 5 cm^3 conical vial. Use approximately 1 cm^3 of clean dichloromethane to wash Na_2SO_4 using the dry cotton plugged Pasteur pipette, then transfer into the vial. Be careful not to transfer any of the Na_2SO_4 into the vial. Use Hickman still head and dry condenser to distil the dichloromethane from the solution until the volume is reduced to 1 cm^3. Discard the distilled dichloromethane from the Hickman still head with a Pasteur pipette or a syringe to a vial (for recovered dichloromethane) and keep the residue for functional group analysis.

Functional Group Analysis: Carry out the functional group analysis of the residue solution (1 cm^3) by using the appropriate reagents at your station. (Note: dichloromethane is immiscible with water.)

Tollen's Reagent: add 1 drop of 5 % aq. $AgNO_3$ in a small test tube followed by 1 drop of 5 % aq. NaOH, brown precipitate will appear. Add 2 % aq NH_3 to the tube until all the precipitate dissolved. The solution is ready for the test.

2. Structure elucidation of the main essential oil (S)

Reaction of the main essential oil (**S**) with CH_3I in the presence of K_2CO_3 gives compound **X** ($C_{11}H_{14}O_2$). Oxidation of **X** gives unknown **Y** ($C_{10}H_{12}O_4$) as the main product and CO_2.

3. Structure elucidation of the unknown Y:

Identify the functional groups of unknown Y (provided in a conical vial) by using the reagents at your station and fill in your results in the answer sheet. Indicate the functional group(s) present or not present.

Hand in your copy of answer sheet PART I (Demonstrator copy) of functional group analysis and ask for ^{1}H NMR spectra. ^{1}H NMR spectra will be given only when the functional group analysis is completed.

4. Draw the structure which represents the main component in the essential oil (S) that was distilled from the sample. Assign each proton from the provided ^{1}H NMR spectra by labelling the peak number on the proton in the structure in the answer sheet.

5. Draw the structures of compound X and unknown Y. Assign each proton of unknown **Y** from the provided ^{1}H NMR spectra in the same manner as in (4).

SOLUTION

1. It was expected to obtain at least 5 cm^3 of distillate.

2. Functional group analysis of the distilled essential oil:

Reagents	Positive test	Negative test
0.2 % $KMnO_4$	✓	
1 % $FeCl_3$	✓	
2,4-DNP		✓
Ceric ammonium nitrate	✓	
Tollen's Reagent		✓

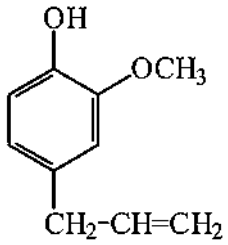
Functional groups in S	Present	Not present
-C=C-	✓	
-OH (alcoholic)		✓
-OH (phenolic)	✓	
-CHO		✓
-CO-		✓
-COOH		✓

3. Funcional group analysis of the unknown compound Y:

Reagents	Positive test	Negative test
5 % HCl		✓
5 % NaOH	✓	
5 % $NaHCO_3$	✓	
0.2 % $KMnO_4$		✓
1 % $FeCl_3$		✓
2,4-DNP		✓
Ceric ammonium nitrate		✓
Tollen's Reagent		✓

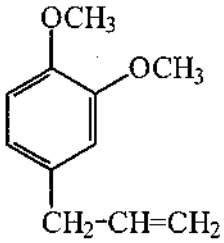
Functional groups in **Unknown Y**	Present	Not present
-C=C-		✓
-OH (alcoholic)		✓
-OH (phenolic)		✓
-CHO		✓
-CO-		✓
-COOH	✓	

4. The structure which represents the main essential oil (S):

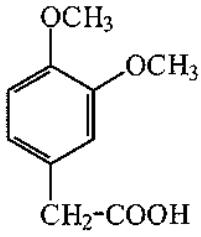


5. The structure of compound **X** and unknown **Y**:

Compound **X**



Compound **Y**

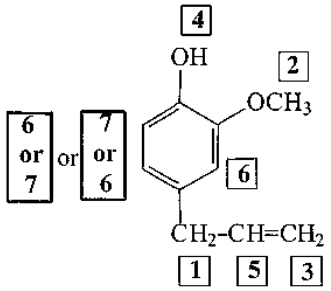


NMR spectrum of the main essential oil (S):

(See peak number in the given 'H NMR spectrum)

Peak No.	Chemical shift (δ, ppm)	No. of proton(s)	Multiplicity
1	3.31	2H	d
2	3.84	3H	S
3 4	5.0 – 5.1	2H	m
5	5.6	1H	S
	5.9 – 6.0	1H	m
6	6.7	2H	S d or m
7	6.87	1H	d

NMR assignment of the main essential oil (S):

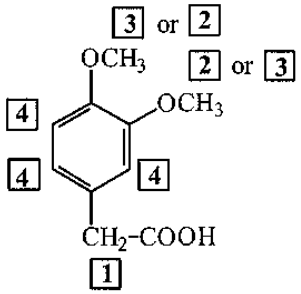


NMR spectrum of the unknown **Y**:

(See peak number in the given 'H NMR spectrum. Labile proton does not appear in the spectrum.)

Peak No.	Chemical shift (δ, ppm)	No. of proton(s)	Multiplicity
1	3.59	2H	s
2	3.86	3H	s
3	3.88	3H	s
4	6.81	3H	s

NMR assignment of the main essential oil (S):



32nd

International Chemistry Olympiad

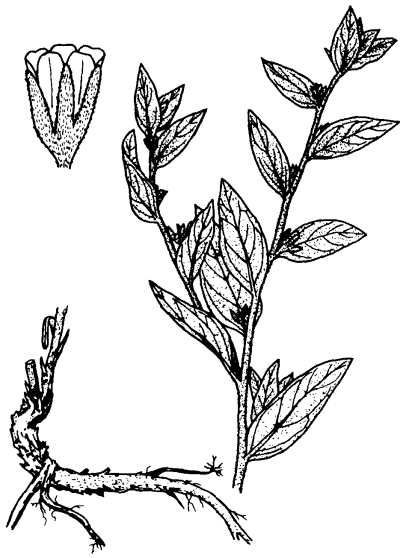
6 theoretical problems
2 practical problems

THE THIRTY-SECOND
INTERNATIONAL CHEMISTRY OLYMPIAD
2–11 JULY 2000, COPENHAGEN, DENMARK

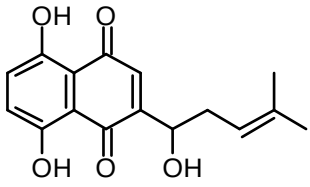
THEORETICAL PROBLEMS

PROBLEM 1

Synthesis of Compounds with Wound Healing Properties



Shikonin is a red compound found in the roots of the plant *Lithospermum erythrorhizon* which grows in Asia. Extracts of the root have been used for centuries in folk medicine and are used today in ointments for healing of wounds.



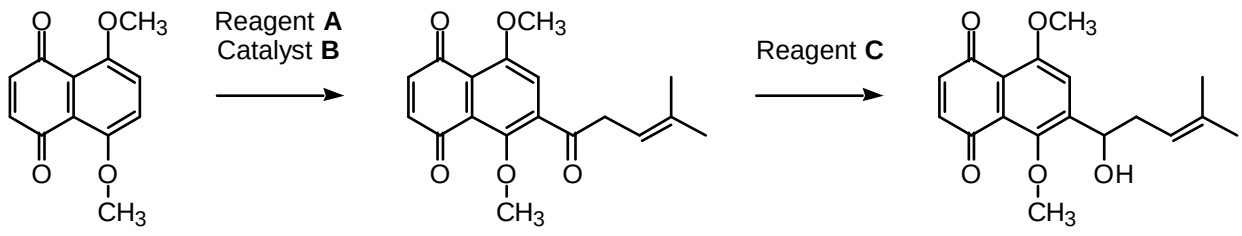
Shikonin

1.1 How many stereoisomers of Shikonin are possible ?

1.2 Do all stereoisomers of Shikonin have the same melting point? Mark with an X.

yes	no

The following sequence is part of a synthetic route to Shikonin:



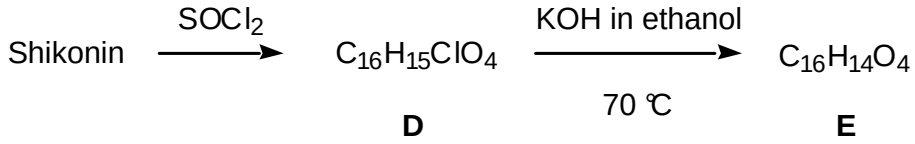
1.3 Draw the structural formula of reagent **A**.

1.4 Indicate (by means of an X in the appropriate check-box) the correct IUPAC name for reagent **A**.

2-Methyl-2-pentenoyl chloride	❑
1-Chloro-4-methyl-3-pentene	❑
4-Methyl-3-pentenoyl chloride	❑
4-Methyl-3-pentene-1-ol	❑
4,4-Dimethyl-3-butenoyl chloride	❑

1.5 Write the molecular formula of reagent **C**.

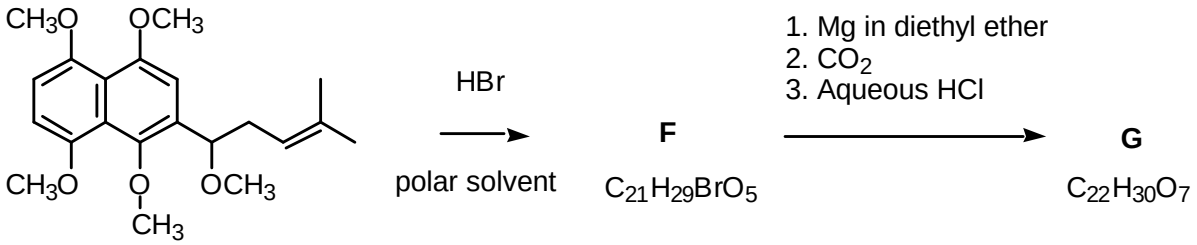
Numerous Shikonin analogues have been synthesized with a view to obtaining more potent compounds. One reaction sequence is shown below:



1.6 Draw the structural formula of compound **E**.

1.7 How many stereoisomers of compound **E,** if any, are possible

Another route to useful Shikonin analogues is the following:



1.8 Draw the structural formula of compound **F**.

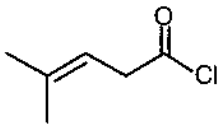
1.9 Draw the structural formula of compound **G**.

SOLUTION

1.1 2 stereoisomers.

1.2 Stereoisomers of Shikonin have the same melting point.

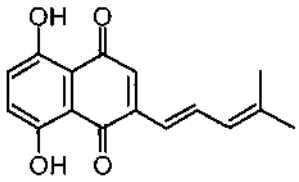
1.3 The structural formula of reagent **A**:



1.4 The correct IUPAC name for reagent **A** is 4-Methyl-3-pentenoyl chloride.

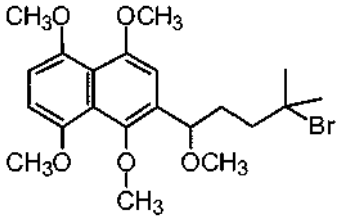
1.5 $NaBH_4$ (LiAlH4 will be acccepted)

1.6 The structural formula of compound **E**:

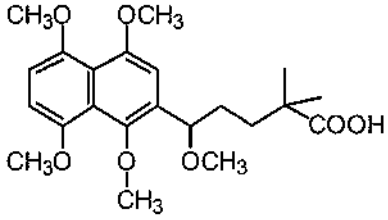


1.7 **2** stereoisomers

1.8 The structural formula of compound **F**:



1.9 The structural formula of compound **G**:



PROBLEM 2

Bridge between Denmark and Sweden

On July 1, 2000, the combined tunnel and bridge connecting Denmark and Sweden was officially opened. It consists of a tunnel from Copenhagen to an artificial island, and a bridge from the island to Malmö in Sweden. The major construction materials employed are concrete and steel. This problem deals with chemical reactions relating to production and degradation of such materials.

Concrete is produced from a mixture of cement, water, sand and small stones. Cement consists primarily of calcium silicates and calcium aluminates formed by heating and grinding of clay and limestone. In the later steps of cement production a small amount of gypsum, $CaSO_4 \cdot 2\ H_2O$, is added to improve subsequent hardening of the concrete. The use of elevated temperatures during the final production may lead to formation of unwanted hemihydrate, $CaSO_4 \cdot ½\ H_2O$. Consider the following reaction:

$$CaSO_4 \cdot 2\ H_2O(s) \rightarrow CaSO_4 \cdot ½\ H_2O(s) + 1½\ H_2O(g)$$

The following thermodynamic data apply at 25 °C, standard pressure: 1.00 bar:

Compound	$\Delta_f H$ (kJ mol^{-1})	S° (J K^{-1} mol^{-1})
$CaSO_4 \cdot 2\ H_2O(s)$	–2021.0	194.0
$CaSO_4 \cdot \frac{1}{2}\ H_2O(s)$	–1575.0	130.5
$H_2O(g)$	–241.8	188.6

Gas constant: $R = 8.314$ J mol^{-1} K^{-1} = 0.08314 L bar mol^{-1} K^{-1}

0 °C = 273.15 K.

2.1 Calculate ΔH (in kJ) for transformation of 1.00 kg of $CaSO_4 \cdot 2\ H_2O(s)$ to hemihydrate $CaSO_4 \cdot \frac{1}{2}\ H_2O(s)$. Is this reaction endothermic or is it exothermic?

2.2 Calculate the equilibrium pressure (in bar) of water vapour in a closed vessel containing $CaSO_4 \cdot 2\ H_2O(s)$, $CaSO_4 \cdot \frac{1}{2}\ H_2O(s)$ and $H_2O(g)$ at 25 °C.

2.3 Calculate the temperature at which the equilibrium water vapour pressure is 1.00 bar in the system described in problem 2-2. Assume that ΔH° and ΔS° are temperature independent.

Corrosion of metals is associated with electrochemical reactions. This also applies for the formation of rust on iron surfaces, where the initial electrode reactions usually are:

(1) $Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^-$

(2) $O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-(aq)$

An electrochemical cell in which these electrode reactions take place is constructed. The temperature is 25 ºC. The cell is represented by the following cell diagram:

$Fe(s)\ |\ Fe^{2+}(aq)\ ||\ OH^-(aq), O_2(g)\ |\ Pt(s)$

Standard electrode potentials (at 25 ºC):

$Fe^{2+}(aq) + 2\ e^- \rightarrow Fe(s)$ $\qquad E^\circ = -0.44$ V

$O_2(g) + 2\ H_2O(l) + 4\ e^- \rightarrow 4\ OH^-(aq)$ $\qquad E^\circ = 0.40$ V

Nernst factor: $RT \ln 10 / F = 0.05916$ volt (at 25 ºC)

Faraday constant: $F = 96485$ C mol^{-1}

2.4 Calculate the standard electromotive force (the standard cell voltage), E°, at 25 ºC.

2.5 Write down the overall reaction which takes place during discharge of the cell under standard conditions.

2.6 Calculate the equilibrium constant at 25 ℃ for th e overall cell reaction.

2.7 The overall reaction referred to above is allowed to proceed for 24 hours under standard conditions and at a constant current of 0.12 A. Calculate the mass of Fe converted to Fe^{2+} after 24 hours. Oxygen and water may be assumed to be present in excess.

2.8 Calculate *E* for the cell at 25 ℃ for the following conditions :
$[Fe^{2+}]$ = 0.015 M, $pH_{\text{right-hand half-cell}}$ = 9.00, $p(O_2)$ = 0.700 bar.

SOLUTION

2.1 ΔH^0 = –1575.0 kJ mol^{-1} + 1.5× (–241.8) kJ mol^{-1} – (–2021.0 kJ mol^{-1}) = 83.3 kJ mol^{-1}

$n = m / M$ = 1000g / 172.18 g mol^{-1} = 5.808 mol

ΔH^0 = 484 kJ

The reaction is endothermic.

2.2 ΔS^0 = 130.5 J K^{-1} mol^{-1} + 3/2 × 188.6 J K^{-1} mol^{-1} – 194.0 J K^{-1} mol^{-1}

= 219.4 J K^{-1} mol^{-1}

$\Delta G^0 = \Delta H^0 - T\Delta S^0$ = 17886 J mol^{-1}

$\Delta G^0 = -RT \ln K$

$K = (p(H_2O))^{3/2} = 7.35 \times 10^{-4}$ (pressure in bar)

$p(H_2O) = 8.15 \times 10^{-3}$ bar

2.3 $p(H_2O)$ = 1.00 bar implies K = 1.00 and $\Delta G^0 = -RT \ln K = 0$

$\Delta G = \Delta H - T\Delta S$

0 = 83300 J K^{-1} – T 219.4 J K^{-1} mol^{-1}

T = 380 K or 107 ºC

2.4 E^0(cell) = E^0(right) – E^0(left) = 0.40 V – (– 0.44 V) = 0.84 V

2.5 Oxidation takes place at the negative, left half-cell.

Left half: $2\ Fe \rightarrow 2\ Fe^{2+} + 4\ e^-$ (multiplied by 2)

Right half: $O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$

Overall: $2\ Fe + O_2 + 2\ H_2O \rightarrow 2\ Fe^{2+} + 4\ OH^-$

2.6 $K = [Fe^{2+}]^2\ [OH^-]^4 / p(O_2)$ (conc. in M and pressure in bar)

$\Delta G = -n\ F\ E$ (cell) $= -RT \ln K$

$K = 6.2 \times 10^{56}$

2.7 $Q = I\ t = 0.12\ A \times 24 \times 60 \times 60\ s = 10\ 368\ C$

$n(e^-) = Q / F = 10\ 368\ C / 96485\ C\ mol^{-1} = 0.1075\ mol$

$m(Fe) = n(Fe)\ M(Fe) = 1/2 \times 0.1075\ mol \times 55.85\ g\ mol^{-1} = 3.0\ g$

2.8 $$E(\text{cell}) = E^0(\text{cell}) - \frac{0.05916\ V}{n} \log \frac{[Fe^{2+}]^2\ [OH^-]^4}{p(O_2)}$$

$pH = 9.00$ implies $[H^+] = 1 \times 10^{-9}$ and $[OH^-] = 1 \times 10^{-5}$

$$E(\text{cell}) = 0.84\ V - \frac{0.05916\ V}{4} \log \frac{0.015^2\ [1 \times 10^{-5}]^4}{0.700} = 1.19\ V$$

PROBLEM 3

Bioinorganic Chemistry

The square planar complex *cis*-diammine dichloroplatinum(II) is an important drug for the treatment of certain cancers.

3.1 Draw the structures of *cis*- and *trans*-diammine dichloroplatinum(II) and label each structure as *cis* or *trans*.

A number of ionic compounds also have the empirical formula $Pt(NH_3)_2Cl_2$.

3.2 Write molecular formulas for all possible ionic compounds which comply with the following conditions: each compound has

1) empirical formula $Pt(NH_3)_2Cl_2$,
2) an anion and a cation and is composed of discrete, monomeric square planar platinum(II) complex,
3) only one type of cation and one type of anion. The answer must clearly reveal the composition of each discrete platinum(II) complex entity in each compound

3.3 How many *5d* electrons are there in the platinum(II) ion?

The valence d-orbital energy splitting diagram for a square planar complex can be regarded as being derived from that for an octahedral complex in which the metal-ligand interactions due to the two ligands coordinated along the *z* axis vanish, while the bonds to the four remaining ligands (coordinated along the *x* and *y* axes) become stronger.

3.4 Which of the five *5d* orbitals attain the highest energy (*i. e.* is the least likely to be occupied by electrons) in the general case of a square-planar Pt(II) complex?

Serum transferrin (abbreviated: Tf) is a monomeric protein whose main function in the human body is the transport of iron(III). Each transferrin molecule can bind up to two iron(III) ions with stepwise binding constants K_1 and K_2 at biological conditions except that the temperature is 25 ℃ corresponding to the react ions:

$Fe^{III} + Tf \rightarrow (Fe^{III})Tf$ $\qquad K_1 = 4.7\times10^{20}$

$Fe^{III} + (Fe^{III})Tf \rightarrow (Fe^{III})_2Tf$ $\qquad K_2 = 2.4\times10^{19}$

In the diferric protein, $(Fe^{III})_2Tf$, the two iron(III) ions are bound at two similar, but non-identical sites, and the two possible monoferric protein products, $(Fe^{III})Tf$, can be denoted $\{Fe^{III} . Tf\}$ and $\{Tf . Fe^{III}\}$. Their relative abundance at equilibrium is given by the constant

$K = [\{Tf . Fe^{III}\}] [\{Fe^{III} . Tf\}]^{-1} = 5.9$.

3.5 Calculate the values of the two constants $K_1' = [\{Fe^{III} . Tf\}] [Fe^{III}]^{-1} [Tf]^{-1}$ and $K_1'' = [\{Tf . Fe^{III}\}] [Fe^{III}]^{-1} [Tf]^{-1}$, respectively, corresponding to the formation of each monoferric form of transferrin.

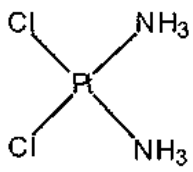
3.6 Calculate the values of the two constants $K_2' = [(Fe^{III})_2Tf] [Fe^{III}]^{-1} [\{Fe^{III} . Tf\}]^{-1}$ and $K_2'' = [(Fe^{III})_2Tf] [Fe^{III}]^{-1} [\{Tf . Fe^{III}\}]^{-1}$ respectively, corresponding to the formation of diferric transferrin from each of the monoferric forms.

The bound iron(III) ion at each binding site is surrounded by six donor atoms from various ligands. Thus, two oxygen atoms of a carbonate anion coordinate to the metal, and the following amino acid side chains from the protein primary structure also coordinate to the iron(III) ion with one potential donor atom each: one aspartate, one histidine and two tyrosine residues.

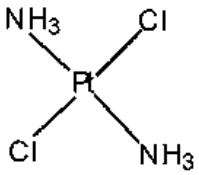
3.7 What is the total number of oxygen donor atoms that surround a 6-coordinate iron(III) ion in transferrin?

SOLUTION

3.1 The structures of *cis*- and *trans*-diammine dichloroplatinum(II)



cis



trans

3.2 $[Pt(NH_3)_4] [PtCl_4]$

$[Pt(NH_3)_3Cl] [Pt(NH_3)Cl_3]$

$[Pt(NH_3)_3Cl]_2 [PtCl_4]$

$[Pt(NH_3)_4] [Pt(NH_3)Cl_3]_2$

3.3 Eight *d*-electrons.

3.4 Orbital $5\,d_{x^2-y^2}$. In a square planar complex the four ligand atoms fall on the *x* and *y* axes along which this orbital, if filled, would also have electron density concentrated.

3.5 The concentration of monoferric forms of transferrin is

$[(Fe^{m})Tf = [\{Fe^{m}\text{-}Tf\}] + [\{Tf\text{-}Fe^{III}\}]$

$K'_1 + K''_1 = K_1 \qquad K'_1 K = K''_1$

$$K'_1 = \frac{K_1}{1+K} = \frac{4.7\times10^{20}}{1+5.9} = 6.8\times10^{19}$$

$$K''_1 = K_1 - K'_1 = (4.7 - 0.68)\times10^{20} = 4.0\times10^{20}$$

3.6 $K'_1 K'_2 = K''_1 K''_2 = K_1 K_2$

$$K'_1 = \frac{K_1 K_2}{K'_1} = \frac{4.7\times10^{20}\times 2.19\times10^{19}}{6.8\times10^{19}} = 1.7\times10^{20}$$

$K''_1 K''_2 = K_1 K_2$

$$K''_2 = \frac{K_1 K_2}{K''_1} = \frac{4.7\times10^{20}\times 2.4\times10^{19}}{4.0\times10^{20}} = 2.8\times10^{19}$$

3.7 (= 2 (CO_3^{2-}) + 1 (Asp(O^-)) + 2 (2 × Tyr(O^-))

PROBLEM 4

A Naturally Occurring Compound

A naturally occurring compound **A** containing only C, H and O has the following elemental composition, percentage mass,

C: 63.2 %, H: 5.3%, O: 31.5%.

4.1 Derive the empirical formula of compound **A**.

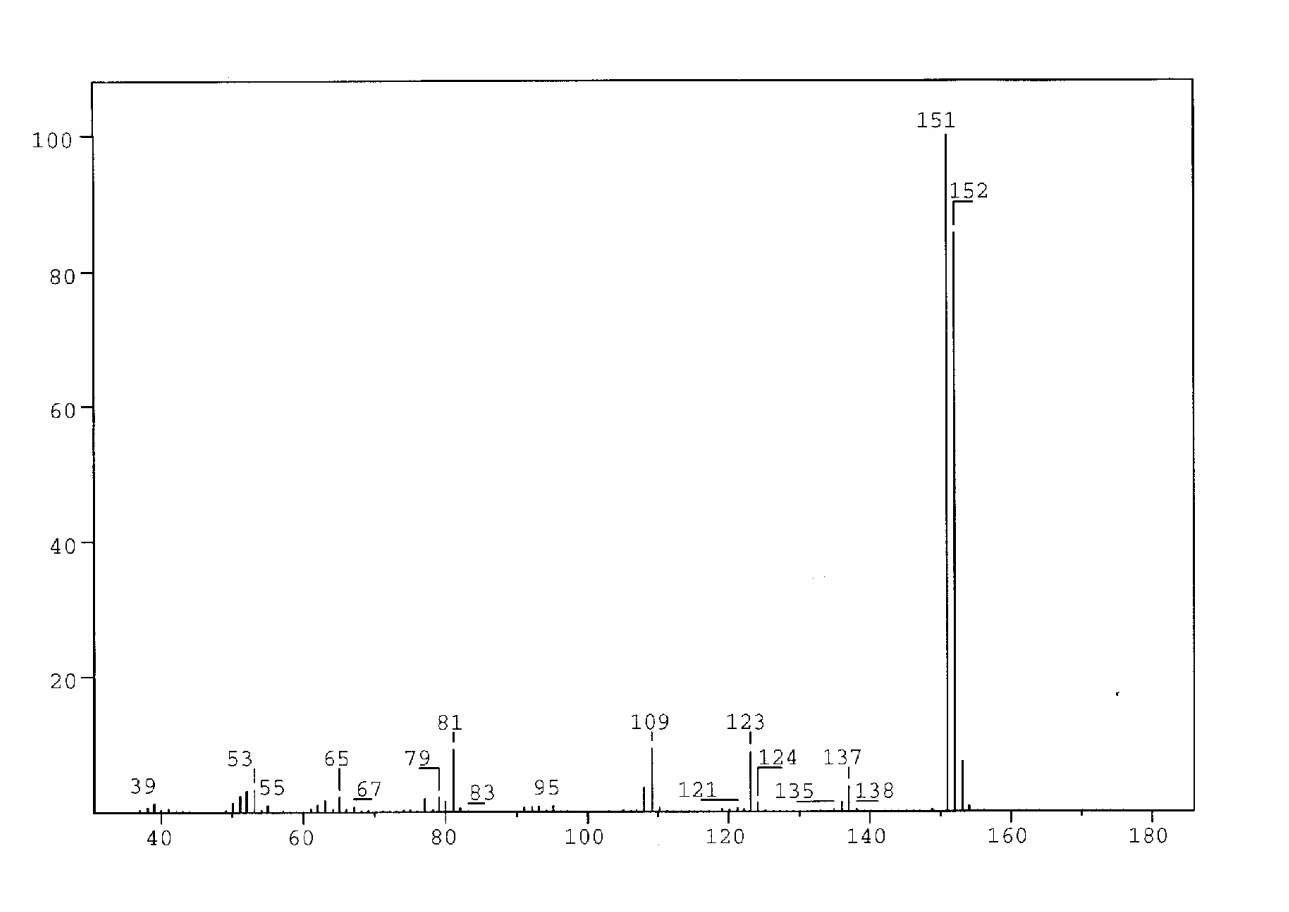


Figure 1

The mass spectrum of compound **A** is shown in Figure 1.

4.2 What is the molecular formula for compound **A**?

A solution of **A** in ether is shaken with an aqueous solution of NaOH. After this, no **A** remains in the ether phase. Another solution of **A** in ether is shaken with an aqueous solution of $NaHCO_3$. **A** remains in the ether phase.

4.3 Which of the following classes of compounds does **A** belong to according to these experiments? Mark with an X.

alcohol ❑	phenol ❑	aldehyde ❑	ketone ❑
acid ❑	ester ❑	ether ❑	

Compound **A** gave rise to formation of a silver mirror with Tollens' reagent ($Ag(NH_3)_2^+$).

4-1 Which of the following functional groups does this indicate the presence of in **A**? Mark with an X.

hydroxy group of an alcohol	❑	hydroxy group of a phenol	❑
carbonyl group of an aldehyde	❑	carbonyl group of a ketone	❑
carboxylic group	❑	ester group	❑
alkoxy group of an ether	❑		

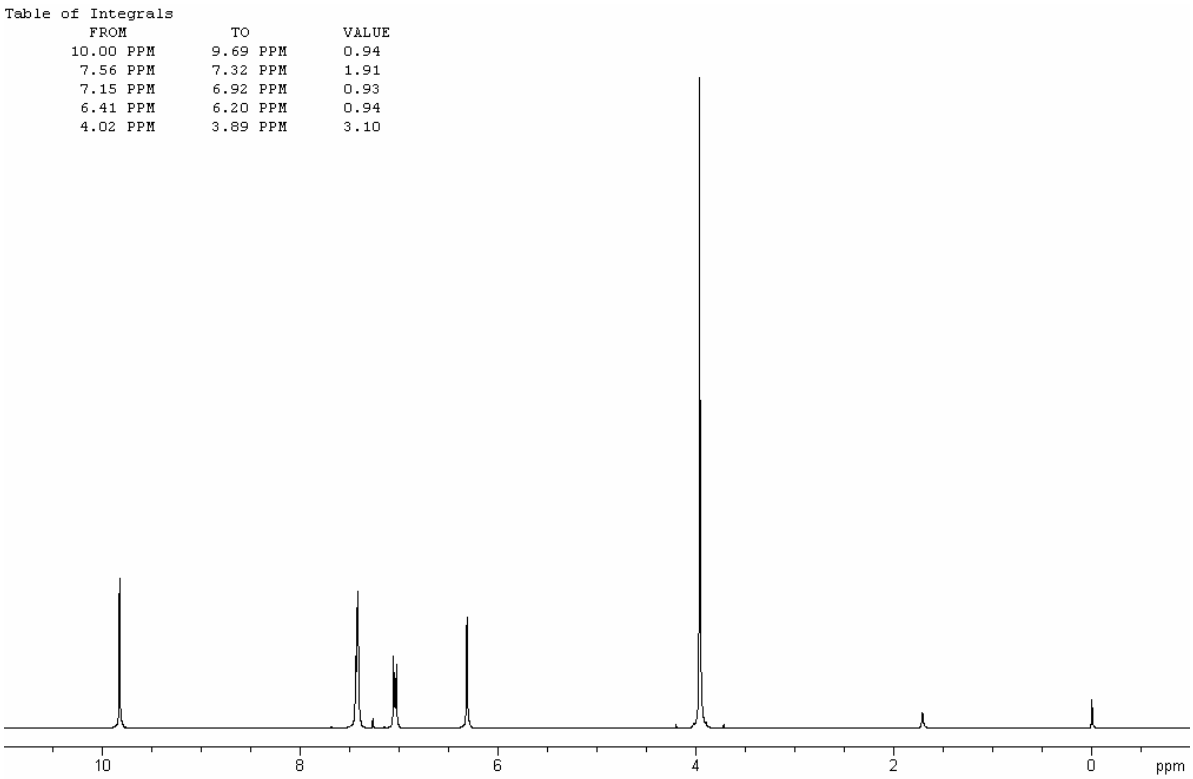


Figure 2a

The ^{1}H NMR spectrum of compound **A** recorded at 300 MHz is shown in Figure 2a (solvent $CDCl_3$ (7.27 ppm), reference tetramethylsilane). The signals at 3.9, 6.3 and 9.8 ppm are singlets. Figure 2b is an expansion of the region 6.9 – 7.6 ppm.

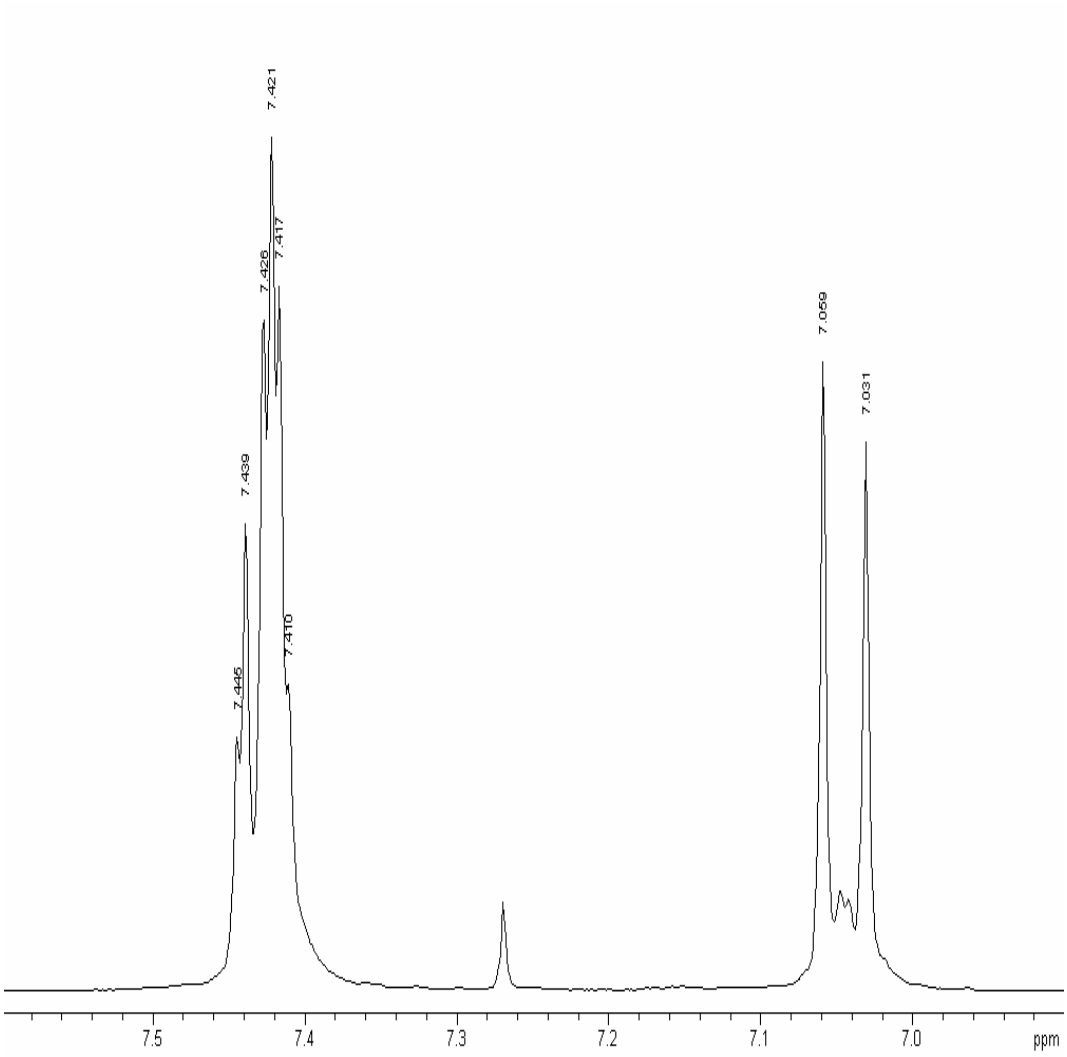


Figure 2b

Selected chemical shift and coupling constant values are given in Table 1.

The signal at 6.3 ppm disappears when a drop of D_2O is added.

4.5 Which of the following does this indicate? Mark with an X.

Exchange of carbon-bonded hydrogen ❑

Exchange of oxygen-bonded hydrogen ❑

Dilution effect ❑

Hydrolysis ❑

The same signal moves to a lower ppm value upon dilution with $CDCl_3$.

4.6 Which of the following does this indicate?

Indicate the true statements (more than one).

Increased hydrogen bonding	❑
Decrease in hydrogen bonding	❑
Intermolecular hydrogen bonding	❑
Intramolecular hydrogen bonding	❑
No hydrogen bonding	❑

4.7 Draw the four possible structural formulas for compound **A** based on the information given above

4.8 Give structural formulas for the fragments lost corresponding to the peaks at 137 and 123 mass units in the mass spectrum.

4.9 Two of the isomers have a lower pK_a value than the others. Write the formulas for those.

Table 1. ^{1}H Chemical Shift δ

Hydrogens attached to carbon		
Methyl	CH_3–C– CH_3–C=O– CH_3–O–R CH_3–OCOR	0.9 – 1.6 ppm 2.0 – 2.4 ppm 3.3 – 3.8 ppm 3.7 – 4.0 ppm
Methylene	CH_2–C– CH_2–C=O– CH_2–OR CH_2–OCOR	1.4 – 2.7 ppm 2.2 – 2.9 ppm 3.4 – 4.1 ppm 4.3 – 4.4 ppm
Methine	CH–	1.5 – 5.0 ppm depending on the substituents. Generally higher than for methyl and methylene
Alkene		4.0 – 7.3 ppm depending on the substituent
Aldehyde	R–CHO	9.0 – 10.0 ppm

Table 1 (continued) ^{1}H Chemical Shift δ

Hydrogens attached to oxygen		
Alcohols	ROH	0.5 – 5.0 ppm
Phenols	ArOH	4.0 – 7.0 ppm
Carboxylic acids	RCOOH	10.0 – 13.0 ppm
Selected spin-spin coupling constants		
Alkanes (free notation)	H-C-C-H vicinal	6 – 8 Hz
Alkenes	trans cis geminal	11 – 18 Hz 6 – 12 Hz 0 – 3 Hz
Aromates	ortho meta para	6 – 10 Hz 1 – 4 Hz 0 – 2 Hz

_____

SOLUTION

4.1 The empirical formula of **A** is $C_8H_8O_3$.

4.2 The molecular formula of compound **A**: $C_8H_8O_3$.

4.3 The compound **A** is a phenol.

4.4 Compound **A** forms a mirror with Tollen's reagent. This indicates the presence of carbonyl group of an aldehyde.

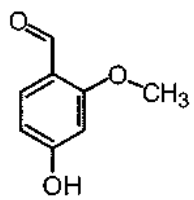
4.5 It indicates exchange of oxygen-bonded hydrogen.

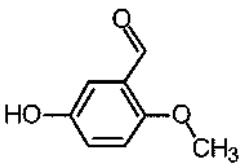
4.6 It indicates:

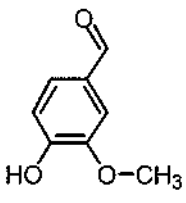
decrease in hydrogen bonding,

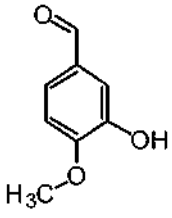
intermolecular hydrogen bonding.

4.7 Four possible structural formulas for compound **A**:



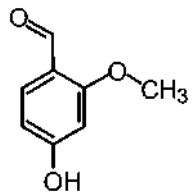


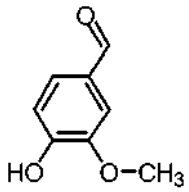




4.8 Formulas for the fragments lost corresponding to the peaks at 137 and 123 mass units in the mass spectrum: CH_3, HC=O.

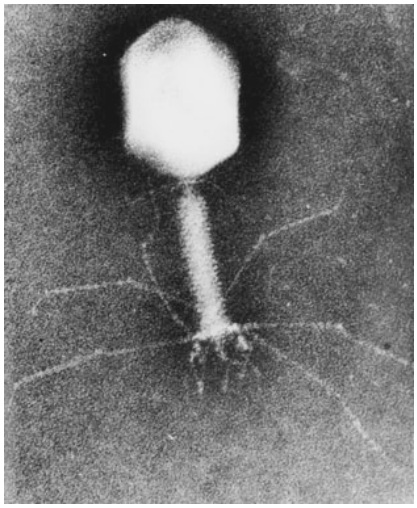
4.9 Two isomers having a lower pK_a value than the others:





PROBLEM 5

Protein and DNA



DNA is composed of 2'-deoxy-nucleotides carrying the bases adenine (A), guanine (G), cytosine (C) and thymine (T). The molar mass of the 2'-deoxy-nucleotide-5'-triphosphates is given in table 2:

Table 2

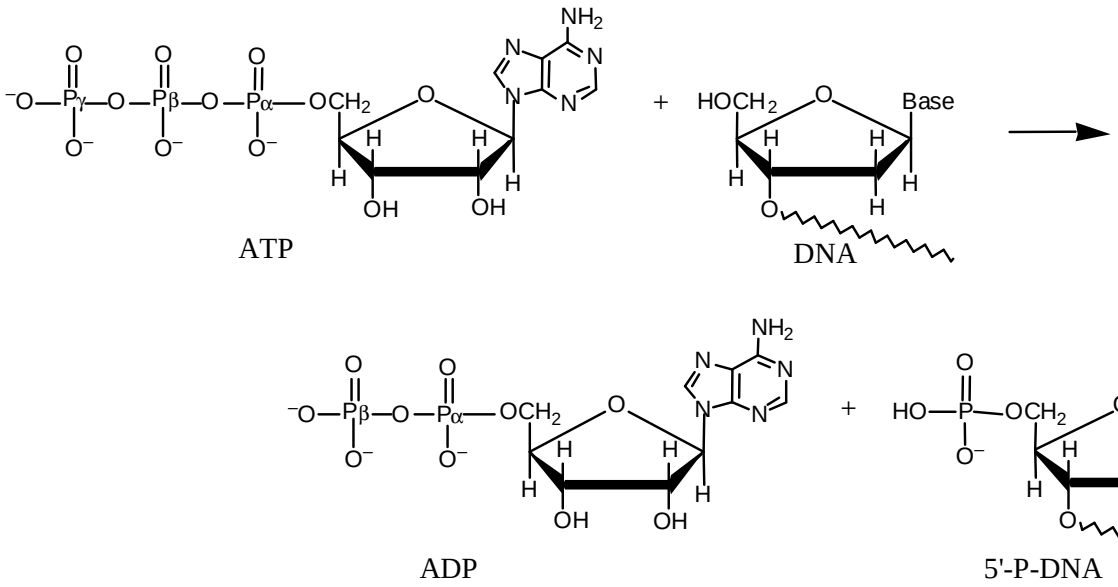
dNTP	Molar mass /g mol^{-1}
dATP	487
dGTP	503
dCTP	464
dTTP	478

5.1 Calculate the molar mass of a double stranded DNA fragment consisting of 1000 base pairs with a uniform distribution of the four bases.

This DNA fragment can be isolated and cloned by using the PCR method (polymerase chain reaction), in which a heat stable DNA polymerase enzyme multiplies the number of molecules of a specific piece of DNA in a cyclic process. Under optimal conditions the number of double-stranded DNA copies doubles in each cycle. Using the PCR method you perform 30 cycles starting from a single double stranded DNA molecule.

5.2 Calculate the approximate mass of the DNA you obtain from this experiment.

The bacteria-virus T4 enzyme - polynucleotide kinase (PNK) catalyzes the transfer of the terminal phosphate of ATP (γ-orthophosphate) to the 5'-hydroxyl termini of ribo- and deoxyribonucleotides:



PNK is commonly used to label DNA at the 5'-end with the radioactive phosphorus isotope ^{32}P using ATP in which the γ-P (the outermost of the phosphorus atoms) is replaced with ^{32}P. The amount of ^{32}P and thus the amount of labelled DNA can be measured.

A 10 μL solution containing double stranded DNA is labelled 100 % with [γ-^{32}P]ATP by PNK. 37 days ago, the specific activity of [γ-^{32}P]ATP was 10 Ci/mmol or 370 $\cdot 10^9$ Bq/mmol. ^{32}P has a half-life of 14.2 days, and during the decay a β-particle is emitted. Now the labelled DNA emits 40000 β-particles/s.

5-3 Calculate the concentration of the DNA solution.

In an experiment in which PNK is incubated with [γ-^{32}P]ATP and single stranded DNA, the reaction can be monitored by isolating labeled DNA and measuring the β-particle emission. Using this kind of measurements in a 1 cm^3 experimental mixture, a labeling of 9 nmol DNA/min was calculated. PNK has a catalytic rate constant (turnover number) of 0.05 s^{-1} and molar mass of 34620 g mol^{-1}.

5.4 Calculate the concentration (in mg/cm3) of PNK in the experimental mixture.

Aromatic amino acids, tryptophan, tyrosine and phenylalanine absorb UV light of a wavelength between 240 nm and 300 nm. In a protein containing several aromatic amino acids, the sum of the molar absorptivity per amino acid $\Sigma\varepsilon_{\text{amino acid}}$, is approximately equal to the molar absorptivity, $\varepsilon_{\text{protein}}$, for the protein. The molar absorptivity, $\varepsilon_{\text{amino acid}}$, at 280 nm for tyrosine, tryptophan and phenylalanine is 1400 M^{-1} cm^{-1}, 5600 M^{-1} cm^{-1} and 5 M^{-1} cm^{-1}, respectively. The absorbance of a 10 μM solution of PNK is 0.644 at 280 nm and with 1.00 cm light path. The amino acid sequence of PNK contains 14 tyrosines and 9 phenylalanines.

(M = mol dm^{-3})

5.5 Calculate the number of tryptophan residues in a PNK molecule.

_____

SOLUTION

5.1 Calculation of the molar mass of a double stranded DNA fragment under given conditions:

dNTP average mass = 483 g mol^{-1}; $M(\text{HP}_2\text{O}_7^{2-})$ = 175 g mol^{-1};

1000 bp double stranded DNA M(DNA) = ((483 – 175) × 2 × 1000 + 2 × 17) g mol^{-1} = 616034 g mol^{-1}.

5.2 Calculation of the approximate mass of the DNA you obtaining from the described experiment.

2^{30} copies = 1073741824 copies

Total mass of DNA: m(DNA) = 1073741824 / N_A × 616350 g mol^{-1} = 1.1 ng

5.3 Calculation of the concentration of the DNA solution.

$$A = A_0\, e^{-kt} \text{ and } k = \frac{\ln 2}{t_{1/2}} \Rightarrow A_0 = \frac{40000}{e^{-0.0488 \times 37}} \text{ dps} = 243464 \text{ dps}$$

It corresponds to $\frac{243464}{370}$ pmol 5'–^{32}P-DNA = 658 pmol 5'–^{32}P-DNA .

Since volume of the labelled DNA is 10 μL, the concentration of the DNA is thus approx. 66 μM.

5.4 Since 9 nmol DNA is labelled per min and the turnover number is 0.05 s^{-1} the amount of PNK that catalyses the labelling is:

$$\frac{9\ \text{nmol}\,\text{min}^{-1}}{0.05 \times 60\ s} = 3\ \text{nmol}$$

which corresponds to 3 nmol $\times$ 34620 g mol^{-1} = 0.1 mg.

The concentration of the PNK in mg cm^{-3} is is thus 0.1 mg cm^{-3}-

5-5 $\varepsilon_{\text{Tryptophan}}$ = 5600 M^{-1} cm^{-1};

$\varepsilon_{\text{Tyrosine}}$ = 1400 M^{-1} cm^{-1};

$\varepsilon_{\text{Phenylalanine}}$ = 5 M^{-1} cm^{-1}

$$\varepsilon = \frac{A}{c\,l} \Rightarrow \varepsilon_{\text{PNK}} = \frac{0.644}{10\ \mu\text{M} \times 1.00\ \text{cm}} = 64400\ \text{M}^{-1}\,\text{cm}^{-1}$$

$\Sigma(\varepsilon_{\text{Tyrosine}} + \varepsilon_{\text{Phenylalanine}})$ = (14 $\times$1400) + (9 $\times$ 5) M^{-1} cm^{-1} = 19645 M^{-1} cm^{-1}

$\Sigma\varepsilon_{\text{Tryptophan}} = \varepsilon_{\text{PNK}} - \Sigma(\varepsilon_{\text{Tyrosine}} + \varepsilon_{\text{Phenylalanine}}) \Rightarrow$

$\Sigma\varepsilon_{\text{Tryptophan}}$ = (64400 – 19645) M^{-1} cm^{-1} = 44755 M^{-1} cm^{-1}

The number of tryptophan residues in a PNK molecule is thus:

$$\frac{44755\ \text{M}^{-1}\,\text{cm}^{-1}}{5600\ \text{M}^{-1}\,\text{cm}^{-1}} = 8\ \text{residues}$$

PROBLEM 6

Hard Water

In Denmark the subsoil consists mainly of limestone. In contact with ground water containing carbon dioxide some of the calcium carbonate dissolves as calcium hydrogen carbonate. As a result, such ground water is hard, and when used as tap water the high content of calcium hydrogen carbonate causes problems due to precipitation of calcium carbonate in, for example, kitchen and bathroom environments.

Carbon dioxide, CO_2, is a diprotic acid in aqueous solution. The pK_a-values at 0 ℃ are:

$$CO_2(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq) \qquad pK_{a1} = 6.630$$

$$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq) \qquad pK_{a2} = 10.640$$

The liquid volume change associated with dissolution of CO_2 may be neglected for all of the following problems. The temperature is to be taken as being 0 ℃.

6.1 The total concentration of carbon dioxide in water which is saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar is 0.0752 mol dm^{-3}. Calculate the volume of carbon dioxide gas which can be dissolved in one litre of water under these conditions.

The gas constant $R = 8.314$ J mol^{-1} K^{-1} = 0.08314 L bar mol^{-1} K^{-1}

6.2 Calculate the equilibrium concentration of hydrogen ions and the equilibrium concentration of CO_2 in water saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar.

6.3 Calculate the equilibrium concentration of hydrogen ions in a 0.0100 M aqueous solution of sodium hydrogen carbonate saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar.

6.4 Calculate the equilibrium concentration of hydrogen ions in a 0.0100 M aqueous solution of sodium carbonate saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar. Ignore water dissociation effects.

6.5 The solubility of calcium carbonate in water at 0 °C is 0.0012 g per 100 cm3 of water. Calculate the concentration of calcium ions in a saturated solution of calcium carbonate in water.

The hard groundwater in Denmark is formed via contact of water with limestone in the subsoil which reacts with carbon dioxide dissolved in the groundwater according to the equilibrium equation:

$$CaCO_3(s) + CO_2(aq) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2\ HCO_3^-(aq)$$

The equilibrium constant, K, for this reaction is $10^{-4.25}$ at 0 °C.

6.6 Calculate the concentration of calcium ions in water in equilibrium with calcium carbonate in an atmosphere with a partial pressure of carbon dioxide of 1.00 bar.

6.7 A 0.0150 M solution of calcium hydroxide is saturated with carbon dioxide gas at a partial pressure of 1.00 bar. Calculate the concentration of calcium ions in the solution by considering the equilibrium equation given above in connection with problem 6.6.

6.8 The calcium hydroxide solution referred to in problem 6.7 is diluted to twice the volume with water before saturation with carbon dioxide gas at a partial pressure of 1.00 bar. Calculate the concentration of calcium ions in the resulting solution saturated with CO_2.

6.9 Calculate the solubility product constant for calcium carbonate from the data given above.

SOLUTION

6.1 $c(CO_2) = 0.0752$ M $n(CO_2) = 0.0752$ mol

The ideal gas equation: $p\,V = n\,R\,T$

$1.00\ \text{bar} \times V = 0.0752\ \text{mol} \times 0.08314\ \text{dm}^3\ \text{bar mol}^{-1}\ \text{K}^{-1} \times 273.15\ \text{K}$

$V = 1.71\ \text{dm}^3$

6.2 $CO_2(aq) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq)$

$[H^+] = [HCO_3^-] = x$ and $[CO_2] + [HCO_3^-] = 0.0752$

$$K_a = 10^{-6.63} = \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{x^2}{0.0752 - x}$$

$[H^+] = 0.000133$ and $[CO_2] = 0.0751$

6.3 $CO_2(aq) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq)$

$[CO_2] = 0.0751$ and $[HCO_3^-] = 0.0100$

$$K_a = 10^{-6.63} = \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{x \ 0.0100}{0.0751}$$

$\underline{x = [H^+] = 1.76\times10^{-6}}$

6.4 $CO_2(aq) + CO_3^{2-}(aq) + H_2O(l) \rightarrow 2\ HCO_3^-(aq)$ $[HCO_3^-] = 0.0200$

$CO_2(aq) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq)$

$$K_a = 10^{-6.63} = \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{x \ 0.0200}{0.0751}$$

$x = [H^+] = 8.8\times10^{-7}$

6.5 0.0012 g $CaCO_3$ in 100 cm^3 of water

0.0012 g /100 $\times$ 0872 g mol^{-1} = 0.000012 mol $CaCO_3$ in 100 cm^3 of water

$[Ca^{2+}] = 1.2\times10^{-4}$ $c(Ca^{2+}) = 1.2\times10^{-4}$ mol dm^{-3}

6.6 $K = \frac{[Ca^{2+}][HCO_3^-]}{[CO_2]} = 10^{-4.25}$ and $2\,[Ca^{2+}] = [HCO_3^-]$

$\frac{4\,[Ca^{2+}]}{0.0751} = 10^{-4.25}$ $[Ca^{2+}] = 1.02\times10^{-2}$ $c(Ca^{2+}) = 1.02\times10^{-2}$ mol dm^{-3}

6.7 $c(Ca(OH)_2) = 0.015$ mol dm^{-3}

$OH^-(aq) + CO_2(aq) \rightarrow HCO_3^-(aq)$

All hydroxide has been consumed ($K = 10^{7.37}$).

From problem 6.6 we found that the maximum possible calcium ion concentration is smaller, *i.e.* precipitation of $CaCO_3$

$[Ca^{2+}] = 1.02\times10^{-2}$ $c(Ca^{2+}) = 1.02\times10^{-2}$ mol dm^{-3}

6.8 $c(Ca(OH)_2) = 0.0075$ mol dm^{-3}

From problem 6.6 we found that the maximum possible calcium ion concentration we can have, is 1.02×10^{-2} mol dm^{-3}, *i.e.* no precipitation of $CaCO_3$ occurs.

$[Ca^{2+}] = 0.75\times10^{-2}$ $c(Ca^{2+}) = 0.75\times10^{-2}$ mol dm^{-3}

6.9

$$K = \frac{[Ca^{2+}][HCO_3^-]}{[CO_2]} = \frac{[Ca^{2+}][HCO_3^-]}{[CO_2]} \times \frac{[CO_3^{2-}][H^+]}{[CO_3^{2-}][H^+]} = \frac{K_{sp}\,K_{a1}}{K_{a2}}$$

$K_{sp} = 10^{-8.26}$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

This experiment includes one preparation of a metal complex salt and two analyses of a provided sample of the same compound. The compound is a "classic" within inorganic photo chemistry.

Preparation of Potassium tris(oxalato)manganate(III) Hydrate, $K_3[Mn(C_2O_4)_3]\cdot xH_2O$

Note 1: The $[Mn(C_2O_4)_3]^{3-}$ ion is photosensitive and should therefore be protected from light as far as possible. Also, the thermal stability of the title compound is low.

Note 2: Before starting the synthesis, write down the thermometer reading in ice-water.

The synthesis comprises a reduction of manganese(VII) to manganese(II) with oxalic acid at 70 – 75 °C. After the addition of the suffi cient amount of potassium ions in form of potassium carbonate, manganese(III) is formed by the addition of manganese(VII) at a temperature below 2 °C.

$$2\ MnO_4^-(aq) + 8\ C_2O_4H_2(aq) \rightarrow 2\ Mn^{2+}(aq) + 10\ CO_2(g) + 3\ C_2O_4^{2-}(aq) + 8\ H_2O(l)$$

$$C_2O_4H_2(aq) + CO_3^{2-}(aq) \rightarrow C_2O_4^{2-}(aq) + CO_2(g) + H_2O(l)$$

$$4\ Mn^{2+}(aq) + MnO_4^-(aq) + 11\ C_2O_4^{2-}(aq) + 4\ C_2O_4H_2(aq) \rightarrow$$

$$\rightarrow 5\ [Mn(C_2O_4)_3]^{3-}(aq) + 4\ H_2O(l)$$

Dissolve 5.00 g of $C_2O_4H_2 \cdot 2\ H_2O$ in 35 cm^3 of water in a 150 cm^3 beaker by heating to 70 °C. Slowly add 1.00 g of $KMnO_4$ with magnetic stirring. The temperature must not exceed 70 - 75 °C. When the mixture is colourless, add 1.10 g of K_2CO_3 in small portions and cool the mixture in ice. When the temperature of the mixture has fallen to 25 - 30 °C, add 25 g of crushed ice. Meanwhile, cool the hotplate with a beaker containing ice.

Maintain the temperature of the reaction mixture not more than 2 ℃ above your reported temperature of ice-water while adding 0.24 g of $KMnO_4$ in small portions with vigorous stirring. Stir for another 10 min and filter off the white precipitate and unmelted ice, if any, using the 60 cm^3 filter syringe (see procedure A). Collect the filtrate in a 250 cm^3 beaker cooled in ice. Add 35 cm^3 of ice-cold ethanol to the cherry-red filtrate (just swirl the beaker; stirring will lead to the formation of tiny crystals), wrap the beaker in aluminium foil and cool it in ice for 2 h (swirl the beaker three or four times during this period).

Clean the filter - first with 4 M HCl, then with water. Collect the cherry-red crystals by filtration using a 60 cm^3 filter syringe, then wash them two times 5 cm3 of ethanol and then two times with 5 cm^3 of acetone, and dry the product in air and protect it from light for at least one hour. A brown vial with lid should be taken to be tared by the lab assistant. When dry, the product is placed in the vial. Write name and student code on the vial. Then close the vial and take it and your answer sheet to the lab. assistant who will weigh your sample. The theoretical yield is 7.6 mmol.

1.1 Record the yield in grams.

1.2 Suggest a molecular formula of the white precipitate which is removed in the first filtration.

_____

Analysis of the Provided Sample of $K_3[Mn(C_2O_4)_3] \cdot x\,H_2O$ for Oxidizing Ability

Note 3: The burette contains a cleanser and should therefore be rinsed 3 - 4 times with water before use.

Manganese(III) is reduced to manganese(II) by iodide ions and the triiodide ions formed are then titrated with thiosulfate.

$$2\,Mn^{III}(aq) + 3\,I^-(aq) \rightarrow 2\,Mn^{II}(aq) + I_3^-(aq)$$

$$I_3^-(aq) + 2\,S_2O_3^{2-}(aq) \rightarrow 3\,I^-(aq) + S_4O_6^{2-}(aq)$$

In a 250 cm^3 conical flask dissolve 1.0 g of KI in 25 cm^3 of demineralized water and add 10 cm^3 of 4 **M** HCl. Immediately after an accurately preweighed sample (approx. 200 mg) of the provided complex is transferred (as much as possible is poured directly into the

liquid in small portions before the residue is washed down) quantitatively with demineralized water to the flask. Titrate the I_3^- formed with the standardized, approx. 0.025 **M** $Na_2S_2O_3$ solution. When the brown colour has faded to light yellow, add 2 cm^3 of starch indicator solution and continue the titration until the colour changes from blue to colourless.

1.3 Calculate the molar mass of the analyzed compound from the titration data.

_____

Analysis of the Provided Sample of $K_3[Mn(C_2O_4)_3] \cdot x\ H_2O$ for Reducing Ability

Note 4: The burette should be rinsed 2 - 3 times with water before this titration.

Manganese(III) is reduced to manganese(II) by the oxalate ligands, and excess oxalate is titrated with permanganate.

$$2\ [Mn(C_2O_4)_3]^{3-}(aq) + 10\ H^+(aq) \rightarrow 2\ Mn^{2+}(aq) + 2\ CO_2(g) + 5\ C_2O_4H_2(aq)$$

$$5\ C_2O_4H_2(aq) + 2\ MnO_4^-(aq) + 6\ H^+(aq) \rightarrow 10\ CO_2(g) + 2\ Mn^{2+}(aq) + 8\ H_2O(l)$$

Transfer an accurately preweighed sample (approx. 200 mg) of the provided complex quantitatively with demineralized water to a 250 cm^3 conical flask. Add 25 cm^3 of 2 **M** sulphuric acid and heat the solution to 75 – 80 °C. Without further heating, titrate with the standardized, approx. 0.025 **M** $KMnO_4$ solution. Near the end of the titration add the titrant slowly, until one drop gives the solution a rose colour which does not fade on standing for 0.5 min.

1.4 Calculate the molar mass of the analyzed compound from the titration data.

The results of the two types of analysis may differ by up to 10 %. Use only the result from the titration with $KMnO_4$ for the following calculation.

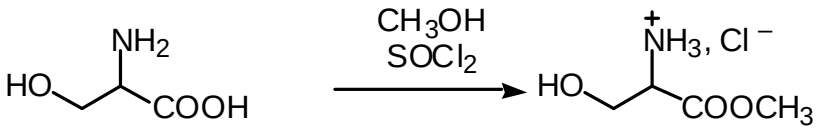
1.5 Calculate the value of x in the formula $K_3[Mn(C_2O_4)_3] \cdot x\ H_2O$ and the yield of your preparation in percent of the theoretical yield.

PROBLEM 2 (Practical)

Synthesis of Amino Acid Methyl Ester Hydrochloride

In the synthesis of peptides, one amino acid is reacted with another to form an amide bond between them. In order to ensure that the individual amino acids do not form amide bonds with themselves and that only one product is formed, the amino group in the first amino acid and the carboxyl group in the second amino acid are masked before the peptide synthesis.

The procedure described below can be used for masking the carboxylic acid groups in amino acids before peptide formation.



The experiment should be performed in a ventilated hood since thionyl chloride is an irritant and since irritating gases are evolved during the reaction.

Thionyl chloride is a corrosive acid chloride. Avoid contact with skin and eyes. Splashes in eyes or on skin should be flushed immediately with water. Thionyl chloride in larger amounts reacts violently with water.

Procedure

Absolute methanol (2.0 cm^3) is transferred quickly to a dry test tube which is then closed with a piece of aluminium foil. The foil is used as a lid throughout the subsequent manipulations with the tube. This protects the content from moisture from the air. The methanol is cooled in an ice-bath for 1 – 2 min. Thionyl chloride, handle with care, see above (0.52 cm^3) is drawn up into a 1 cm^3 graduated syringe with polyethylene tube tip, as described in separate procedure B, and is cautiously added to the methanol over a period of approximately 5 min.

The mixture is kept at 0 ℃ for approx. 2 min. (*S*)-Serine (0.210 g, weighed sample provided) is added and the mixture is kept at room temperature for approx. 2 min before gently heating to boiling (using a sand bath) for 10 min. All material should then have dissolved.

The mixture is cooled in an ice-bath for approx. 2 min. Dry *tert*.-butyl methyl ether (10 cm^3) is then added. The inside wall of the test tube is scratched at the surface region of the solution with a glass spatula for about 1 min. and the test tube is then left in the ice-bath for a further 5 –15 min for crystallization. The separated crystals are then isolated by filtration as described in separate procedure A. The filtrate is collected in a 100 cm^3 beaker.

The crystals are washed two times on the filter, each time with 1 cm^3 of *tert*.-butyl methyl ether. The filter cake is finally pressed with the piston, and the crystals are pre-dried by pumping air through the filter cake with the piston.

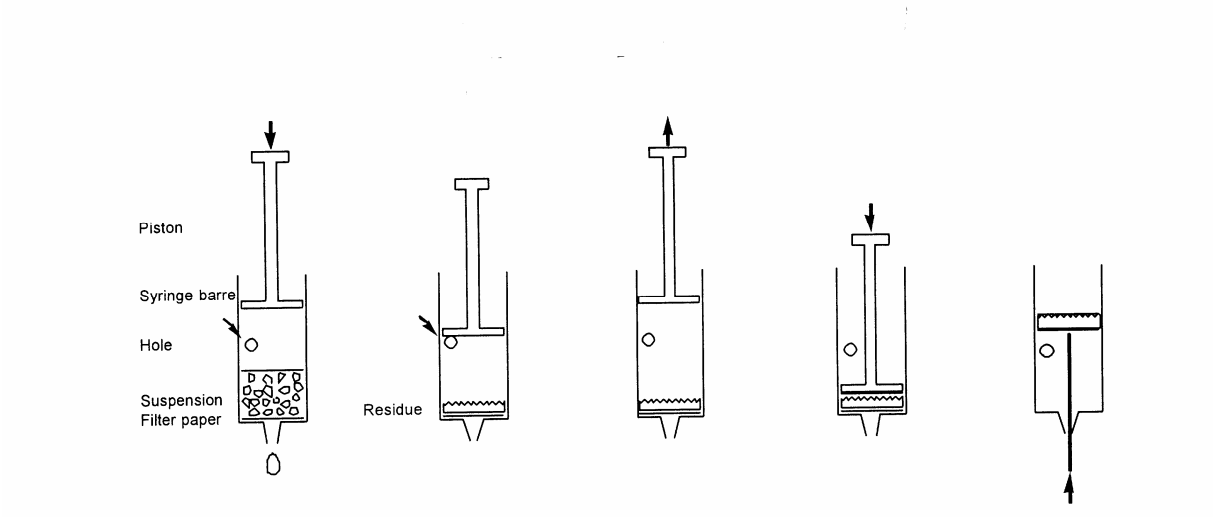
The solid is then collected on a piece of filter paper in order to absorb residual solvent. When dry, the residue is placed in a tarred plastic sample tube with lid (Eppendorf tube) found in the box. The sample tube is then closed and weighed.

PROCEDURE A

Filtration procedures

Modified syringes are used for filtration in the laboratory tasks. A 60 cm^3 syringe with a disc of porous polypropylene is used in task 1, while a 10 cm^3 syringe with a disc of filtration paper is used in task 2. The procedure is sketched on Fig. 1.

Fig. 1: Micro-scale filtration in plastic syringe



Procedure:

1. Fill the syringe from above with suspension to be filtered. The syringe can be filled to the level of the hole. Replace piston.
2. Close hole and press piston for filtration.
3. Stop before passing the hole.
4. Open hole and draw piston back.
5. Repeat steps 2-4 a couple of times.
6. Remove piston and place filter paper on top of the filter cake.
7. Press piston against filter cake.
8. Push filter cake out with straightened- out paper clip.

Filtration procedure for practical problem 1

The provided filter syringe to be used in this experiment is made from a 60 cm^3 standard medical polypropylene syringe from which the piston has been temporarily removed and a 3 mm hole drilled at the 35 cm^3 mark. With a plastic spatula a disc of porous polypropylene, which fits tightly inside the syringe, is pressed down to be positioned at the base of the syringe. The mixture to be filtered is applied without the piston inserted. Drops of solution may be moved downwards by tapping the syringe against a solid surface,

The piston is now placed in the syringe and gently pressed down while keeping the hole closed with a finger so to promote the passage of solvent through the filter. When the piston reaches just above the hole, the finger is removed from the hole, and the piston is drawn back again to the top position. This cycle can then be repeated a couple of times, until the filter cake looks dry. Remember to close the drilled hole, then the piston is moved downwards and to open the hole, when the piston is moved upwards. The filter cake can be washed and the washing solution pressed out using similar cycles.

Solvent remaining in the outlet can be sucked up with a small piece of tissue paper. The solid is then removed from the syringe and collected on a piece of weighing paper for drying.

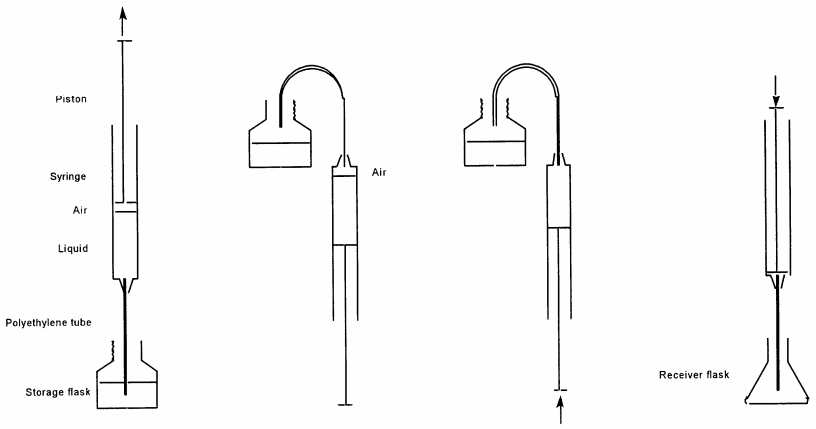
Filtration procedure for practical problem 2

The provided filter syringe to be used in this experiment is made from a 10 cm^3 standard medical polypropylene syringe from which the piston has been temporarily removed and a 3 mm hole drilled at the 5.5 cm^3 mark. A piece of filter paper which fits snugly in the syringe is pressed down to the bottom with the piston. Filtration and washing are then performed as described for task 1. Before removing the filter cake the piston is withdrawn. A piece of filter paper fitting the syringe is then pressed all the way down to the filter cake using the piston. The filter cake is pressed by means of the piston. Then the piston is then drawn back and out the syringe (slowly, until the hole is reached).
This leaves the filter cake between two pieces of filter paper. Solvent remaining in the outlet can be sucked up with a small piece of tissue paper.

The filter cake is cautiously pushed out of the syringe using an straightened-out metal paper clip introduced through the outlet of the syringe. The solid material is then removed from the syringe, if possible as a coherent plug. The residue is collected on a piece of filter paper for drying by using a small metal spatula. Filter paper from the filtration can be fixed with the paper clip tip while adhering solid is removed using the spatula.

PROCEDURE B

Fig. 2. Measuring volumes of liquids using a syringe



Procedure:

1. Suck up a slight excess of liquid in syringe.

2. Turn syringe upside down; the tip of the tube is kept in the storage nottle. Air in the syringe is accumulated at its top.
3. Air in the syringe is removed by pressing the piston. Press further until desired volume of liquid is left in the syringe. The tip of the tube is kept in the storage bottle.
4. Turn the syringe, place tip of the tube in the receiver flask and press piston until desired volume of liquid has left the syringe.

33rd

International Chemistry Olympiad

7 theoretical problems
3 practical problems

THE THIRTY-THIRD
INTERNATIONAL CHEMISTRY OLYMPIAD
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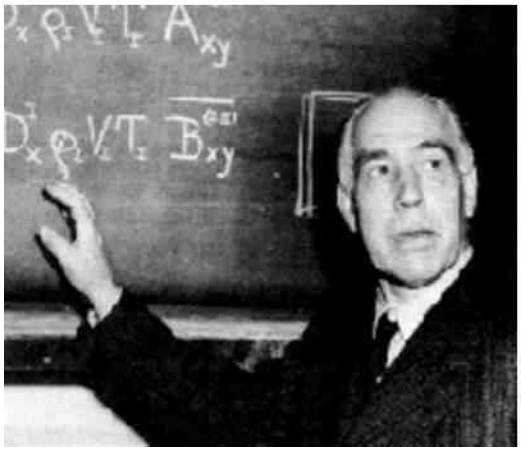
THEORETICAL PROBLEMS

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

$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right); \quad n = 3, 4, 5, ...$$

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

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, $a_0 = \frac{\varepsilon_0 h^2}{m_e e^2 \pi}$) 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)

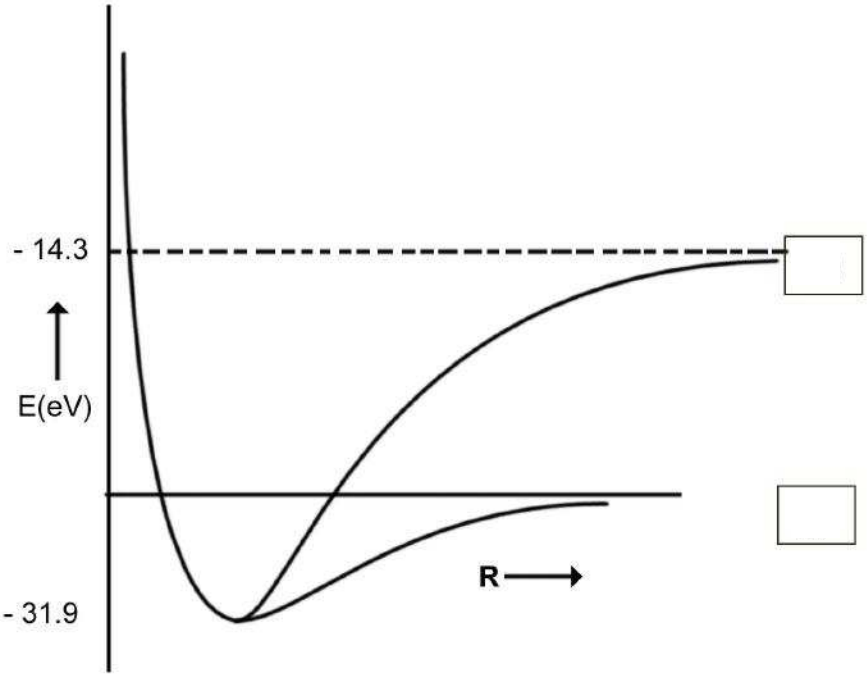
The graph of energy (E) vs internuclear distance (R) for H_2 is shown schematically in the figure. The atomic and molecular energies are given in the same scale.

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

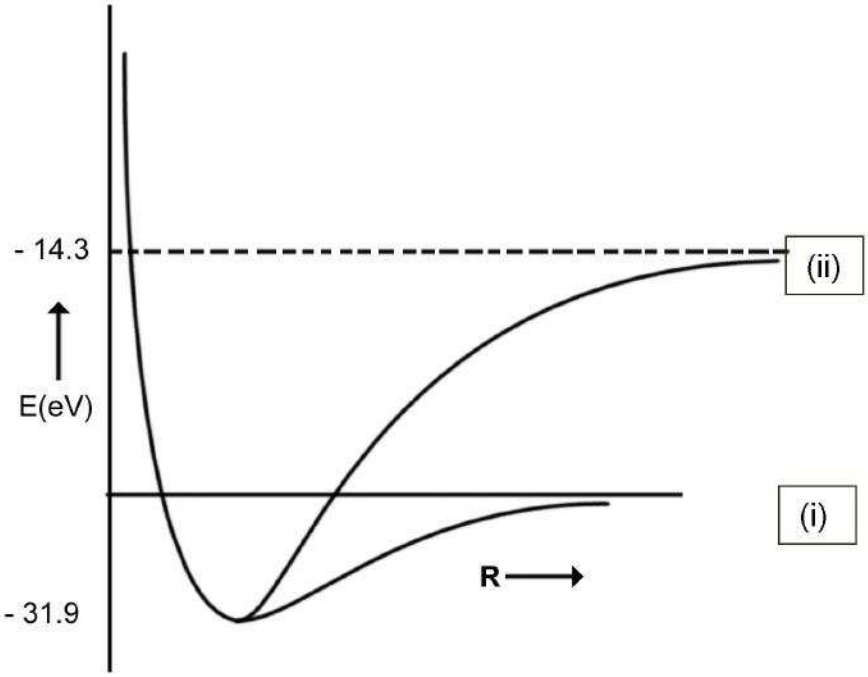
$E = -hcR_H = -13.6$ eV

1.3 Lowest energy = $-207 \times 13.6 = -2.82$ keV

Radius of the first Bohr orbit = $0.53 / 207 = 2.6\times10^{-3}$ Å

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

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 ℃ 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-}) :

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

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

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

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

$pK_{2b} = 6.79$

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

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

$0.0051\text{-}x \qquad\qquad x \quad + \quad x$

$pK_{1a} = 2.12$ 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 $\quad f_0 = \dfrac{[H_3X]}{C}, \quad f_1 = \dfrac{[H_2X^-]}{C},$

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

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

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

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

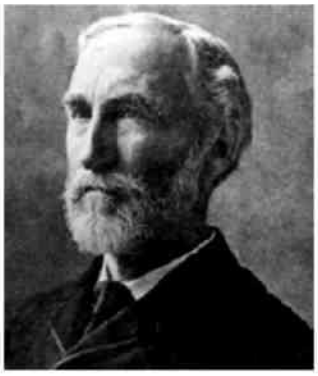
$[Zn^{2+}] = 9\times10^{-5}$

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

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 ℃) 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.

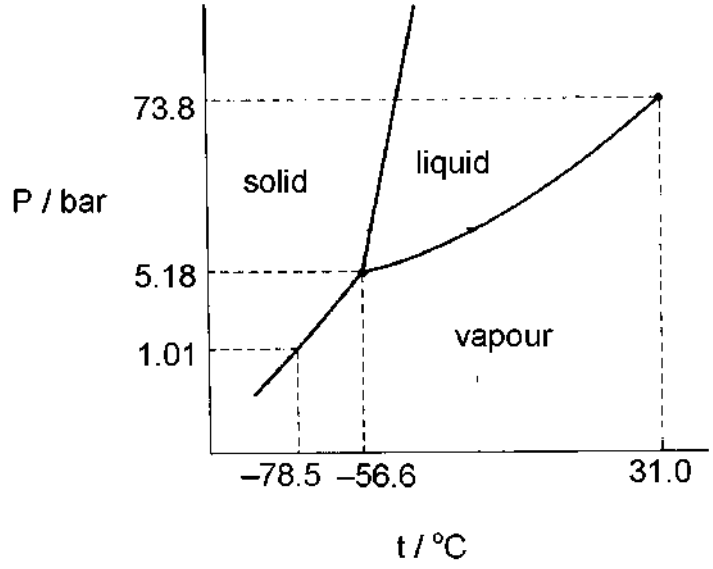
3.3 Calculate ΔS_{sur}.

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 ℃ 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): $\Delta H_f^0 = -393.51$ kJ mol^{-1}; $S^0 = 213.79$ J K^{-1} mol^{-1}

CO(g): $\Delta H_f^0 = -110.53$ 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 ℃ 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.

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

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

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

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

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

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

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

$\Delta G^0 > 0$ implies $K < 1$

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

$T = 980 \text{ K}$

3.10

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

$1 - \alpha$ $\qquad$ 2α

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

$$K_p = \frac{p^2(CO)}{p(CO_2)}$$

$p(CO) = 3.7$ 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 $N = N_0\, e^{-\frac{0.6931\, t}{t_{1/2}}}$

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

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

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

$$e^{\frac{0.6931\, t}{1.41\times 10^{10}}} = 1.104$$

t = 2.01×10^9 years.

4.2 Let x be the required ratio.

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

where t = 2.01×10^9 years, and $t_{1/2}$ = 4.47×10^9 years.

x = 0.366

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

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

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

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

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

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

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.

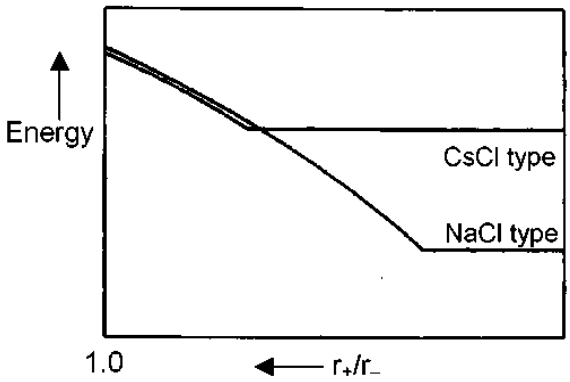
5.8 Chlorine dioxide reacts with sodium hydroxide as shown below. Identify the products X and Y (both containing chlorine) and balance the equation.

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

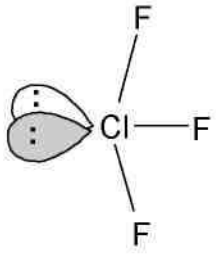
5.2 $AgBr(s) + 2\ Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

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

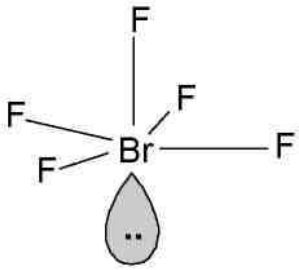
$2\ [Ag(CN)_2]^- + Zn \rightarrow [Zn\ (CN)_4]^{2-} + 2\ Ag \downarrow$

5.4

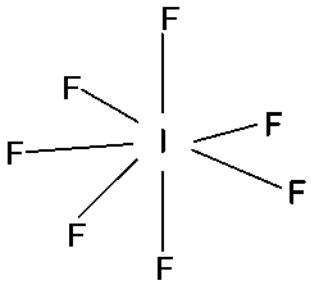
ClF_3



BrF_5



IF_7

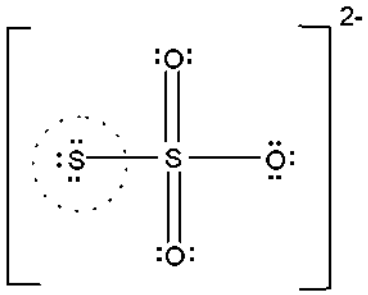


5.5.

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 $2\ ClO_2 + 2\ NaOH \rightarrow NaClO_2 + NaClO_3 + H_2O$

X Y

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

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.

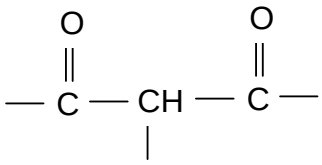
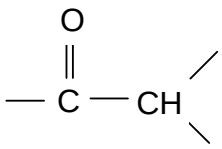
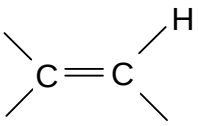
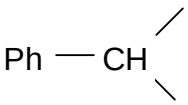
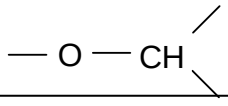
Table 1: ^{1}H NMR spectral data on Zingerone

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

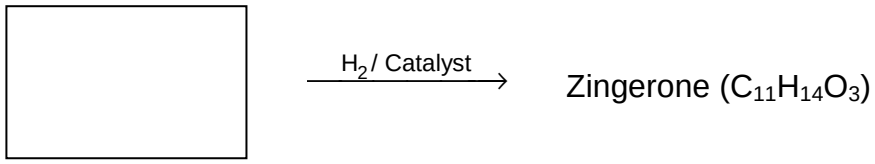
ii) substituent on the aromatic ring

iii) relative positions of the substituents on the ring

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

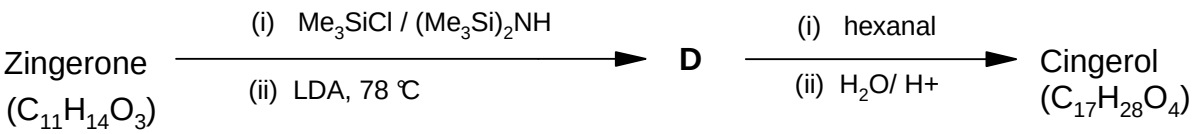
6.4 Complete the following reaction sequence for the synthesis of Zingerone.

A + **B** (C_3H_6O)



C

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



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

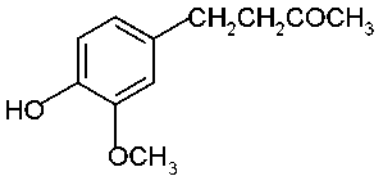
(d) phenolic hydroxyl

6.2 i) side chain in Zingerone: $CH_2CH_2COCH_3$

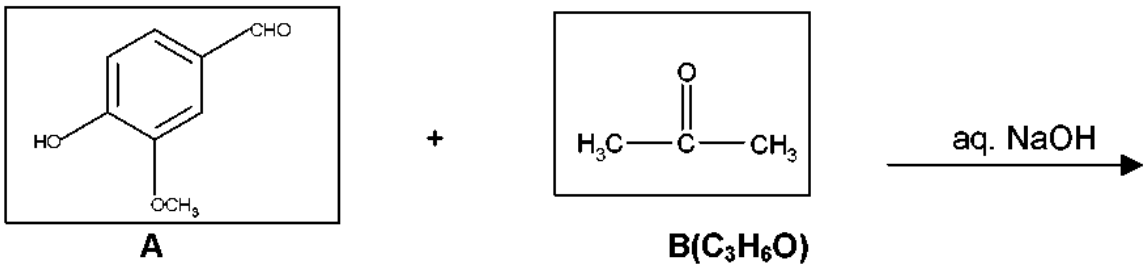
ii) substituents on the aromatic ring: OH, OCH_3

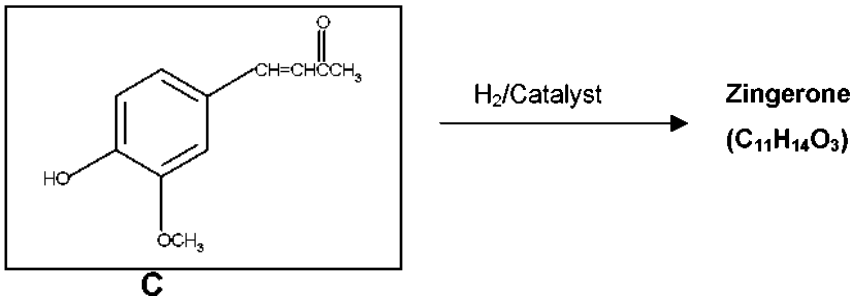
iii) relative positions of the substituents on the ring: 1, 2, 4

6.3

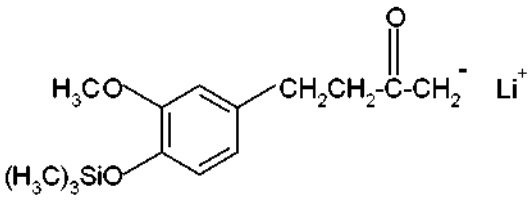


6.4

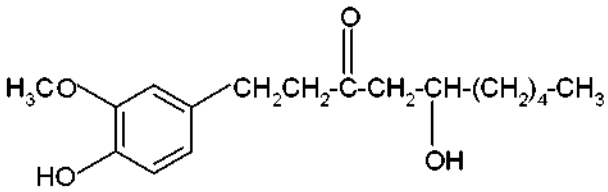




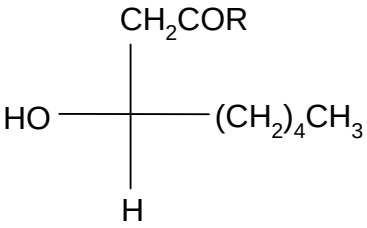
6.5 i)



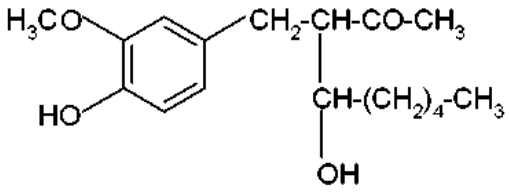
ii)



iii)

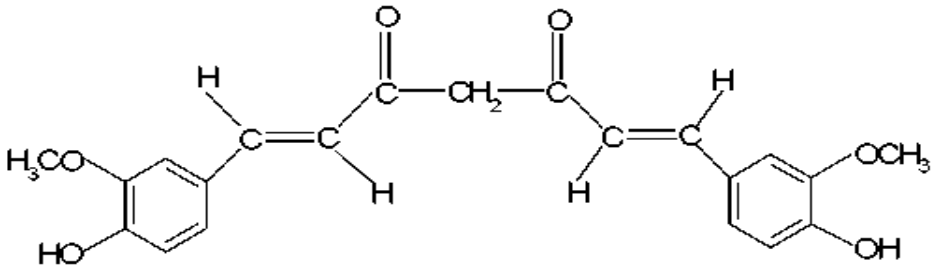


iv)

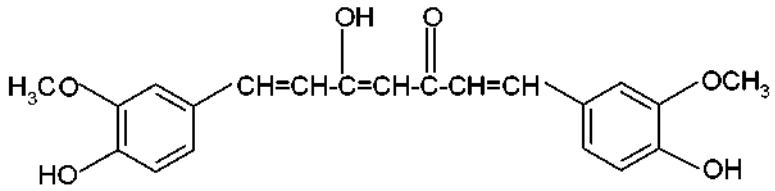


v) Compound **E** will be formed as: (b) a mixture of diastereomers

6.6 i)



ii)

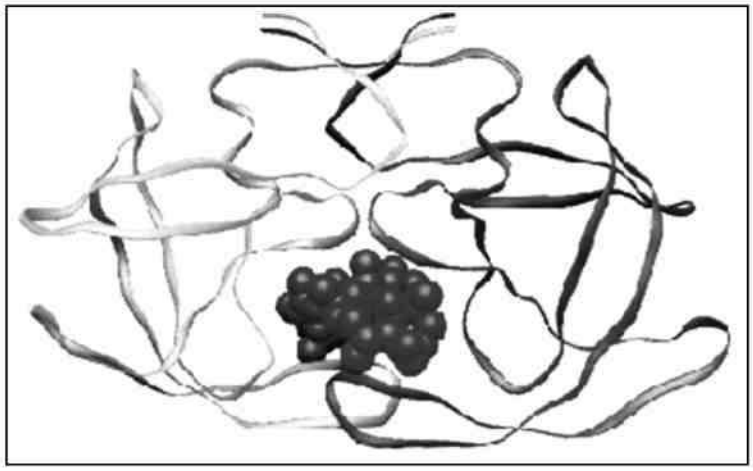


iii) Curcumin is yellow in coulour because it has:

(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.

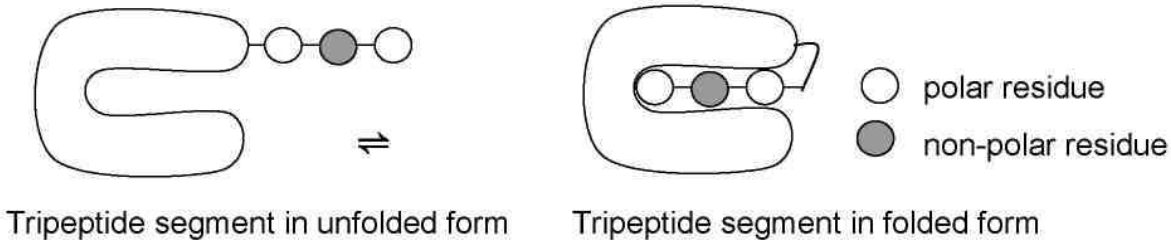
Consider the following process of folding/unfolding of a tripeptide segment in a large protein. The free energy change (AG) will depend on the interaction of the unfolded tripeptide with the solvent (water) and with the rest of the protein in the folded state (see below). Assume that the tripeptide is 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}

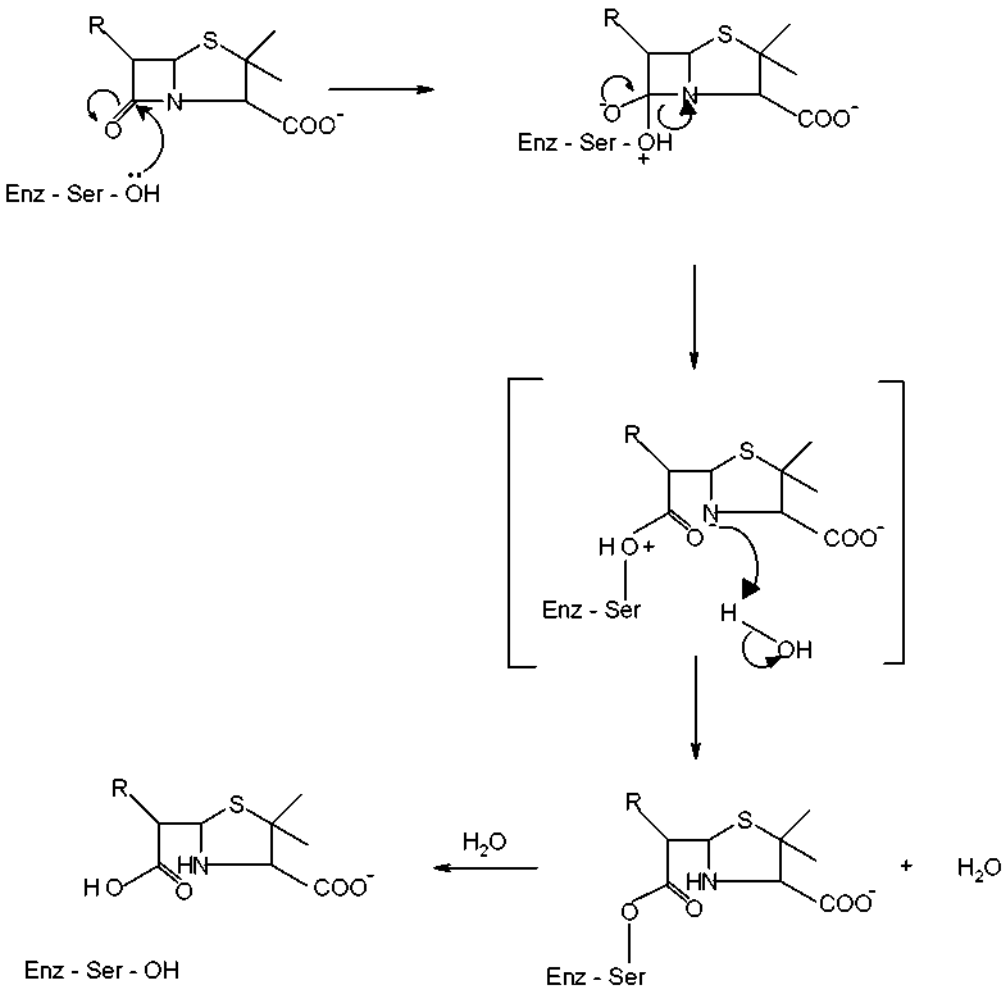


7.4 Calculate ΔG for the foldinq of the tripeptide segment.

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

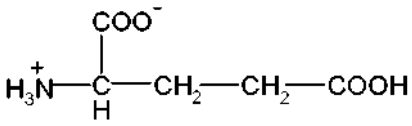
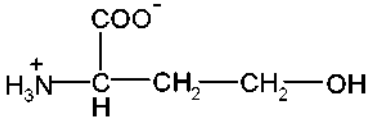
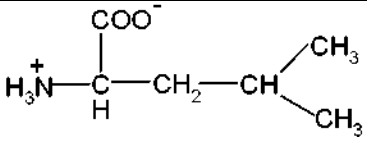
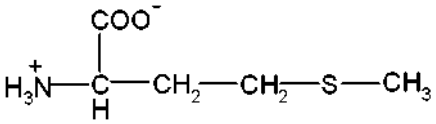
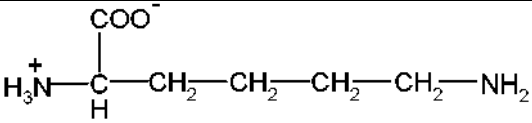
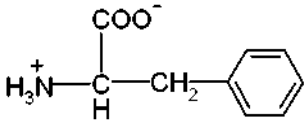
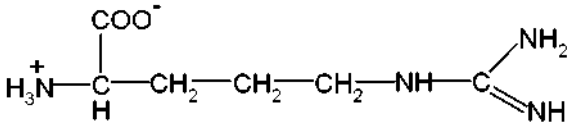
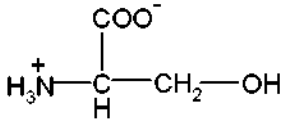
Amino Acid	Structure	Molecular mass (Da)
Glu – Glutamic acid		147
Hms – Homoserine		119
Leu – Leucine		131
Met – Methionine		149
Lys – Lysine		146
Phe – Phenylalanine		165

Table (continued)

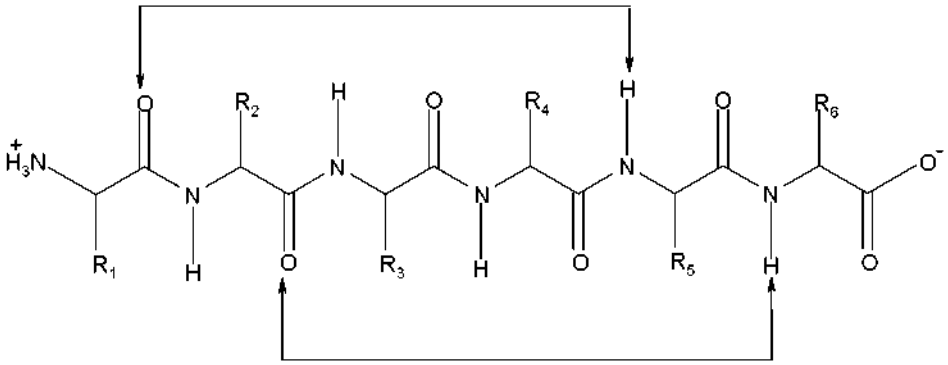
Arg – Arginine		174
Ser – Serine		105

SOLUTION

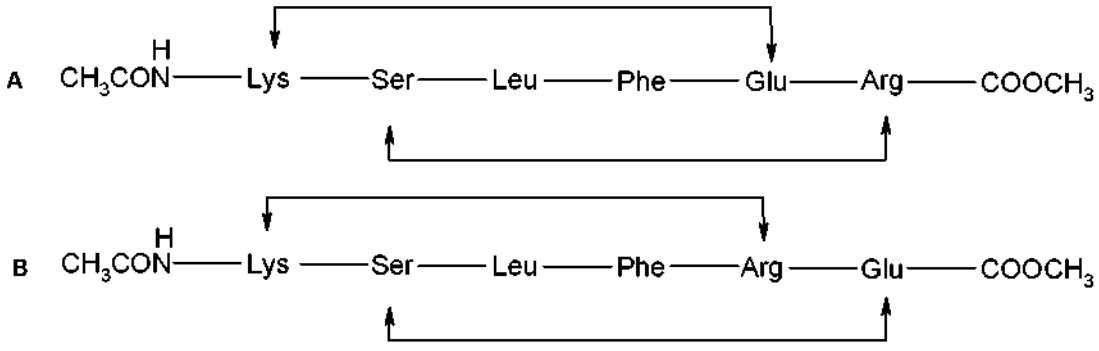
7.1 The end-to-end distance in a hexapeptide when it is in a fully extended conformation is approximately :

(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 $\frac{105 \times 100}{0.35} = 30000$ 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

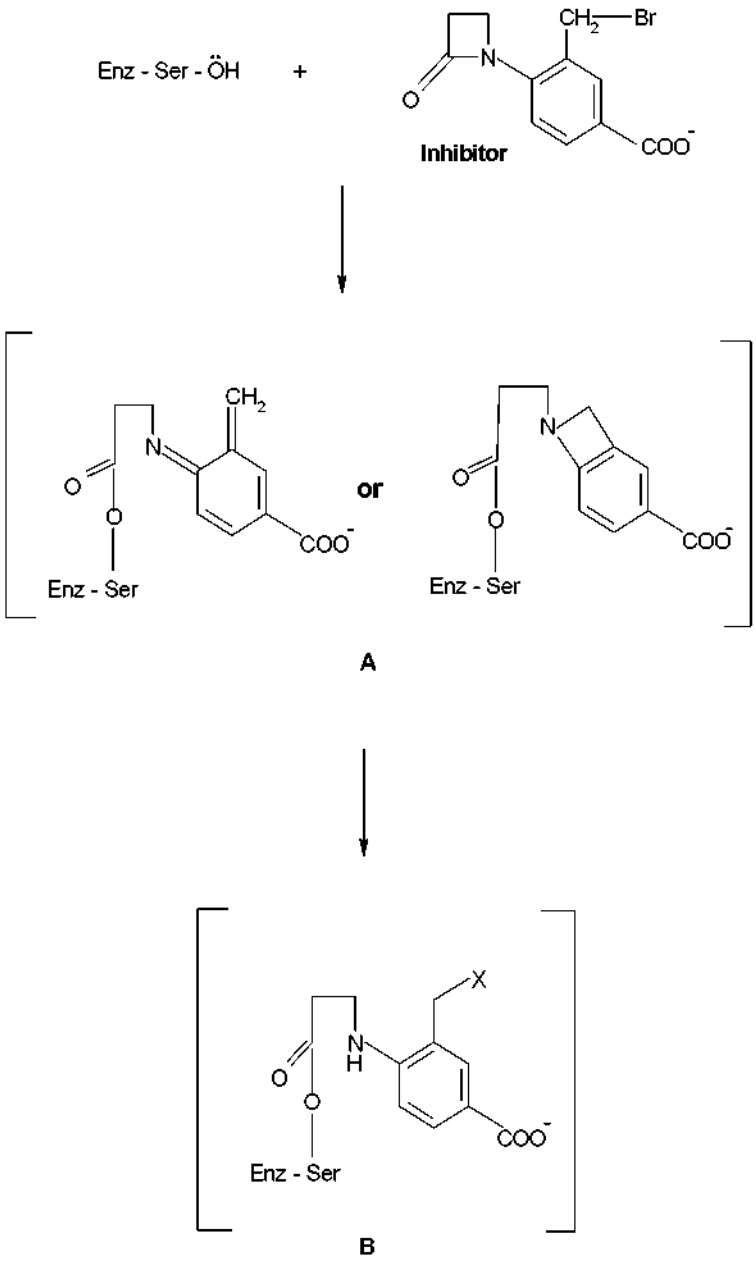
7.9 Phe - Glu - Ser - Hms

(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
COO-
Enz - Ser
or
N
O
O
COO-
Enz - Ser
A
X
N
H
O
O
COO-
Enz - Ser
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:

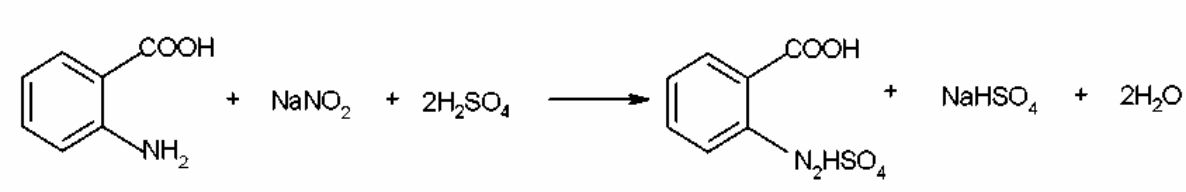
(a) diazotization of 2-aminobenzoic acid using $NaNO_2$ and H_2SO_4.

(b) the reaction of K**I** with the diazotized product.

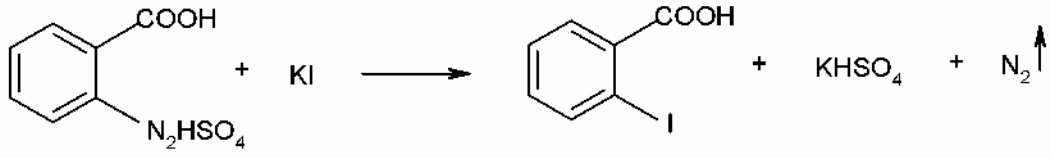
_____

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(ll) and Mn(ll) 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

$$\text{rate} = k[HCrO_4^-]^x$$

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.

34th

International Chemistry Olympiad

10 theoretical problems
3 practical problems

THE THIRTY-FOURTH
INTERNATIONAL CHEMISTRY OLYMPIAD
5–14 JULY 2002, GRONINGEN, THE NETHERLANDS

THEORETICAL PROBLEMS

Theme 1 - Chemistry of Life

Life runs on chemistry. Understanding and monitoring life processes receive much attention in chemistry.

PROBLEM 1

OXYGEN IN YOUR LIFE

Oxygen is of vital importance for all of us. Oxygen enters the body via the lungs and is transported to the tissues in our body by blood. There it can deliver energy by the oxidation of sugars:

$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$

This reaction releases 400 kJ of energy per mol of oxygen. O_2 uptake by blood is at four heme (Hm) groups in the protein hemoglobin (Hb).

Free Hm consists of an Fe^{2+} ion attached to four N atoms of a porphyrin^{2-} ligand. Oxygen can bind at the coordination site of Fe^{2+} giving a Hm·O_2 complex. Carbon monoxide can be complexed similarly, giving a Hm·CO complex. CO is a poison as it binds more strongly to Hm than O_2 does. The equilibrium constant K_1 for the reaction:

$$Hm + CO \rightleftharpoons Hm{\cdot}CO \qquad (1)$$

is 10 000 times larger than the equilibrium constant K_2 for the reaction:

$$Hm + O_2 \rightleftharpoons Hm{\cdot}O_2 \qquad (2)$$

Each Hb molecule can take up four molecules of O_2. Blood in contact with O_2 absorbs a fraction of this amount, depending on the oxygen pressure, as shown in Figure 1 (curve 1). Also shown are the curves (2) and (3) for blood with two kinds of deficient Hb. These occur in patients with certain hereditary diseases.

Relevant data: O_2 pressure in lungs is 15 kPa; in the muscles it is 2 kPa. The maximum

flow of blood through heart and lungs is 4×10^{-4} m^3 s^{-1}. The red cells in blood occupy 40 % of the blood volume; inside the cells the concentration of Hb is 340 kg m^{-3}; Hb has a molar mass of 64 kg mol^{-1}. R = 8.314 J mol^{-1} K^{-1}. T = 298 K.

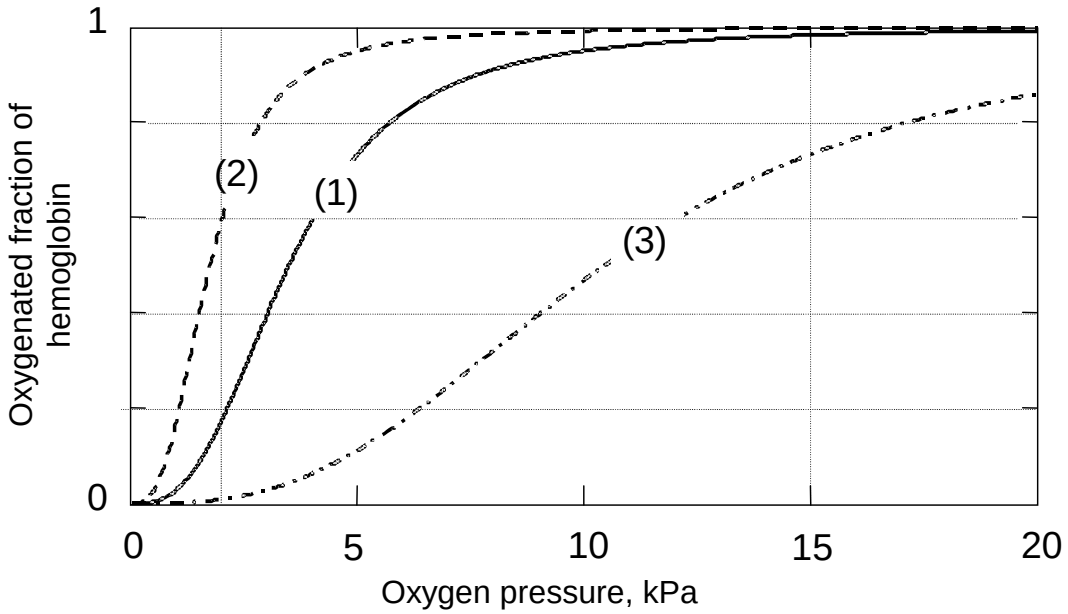


Figure 1

1.1 Using the relation between K and the standard Gibbs energy ΔG^0 for a reaction, calculate the difference between the ΔG^0 values for the heme reactions (1) and (2).

1.2 Estimate from Figure 1 (to 2 significant figures) how many moles of O_2 are deposited in muscle tissue when one mole of Hb travels from the lungs to the muscles and back again for the three different types of Hb.

1.3 The special S-shaped uptake curve 1 is the result of subtle structural features of Hb. The deficient Hb shown in curve 2 is not optimal because:

- ❑ The binding with O_2 is too weak.
- ❑ The binding with O_2 is too strong.
- ❑ The maximum oxygen capacity is too low.
- ❑ The deficiency is caused by carbon monoxide poisoning.

1.4 Calculate how much oxygen (in mol s^{-1}) can be deposited in tissue by blood with normal Hb (1).

1.5 Calculate the maximum power that the body can produce (assuming it is limited by oxygen transfer).

SOLUTION

1.1 $\Delta G_1^0 = -RT \ln K_1 \qquad \Delta G_2^0 = -RT \ln K_2$

$$\Delta G_2^0 - \Delta G_1^0 = RT \ln \frac{K_1}{K_2}$$

$\Delta G_2^0 - \Delta G_1^0 = (8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \ln 10\,000) \text{ J} = 23 \text{ kJ mol}^{-1}$

1.2 Hb-Typ 1: $(0.98 - 0.17) \text{ mol} \times 4 = 3.2 \text{ mol}$

Hb-Typ 2: $(1.00 - 0.60) \text{ mol} \times 4 = 1.6 \text{ mol}$

Hb-Typ 3: $(0.73 - 0.01) \text{ mol} \times 4 = 2.9 \text{ mol}$

1.3 Correct answer: The binding with O_2 is too strong.

1.4 $(4\times10^{-4} \text{ m}^3 \text{ s}^{-1}) \times 0.4 \times (340 \text{ kg m}^{-3}) \times (3.2 \text{ mol } O_2 \text{ / mol Hb}) / (64 \text{ kg mol}^{-1}) =$

$= 2.72\times10^{-3} \text{ mol s}^{-1}$

1.5 $(2.72\times10^{-3} \text{ mol s}^{-1}) \times (400 \text{ kJ mol}^{-1}) = 1088 \text{ W}$

PROBLEM 2

Nitrogen Cycle in Nature

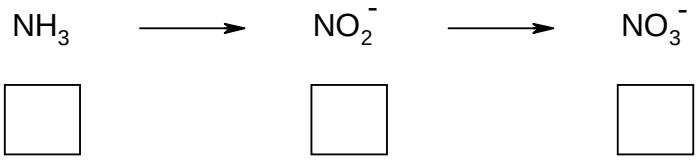
Ammonia is a toxic substance to marine animals at levels exceeding 1 ppm. Nitrifying bacteria play an important role in the conversion of NH_3 first to nitrite and then to nitrate, the storage form of nitrogen in the soil.

$$NH_3 + 2\,O_2 + NADH \xrightarrow[\text{bacteria}]{\text{Nitrosomonas}} NO_2^- + 2\,H_2O + NAD^+$$

NADH is the biochemical reducing agent of the coenzyme nicotinamide dinucleotide (NAD), NAD^+ is the oxidized form of the coenzyme NAD.

$$2\,NO_2^- + O_2 \xrightarrow[\text{bacteria}]{\text{Nitrobacter}} 2\,NO_3^-$$

2.1 Give the oxidation states of N in the following series: (Use the boxes below the compounds)



The spectrophotometric analysis of nitrite is based on a reaction with an indicator. The coloured product then obtained has an absorbance maximum at λ = 543 nm. For quantitative analyses a calibration curve has to be made, in which absorbance at the maximum absorbance wavelength λ = 543 nm is plotted against nitrite concentration in a series of standards.

2.2 The measurements are performed at the wavelength with the maximum absorbance because:

- ❑ There is no interference of impurities.
- ❑ There is no contribution of stray light.
- ❑ There is optimal accuracy of the measurement.
- ❑ None of these statements.

Mark the correct answer.

The absorption is measured with a single beam spectrophotometer. However 5 % of the light, the so-called stray light I_s, strikes the detector directly (see Figure 2).

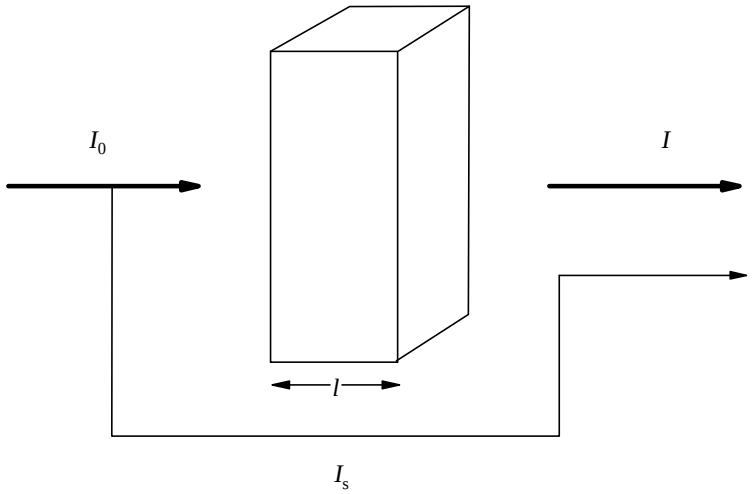


Figure 2

2.3 Calculate the value of the absorbance A shown by the spectrophotometer if ε = 6 000 M^{-1} cm^{-1}, l = 1 cm and $c = 1 \times 10^{-4}$ M

For a nitrite determination in water the following data have been measured.

Table 1

concentration of nitrite nitrogen (ppm)	absorbance at 543 nm (1.000 cm cell)
blank	0.003 (due to impurities in the solvent)
0.915	0.167
1.830	0.328

2.4 Determine (show calculation) from the data given above, using the values corrected for the solvent impurities, the slope m and the intercept b of the calibration curve $A = m\,c$ + b.

The duplicate analyses of a water sample are given below. The measurements have been performed at a wavelength of 543 nm and in a 2.000 cm cell.

Table 2

water sample	absorbance
analysis 1	0.562
analysis 2	0.554

For the calculation of the concentration of the nitrite nitrogen (c in ppm) the equation obtained by the method of least squares

corrected absorbance = 0.1769 c + 0.0015 (a)

may be applied, using the measurements in a 1.000 cm cell.

2.5 Calculate the average nitrite nitrogen concentration in ppm and μg cm^{-3}.

Hint: Take the blank from problem 2.4.

_____

SOLUTION

2.1 NH_3: –III (–3) NO_2^-: III (3) NO_3^-: V (5)

2.2 Correct answer: There is optimal accuracy of the measurement.

2.3 $I_S = 0.05 \times I_0$ $A = \log \frac{I_0}{I + I_S}$ (see Figure 2)

The absorption of the solution A_{sol} is given by the relation:

$$A_{sol} = \log\ 0.95 \times \frac{I_0}{I} = \varepsilon\, c\, d$$

$$I = 0.95 \times I_0 \times 10^{-6000 \cdot 0.0001 \cdot 1} = 0.95\ I_0 \times 10^{-0.6}$$

$$A = \log \frac{I_0}{0.95 \times I_0 \times 10^{-0.6} + 0.05 \times I_0} = 0.54$$

2.4 The absorbance of the blank solution (see Table): A = 0.003.

Slope m of the calibration curve:

$$m = \frac{\Delta A}{\Delta c} = \frac{A_2 - A_1}{c_2 - c_1} = \frac{0.325 - 0.164}{1.830 - 0.915} = \frac{0.161}{0.915\ \mathrm{M}} = 0.176\ \mathrm{M}^{-1}$$

Note: Corrected absorbance values were used in the calculation.

A = 0.176 c + b

For c = 0, A = 0.003.

Thus: b = 0.003

2.5 The average absorption in a 2 cm cell is 0.558; thus, in a 1 cm cell is 0.279. Regarding the blank value (0.003) the corrected absorption has the value 0.276. Substituting this value into the equation (a) gives:

$$c = \frac{0.276 - 0.0015}{0.1769} \text{ ppm}$$

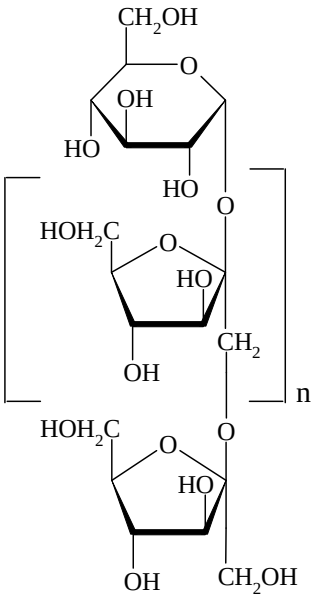
c = 1.55 ppm = 1.55 μg cm^{-3}

Theme II - Chemistry of Industrial Relevance

In our daily life we use many products that are produced on an industrial scale. Mastering the underlying chemistry is at the heart of this business.

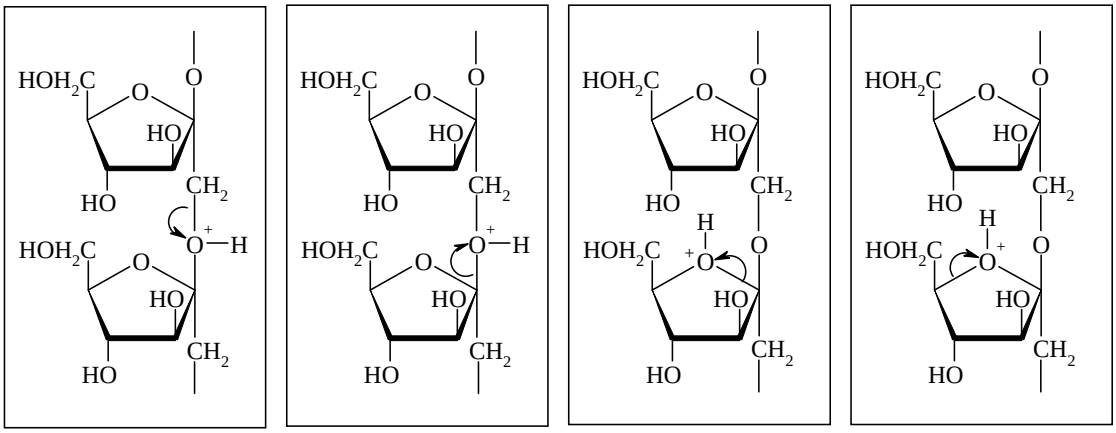
PROBLEM 3

Inulin, a New Renewable Raw Material



Inulin, which is produced from chicory roots in Belgium and The Netherlands, is used as a food additive as it has a beneficial effect on the intestinal flora. It is also used as source of fructose which is 1.9 times sweeter than sucrose, and for the production of mannitol which is used in chewing gum. Inulin is a linear polymer of fructose units with a glucose unit at one end; its Haworth projection formula is shown at the left. In this problem inulin has 10 fructose units (n = 9).

3.1 Inulin may be hydrolyzed under H^+-catalysis conditions. Of the four options below (**A**, **B**, **C** and **D**) indicate which C-O bond cleavage is most likely to occur.



A ☐ **B** ☐ **C** ☐ **D** ☐

Mark the correct cleavage mechanism for the most efficient hydrolysis.

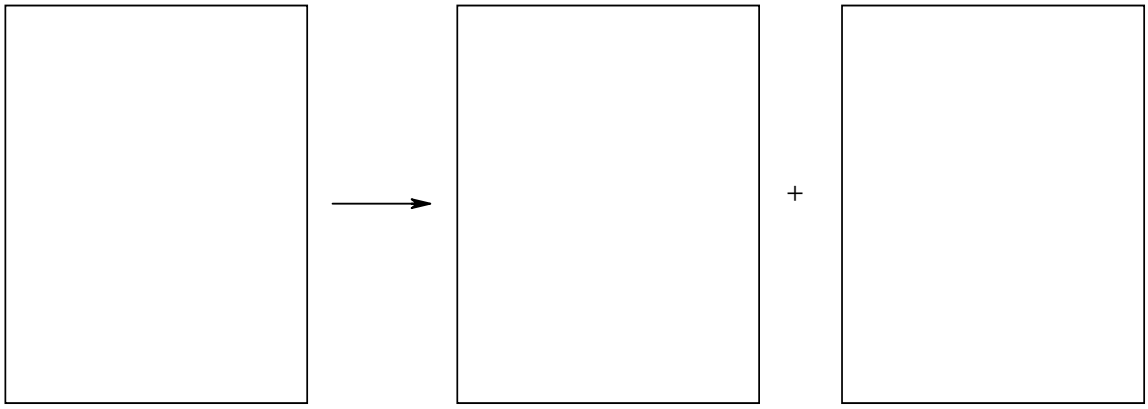
Hydrolysis with isotopically labelled water can provide information about the mechanism of hydrolysis using modern NMR techniques, which can "see" deuterium (^2H) and the oxygen isotope ^{17}O.

3.2 Indicate which labelled water can best be used for this purpose. Mark the correct answer.

- ❑ ^2H_2O
- ❑ $H_2{}^{17}O$
- ❑ $^2H_2{}^{17}O$
- ❑ None of them.

Upon catalytic hydrogenation glucose gives sorbitol (**S**), whilst fructose (**F**) gives mannitol (**M**) and sorbitol (**S**).

3.3 Draw the Fischer projections of fructose (**F**), sorbitol (**S**) and mannitol (**M**).



F **S** **M**

1.00 mol of inulin in 2.00 kg of water with added catalysts, is subjected to hydrolysis and hydrogenation at 95 ^oC in a one step process. The selectivity of the hydrogenation of fructose to mannitol / sorbitol is 7 / 3.

3.4 How many moles of mannitol and sorbitol are obtained?

M:	**S**:

After completion of the reactions the catalysts are removed and the reaction mixture is cooled to 25 ^oC. The solubility of **M** is 0.40 mol kg^{-1} in water at 25 ^oC and the solubility of **S** is so high that it will not precipitate.

3.5 Calculate how many moles of **M** will precipitate.

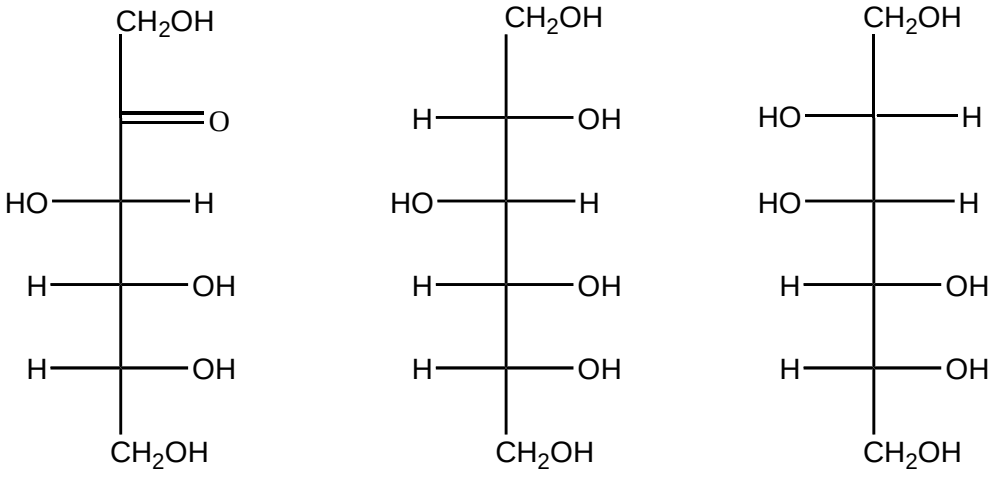
———————

SOLUTION

3.1 B is correct.

3.2 $H_2{}^{17}O$

3.3



F S M

3.4 n(M): 7 mol n(S): 4 mol

3.5 Remaining amount of water:

$m(H_2O) = 2\ kg - (10 \times 0.018\ kg) = 1.82\ kg$

$n(M)_{total} = 7\ mol$

$n(M)_{dissolved} = 1.82 \times 0.4\ mol = 0.73\ mol$

$n(M)_{precipitated} = 7.00 - 0.73 = 6.27\ mol$

PROBLEM 4

Production of Methanol

Methanol (CH_3OH) is a chemical that is used for the production of additives in gasoline and many common plastics. A factory, producing methanol, is based on the reaction:

$$CO + 2\,H_2 \rightleftharpoons CH_3OH$$

Hydrogen and CO are obtained by the reaction:

$$CH_4 + H_2O \rightleftharpoons CO + 3\,H_2$$

The three units of the factory, namely, the "reformer" for the hydrogen / carbon monoxide production, the "methanol reactor" and a "separator" to separate methanol from CO and H_2, are schematically shown in Figure 1. Four positions are indicated by α, β, γ and δ.

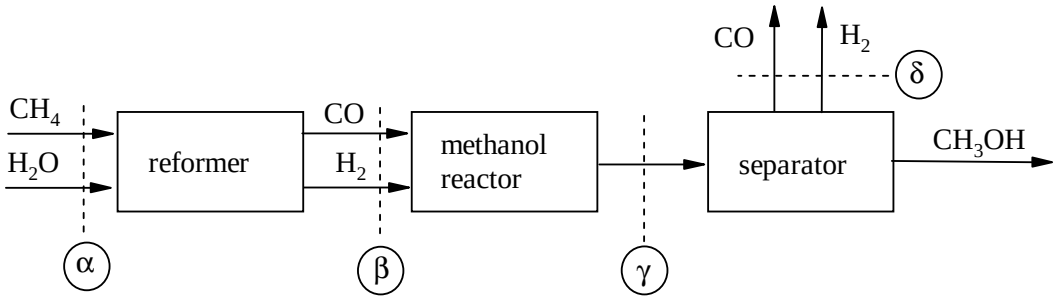


Figure 1

The flow of methanol at position **γ** is $n[CH_3OH, \gamma] = 1000$ mol s^{-1}. The factory is so designed that 2/3 of the CO is converted to methanol. Excess CO and H_2 at position **δ** are used to heat the first reactor. Assume that the reformer reaction goes to completion.

4.1 Calculate the flow of CO and H_2 at position **β**.

4.2 Calculate the flow of CO and H_2 at position **γ**.

4.3 Calculate the flows of CH_4 and H_2O needed at position **α**.

4.4 At point **γ** all species are gases. Calculate the partial pressures in MPa for CO, H_2 and CH_3OH at position γ using the equation:

$$p_i = p\,\frac{n_i}{n_{tot}}$$

wherein n_i is the flow and p_i the partial pressure of the compound i, n_{tot} is the total flow at the position considered, and p the total pressure in the system. (p = 10 MPa)

When the methanol reactor is large enough the reaction goes to equilibrium. The partial pressures at point γ obey the equation:

$$K_p = \frac{p_{CH_3OH}\, p_0^2}{p_{CO}\, p_{H_2}^2}$$

wherein p_0 is a constant (0.1 MPa) and K_p is a function of temperature as is shown in Figure 2 (the vertical scale is logarithmic).

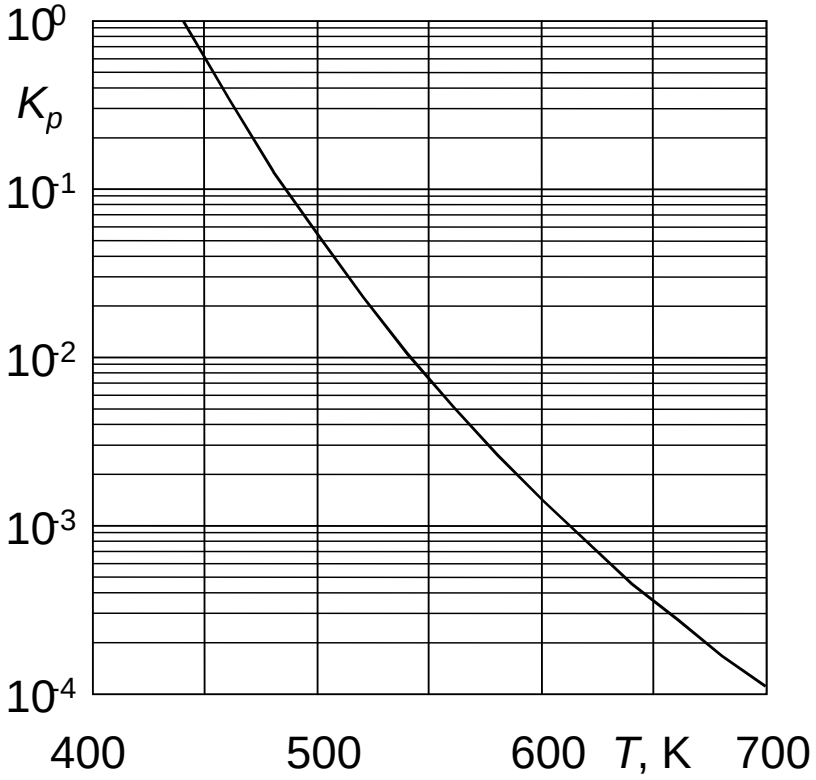


Figure 2

4.5 Calculate K_p and indicate at which temperature T the reaction must be operated to achieve this equilibrium.

SOLUTION

4.1 $n(CO, \beta) = 3/2 \times n(CH_3OH, \gamma) = 1500$ mol s^{-1}

$n(H_2, \beta) = 3 \times n(CO, \beta) = 4500$ mol s^{-1}

4.2 $n(CO, \gamma) = n(CO, \beta) - n(CH_3OH, \gamma) = (1500 - 1000)\ mol\ s^{-1} = 500\ mol\ s^{-1}$

$n(H_2, \gamma) = n(H_2, \beta) - 2 \times n(CH_3OH, \gamma) = (4500 - 2 \times 1000)\ mol\ s^{-1} = 2500\ mol\ s^{-1}$

4.3 $n(CH_4, \alpha) = n(CO, \beta) = 1500\ mol\ s^{-1}$

$n(H_2O, \alpha) = n(CO, \beta) = 1500\ mol\ s^{-1}$

4.4 $n_{tot} = (1000 + 500 + 2500)\ mol\ s^{-1} = 4000\ mol\ s^{-1}$

$p_i = p_{tot} \cdot (n_i/n_{tot})$

$p(CO, \gamma) = 10\ MPa \times (500/4000) = 1{,}25\ MPa$

$p(H_2, \gamma) = 10\ MPa \times (2500/4000) = 6{,}25\ MPa$

$p(CH_3OH, \gamma) = 10\ MPa \times (1000/4000) = 2{,}50\ MPa$

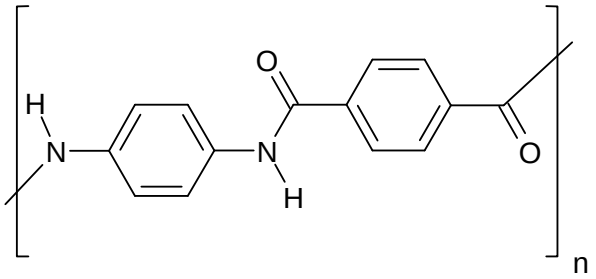
4.5 Calculation of K_p: $K_p = (2.5 \times 0.1^2) / (1.25 \times 6.25^2) = 5.12 \times 10^{-4}$.

The temperature corresponding to this value (see Fig. 2) is $\approx$ 630 K.

PROBLEM 5

Aramids, High-performance Polymeric Materials

Aromatic polyamides (aramids) are high strength, high performance polymer fibers that find use in composite materials, bullet-proof vests, high quality skis, safety helmets, etc. Aramid PPTA is marketed under the names Kevlar® (DuPont) and Twaron® (Teijin), and amongst others manufactured in the north of The Netherlands. The PPTA chains are neatly packed into fibers with a sheet type structure.



PPTA

5.1 Draw the structure of these sheets (three chains suffice).

For a polymerisation of equimolar amounts of two monomers the average chain length is $\overline{P}_n$, the degree of conversion is *p*, which equals the fraction of functional groups that have reacted, the total number of chains is N_t and the total initial number of monomers is U_0.

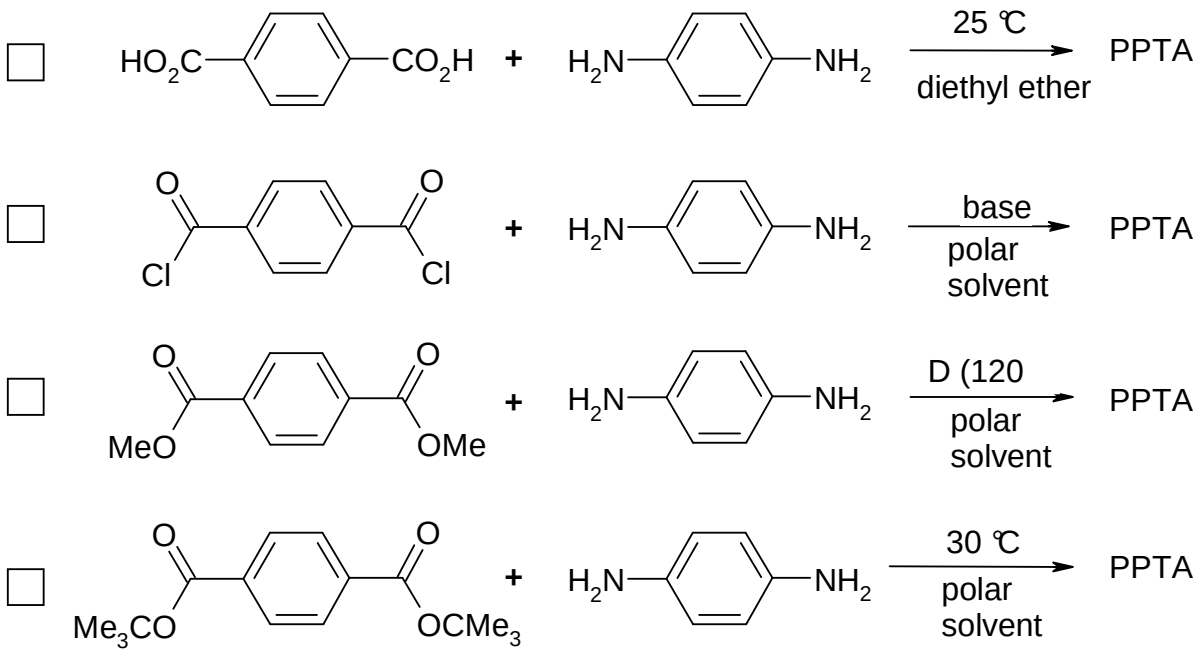
Assuming that the polymerization equilibrium can fully be described by:

$$C + A \rightleftharpoons Am + H_2O$$

where C stands for any $–CO_2$ group, A stands for any $–NH_2$ group and Am stands for any amide group.

5.2 Calculate the degree of conversion needed to obtain an average chain length of 500.

5.3 For the synthesis of PPTA the following possibilities are considered. Which of the following reactions will work? Mark the correct answer(s).



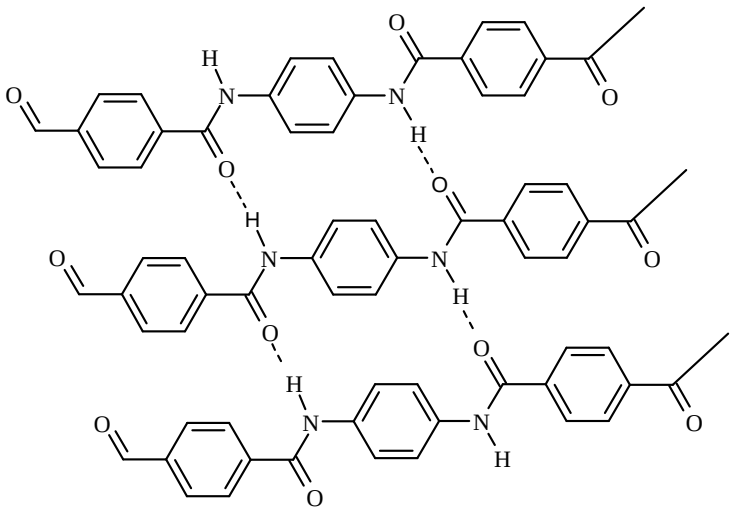
5.4 Another type of aramid can be produced from 4-aminobenzoic acid (4-aminobenzene-carboxylic acid) by heating.

(a) Give the structure of this aramid (n = 4)

(b) Calculate the average chain length at equilibrium (reaction is carried out in a closed vessel). The equilibrium constant K = 576.

SOLUTION

5.1



5.2 $\bar{P}_n = \frac{U_0}{N_t}$, $p = \frac{U_0 - N_t}{U_0}$ ➜

$p = 1 - \frac{N_t}{U_0}$, $\frac{N_t}{U_0} = 1 - p$ ➜ $\bar{P}_n = \frac{1}{1-p}$

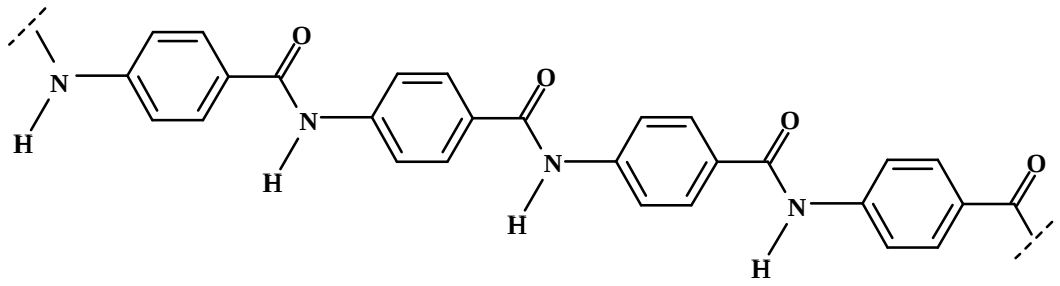
$500 = \frac{1}{1-p}$ $p = \frac{499}{500} = 0.998$

5.3

2 and 3

5.4

a)



b) $K = \frac{[Am] \times [H_2O]}{[C] \times [A]} = \frac{p\,U_0 \times p\,U_0}{(1-p)^2 \times U_0^2} = \frac{p^2}{(1-p)^2} = 576 \Rightarrow p = 0.96$

$\bar{P}_n = \frac{1}{1-p} = \frac{1}{1-0.96} = 25$

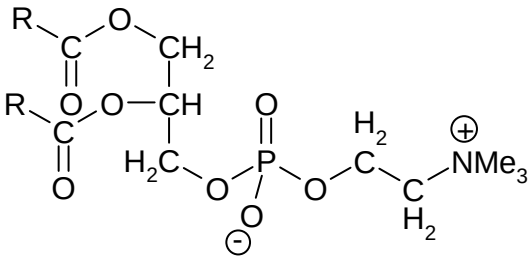
Theme III - Chemistry of Functional Molecules in Nature

A challenge in chemistry is to discover what nature does and how the structures of biologically active molecules are related to what they do.

PROBLEM 6

Phospholipids in Membranes

Biological cell membranes are complex, functional, non-covalent molecular assemblies, largely consisting of lipids and proteins. Their function is of vital importance for life processes. They separate the cell from its environment and also determine the specific flow of information between the cell contents and the environment. Phospholipids are among the most important components of cell membranes. An example is compound **A**.

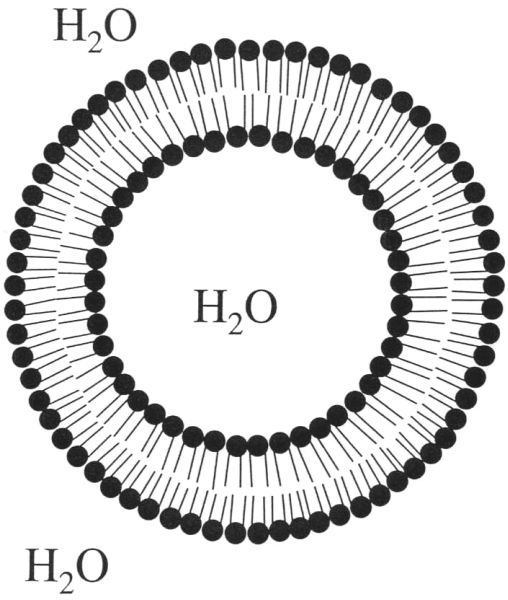


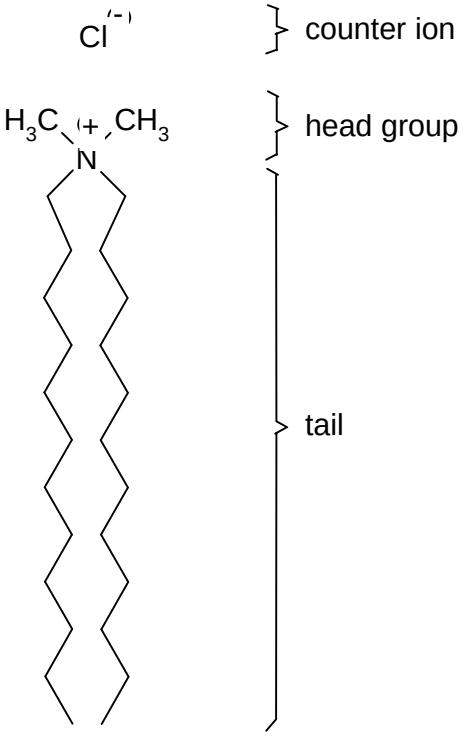
A

R = *n*-$C_{17}H_{35}$

Upon dispersion in water (above a low critical concentration) compound **A** forms closed bilayer structures, called liposomes, which are employed as model compounds for aspects of the chemistry of the structurally much more complex cell membranes. Liposomes are globular aggregates with the polar or ionic head groups in contact with water and with the alkyl tails sequestered in a hydrophobic core. The bilayer structure encloses an aqueous inner compartment.

Double-tailed *synthetic* surfactants also form closed bilayer assemblies similar to liposomes but now called vesicles. An example is di-*n*-dodecyldimethylammonium chloride (**DDAC**).

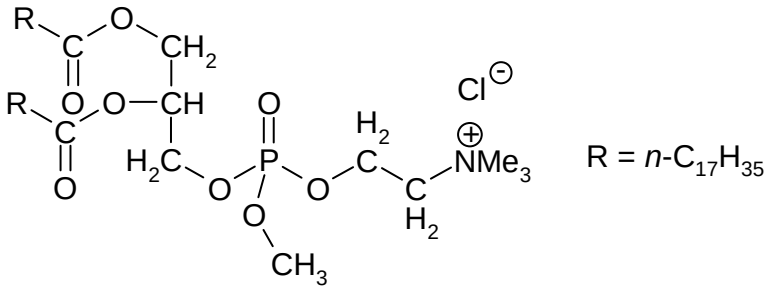




DDAC

6.1 **(a)** How many stereoisomers are possible for compound **A**?

(b) How many stereoisomers are possible for the trialkylphosphate **B**?

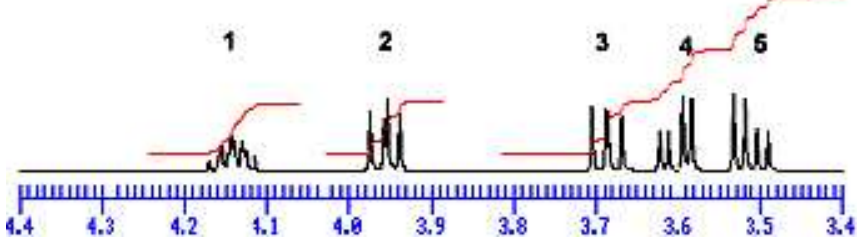


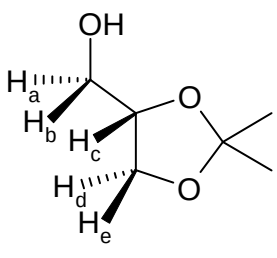
R = *n*-$C_{17}H_{35}$

B

A precursor for the synthesis of compound **A** is the acetonide **C** derived from glycerol. Part of the ^{1}H-NMR spectrum of compound **C** is shown below.

6.2 Which signal number in the ^{1}H-NMR spectrum corresponds to proton $\mathbf{H_c}$?





C

The bilayer of a liposome can be characterized by V (the volume of the hydrocarbon chains), a_0 (optimal cross-sectional surface area of the head groups of the phospholipid in the aggregate) and l_c (the maximum chain length that the alkyl group can assume). A good approximation for unbranched alkyl tails containing n carbon atoms yields:

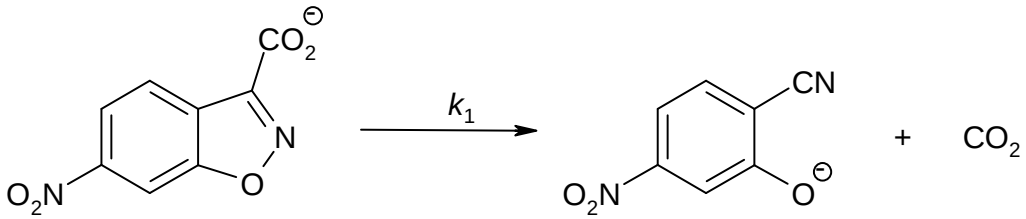
$V = (27.4 + 26.99\ n) \times 10^{-3}\ nm^3$

$l_c = (0.154 + 0.1265\ n)\ nm$

For very large n values, the intertail interactions dominate over the head group repulsions.

6.3 Calculate the minimum cross-sectional surface area of the head groups for such very large n values.

Vesicles formed from **DDAC** (above its critical vesicle concentration, cvc) catalyse the unimolecular decarboxylation of 6-nitro-benzisoxazole-3-carboxylate (**6-NBIC**).



6-NBIC

In water at 25 ºC $k_1 = 3.1 \times 10^{-6}\ s^{-1}$. At the concentration c_1 of **DDAC** at which **6-NBIC** becomes fully bound to the vesicles, $k_1 = 2.1 \times 10^{-3}\ s^{-1}$.

6.4 Sketch a plot of k_1 vs. [**DDAC**] for [**DDAC**] = 0 → 3 c_1.

6.5 The main reason for the efficient catalysis of the decarboxylation of **6-NBIC** by **DDAC** vesicles is:

- ❑ The decarboxylation is catalysed by the Cl^- ions bound to the surface of the vesicles.
- ❑ Efficient loss of hydration of the carboxylate group of vesicle-bound 6-NBIC.
- ❑ Strong binding of CO_2 in the interior of the vesicle.
- ❑ Strong binding of the organic reaction product to the vesicles relative to that of 6-NBIC.

Mark the correct answer.

SOLUTION

6.1 (a) 2; (b) 4

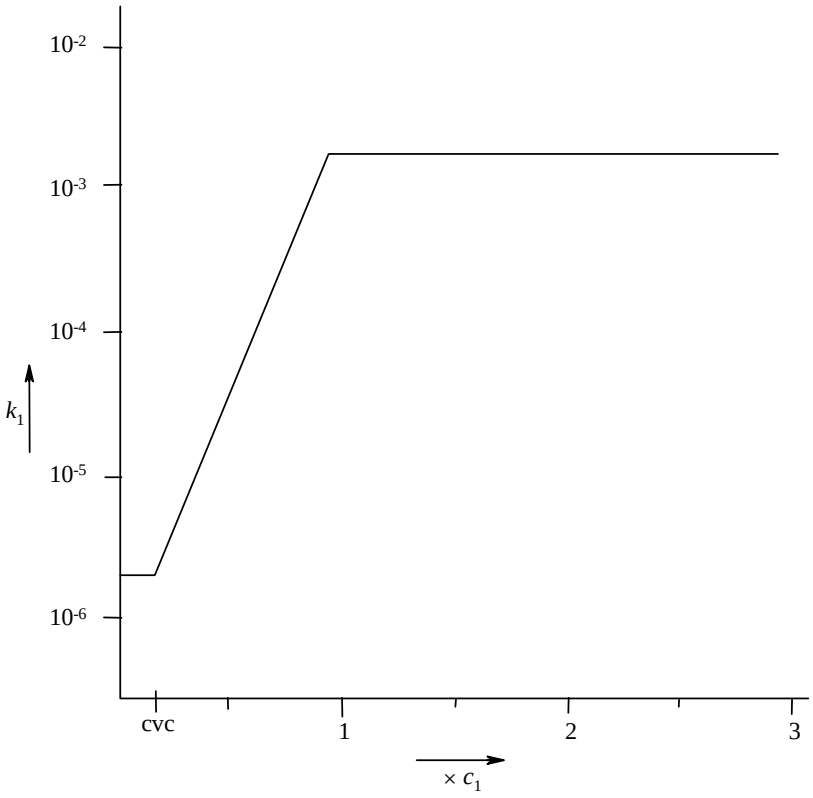
6.2 Signal No 1.

6.3 $a_0(\text{min}) = \dfrac{V}{l_c} = \dfrac{(27.4 + 26.99\,n)\times 10^{-3}}{(0.154 + 0.1265\,n)}\ \text{nm}^2$

For a large value of n: $a_0(\text{min}) = \dfrac{26.99\times 10^{-3}}{0.1265}\ \text{nm}^2$

$a_0(\text{min}) = 0.213\ \text{nm}^2$

6.4



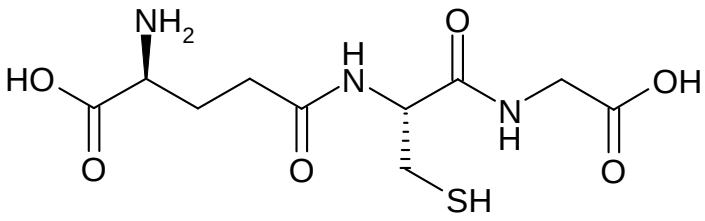
We expect curved bends in the graph, however, sharp corners (see the Figure) are also accepted.

6.5 The second answer is correct: Efficient loss of hydration of the carboxylate group of vesicle-bound 6-NBIC.

PROBLEM 7

Glutathione, an Essential Mini-Peptide

Glutathione, abbreviated as GSH, is a small peptide that is present in almost all tissues of animals. GSH fulfils important biological functions, such as detoxification of electrophilic chemicals and reduction of (organic) peroxides in blood. An electrophilic compound reacts irreversibly with GSH, especially in the liver, to give a primary product that is converted by a series of biotransformations into a so-called *mercapturic acid*, which is excreted via the urine. Oxidants react with GSH to give the disulfide GSSG, which can be enzymatically reverted to GSH with reductases. The ratio GSH/GSSG in most cells is ≥ 500.

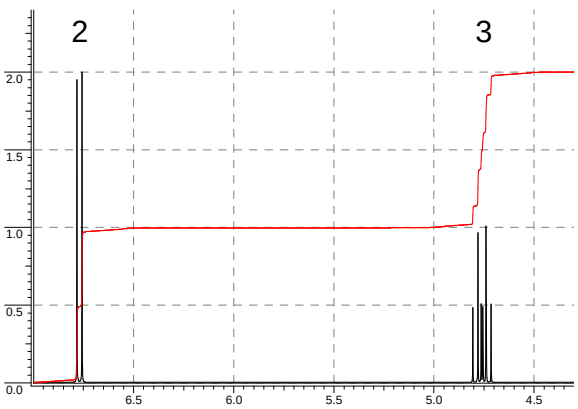


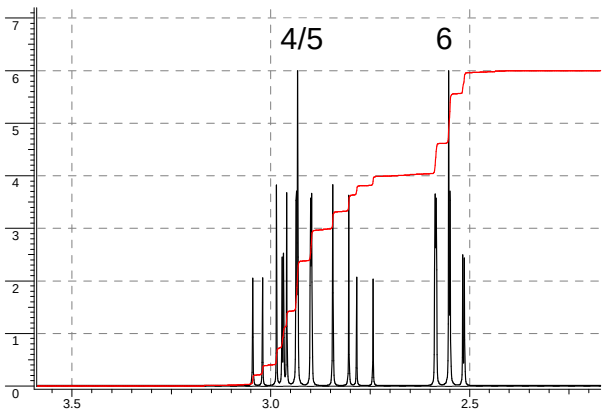
GSH

7.1 **(a)** How many amino acid residues are present in GSH?

(b) Draw the structures of the corresponding amino acids and mark the chiral centers with an asterisk.

A mercapturic acid **A** isolated from urine of a person who has been exposed to acrylonitrile (H_2C=CH-CN) has the molecular formula $C_8H_{12}N_2O_3S$. The ^{1}H-NMR spectrum of **A** in $(CD_3)_2SO$ is shown in Figure 1. When the product is pretreated with D_2O, the signals at δ 12.8 and δ 6.8 are no longer present and the signal 3 is simplified.





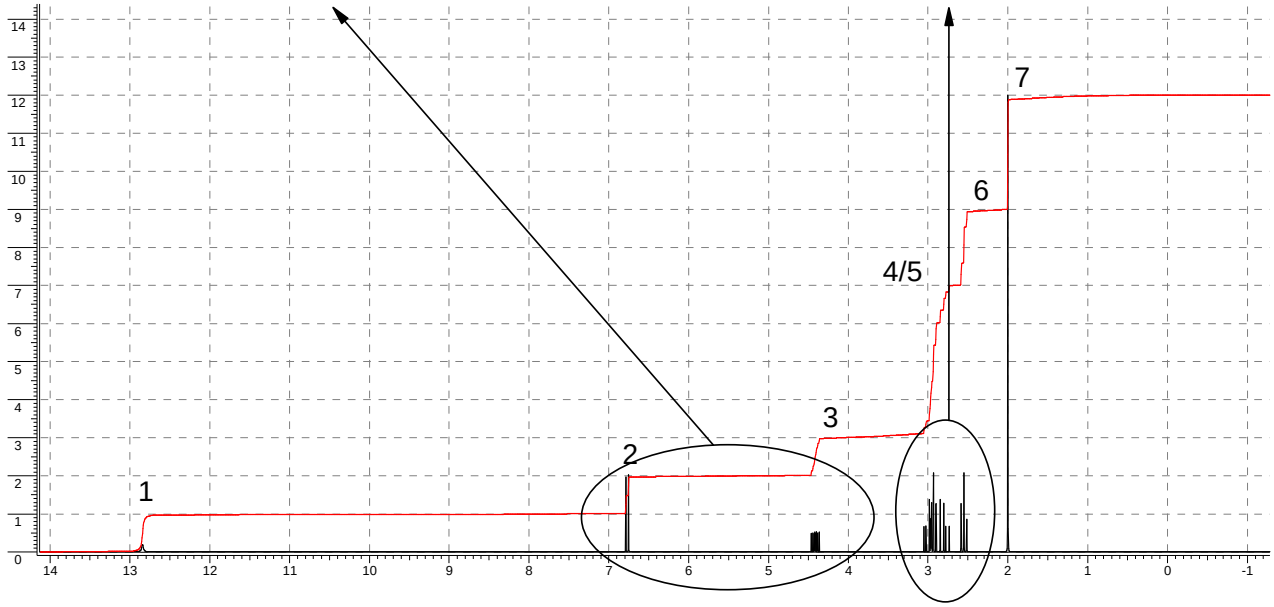


Figure 1

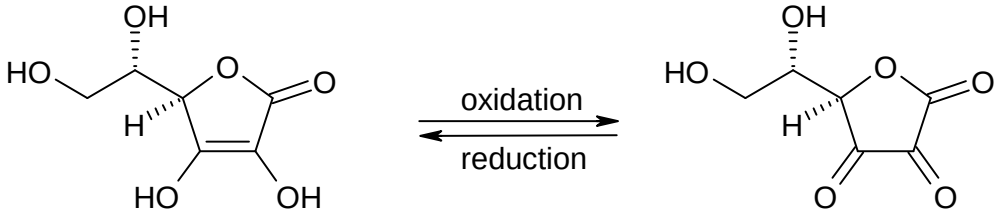
7.2 **(a)** The NMR-signals correspond with protons in the following groups: CH, CH_2, CH_3, OH and NH. Indicate the appropriate proton group in the boxes for the signals 1 – 7.

Signals	1	2	3	4/5	6	7
Protons						

(b) How many carbon atoms are present in compound **A** that do not carry any protons?

(c) Draw the structure of compound **A**.

Vitamin C (ascorbic acid) reacts with oxidants to give dehydroascorbic acid **D**



vitamin C **D**

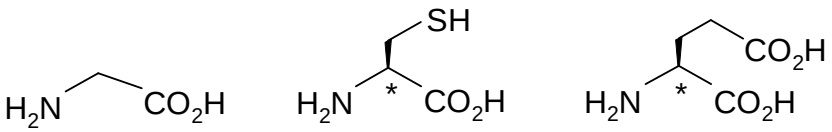
7.3 Eating fresh fruit and vegetables is healthy

- ❑ because vitamin C forms a complex with GSH.
- ❑ because vitamin C reacts with electrophilic compounds.
- ❑ because vitamin C removes oxidants and prevents undesired depletion of GSH.
- ❑ for many reasons, but none of them has anything to do with GSH.

SOLUTION

7.1 a) Three amino acid residues.

b)

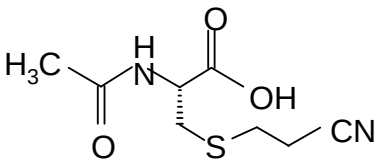


7.2 a)

Signal	1	2	3	4/5	6	7
Group of protons	OH	NH	CH	CH_2	CH_2	CH_3

b) 3

c)



7.3 The third answer is correct: Vitamin C removes oxidants and prevents undesired depletion of GSH.

Theme IV - Chemistry Related to Light and Energy

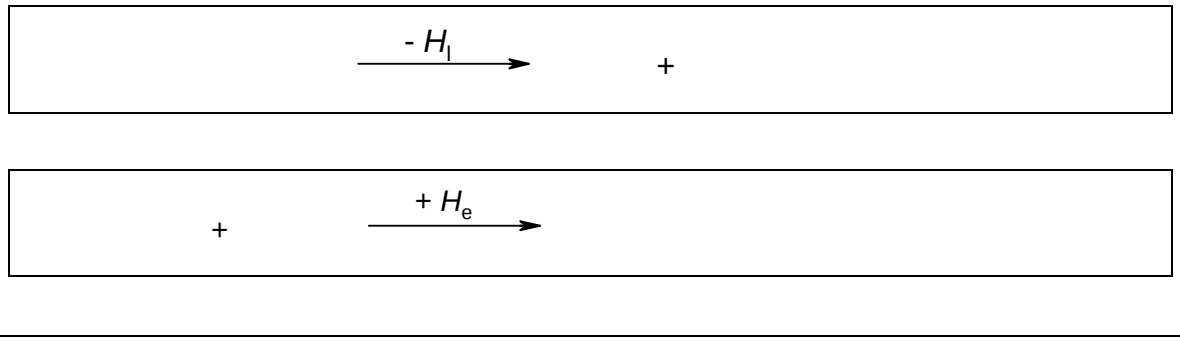
Chemistry plays a major role in meeting our needs of light and energy. Our life is unthinkable without artificial light and energy for mobility.

PROBLEM 8

LIGHTING LAMPS

Since 1891 lighting lamps have been manufactured in The Netherlands. The improvement today in comparison to the first lamp is enormous, especially with the introduction of the gas discharge lamps. The life-time has increased by orders of magnitude. The colour is also an important aspect. Rare earth metal compounds like $CeBr_3$ are now included to reach a colour temperature of 6000 K in the lamp. These compounds are ionic solids at room temperature, and upon heating they sublime partially to give a vapour of neutral metal halide molecules. To achieve a high vapour pressure, the sublimation enthalpy should be as low as possible.

8.1 Give a thermochemical cycle (Law of Hess) for sublimation of $CeBr_3$, via a vapour of mononuclear ions. ($H_l = H_{lattice}$; $H_e = H_{electrostatic}$; $H_s = H_{sublimation}$;H is not absolute, H means ΔH)



The lattice energy of the solid can be calculated using the Born–Landé formula:

$$H_l = f\,\frac{Z_+ Z_- A e^2}{r_+ + r_-}\left(1-\frac{1}{n}\right)$$

The factor fe^2 (necessary in order to calculate the lattice energy in kJ mol^{-1}) amounts to 139 when the ionic radii are substituted in nm. The Madelung constant A for the lattice is

2.985. The Born exponent n is 11. The charges of the ions Z_+ and Z_- are integer numbers (Z_- is negative). For the calculation of the energy of gaseous $CeBr_3$ (when formed from ions) the same Born-Landé formula can be used without A. The structure of $CeBr_3$ in the gas phase is planar triangular. The radius of Ce^{3+} is 0.115 nm and of Br^- is 0.182 nm.

8. 2 Calculate the enthalpy of sublimation of $CeBr_3$ (in integers; be aware of the signs!)

Attempts to make a better lamp have been undertaken by adding a stoichiometric amount of CsBr to the $CeBr_3$ in the lamp leading at room temperature to solid $CsCeBr_4$. When the sublimation temperature decreases the life time of the lamp will increase likewise. The $CsCeBr_4$ lattice has a NaCl structure with Cs^+ as cations and tetrahedral $CeBr_4^-$ as complex anions. Sublimation of $CsCeBr_4$ leads to a vapour of CsBr and $CeBr_3$ molecules.

8.3 Give the reaction equations of the thermochemical cycle (Law of Hess) for this process in which some steps involve $CeBr_4^-$ ions, mononuclear ions and/or neutral molecules in the gas phase.

Step 1: $\xrightarrow{+ H_1}$ +

Step 2: + $\xrightarrow{+ H_2}$

Step 3: + $\xrightarrow{+ H_3}$

Step 4: + $\xrightarrow{+ H_4}$

Total: $(CsCeBr_4)_{lattice} \xrightarrow{+ H_{total}} (CeBr_3)_{molecule} + (CsBr)_{molecule}$

8.4 Calculate the enthalpy of sublimation of $CsCeBr_4$ (in integers).

Use the Born–Landé formula for all steps in the process and report the separate energies also (be aware of the signs!). The Madelung constant for NaCl is 1.75. The

Cs–Ce distance in the lattice is 0.617 nm. The $CeBr_4^-$ anion is a tetrahedron in which the ratio between the edge and the distance between a corner of the tetrahedron and the centre of gravity (body-radius) amounts to $(2\sqrt{6})/3 = 1.633$. The Born exponent of CsBr is 11. The radius of Cs^+ is 0.181 nm.

8.5 Conclusion in relation to the previous answers: Was adding CsBr a good idea? Mark the correct answer.

- ❑ Adding CsBr is counterproductive.
- ❑ Adding CsBr has no influence.
- ❑ Adding CsBr is advantageous.
- ❑ From these data no clear answer can be given.

SOLUTION

8.1 $(CeBr_3)_{latitce} \xrightarrow{-H_l} Ce^{3+} + 3\ Br^-$

$Ce^{3+} + 3\ Br^- \xrightarrow{-H_e} (CeBr_3)_{molecule}$

$(CeBr_3)_{lattice} \xrightarrow{+H_s} (CeBr_3)_{molecule}$ $\qquad H_s = -H_l + H_e$

8.2 $H_l = -\frac{139\times 3\times 1\times 2.985}{0.297}\times\frac{10}{11}$ kJ mol^{-1} = – 3810 kJ mol^{-1}

$H_e = \left(-3\times\frac{139\times 3\times 1}{0.297}\times\frac{10}{11}\right)+\left(3\times\frac{139\times 1\times 1}{0.297\sqrt{3}}\times\frac{10}{11}\right)$ kJ mol^{-1} = - 3092 kJ mol^{-1}

H_s = 718 kJ mol^{-1}

8.3 Step 1: $(CsCeBr_4)_{lattice} \xrightarrow{+H_1} Cs^+ + CeBr_4^-$

Step 2: $CeBr_4^- \xrightarrow{+H_2} Ce^{3+} + 4\ Br^-$

Step 3: $Ce^{3+} + 3\ Br^- \xrightarrow{+H_3} (CeBr_3)_{molecule}$

Step 4: $Cs^+ + Br^- \xrightarrow{+H_4} (CsBr)_{molecule}$

Total $(CsCeBr_4)_{lattice} \xrightarrow{+H_{total}} (CeBr_3)_{molecule} + (CsBr)_{molecule}$

8.4 Step 1: The lattice energy of $CsCeBr_4$ with opposite sign is:

$$H_1 = \frac{139 \times 1 \times 1 \times 1.75}{0.617} \times \frac{10}{11} \text{ kJ mol}^{-1} = 358 \text{ kJ mol}^{-1}$$

Step 2:

$$H_2 = 4 \times \frac{139 \cdot 3 \cdot 1}{0{,}297} \cdot \frac{10}{11} - 6 \times \frac{139 \times 1 \times 1}{0.297 \times \frac{2}{3} \times \sqrt{6}} \times \frac{10}{11} \text{ kJ mol}^{-1} = 3543 \text{ kJ mol}^{-1}$$

Step 3: The electronic energy in the gas phase of $CeBr_3$ is (see answer 8.2):

$$H_3 = -3 \times \frac{139 \times 3 \times 1}{0.297} \times \frac{10}{11} + 3 \times \frac{139 \times 1 \times 1}{0.297 \times \sqrt{3}} \times \frac{10}{11} \text{ kJ mol}^{-1} = -3092 \text{ kJ mol}^{-1}$$

Step 4: The electrostatic energy in the gas phase of CsBr is

$$H_4 = -\frac{139 \times 1 \times 1}{0.363} \times \frac{10}{11} \text{ kJ mol}^{-1} = -348 \text{ kJ mol}^{-1}$$

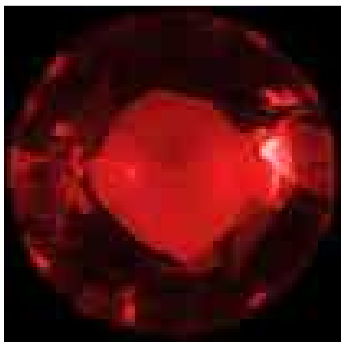
Total sum:

$H_{total} = H_1 + H_2 + H_3 + H_4 = 461 \text{ kJ mol}^{-1}$

8.5 The third answer is correct: Adding CsBr is advantageous.

PROBLEM 9

RED RUBY



Ruby crystals have a deep red colour and are well known for their use in jewellery. Not many people know that the heart of the first laser, built in 1960 by Maiman, was a big ruby crystal. The red colour of ruby originates from the absorption of light by Cr^{3+} ions that are incorporated in colourless aluminium oxide (Al_2O_3) crystals. The Cr^{3+} ion has 3 electrons in the 3*d* shell and the absorption of light is due to electronic transitions between 3*d* orbitals of lower and higher energy.

9.1 Indicate which of the four absorption spectra belongs to ruby.

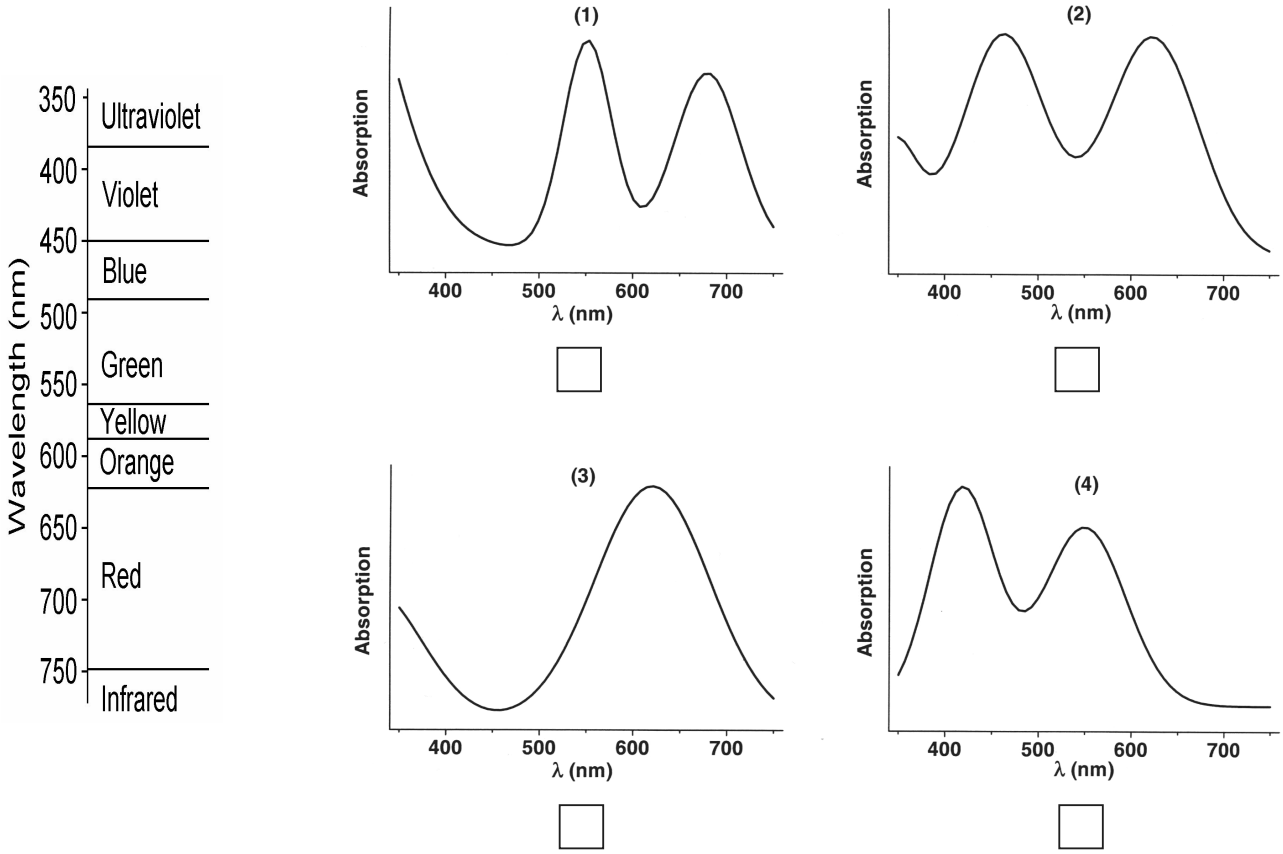


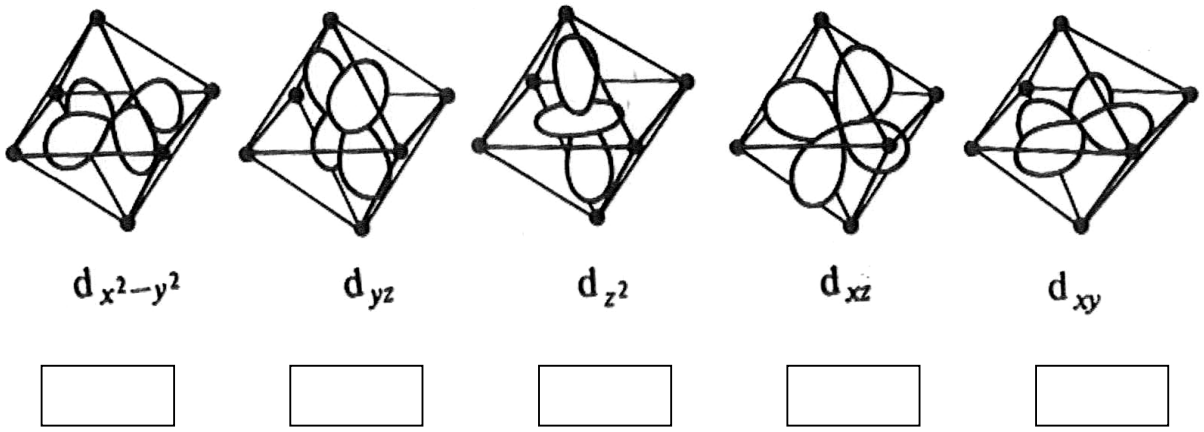
Figure 1

The rod used in ruby lasers is a cylinder with a length of 15.2 cm and a diameter of 1.15 cm. The amount of Cr^{3+} ions is 0.050 mass %. The density of Al_2O_3 is 4.05 g cm^{-3}. The atomic mass of Cr = 52u. (1u = 1.67×10^{-27} kg).

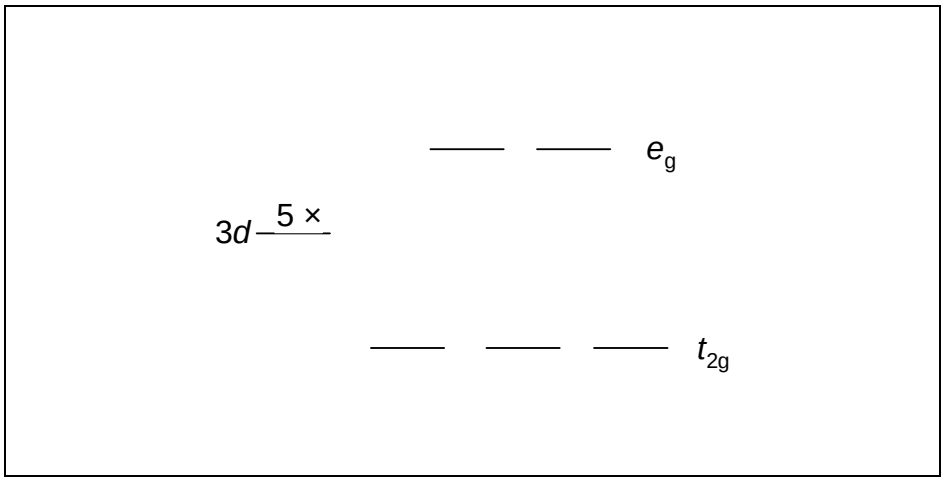
9.2 Calculate how many Cr^{3+} ions are in this laser rod.

In rubies the Cr^{3+} ions are coordinated by an octahedron of 6 oxygen ions. The shape of the five 3*d* orbitals is shown below. The box below shows the splitting of the five 3*d* orbitals into a group of three orbitals at lower energy (t_{2g}) and a group of two at higher energy (e_g)..

9.3 Indicate in the boxes below which of the 3*d* orbitals (d_z^2, d_{xy}, d_{yz}, $d_{x^2-y^2}$, d_{xz}) belong to the t_{2g} group and which belong to the e_g group.



9.4 Indicate with arrows the distribution and the direction of the magnetic spin moment of the three 3*d* electrons of Cr^{3+} over the five *d* orbitals in the lowest energy state of Cr^{3+}.



The ruby is placed on a (non-magnetic) scale. When the scale is in balance (Figure 2) a magnet is placed directly under the side with the ruby.

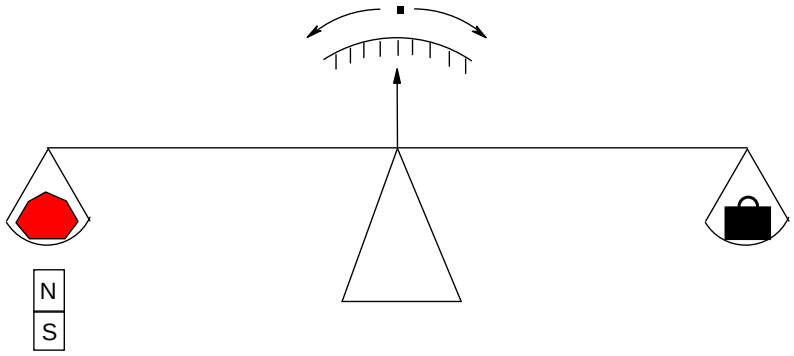


Figure 2

9.5 Indicate what will happen with the ruby (mark the correct answer)

- ❑ The magnet attracts the ruby (the ruby moves down)
- ❑ The magnet has no influence on the ruby (the ruby does not move)
- ❑ The magnet repels the ruby (the ruby moves up)
- ❑ The magnet has an oscillating effect on the ruby (the ruby moves up and down)

SOLUTION

9.1 The fourth spectrum is correct.

9.2 Volume of the rod = $\pi \times r^2 \times l$

$V = \pi \times 0.575^2 \times 15.2\ \text{cm}^3 = 15.79\ \text{cm}^3$

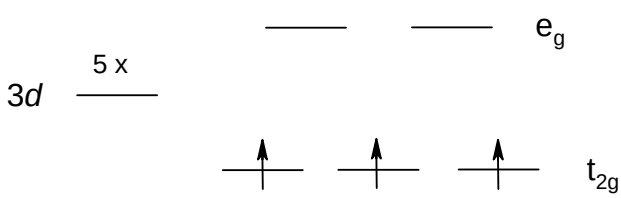
Mass of the rod: $m = 15.79 \times 4.05\ \text{g} = 63.94\ \text{g}$

Mass of chromium in the rod: $m_{Cr} = 63.94\ \text{g} \times 0.05 / 100 = 0.0319\ \text{g}$

Number od chromium ions: $N = 0{,}0319 \times 10^{-3}\ \text{kg} / (52 \times 1{,}67 \times 10^{-27}) = 3{,}68 \times 10^{20}$.

9.3 $d_{x^2-y^2}$: e_g d_{yz}: t_{2g} d_{z^2}: e_g d_{xz}: t_{2g} d_{xy}: t_{2g}

9.4



9.5 The correct answer: The magnet attracts the ruby (the ruby moves down).

PROBLEM 10

Vehicle Traction Batteries

Battery-powered electric vehicles (EV's) are likely to become increasingly common in the next 50 years because of growing concern over pollution caused by vehicles using combustion engines. The reason for the current meagre commercial success of EV's is that the battery specifications must have a performance and cost profile comparable to conventionally powered vehicles.

Lead-acid batteries are extensively used as portable power sources for vehicles and traction. A lead-acid battery capable of efficient recharging has an energy density of 45 Wh/kg.

In the current evolution of EV batteries, the most promising long-term solution is the rechargeable light weight lithium-ion battery. Such batteries are under intensive investigation worldwide and hold also promise for the storage of electricity from solar cells. Their weight is 1/3 of a lead-acid battery. Lithium is used as a negative electrode. It has a high specific capacity and electrode potential. A common positive electrode material is the environmentally benign spinel-type $LiMn_2O_4$. The spinel structure comprises a matrix of cubic close-packed oxide ions, stabilised by lithium ions in tetrahedral sites and manganese ions in octahedral sites. In $LiMn_2O_4$ half of the manganese ions has an oxidation state +3 and half the oxidation state +4.

A lead-acid battery is represented by:

$$Pb(s) \mid PbSO_4(s) \mid H_2SO_4(aq) \mid PbSO_4(s) \mid PbO_2(s) \mid (Pb(s))$$

A lithium battery is represented by:

$$Li(s) \mid Li^+\text{-conducting (solid) electrolyte(s)} \mid LiMn_2O_4(s)$$

Upon discharge the insertion product $Li_2Mn_2O_4$ is formed. Charging the battery leads to the products Li(s) and $LiMn_2O_4$.

10.1 Give the electrochemical reactions at the electrodes of the lead-acid battery during discharge.

10.2 Give the electrochemical reactions at the electrodes of the lithium-ion battery upon discharge.

10.3 Give the coordination numbers of the lithium ions and of the manganese ions in the spinel structure of $LiMn_2O_4$.

A typical family car of 1000 kg requires at least 5 kWh of energy to move 50 km, which corresponds with the consumption of about 5.0 litres or 3.78 kg of petrol. This conventional car has a petrol tank volume of 50 L. The weight of the tank is 10 kg. The fuel consumption is 10 km L^{-1}.

10.4 Calculate the extra weight of the car if the petrol tank is replaced by an equivalent battery in an EV based on (**a**) lead-acid battery and (**b**) lithium battery. Assume that in all cases the engine efficiency is the same. Calculate:

(**a**) Extra weight of a lead-acid battery car.

(**b**) Extra weight of a lithium battery car.

SOLUTION

10.1 Reaction at the negative electrode:

$$Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2\ e^-$$

Reaction at the positive electrode:

$$PbO_2(s) + 3\ H^+(aq) + HSO_4^-(aq) + 2\ e^- \longrightarrow PbSO_4(s) + 2\ H_2O(l)$$

10.2 Reaction at the negative electrode:

$$Li(s) \longrightarrow Li^+ + e^-$$

Reaction at the positive electrode:

$$Li^+ + e^- + LiMn_2O_4(s) \longrightarrow Li_2Mn_2O_4(s)$$

10.3 Li – ions: coordination number = 4 Mn – ions: cordination number = 6

10.4 Distance of the petrol car = 500 km $\Rightarrow$ 50 kWh

Mass of petrol tank = 10 kg + 50 $\times$ (3.78 / 5) = 47.8 kg

(a) Mass of a lead-acid battery = 50000 Wh / 45 Wh kg^{-1} = 1111.1 kg

Extra weight of a lead-acid battery car = 1111.1 kg – 47.8 kg = 1063.3 kg

(b) Mass of the lithium battery = 1/3 of the mass of a lead-acid battery

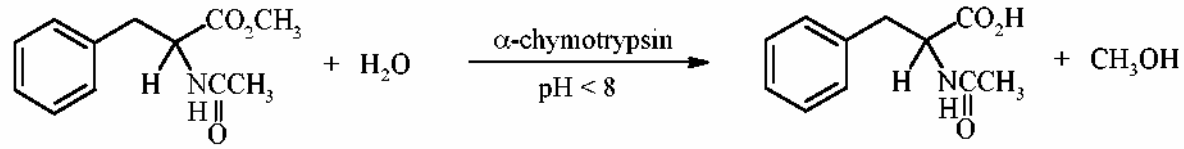
Extra weight of a lithium battery car = 1111.1 kg / 3 – 47.8 kg = 322.6 kg.

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

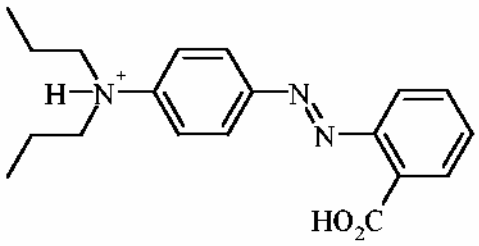
Enzymatic Hydrolysis of Methyl *N*-Acetyl-phenylalaninate

α-Chymotrypsin, a protease enzyme recognizing derivatives of natural α-amino acids, catalyses the hydrolysis of esters. In this experiment the enzymatic hydrolysis of racemic methyl N-acetyl-phenylalaninate **A** is investigated (Scheme).



A **B**

The rate of formation of *N*-acetyl-phenylalanine **B** can be monitored by titration with 0.100 M NaOH in the presence of propyl red as a pH indicator.



Propyl red (protonated form)
At pH < 5: pink; at pH > 6: yellow

Procedure

Note: the required amount of α-chymotrypsin will be supplied in a sample vial by the laboratory assistant on request.

Racemic methyl *N*-acetyl-phenylalaninate **A** [500 mg, the exact mass (± 1 mg) is indicated on the label of the vial marked as NacPheOMe] is transferred quantitatively into a 50 cm^3 Erlenmeyer flask and dissolved in methanol (~ 2.5 cm^3). Subsequently, propyl red (0.02 % solution in ethanol; 4 drops) is added. The kinetic experiment is started by adding α-chymotrypsin (10.0 cm^3 of a 0.05 % solution in distilled water) in one portion (*start the stopwatch*).

When the reaction mixture turns pink, it is immediately titrated with 0.100 M NaOH

until the colour changes to yellow. When the pink colour reappears, add just enough titrant to restore the pale yellow colour, swirling the flask continually during the addition. You only need to record the reading on the burette every 5 minutes. (*Note: at the beginning colour changes occur very frequently.*)

Monitor the reaction for 75 minutes. A graph showing the amounts of NaOH consumed in cm^3 versus time is constructed, in order to visualize the kinetic course of this enzymatic reaction.

SOLUTION

The competitors were expected to show on the answer sheet the following data, tables, graphs or calculations:

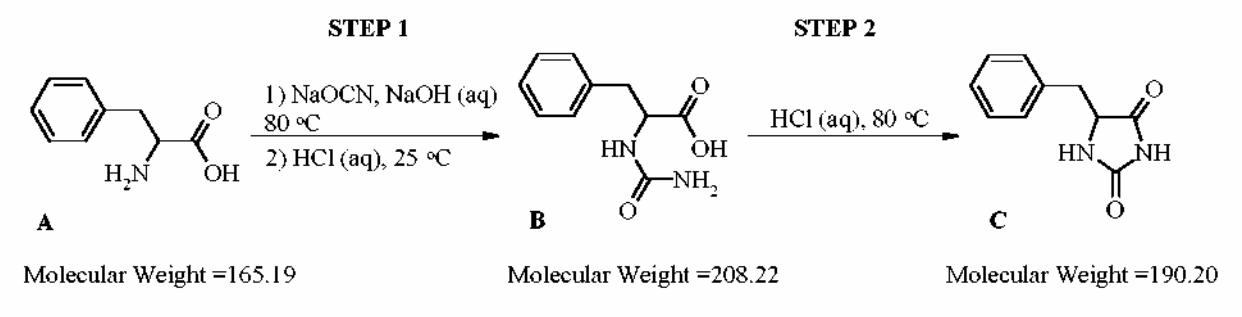
1. Amount of the starting racemic methyl *N*-acetyl-phenylalaninate **A** (in mg and mmol).
2. Table with time measured and the total consumption of NaOH in cm^3.
3. A graph of the total consumption of NaOH vs time.
4. Calculation of the amount of 0.100 M NaOH consumed in this experiment in mmol.
5. Calculation of the degree of hydrolysis of methyl *N*-acetyl-(*R,S*)-phenylalaninate **A** in mol %.

PROBLEM 2 (Practical)

Synthesis of Benzylhydantoin

Introduction

α-Amino acids are the building blocks for peptides and proteins. They are also frequently used as starting material for the synthesis of pharmaceuticals. In this experiment natural *S*-phenylalanine **A** is converted in two steps into benzylhydantoin **C**, which is a useful intermediate for the preparation of various physiologically active derivatives.



Procedure

STEP 1

*Retain a tiny amount of starting material **A** for the TLC analysis (see below).* A long-necked round-bottomed flask is charged with (*S*)-phenylalanine **A** (500 mg, 3 mmol, the exact amount is indicated on the label of the vial), sodium cyanate (300 mg, 4.6 mmol), water (3 cm^3) and a stirring bar. Two drops of aqueous sodium hydroxide (1 M) are added to the stirred suspension. The flask is equipped with a condenser (distillation column) and the reaction mixture is heated to 80 ^oC on a sand bath while stirring magnetically.

Important

In order to reach the appropriate temperature in time and not lose too much time, start the electric heating of the sand bath immediately at the beginning of this experiment. Check the temperature of the sand bath regularly and carefully with a thermometer.

After heating the reaction mixture at 80 ^oC for at least 30 minutes, the resulting clear solution is cooled to room temperature and poured into a small Erlenmeyer flask. Rinse the round-bottomed flask with a little water. The solution is acidified by dropwise addition

of hydrochloric acid (4 M) to pH < 3 with magnetic stirring. Some water is added to the resulting white suspension in order to facilitate stirring.

The white precipitate is then filtered off by suction, washed with ample water (on the filter) and then washed twice with a small amount of di-isopropyl ether to remove most of the adhering water. The urea derivative **B** is left on the filter under suction for at least 3 minutes to remove as much solvent as possible.

A small amount of the obtained urea derivative **B** is retained for TLC-analysis later.

STEP 2

The urea derivative **B** is now transferred into a long-necked round-bottomed flask and hydrochloric acid (4 M, 3 cm^3) is added. A stirring bar is introduced and the suspension is stirred thoroughly whilst heating at 80 ^oC on a sand bath. A clear solution is obtained. After a reaction time of 30 minutes, the reaction mixture, which may already contain some precipitate, is cooled to room temperature. The obtained suspension is filtered by suction, washed thoroughly with water and finally washed twice with a small amount of di-isopropyl ether. The product is left on the filter under suction for at least 3 minutes. It is then collected on a filter paper and dried in the air for at least 30 minutes.

The final product **C**, its precursor **B** and starting material **A** (see above) are subjected to TLC-analysis. For this purpose small amounts of either compound are dissolved in a tiny amount of pure acetone. Small samples of these solutions are applied to a TLC plate, using the supplied capillary tubes. The analysis is carried out with two TLC plates in one run. The TLC-plates are developed with a solution of 2% formic acid in ethyl acetate as the eluent. After the elution the TLC-plates are analysed using a UV-lamp. The starting line, solvent front and the UV-active spots are clearly marked with a pencil. Copy the diagram in the box on the answer sheet. The R_f values are determined. Finally, the TLC-plate with the best analysis is wrapped in parafilm and placed in a plastic bag with a sealing strip.

The final product **C** is transferred into a sample vial of which the empty weight has been pre-determined (weight is indicated on the label). Weigh the vial with product and calculate the yield of the product **C**.

The examination committee will check the quality of the benzylhydantoin that you have prepared by determining its melting point using an automatic melting point apparatus.

SOLUTION

The competitors were expected to show the following data, tables, graphs or calculations on the answer sheet:

1. Mass of your starting material **A** (see label on the vial) in mg.
2. Amount of benzylhydantoin **C** obtained.
3. Calculation of the yield of benzylhydantoin **C** in %.
4. R_f value of urea derivative **B.**
5. R_f value of benzylhydantoin **C.**
6. A copy of the TLC diagram with indication of the front base line of the solvent.
7. Conclusions from the TLC analysis:

   Compound **B**: is pure; contains some **A**; contains several contaminants.

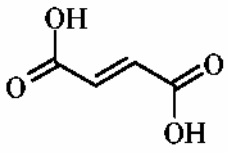
   Compound **C**: is pure; contains some **B**; contains some **A** and **B**; contains several contaminants.
8. Appearance of benzylhydantoin **C**: white colour, yellowish colour, sticky, crystalline, powder.
9. Melting point of benzylhydantoin **C** was determined by the examination committee.
10. The TLC plate was necessary to pack in an envelope and leave it to a laboratory superviser.

PROBLEM 3 (Practical)

Determination of Iron in Iron Pills

Introduction

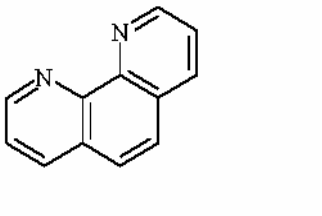
Iron is an essential component of hemoglobin, transporting oxygen in the blood to all parts of the body. It also plays a vital role in many metabolic reactions. Iron deficiency can cause anaemia resulting from low levels of hemoglobin in the blood. Iron deficiency is the most widespread mineral nutritional deficiency worldwide. One way to reduce iron shortage is by treatment with iron pills. The active ingredient in the iron pill to be examined, is iron(II) present as iron(II) fumarate. Besides this organic iron(II) compound the pill contains other compounds such as binding agents. The structure of fumaric acid is:



Fumaric acid

Iron(II) and 1,10-phenanthroline form an orange/red coloured complex $[(C_{12}H_8N_2)_3Fe]^{2+}$. The absorbance of this complex, determined at 510 nm in a buffer solution (pH=8) is a measure for the iron content of the iron pill. Since 1,10-phenanthroline only binds to iron(II) and iron(II) is readily oxidized to iron(III), hydroxylammonium chloride is added to reduce all iron(III) to iron(II). A simplified reaction scheme is:

$$2\ NH_2OH + 4\ Fe^{3+} \rightarrow\ N_2O + 4\ H^+ + H_2O + 4\ Fe^{2+}$$



1,10-Phenanthroline

Procedure

The weight of the iron pill is determined with an accuracy of 1 mg using a balance. The pill is carefully pulverized in a mortar and transferred quantitatively into a 100 cm^3 beaker with the aid of a small amount of distilled water. Hydrochloric acid (5 cm^3, 4 M) is added. The content of the beaker is heated up to approximately 60 ℃ on a hotplate. The solution turns a yellow colour.

The beaker is then placed in an ultrasonic bath for at least 5 minutes. The beaker is kept in place by styrofoam. The suspension is filtered by suction using a Hirsch funnel containing a small layer of moistened hi-flow filter aid pressed onto the filter. The hi-flow filter aid is washed with ample distilled water. The filtrate is carefully transferred into a volumetric flask (250 cm^3) and the final volume adjusted by adding distilled water and with regular mixing. An amount of 10 cm^3 is pipetted from this solution and transferred into a volumetric flask of 100 cm^3. Again the volume is adjusted with distilled water while mixing the content of the flask.

From this solution, 10 cm^3 is pipetted and transferred into a volumetric flask of 100 cm^3. Subsequently, 1,10-phenanthroline solution (10 cm^3) and hydroxylammonium chloride solution (1 cm^3) are added. Then the volume is adjusted with buffer solution (pH 8).

The absorbance of this solution is measured with a spectrophotometer at 510 nm against water as a blank in a 1.000 cm cell.

Calculate the amount of iron in the iron pill on basis of the known molar absorptivity (extinction coefficient, ε) of the iron(II)phenanthroline complex at 510 nm. The molar absorptivity of the iron(II)phenanthroline complex at 510 nm is 11100 $M^{-1}cm^{-1}$.

Important

In order to eliminate deviations in absorbance typically connected to the spectrophotometer used, a correction factor is denoted on the spectrophotometer you will be using for your experiment. The absorbance observed must be multiplied by this factor in order to obtain the correct absorbance of the solution of the iron complex.

SOLUTION

The competitors were expected to show the following data, tables, graphs or calculations:

1. Weight of the iron pill in mg.
2. Reading of the spectrophotometer and corrected absorbance.
3. Calculation of the concentration of iron(II)phenanthroline complex in the cell in mmol dm^{-3}.
4. Calculation of the total amount of iron(II) in the pill in mg.
5. Calculation of the iron content of the pill in weight %.

35th

IChO

International Chemistry Olympiad

35 theoretical problems
2 practical problems

THE THIRTY-FIFTH
INTERNATIONAL CHEMISTRY OLYMPIAD
5–14 JULY 2003, ATHENS, GREECE

THEORETICAL PROBLEMS

SECTION A: General Chemistry

QUESTION 1

The molar solubility s (mol dm^{-3}) of $Th(IO_3)_4$ as a function of the solubility product K_{sp} of this sparingly soluble thorium salt is given by the equation:

(a) $s = (K_{sp} / 128)^{1/4}$ ( )

(b) $s = (K_{sp} / 256)^{1/5}$ ( )

(c) $s = 256\ K_{sp}^{1/4}$ ( )

(d) $s = (128\ K_{sp})^{1/4}$ ( )

(e) $s = (256\ K_{sp})^{1/5}$ ( )

(f) $s = (K_{sp} / 128)^{1/5} / 2$ ( )

QUESTION 2

Which one of the following equations must be used for the exact calculation of $[H^+]$ of an aqueous HCl solution at any concentration c_{HCl}? ($K_w = 1\times10^{-14}$).

(a) $[H^+] = c_{HCl}$ ( )

(b) $[H^+] = c_{HCl} + K_w / [H^+]$ ( )

(c) $[H^+] = c_{HCl} + K_w$ ( )

(d) $[H^+] = c_{HCl} - K_w / [H^+]$ ( )

QUESTION 3

The molar mass of glucose ($C_6H_{12}O_6$) is 180 g mol^{-1} and N_A is the Avogadro constant. Which <u>one</u> of the following statements <u>is not correct</u>?

(a) An aqueous 0.5 M solution of glucose is prepared by dissolving 90 g of glucose to give 1000 cm^3 of solution. ( )

(b) 1.00 mmol amount of glucose has a mass of 180 mg. ( )

(c) 0.0100 mol of glucose comprises of $0.0100 \times 24 \times N_A$ atoms. ( )

(d) 90.0 g glucose contain $3 \times N_A$ atoms of carbon. ( )

(e) 100 cm^3 of a 0.10 M solution contain 18 g of glucose. ( )

QUESTION 4

If the density of a liquid compound B is ρ (in g cm^{-3}), M is the molar mass of B and N_A is the Avogadro constant, then the number of molecules of B in 1 dm^3 of this compound is:

(a) $(1000 \times \rho) / (M \times N_A)$ ( )

(b) $(1000 \times \rho \times N_A) / M$ ( )

(c) $(N_A \times \rho) / (M \times 1000)$ ( )

(d) $(N_A \times \rho \times M) / 1000$ ( )

QUESTION 5

The equilibrium constant of the reaction:

$Ag_2CrO_4(s) + 2\ Cl(aq)^- \rightleftharpoons 2\ AgCl(s) + CrO_4^{2-}(aq)$

is given by the equation:

(a) $K = K_{sp}(Ag_2CrO_4) / K_{sp}(AgCl)^2$ ( )

(b) $K = K_{sp}(Ag_2CrO_4) \times K_{sp}(AgCl)^2$ ( )

(c) $K = K_{sp}(AgCl) / K_{sp}(Ag_2CrO_4)$ ( )

(d) $K = K_{sp}(AgCl)^2 / K_{sp}(Ag_2CrO_4)$ ( )

(e) $K = K_{sp}(Ag_2CrO_4) / K_{sp}(AgCl)$ ( )

QUESTION 6

How many cm^3 of 1.00 M NaOH solution must be added to 100.0 cm^3 of 0.100 M H_3PO_4 solution to obtain a phosphate buffer solution with *pH* of about 7.2? (The *pK* values for H_3PO_4 are $pK_1 = 2.1$, $pK_2 = 7.2$, $pK_3 = 12.0$)

(a) 5.0 cm^3 ( )

(b) 10.0 cm^3 ( )

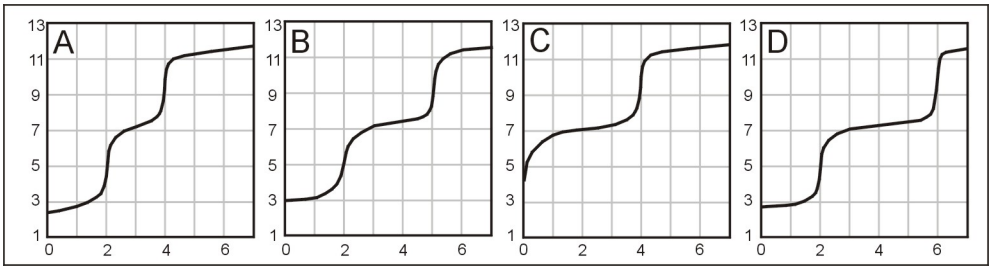
(c) 15.0 mL ( )

(d) 20.0 mL ( )

QUESTION 7

Solutions containing H_3PO_4 and/or NaH_2PO_4 are titrated with a strong base standard solution. Associate the contents of these solutions with the titration curves (*pH vs*. volume of titrant) shown in the figure:

(For H_3PO_4: pK_1 = 2.1, pK_2 = 7.2, pK_3 = 12.0)



a) The sample contains H_3PO_4 only.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

b) The sample contains both in a mole ratio H_3PO_4 : NaH_2PO_4 = 2 : 1.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

c) The sample contains both in a mole ratio H_3PO_4 : NaH_2PO_4 = 1 : 1.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

QUESTION 8

A fuel/oxidant system consisting of N,N-dimethylhydrazine $(CH_3)_2NNH_2$ and N_2O_4 (both liquids) is commonly used in space vehicle propulsion. Components are mixed stoichiometrically so that N_2, CO_2 and H_2O are the only products (all gases under the same reaction conditions). How many moles of gases are produced from 1 mol of $(CH_3)_2NNH_2$?

(a) 8 ( )

(b) 9 ( )

(c) 10 ( )

(d) 11 ( )

(e) 12 ( )

QUESTION 9

The complete electrolysis of 1 mol of water requires the following amount of electric charge (F is the Faraday constant):

(a) F ( )

(b) (4/3) F ( )

(c) (3/2) F ( )

(d) 2 F ( )

(e) 3 F ( )

QUESTION 10

Identify particle X in each of the following nuclear reactions:

a) $^{68}_{30}Zn + {}^{1}_{0}n \rightarrow {}^{65}_{28}Ni + X$ alpha ( ), beta ( ), gamma ( ), neutron ( )

b) $^{130}_{..52}Te + {}^{2}_{1}H \rightarrow {}^{131}_{..53}I + X$ alpha ( ), beta ( ), gamma ( ), neutron ( )

c) $^{214}_{..82}Pb \rightarrow {}^{214}_{83}Bi + X$ alpha ( ), beta ( ), gamma ( ), neutron ( )

d) $^{23}_{11}Na + {}^{1}_{0}n \rightarrow {}^{24}_{11}Na + X$ alpha ( ), beta ( ), gamma ( ), neutron ( )

e) $^{19}_{..9}F + {}^{1}_{0}n \rightarrow {}^{20}_{..9}F + X$ alpha ( ), beta ( ), gamma ( ), neutron ( )

QUESTION 11

10.0 cm^3 of 0.50 M HCl and 10.0 cm^3 of 0.50 M NaOH solutions, both at the same temperature, are mixed in a calorimeter. A temperature increase of ΔT is recorded. Estimate the temperature increase if 5.0 cm^3 of 0.50 M NaOH were used instead of 10.0 cm^3. Thermal l osses are negligible and the specific heats of both solutions are taken as equal.

(a) (1/2) ΔT ( )

(b) (2/3) ΔT ( )

(c) (3/4) ΔT ( )

(d) ΔT ( )

QUESTION 12

Natural antimony consists of the following 2 stable isotopes: ^{121}Sb, ^{123}Sb. Natural chlorine consists of the following 2 stable isotopes: ^{35}Cl, ^{37}Cl. Natural hydrogen consists of the following 2 stable isotopes: ^{1}H, ^{2}H. How many peaks are expected in a low resolution mass spectrum for the ionic fragment $SbHCl^{+}$?

(a) 4 ( )

(b) 5 ( )

(c) 6 ( )

(d) 7 ( )

(e) 8 ( )

(f) 9 ( )

QUESTION 13

The smallest diffraction angle of a monochromatic beam of X-rays in a certain experiment is 11.5°. Based on this we must expect a beam of X-rays diffracted at:

(a) 22.0 degrees ( )

(b) 22.5 degrees ( )

(c) 23.0 degrees ( )

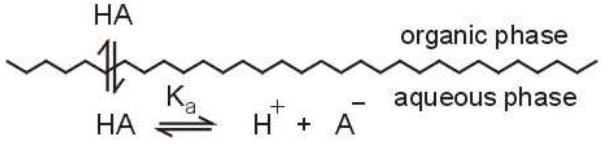
(d) 23.5 degrees ( )

(e) 24.0 degrees ( )

(f) 24.5 degrees ( )

QUESTION 14

The undissociated form of a weak organic acid HA can be extracted from the aqueous phase by a water-immiscible organic solvent according to the scheme:



Regarding this extraction, are the following statements correct (Y) or not (N)?

(a) The distribution constant (K_D) of the acid HA depends on the *pH* of the aqueous phase. (Y) (N)

(b) HA can be efficiently extracted only from acidic aqueous solutions. (Y) (N)

(c) The distribution ratio (D) of the acid HA depends on the pH of the aqueous phase. (Y) (N)

(d) The distribution ratio (D) of the acid HA depends mainly on its concentration. (Y) (N)

QUESTION 15

Regarding Beer's law, are the following statements correct (Y) or not (N)?

(a) The absorbance is proportional to the concentration of the absorbing compound. (Y) (N)

(b) The absorbance is linearly related to the wavelength of the incident light. (Y) (N)

(c) The logarithm of transmittance is proportional to the concentration of the absorbing compound. (Y) (N)

(d) The transmittance is inversely proportional to the logarithm of absorbance. (Y) (N)

(e) The transmittance is inversely proportional to the concentration of the absorbing compound. (Y) (N)

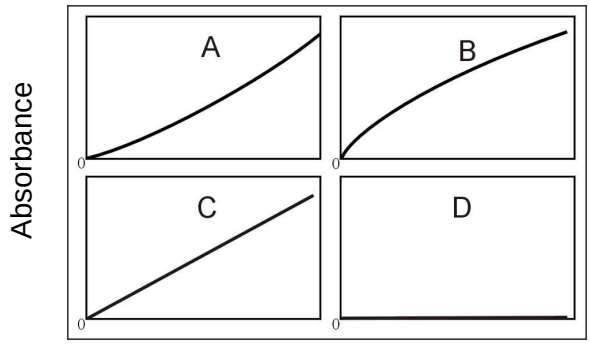
QUESTION 16

Calculate the corresponding wavelength in nanometers (nm) for monochromatic radiation with the following numerical characteristics:

a)	3000 Å	150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )
b)	5×10^{14} Hz	150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )
c)	2000 cm^{-1}	150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )
d)	2×10^{6} GHz	150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )

QUESTION 17

The absorbance of solutions of the weak acid HX were obtained. Associate the expected form of the resulting working curve with those shown in figure, under the following conditions:



a) Pure aqueous solutions of HX were used. Only the undissociated species HX absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

b) Pure aqueous solutions of HX were used. Only the anionic species X^- absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

c) All solutions of HX contain an excess of a strong base. Only the undissociated HX species absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

d) All solutions of HX contain an excess of a strong acid. Only the undissociated HX species absorb. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

e) Pure aqueous solutions of HX were used. Both HX and X^- absorb. Measurements were obtained at a wavelength where the molar absorptivities of X^- and HX are equal and different than zero. Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

QUESTION 18

Which of the following acids is the strongest?

a) perchloric acid, $HClO_4$ ( )

b) chloric acid, $HClO_3$ ( )

c) chlorous acid, $HClO_2$ ( )

d) hypochlorous, HClO ( )

(e) All of them are equally strong because they all contain chlorine ( )

QUESTION 19

Which structure describes best the crystal system of iron in which the coordination number is 8?

a) simple cubic ( )

b) body-centered cubic ( )

c) cubic closest packed ( )

d) hexagonal closest packed ( )

e) none of the above ( )

QUESTION 20

Which of the following elements has the largest third ionization energy?

a) B ( )

b) C ( )

c) N ( )

d) Mg ( )

e) Al ( )

QUESTION 21

Which second period (row) element has the first six ionization energies (*IE* in electron volts, eV) listed below?

IE_1	IE_2	IE_3	IE_4	IE_5	IE_6
11	24	48	64	392	490

a) B ( )

b) C ( )

c) N ( )

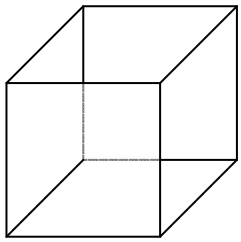
d) O ( )

e) F ( )

QUESTION 22

Silver metal exists as a face-centered cubic (fcc) packed solid.

a) Draw an fcc unit cell.



b) How many atoms are present in the fcc unit cell?

c) The density of silver has been determined to be 10.5 g cm^{-3} . What is the length of each edge of the unit cell?

d) What is the atomic radius of the silver atoms in the crystal?

QUESTION 23

Are the following statements correct (Y) or not (N)?

a) HF boils at a higher temperature than HCl. (Y) (N)

b) HBr boils at a lower temperature than HI (Y) (N)

c) Pure HI can be produced by reacting concentrated sulfuric acid with KI. (Y) (N)

d) Ammonia solutions are buffer solutions because they contain the conjugate pair $NH_3 – NH_4^+$. (Y) (N)

e) Pure water at 80 ℃ is acidic. (Y) (N)

f) During electrolysis of an aqueous KI solution with graphite electrodes, the *pH* near the cathode is below 7. (Y) (N)

QUESTION 24

Under certain conditions of concentration and temperature HNO_3 reacts with Zn and its reduction products are NO_2 and NO in a molar ratio 1 : 3. How many moles of HNO_3 are consumed by 1 mol of Zn?

a) 2.2 ( )

b) 2.4 ( )

c) 2.6 ( )

d) 2.8 ( )

e) 3.0 ( )

f) 3.2 ( )

SOLUTIONS FOR SECTION A

1: (b); :

2: (b);

3: (e) is not correct;

4: (b);

5: (a);

6: (c);

7: **a)** curve A;

b) curve B;

c) curve D;

8: (b);

9: (d);

10: **a)** alpha;

b) neutron;

c) beta;

d) gamma;

e) gamma;

11: (b);

12: (c);

13: (d);

14: **a)** N;

b) Y;

c) Y;

d) N;

15: **a)** Y;

b) N;

c) Y;

d) N;

e) N;

16: **a)** 300 nm;

b) 600 nm;

c) 5000 nm;

d) 150 nm;

17: **a)** Curve A;

b) Curve B;

c) Curve D;

d) Curve C;

e) Curve C;

18: (a);

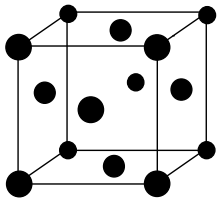
19: (b);

20: (d);

21: (b);

22:

a)



b) 4 atoms,

c) The length of each edge of the unit cell is 0.409 nm,

d) The atomic radius of the silver atoms in the crystal is 0.145 nm.

23: **a)** Y;

b) Y;

c) N;

d) N;

e) N;

f) N;

24: (d)

SECTION B: PHYSICAL CHEMISTRY

PROBLEM 25 Muon

The muon (μ) is a subatomic particle of the lepton family which has same charge and magnetic behavior as the electron, but has a different mass and is unstable, i.e., it disintegrates into other particles within microseconds after its creation. Here you will attempt to determine the mass of the muon using two rather different approaches.

a) The most common spontaneous disintegration reaction for the muon is:

$\mu \rightarrow e + \bar{\nu}_e + \nu_\mu$,

where $\bar{\nu}_e$ is the electron antineutrino, and ν_μ the muon neutrino. In a given experiment using a stationary muon, $\bar{\nu}_e + \nu_\mu$, carried away a total energy of 2.000×10^{-12} J, while the electron was moving with a kinetic energy of 1.4846×10^{-11} J. Determine the mass of the muon.

b) Many experiments have studied the spectroscopy of atoms that have captured a muon in place of an electron. These exotic atoms are formed in a variety of excited states. The transition from the third excited state to the first excited state of an atom consisting of a ^{1}H nucleus and a muon attached to it was observed at a wavelength of 2.615 nm. Determine the mass of the muon.

SOLUTION

a) Energy of a stationary muon:

$E_\mu = m_\mu c^2 = E_e + E_{\nu,\nu}$

$m_\mu c^2 = m_e c^2 + (T_e + E_{\nu,\nu})$

$$m_\mu = \frac{m_e + (T_e + E_{\nu,\nu})}{c^2} = \frac{9.109\times10^{-31} + (1.4846\times10^{-11} + 2.000\times10^{-12})}{(2.998\times10^8)^2} =$$

$= 1.883\times10^{-28}$ kg

b) From Bohr theory:

$$E_n = -\frac{me^4}{2n^2h^2} = -109700\ \text{cm}^{-1} \times \frac{1}{n^2} \times \left(\frac{m}{m_e}\right),$$

where

$$m = \frac{m_\mu\, m_H}{m_\mu + m_H}$$

$$\lambda = \frac{1}{E_4 - E_2} = \frac{1}{109700\left(\frac{m}{m_e}\right)\left(\frac{1}{4} - \frac{1}{16}\right)} = 2.615\times10^{-7}\ \text{cm}$$

$$\frac{m}{m_e} = 185.9$$

$$m = 185.9 \times 9.109\times10^{-31} = 1.693\times10^{-28}\ \text{kg}$$

The mass of a proton from Tables attached :

$m_H = 1.673\times10^{-27}$ kg

$$m_\mu = \frac{m\, m_H}{m_H - m} = \frac{1.693\times10^{-28}\ \times\ 1.673\times10^{-27}}{1.673\times10^{-27} - 1.693\times10^{-28}} = 1.884\times10^{-28}\ \text{kg}$$

PROBLEM 26 Spectrum of CO

Rotational energy levels of diatomic molecules are well described by the formula $E_J = B\ \mathrm{J(J+1)}$, where J is the rotational quantum number of the molecule and B its rotational constant. Constant B is related to the reduced mass μ and the bond length R of the molecule through the equation

$$B = \frac{h^2}{8\pi^2 \mu R^2}\,.$$

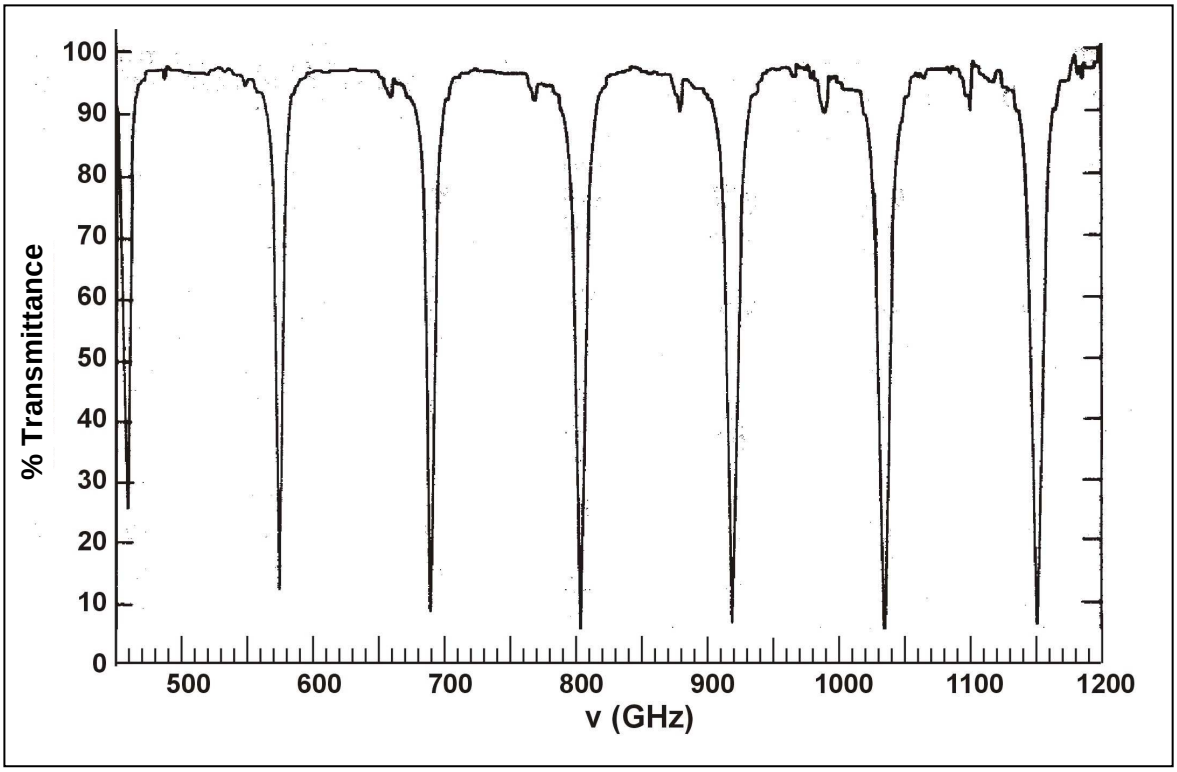
In general, spectroscopic transitions appear at photon energies which are equal to the energy difference between appropriate states of a molecule ($h\ \nu = \Delta E$). The observed rotational transitions occur between adjacent rotational levels, hence $\Delta E = E_{J+1} - E_J = 2\ B\ (J+1)$. Consequently, successive rotational transitions that appear on the spectrum (such as the one shown here) follow the equation $h\ (\Delta \nu) = 2\ B$.

By inspecting the spectrum provided, determine the following quantities for $^{12}C^{16}O$ with appropriate units:

a) $\Delta \nu$

b) B

c) R



SOLUTION

a) For example: $\Delta\nu$ = 1150 – 1035 = 115 GHz

b) $$B = \frac{h\ \Delta\nu}{2} = \frac{6.63\times10^{-34}\times115\times10^{9}}{2} = 3.81\times10^{-23}\ \text{J}$$

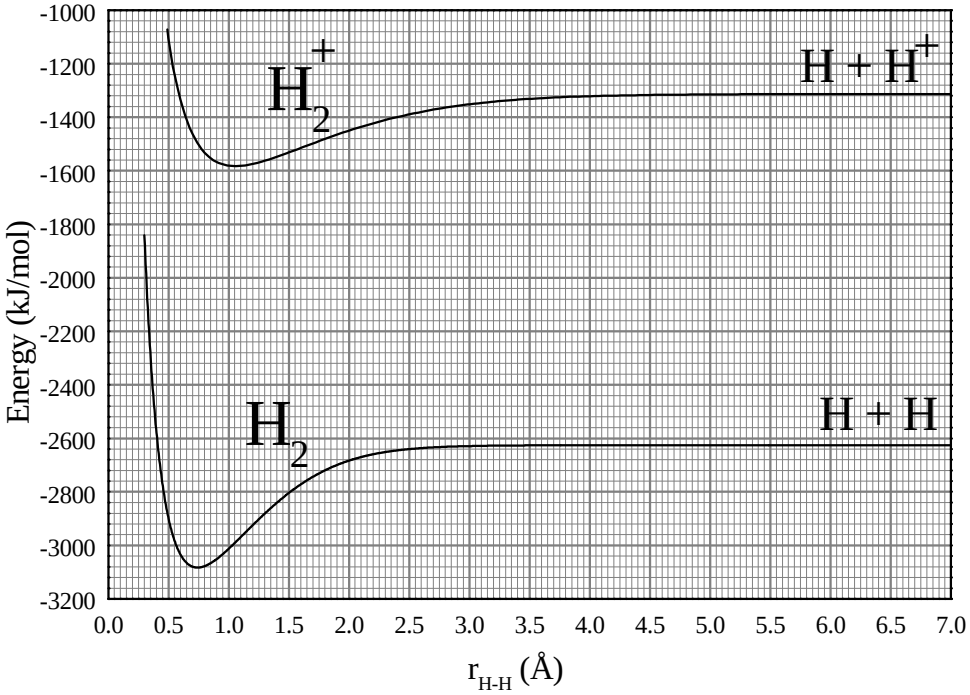
c) $$\mu = \frac{m(\text{C})\times m(\text{O})}{m(\text{CO})} = \frac{12\times16}{28} = 6.86\ \text{a.u.} = 1{,}14\times10^{-26}\ \text{kg}$$

For interatomic distance *R*:

$$R = \frac{h}{2\pi\sqrt{2\mu B}} = \frac{6.63\times10^{-34}}{2\times3.14\sqrt{2\times1.14\times10^{-26}\times3.81\times10^{-23}}} = 1.13\times10^{-10}\ \text{m} = 1.13\ \text{Å}$$

PROBLEM 27 Hydrogen molecule

Using the information provided on this graph, give numerical answers with appropriate units to the following questions:



1. What are the equilibrium bond lengths of H_2 and H_2^+?
2. What are the binding energies of H_2 and H_2^+?
3. What is the ionisation energy of the H_2 molecule?
4. What is the ionisation energy of the H atom?
5. If we use electromagnetic radiation of frequency 3.9×10^{15} Hz in order to ionise H_2, what will be the velocity of the extracted electrons? (Ignore molecular vibrational energy.)

SOLUTION

1. The equilibrium bond lengths of H_2 and H_2^+ can be read from the minimum of the curves: $r(H_2) = 0.75$ Å; $r(H_2^+) = 1.05$ Å

2. The binding energies of H_2 and H_2^+ can be calculated as the differences in the values for infinitive bond lengths and those for minima of the particular curves:

$E_{bond}(H_2) = -2620 - (-3080) = 460$ kJ mol^{-1}

$E_{bond}(H_2^+) = -1310 - (-1580) = 270$ kJ mol^{-1}

3. The ionization energy $E_{ion}(H_2)$:

$E_{ion}(H_2) = -1580 - (-3080) = 1500$ kJ mol^{-1}

4. $E_{ion}(H) = -1310 - (-2620) = 1310$ kJ mol^{-1}

5. $H_2 + h\nu \rightarrow H_2^+ + e^-$

$$E(H_2) + h\nu \rightarrow E(H_2^+) + \frac{m_e v_e^2}{2}$$

$$v_e = \sqrt{\frac{2\,(E(H_2) - E(H_2^+) + h\nu}{m_e}} =$$

$$= \sqrt{\frac{2\left(\frac{-3080\times10^3 - (-1510\times10^3)}{6.02\times10^{23}}\right) + 6.63\times10^{-34}\times4.1\times10^{15}}{9.11\times10^{-31}}} = 492\times10^3 \text{ m s}^{-1}$$

PROBLEM 28 Cryoscopy

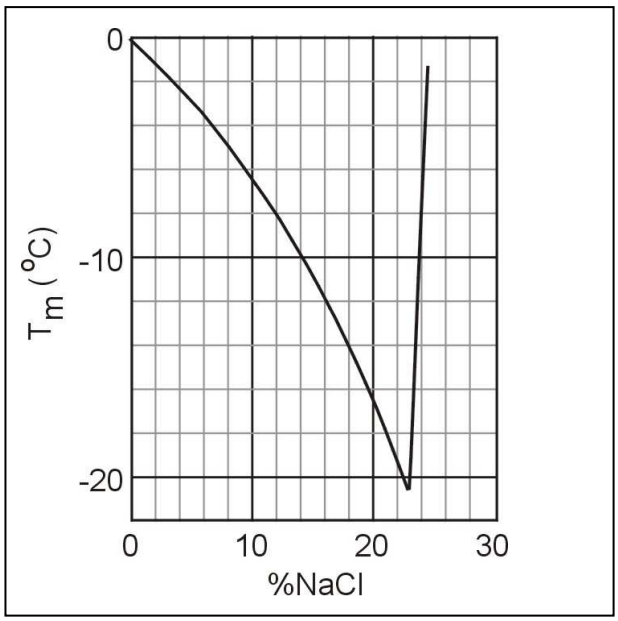
Chemists often need a bath in which to carry out a process that has a temperature below the water freezing point (0 °C) and well above the CO_2 sublimation point (–78 °C) this case they mix water ice prepared at its melting point and NaCl. Depending on the quantities used temperatures as low as –20 °C can be reached.

We prepare a cold bath mixing 1 kg of ice at 0 °C with 150 g of NaCl in a thermally insulated container. Circle the letters Y or N to indicate if the following statements are correct (Y) or not (N).

a) The mixing process is spontaneous. (Y) (N)

b) The change of entropy during the mixing process is negative. (Y) (N)

c) The following diagram depicts the freezing point of aqueous solutions of NaCl as a function of the composition of the solution (per cent by weight). What is is the freezing point of the bath based on the diagram?



d) If an equal mass of $MgCl_2$ were used instead of NaCl, would the freezing point be higher? (Y) (N)

SOLUTION

The correct answers are as follows:

a) Y (Yes)

b) N (No)

c) The freezing point of the bath is –9 °C.

d) Y (Yes)

PROBLEM 29 Pool

A very large swimming pool filled with water of temperature equal to 20 ^{o}C is heated by a resistor with a heating power of 500 W for 20 minutes. Assuming the water in the pool is not in any contact with anything besides the resistor, determine:

a) The heat delivered to the water.

b) Is the change of entropy of the resistor positive, negative, or zero?

(i) $\Delta S_{res} > 0$ ( )

(ii) $\Delta S_{res} = 0$ ( )

(iii) $\Delta S_{res} < 0$ ( )

c) Is the change of entropy of the water positive, negative, or zero?

i) $\Delta S_{pool} > 0$ ( )

(ii) $\Delta S_{pool} = 0$ ( )

(iii) $\Delta S_{pool} < 0$ ( )

d) Is the change of entropy of the system positive, negative, or zero?

(i) $\Delta S_{total} > 0$ ( )

(ii) $\Delta S_{total} = 0$ ( )

(iii) $\Delta S_{total} < 0$ ( )

e) Is the process reversible? (Y) (N)

SOLUTION

a) Q = 500 W$\times$ 20 min $\times$ 60 = 600 kJ

b) $\Delta S_{res} = 0$

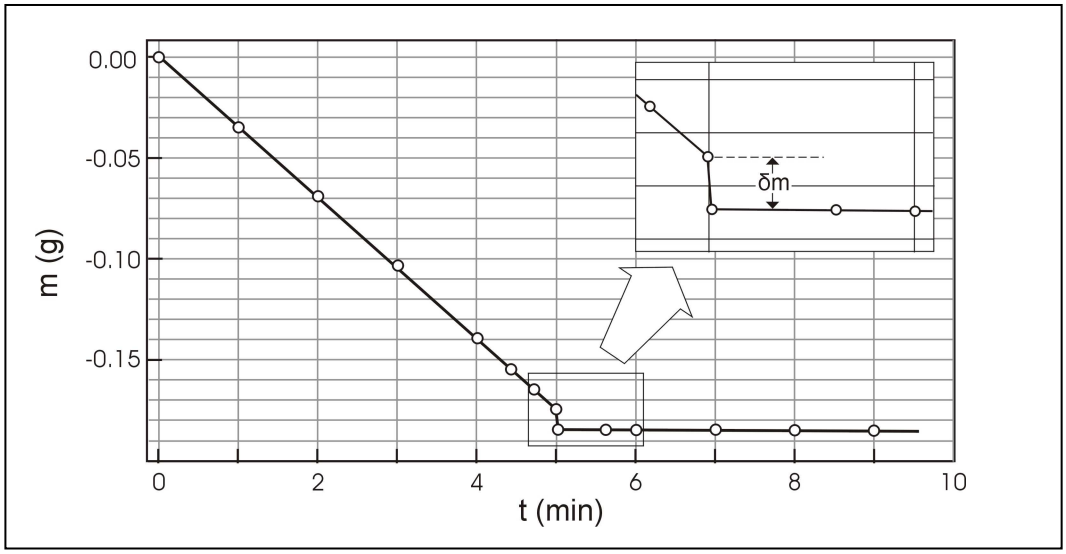
c) $\Delta S_{pool} > 0$

d) $\Delta S_{total} > 0$

e) The answer is No (N).

PROBLEM 30 Gas velocity

The experiment described here gives a simple way to determine the mean velocity *u* of the molecules in the gas phase of a volatile liquid. A wide shallow container (a Petri dish) half filled with ethanol is placed on an electronic balance with its lid next to it and the balance is zeroed at time *t* = 0. Balance readings are recorded as shown on the diagram.



At *t* = 5 min the lid is placed over the dish. The liquid no longer evaporates, but the trapped molecules push against the lid, hence lowering the measurement of the balance by δm. Therefore, the force exerted on the lid is $f = \delta m\, g$. The force is also equal to the rate of change of the momentum of the evaporating molecules, i.e., $f = \frac{1}{2} u\, \mathrm{d}m/\mathrm{d}t$. Using the data provided determine the mean velocity of ethanol molecules at 290 K. Assume $g = 9.8\ \mathrm{m\ s^{-2}}$.

SOLUTION

$$\frac{dm}{dt} = \frac{\Delta m}{\Delta t} = \frac{0.14\ \mathrm{g}}{4\ \mathrm{min}} = 0.035\ \mathrm{g\,min^{-1}} = 5.8\times10^{-4}\ \mathrm{g\,s^{-1}}$$

$$\delta m\ g = \frac{1}{2} u \frac{dm}{dt}$$

$$u = \frac{0.01\times 9.81\times 2}{5.8\times10^{-4}} = 338\ \mathrm{m\,s^{-1}}$$

SECTION C: Organic Chemistry

PROBLEM 31 Ester identification

2.81 g of an optically active diester **A**, containing only C, H and O were saponified with 30.00 cm^3 of a 1.00 M NaOH solution. Following the saponification, the solution required 6.00 cm^3 of a 1.00 M HCl solution to titrate the unused NaOH only. The saponification products were an optically inactive dicarboxylic acid **B**, MeOH and an optically active alcohol **C**. Alcohol **C** reacted with I_2/NaOH to give a yellow precipitate and C_6H_5COONa. The diacid **B** reacted with Br_2 in CCl_4 to give a single, optically inactive product (compound **D**). Ozonolysis of **B** gave only one product.

a) Determine the molecular mass of compound **A**.

b) Give the structural formulas of **A**, **B**, and **C** without stereochemical information.

c) Give the possible stereochemical formulas (with bold and dashed bonds) for **C**.

d) Give the stereochemical formula for **D**, using a Fischer projection.

e) Give the stereochemical formula for **B**.

The diester **A** also reacted with Br_2 in CCl_4 and was converted to a mixture of two compounds (**E**, **F**) both optically active.

f) Give all the possible stereochemical formulas for **E** and **F**, using Fischer projections. Name all the stereogenic centers as either *R* or *S* on all the formulas.

If we use $Na^{18}OH$ for the saponification of compound **A**, would the oxygen isotope be incorporated in (either or both of) the products **B** and **C**?

g) Mark the correct answer:

i) Only **B** ( )

ii) Only **C** ( )

iii) Both **B** and **C** ( )

SOLUTION

a) For reaction with diester A 30 – 6 = 24 cm^3 of 1.00 M NaOH (0.024 mol NaOH)

Reaction:

ROOC – X – COOR + 2 NaOH $\rightarrow$ NaOOC – X – COONa + 2 ROH

The amount of diester: 0.024 mol / 2 = 0.012 mol

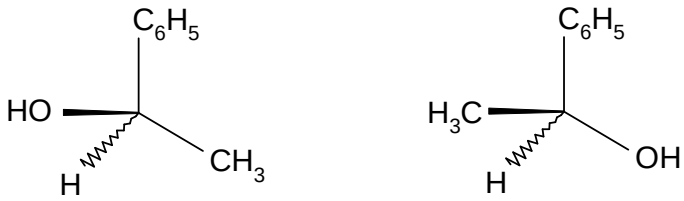
M(A) = 2.81 g / 0.012 mol = 234 g mol^{-1}

b) **A**: $H_3COCO\text{-}CH{=}CH\text{-}COO(CH_3)C_6H_5$

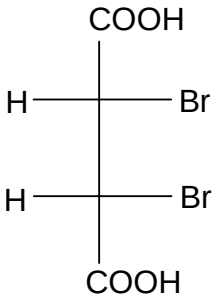
B: HOOC-CH=CH-COOH

C: $C_6H_5CH(OH)CH_3$

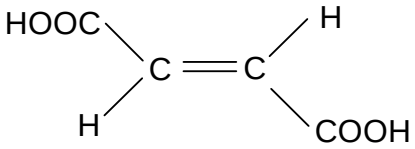
c) Possible stereochemical formulas for **C**:



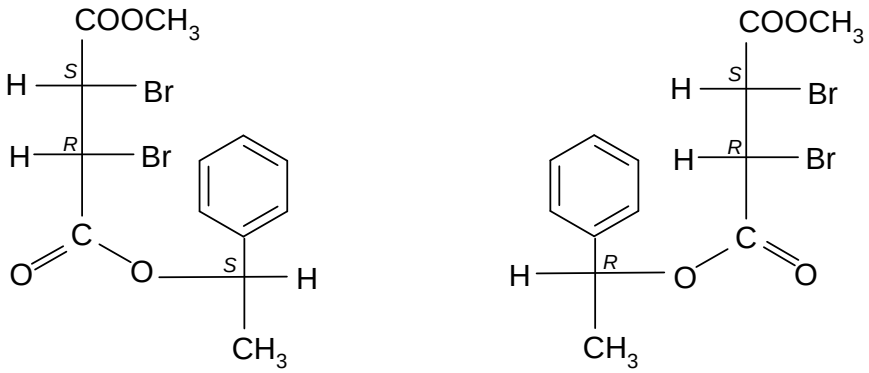
d) Stereochemical formula for **D**:



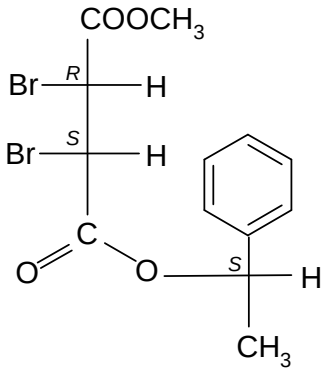
e) Stereochemical formula for **B**:

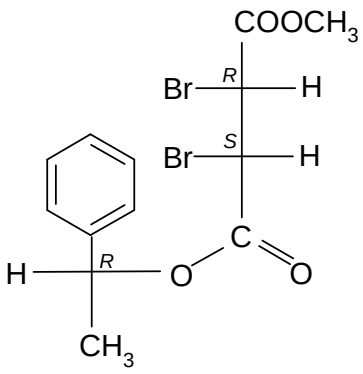


f) Possible stereochemical formula(s) for **E**:



Possible stereochemical formula(s) for **F**:

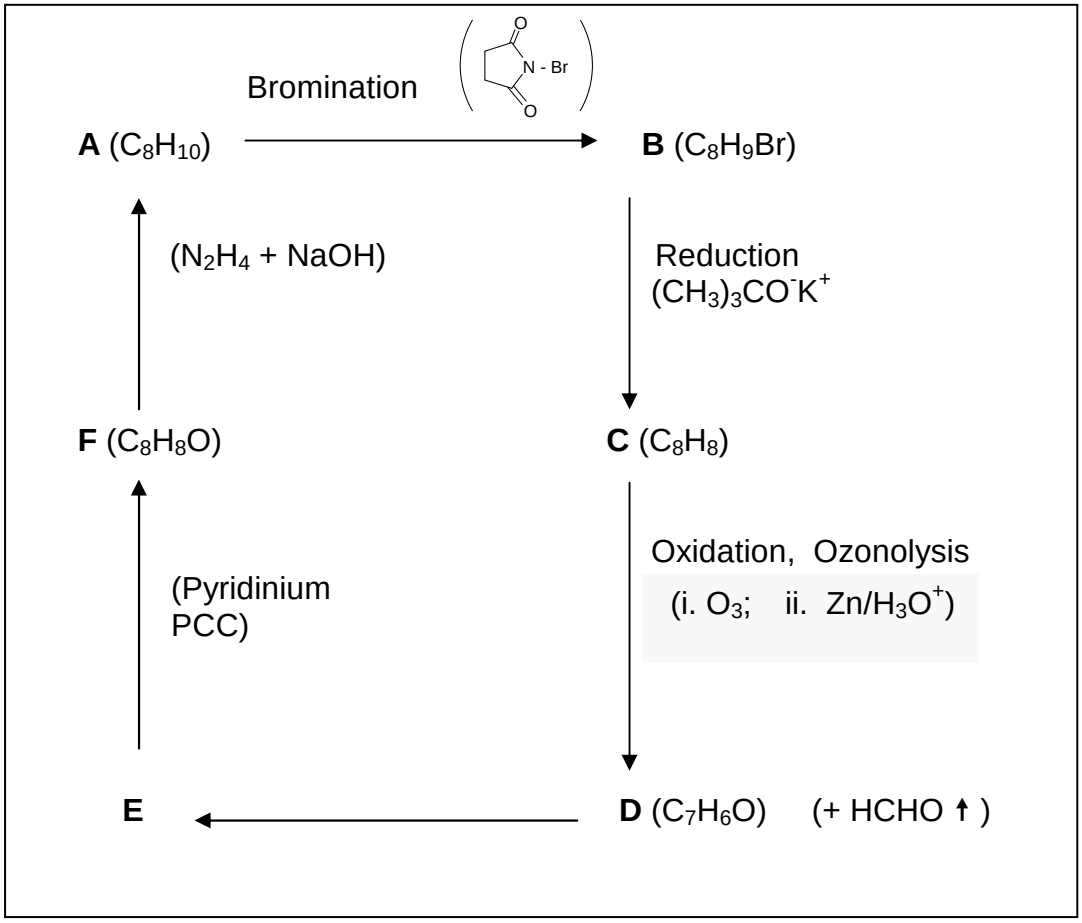




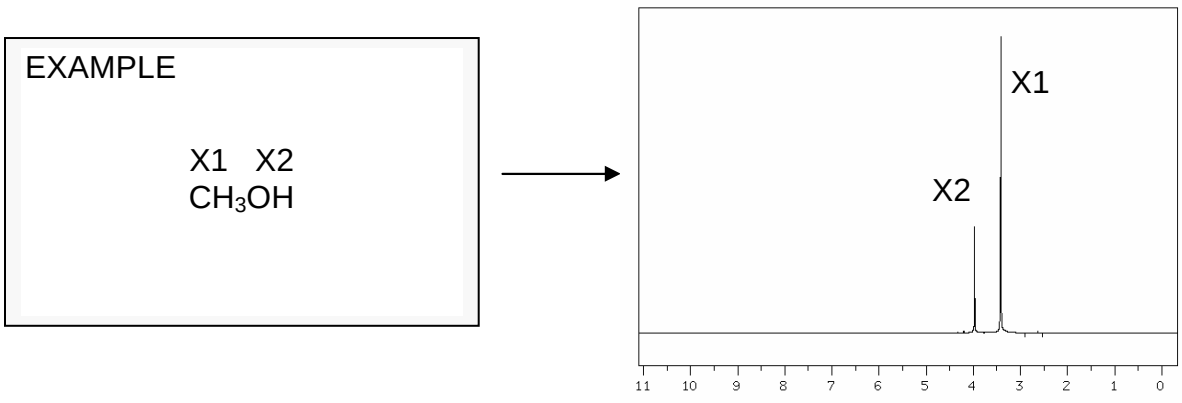
g) Correct answer is ii).

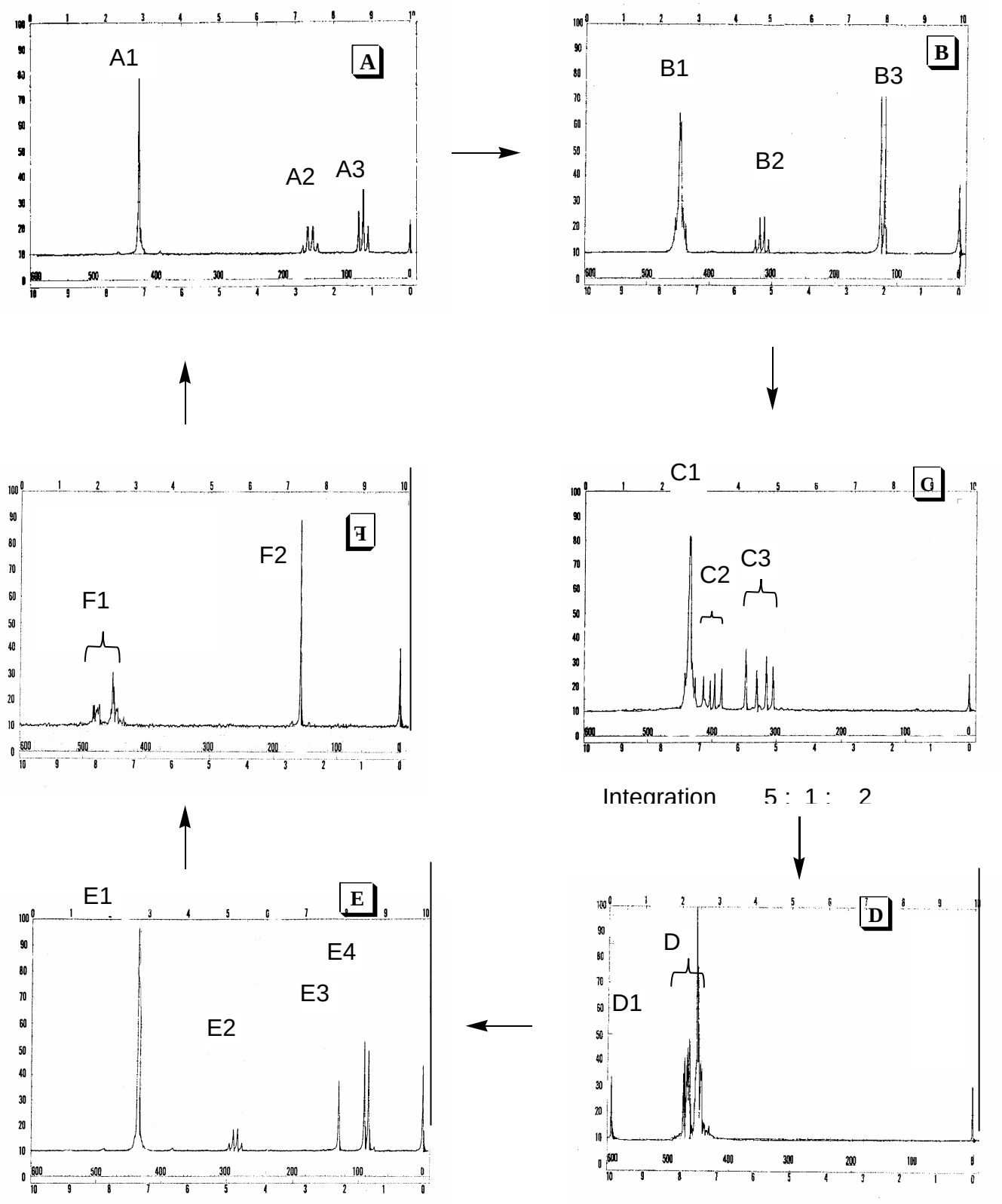
PROBLEM 32 NMR puzzle

An organic compound **A** (C_8H_{10}) gives the following chain of reactions:



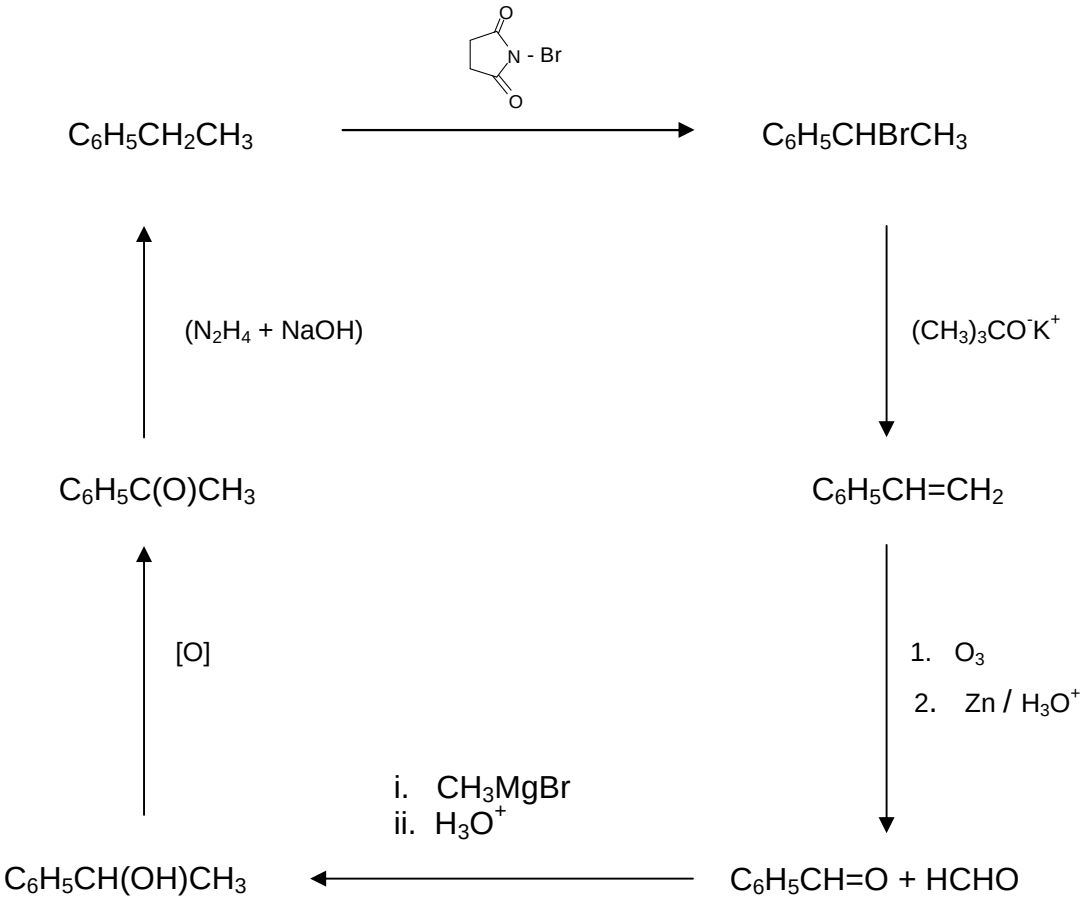
Based on the ^{1}H-NMR spectra given, draw the structures of compounds **A**, **B**, **C**, **D**, **E** and **F**, and match the groups of the hydrogen atoms of each compound to the corresponding ^{1}H-NMR peaks, as shown in the example.

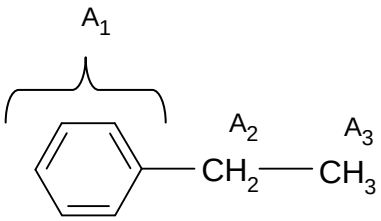




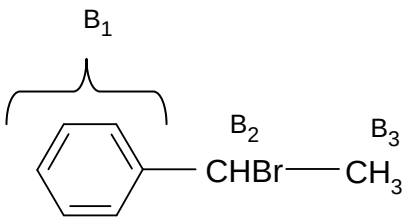
General remarks: NMR spectra were ecorded in $CDCl_3$ on a 60 MHz Perkin Elmer Spectrometer. Under ordinary conditions (exposure to air, light and water vapour) acidic impurities may develop in $CDCl_3$ solutions and catalyse rapid exchange of some particular protons.

SOLUTION

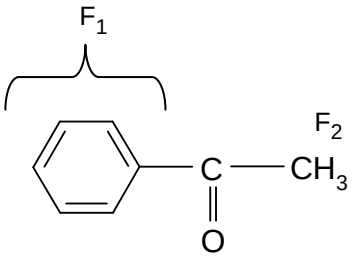




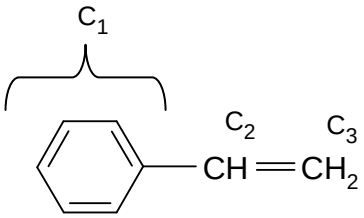
A



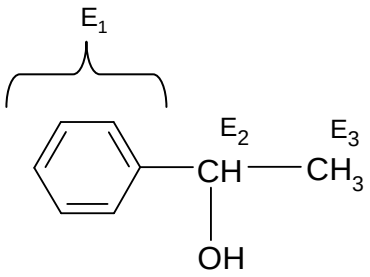
B



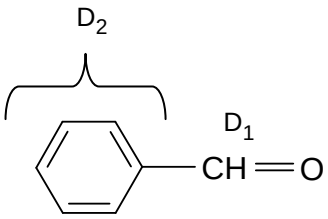
F



C



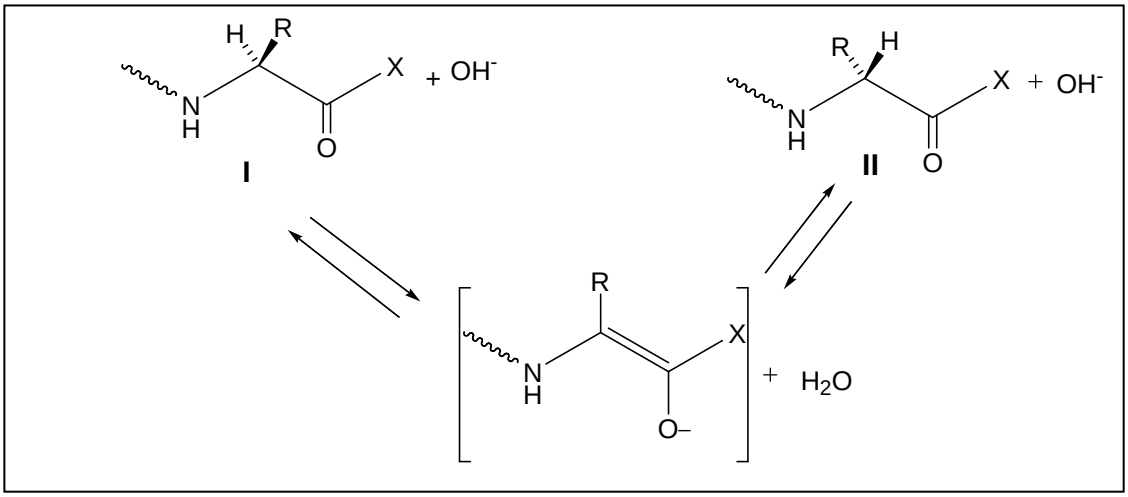
E



D

PROBLEM 33 Peptides

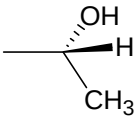
Racemization of α-aminoacids and peptides can occur by an α-enolization mechanism and both heat and the presence of strong bases greatly accelerate the process:



intermediate

1. Draw stereochemical formulas **I** and **II** (with bold and dashed bonds) for the aminoacid components of the mixture that has reached equilibrium through the α-enolization mechanism described above operating on each of the following hydroxyaminoacids **A** and **B**:

A: serine (R = $-CH_2OH$)

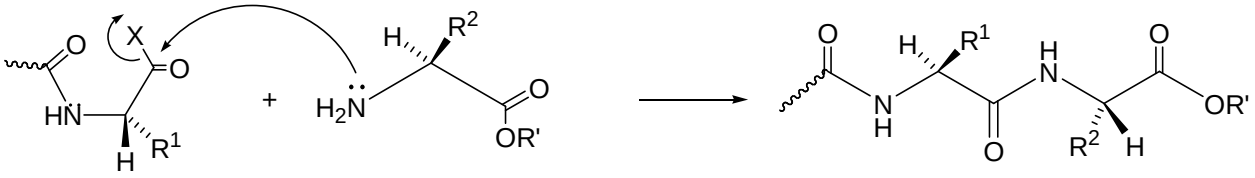
B: (2*S*,3*R*)-threonine (R = 

)

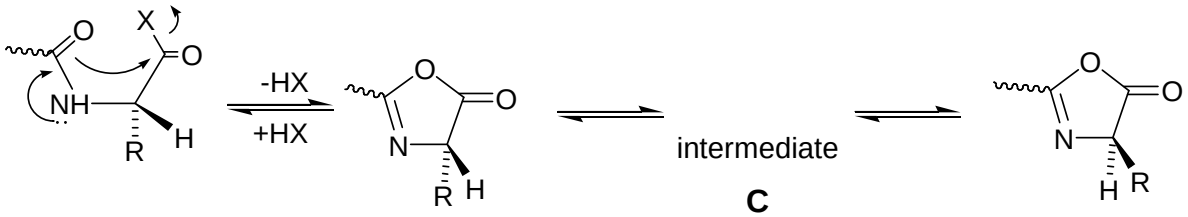
2. Mark the box that corresponds to the correct definition of the relationship between the structures you have drawn in each of the above cases A and B.

	enantiomers	diastereomers
A I, II	☐	☐
	enantiomers	diastereomers
B I ,II	☐	☐

During peptide synthesis, in order to form a new peptide bond the carboxyl group has to be activated, that is, it must bear a good leaving group, represented in a simplified scheme below:



It is at this stage of the synthesis that a second racemization mechanism may occur; the amidic carbonyl oxygen is five atoms away from the activated carboxyl group and can intramolecularly attack the activated carboxyl forming a five membered cyclic intermediate (an azalactone) which quickly equilibrates its hydrogen at the stereogenic center, represented in a simplified scheme below:



azalactone intermediate **C** azalactone

3. Write the structural formula for the intermediate **C** that interconverts the two azalactones and thus explains the scrambling of the stereochemistry at the stereogenic center.

Azalactones are very reactive substances that can still react with the amino group of an aminoacid. Therefore, the coupling reaction can proceed to completion albeit affording racemized or epimerized products.

4. If *N*-benzoyl glycine, $C_9H_9NO_3$, is warmed to 40 ˚C with acetic anhydride it is converted into a highly reactive substance, $C_9H_7NO_2$ (**P_1**).

a) Propose a structure for substance **P_1**.

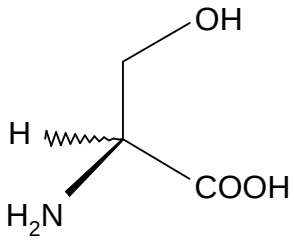
b) Write the reaction product(s) of the substance **P_1** with *S*-alanine ethyl ester (**P_2**) (the side chain R of the aminoacid alanine is a methyl group) using

stereochemical formulas (with bold and dashed bonds) for both reactants and product.

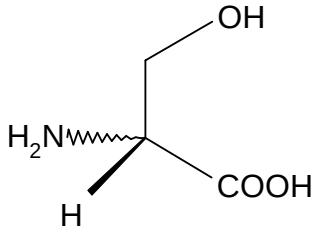
SOLUTION

1.

A:

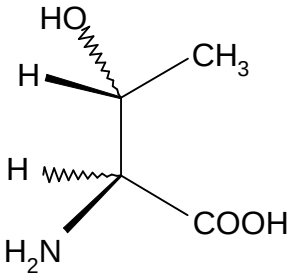


I

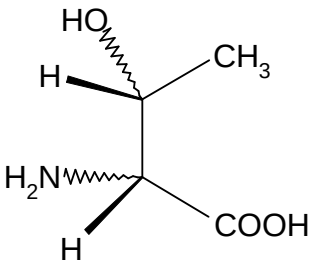


II

B:



I

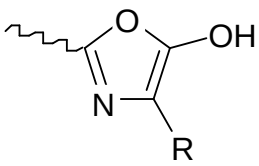


II

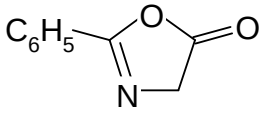
2. **A(I)** and **A(II)** are enantiomers**.**

B(I) and **B(II)** are diastereomers**.**

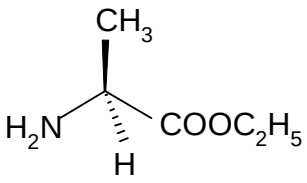
3. Intermediate **C**



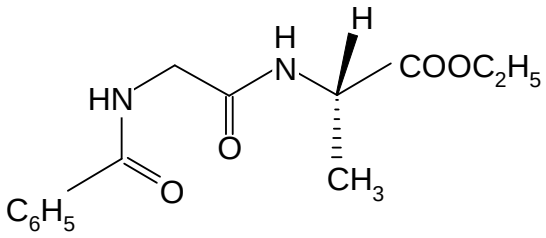
4.



Substance **P_1**



Ester **P_2**



Product

SECTION D: Inorganic Chemistry

PROBLEM 34 Aluminium

One of the largest factories in Greece, located near the ancient city of Delphi, produces alumina (Al_2O_3) and aluminium metal using the mineral bauxite mined from the Parnassus mountain. Bauxite is a mixed aluminium oxide hydroxide – $AlO_x(OH)_{3-2x}$ where $0<x<1$.

Production of Al metal follows a two-stage process:

(i) Bayer process: Extraction, purification and dehydration of bauxite (typical compositions for industrially used bauxites are Al_2O_3 40 – 60 %, H_2O 12 – 30 %, SiO_2 free and combined 1 – 15 %, Fe_2O_3 7 – 30 %, TiO_2 3 – 4 %, F, P_2O_5, V_2O_5, etc., 0.05 – 0.2 %). This involves dissolution in aqueous NaOH, separation from insoluble impurities, partial precipitation of the aluminium hydroxide and heating at 1200 ^oC. Complete and balance the following chemical reactions:

$Al_2O_3 + OH^- + \rightarrow [Al(OH)_4(H_2O)_2]^-$

$SiO_2 + OH^- \rightarrow SiO_2(OH)_2^{2-}$

$SiO_2(OH)_2^{2-} + \rightarrow CaSiO_3\downarrow +$

$[Al(OH)_4(H_2O)_2]^- \rightarrow \downarrow + OH^- + H_2O$

$Al(OH)_3 \rightarrow Al_2O_3 +$

ii) Héroult-Hall process: Electrolysis of pure alumina dissolved in molten cryolite, Na_3AlF_6. Typical electrolyte composition ranges are Na_3AlF_6 (80 – 85 %), CaF_2 (5 – 7 %), AlF_3 (5 – 7 %), Al_2O_3 (2 – 8 % intermittently recharged). Electrolysis is carried out at 940^oC, under constant pressure of 1 atm, in a carbon-lined steel cell (cathode) with carbon anodes. Balance the main reaction of the electrolysis:

$Al_2O_3(l) + C(anode) \rightarrow Al(l) + CO_2(g)$

Since cryolite is a rather rare mineral, it is prepared according to the following reaction.

Complete and balance this reaction:

$HF + Al(OH)_3 + NaOH \rightarrow Na_3AlF_6 +$

During the electrolysis process several parallel reactions take place that degrade the graphite (C) anodes or reduce the yield.

iii) By using the thermodynamic data given below, which are taken to be independent on temperature, determine the thermodynamic quantities ΔH, ΔS and ΔG at 940 ℃ for the reaction:

$C(graphite) + CO_2(g) \rightarrow 2\ CO(g)$.

	Al(s)	Al_2O_3(s)	C (graphite)	CO(g)	CO_2(g)	O_2(g)
$\Delta_f H^o$ (kJ mol^{-1})	0	–1676	0	–111	–394	
S^o (J.K^{-1} mol^{-1})	28	51	6	198	214	205
$\Delta_{fus} H$ (kJ mol^{-1})	11	109				

iv) At the same temperature and using the data from the table in part (iii) determine the quantities ΔH and ΔG for the reaction

$2\ Al(l) + 3\ CO_2(g) \rightarrow Al_2O_3(l) + 3\ CO(g)$

given that $\Delta S = -126$ J K^{-1} mol^{-1}. (Show your calculations)

v) Pure aluminium is a silvery-white metal with a face-centered cubic (fcc) crystal structure. Aluminium is readily soluble in hot concentrated hydrochloric acid producing the cation $[Al(H_2O)_6]^{3+}$, as well as in strong bases at room temperature producing hydrated tetrahydroxyaluminate anion, $[Al(OH)_4]^-$(aq). In both cases liberation of H_2 occurs. AlF_3 is made by treating Al_2O_3 with HF gas at 700 ^oC, while the other trihalides, AlX_3, are made by the direct exothermic reaction of Al with the corresponding dihalogen. Write all 4 chemical reactions described above.

vi) The $AlCl_3$ is a crystalline solid having a layer lattice with 6-coordinate Al(III), but at the melting point (192.4^oC) the structure changes to a 4-coordinate molecular dimer, Al_2Cl_6. The covalently bonded molecular dimer, in the gas phase and at high temperature, dissociates into trigonal planar $AlCl_3$ molecules.

For the molecular dimer Al_2Cl_6, in the gas phase, two different Al–Cl distances (206 and 221 pm) were measured. Draw the stereostructure of the dimer, and write down the corresponding Al–Cl distances.

vii) What is the hybridization of the Al atom(s) in Al_2Cl_6 and $AlCl_3$?

SOLUTION

i) $Al_2O_3 + 2\ OH^- + 7\ H_2O \rightarrow 2\ [Al(OH)_4(H_2O)_2]^-$

$SiO_2 + 2\ OH^- \rightarrow SiO_2(OH)_2^{2-}$

$SiO_2(OH)_2^{2-} + Ca^{2+} \rightarrow CaSiO_3\downarrow + H_2O$

$[Al(OH)_4(H_2O)_2]^- \rightarrow Al(OH)_3\downarrow + 2\ OH^- + 2\ H_2O$

$2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O$

ii) $2\ Al_2O_3(l) + 3\ C(anode) \rightarrow 4\ Al(l) + 3\ CO_2(g)$

$6\ HF + Al(OH)_3 + 3\ NaOH \rightarrow Na_3AlF_6 + 6\ H_2O$

iii) $\Delta_r H^0_{1213} = 2\Delta_f H^0_{1213}(CO) - \Delta_f H^0_{1213}(CO_2) = 2\times(-111) - (-394) = 172\ kJ$

$\Delta_r S^0_{1213} = 2S^0_{1213}(CO) - S^0_{1213}(CO_2) - S^0_{1213}(C) = 2\times(-198) - 214 - 6 = 176\ J\,K^{-1}$

$\Delta_r G^0_{1213} = \Delta_r H^0_{1213} - T\Delta S^0_{1213} = 172 - 1213\times 0.176 = -41.5\ kJ\,K^{-1}$

iv)

$$\Delta_r H^0_{1213} = 3\Delta_f H^0_{1213}(CO) + \Delta_f H^0_{298}(Al_2O_3) + \Delta_{melt}H(Al_2O_3) - 3\Delta_f H^0_{1213}(CO_2) - 2\Delta H_{melt}H(Al) =$$
$$= 3\times(-111) - (-1676) + 109 - 3\times(-394) - 2\times 11 = -740\ kJ$$

$$\Delta_r H^0_{1213} = 3\Delta_f H^0_{1213}(CO) + \Delta_f H^0_{298}(Al_2O_3) + \Delta_{melt}H(Al_2O_3) - 3\Delta_f H^0_{1213}(CO_2) - 2\Delta H_{melt}H(Al) =$$
$$= 3\times(-111) - (-1676) + 109 - 3\times(-394) - 2\times 11 = -740\ kJ$$

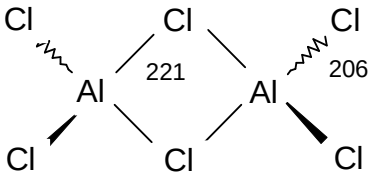
v) $2\ Al + 6\ H^+ + 12\ H_2O \rightarrow 2\ [Al(H_2O)_6]^{3+} + 3\ H_2$

$2\ Al + 2\ OH^- + 6\ H_2O \rightarrow 2[Al(OH)_4]^- + 3\ H_2$

$Al_2O_3 + HF \rightarrow 2\ AlF_3 + 3\ H_2O$

$2\ Al + 3\ X_2 \rightarrow 2\ AlX_3$

vi)



vii) Al_2Cl_6 - sp^3 hybridization

$AlCl_3$ - sp^2 hybridization

PROBLEM 35 Kinetics

The acid-catalyzed reaction $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$ was found to be of first order with respect to hydrogen ions. At constant hydrogen ion concentration the time needed for the concentration of iodine to be reduced by 0.010 mol dm^{-3} was measured under various concentrations of the reactants.

Based on the information provided in the table, answer fulfil the following tasks:

$[CH_3COCH_3]$	$[I_2]$	Time
(mol dm^{-3})	(mol dm^{-3})	(min)
0.25	0.050	7.2
0.50	0.050	3.6
1.00	0.050	1.8
0.50	0.100	3.6
0.25	0.100	…
1.50	…	…
…	…	0.36

a) Derive the rate law for the reaction and calculate the rate constant.

b) Calculate the time needed for 75 % of CH_3COCH_3 to react in excess I_2.

c) Show graphically the dependence of the rate on $[CH_3COCH_3]$ and on $[I_2]$, for fixed initial concentration of the other reagents.

d) If the rate is doubled by raising the temperature by 10 ℃ from 298 K, calculate the activation energy for this reaction.

SOLUTION

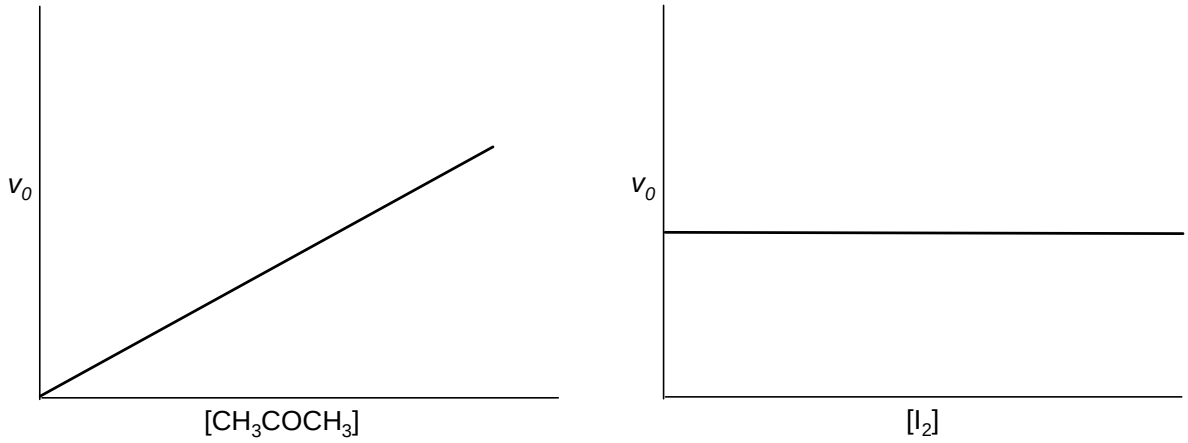
a) $v = k\,[CH_3COCH_3]$

$$k = \frac{v}{[CH_3COCH_3]} = \frac{\frac{0.010}{7.2}}{0.25} = 5.56\times10^{-3}\ \text{min}^{-1} = 9.26\times10^{-5}\ \text{s}^{-1}$$

b) $\tau = \ln 2 / k = 125$ min

$t = 2\ \tau = 250$ min

c)



d)

$$k = A \exp\left(-\frac{E_A}{RT}\right)$$

$$\frac{v_2}{v_1} = \frac{k_2}{k_1} = \frac{\exp\left(-\frac{E_A}{RT_2}\right)}{\exp\left(-\frac{E_A}{RT_1}\right)} = \exp\left(-\frac{E_A}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right)$$

$$\ln\frac{v_2}{v_1} = -\frac{E_A}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$E_A = -R\left(\frac{1}{T_2} - \frac{1}{T_1}\right)^{-1} \ln\frac{v_2}{v_1}$$

$$E_A = -8.314\left(\frac{1}{308} - \frac{1}{298}\right)^{-1} \ln\frac{2}{1} = 52.9\ \text{kJ mol}^{-1}$$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis of the Dipeptide *N*-acetyl-*L*-prolinyl-*L*-phenylalanine Methyl Ester (Ac-*L*-Pro-*L*-Phe-OCH_3)

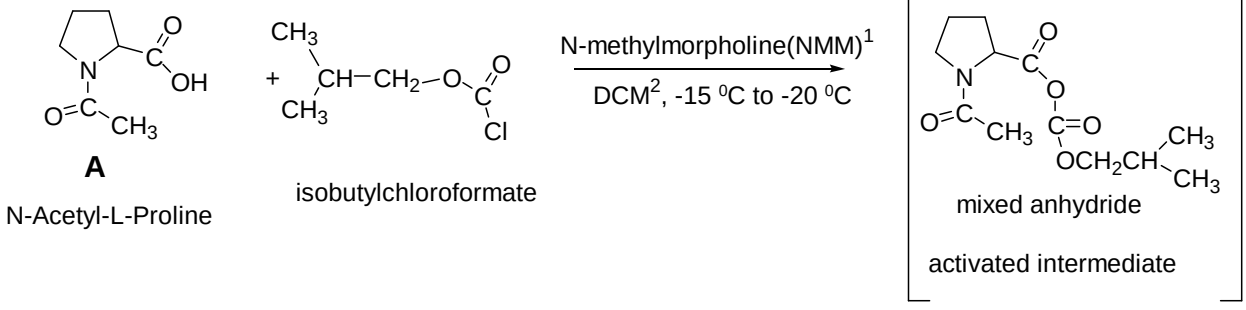
Introduction

Peptide synthesis is now a well-refined art and many of their synthetic procedures can be readily adapted to the elementary laboratory. Interest in peptides, always high, has heightened even more with the recent discovery of the importance of the so-called “opiate” peptides as well as of other biological active peptides.

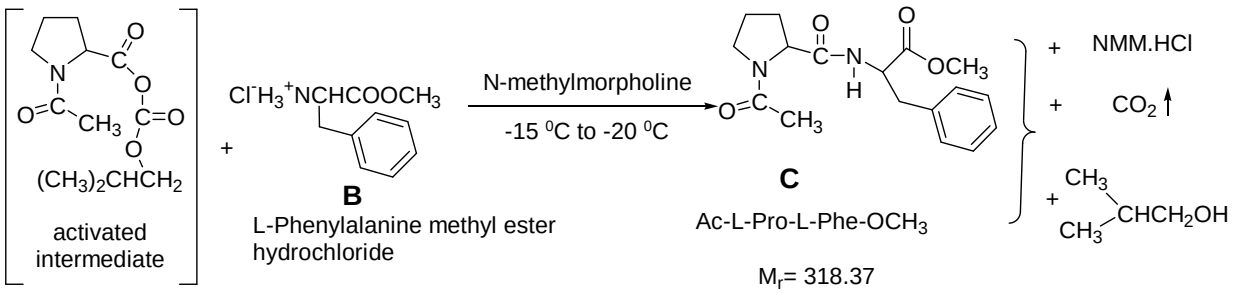
In this experiment the one-pot procedure for synthesizing the title dipeptide from its components, suitably protected amino acids, is described.

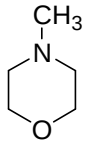
Reactions

STEP 1



STEP 2



[1] *N*-methylmorpholine (NMM) = 

[2] DCM = Dichloromethane

Procedure

STEP 1

Place the 1.50 g (0.0095 mol) sample of *N*-acetyl-*L*-proline (labelled AcPro), which you have been given, into a 50-cm^3 round-bottom flask. Add 20 cm^3 dichloromethane (labelled DCM) in the graduated cylinder. Use some of the 20 cm^3 DCM to wash out the AcPro vial and add the remaining DCM also into the round-bottomed flask. Plug the flask with a septum, clamp it loosely to a support stand and cool it to –15 ℃ to –20 ℃ in the ice/sodium chloride cold bath provided by the supervisor. Allow approximately 5 minutes for cooling. Add 1.2 cm^3 (0.0109 mol) of *N*-methylmorpholine (labelled NMM) to the flask, by means of a syringe. Then, slowly add 1.5 cm^3 (0.0116 mol) isobutyl-chloroformate (labelled IBCF) to the flask by means of a second syringe. During the addition, swirl the reaction mixture gently by hand, and continue swirling for another 10 min. The temperature should remain in the range –20 ^{o} to –15 ^{o}C.

STEP 2

Remove the septum and quickly add all the *L*-phenylalanine methyl ester hydrochloride (2.15 g, 0.0100 mol), (labelled $HCl{\cdot}H_2NPheOCH_3$) using the polypropylene powder funnel. Plug the flask again with the septum. Immediately add 1.2 cm^3 (0.0109 mol) of *N*-methylmorpholine (labelled NMM) using a third syringe, while the reaction mixture is swirled by hand. *ATTENTION: Leave the needle part of the syringe in the septum for the remainder of the reaction*. Allow the reaction to proceed for 60 min at –15 ℃ to –20 ℃, swirling periodically by hand.

During this waiting period you are highly advised to start working on the Analytical Chemistry experiment.

After 60 min at –20 ^{o}C to –15 ^{o}C, remove the 50 cm^3 round-bottomed flask from the ice/sodium chloride bath and place the flask in the 250 cm^3 beaker and let it warm up to

room temperature. Transfer the contents of the flask into the 50 cm^3 separating funnel by means of the glass funnel. Rinse the flask with a small amount of dichloromethane (3 – 5 cm^3), which is in a vial (labelled DCM). Wash the organic layer successively with two 20 cm^3 portions of 0.2 M aqueous HCl solution, two 20 cm^3 portions of 1 % aqueous

$NaHCO_3$ solution (read caution comment in next paragraph) and finally one 10 cm^3 portion of saturated solution of sodium chloride (labelled brine).

Important

After each washing allow the separating funnel to stand for enough time, so that the two phases separate completely. Also, take into consideration that the organic phase (DCM) is always the lower layer and contains the product. All the aqueous washings are collected in the same Erlenmeyer flask (empty if necessary).

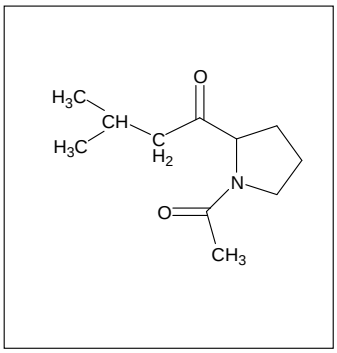
CAUTION: Keep in mind, also, that during washing with 1 % $NaHCO_3$, the CO_2 liberated is exerting pressure on the separating funnel stopper, so be sure to let the gas out through the stopcock before and after each shaking, while holding the funnel upside down.

Before continuing, wash the glass funnel, the 50 cm^3 cylinder and the 50 cm^3 round-bottom flask with water and then dry them with acetone. Your supervisor will show you where to dispose of the water and the acetone.

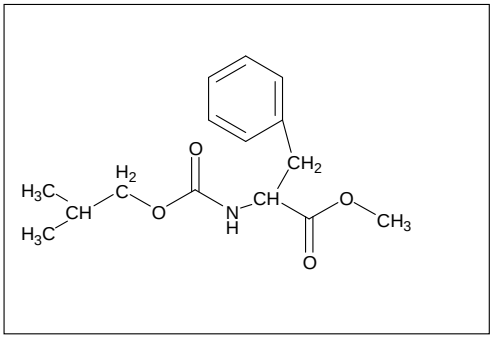
Pour the organic layer into a clean 50 cm^3 Erlenmeyer flask. Add the anhydrous sodium sulphate, which is in a vial labelled Na_2SO_4, to the Erlenmeyer flask containing the organic layer. The organic phase should become clear. Filter it through the cleaned and dried funnel, whose stem you have previously stuffed with a small piece of cotton to trap any solids, into the cleaned and dried 50 cm^3 round-bottom flask. Rinse the Erlenmeyer flask with a small amount of dichloromethane (3 – 5 cm^3). Removal of the organic solvent is done under reduced pressure, using a rotary evaporator apparatus. This will be done for you by a laboratory supervisor, who will add 20 cm^3 of diethylether to the residue in your flask, which will cause precipitation of your product. After cooling for 5 minutes in the ice bath, scrape the walls of the flask with a spatula, filter by suction the crystallized dipeptide through a fritted glass funnel. Wash twice with diethylether (5 cm^3 each time).

Leave the product on the filter under suction for at least 3 minutes. Then collect it on weighing paper, weigh it in the presence of a supervisor and then transfer it into a sample vial and label it with your student code. Write the mass of your product (**C**) on the label and on your answer sheet (on the next page).

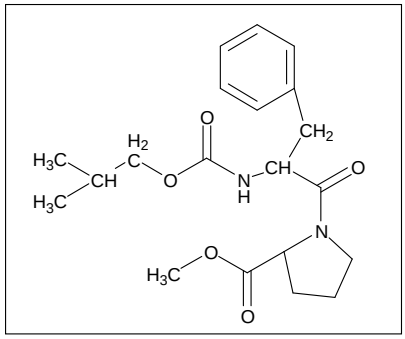
During the reaction between the phenylalanine methylester **B** and the activated mixed anhydride intermediate (step 2) the formation of the desired dipeptide product **C** is usually accompanied by a by-product the correct structure of which is one of the three structures **I**, **II**, **III** given below. Circle the Roman numeral corresponding to the correct structure.



I



II



III

TLC- Analysis

You have two Eppendorfs, one empty and one with a tiny amount of substance **B**. Put a small amount of **C** into the empty Eppendorf, and dissolve both **B** and **C** in a few drops of methanol. Use the supplied capillary tubes to apply small samples of these solutions to the TLC plate. Develop the TLC plate with a solution of chloroform-methanol-acetic acid (7 : 0.2 : 0.2) as eluant. The appropriate amount of eluant has been placed in the proper vial by the supervisor.

After the elution, analyze the TLC-plate using a UV-lamp. Clearly mark the starting line, solvent front and the UV-active spots.

Draw the diagram in the box on the answer sheet. Determine the R_f values.

Finally place the TLC-plate in a small plastic bag with a sealing strip and put it in an envelope provided by the supervisor. Write your student code on the envelope.

The examination committee will check the quality of the *N*-acetyl-*L*-prolinyl-*L*-phenylalanine methyl ester that you have prepared by determining its angle of optical rotation and consequently its specific rotation, $[a]^t_{D,}$ using an accurate polarimeter apparatus.

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SOLUTION

The following values were required to be written in the Answer Sheet

- Mass of Ac-*L*-Pro-*L*-Phe-OCH_3 obtained (product **C**).
- The yield of Ac-*L*-Pro-*L*-Phe-OCH_3 **C.**
- The TLC diagram with indication of the base line and the front of the solvent.
- R_f value of *L*-phenylalanine methyl ester hydrochloride (material B) and that of R_f value of Ac-*L*-Pro-*L*-Phe-OCH_3 (product C).

- Conclusions from the TLC analysis:
  Compound **C:**
  - Is pure,
  - Contains some **B**,
  - Contains several contaminants,
  - No conclusion.

- Specific rotation of the dipeptide Ac-*L*-Pro-*L*-Phe-OCH_3 C (to be measured later by the examination committee)
  $[a]_D^T$ = 45 °

- The correct structure of the by-product: **II.**