

31st



International Chemistry Olympiad

**6 theoretical problems
2 practical problems**

THE THIRTY-FIRST INTERNATIONAL CHEMISTRY OLYMPIAD 3–12 July 1999, BANGKOK, THAILAND

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 $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ at $25.00 \text{ }^\circ\text{C}$ are -393.51 and $-285.83 \text{ kJ mol}^{-1}$, respectively. The gas constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

(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 $25.000 \text{ }^\circ\text{C}$. After the reaction is completed, the temperature is observed to be $27.250 \text{ }^\circ\text{C}$, and 1.5144 g of $\text{CO}_2(\text{g})$ and 0.2656 g of $\text{H}_2\text{O}(\text{l})$ 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 $4.184 \text{ J g}^{-1} \text{ K}^{-1}$ and the internal energy change of the reaction (ΔU°) $-3079 \text{ kJ mol}^{-1}$.

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

1.3 Calculate the standard enthalpy of formation (ΔH_f°) of **Q**.

PART B

The following data refer to the distribution of **Q** between benzene and water at $6 \text{ }^\circ\text{C}$, 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 °C. 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.

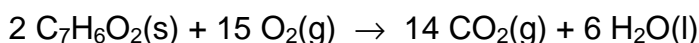
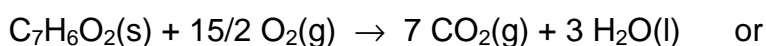
SOLUTION

PART A

$$1.1 \text{ Mole C : H : O} = \frac{1.5144 \times 12.0}{44.0} : \frac{0.2656 \times 2.0}{18.0} : \frac{0.1575}{16.0}$$

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

The formula mass of C₇H₆O₂ = 122 which is the same as the molar mass given.



$$1.2 \quad n(\text{Q}) = \frac{0.6000}{122.0} = 4.919 \times 10^{-3} \text{ mol}$$

$$q_v = n \Delta U^\circ = \frac{0.6000}{122.0} \times (-3079) = -15.14 \text{ kJ}$$

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

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

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

$$1.3 \quad \Delta n_g = 7 - 15/2 = -0.5 \text{ mol}$$

$$\Delta H^\circ = \Delta U^\circ + RT \Delta n_g = -3079 + (8.314 \times 10^{-3}) \times (298) \times (-0.5) = -3079 - 1 = -3080$$

$$\Delta H^\circ = (7 \Delta_f H^\circ, \text{CO}_2(\text{g}) + 3 \Delta_f H^\circ, \text{H}_2\text{O}(\text{l})) - (\Delta_f H^\circ, \text{Q})$$

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

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.

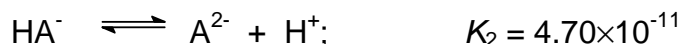
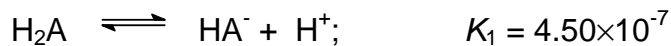
$$\text{Mole fraction of Q}_2 = \frac{\frac{0.244}{244}}{\frac{0.244}{244} + \frac{5.85}{78.0}} = 1.32 \times 10^{-2} \quad (0.01316)$$

$$\Delta T_f = \frac{8.314 \times 278.55^2}{9.89 \times 10^3} \times 1.32 \times 10^{-2} = 0.861$$

$$T_f = 5.40 - 0.861 = 4.54 \text{ }^\circ\text{C}$$

PROBLEM 2**PART A**

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



A 20.00 cm³ 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 :

<u>cm³ HCl added</u>	<u>pH</u>
1.00	10.33
10.00	8.34

- 2.1 On adding 1.00 cm³ 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 ($K_{In} = 4.19 \times 10^{-4}$) 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 H₂O, 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)?

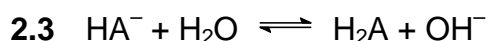
SOLUTION

PART A

- 2.1 Species which reacts first is A²⁻.

The product is HA⁻.

2.2 $n(\text{product}) = 1.00 \times 0.300 = 0.300 \text{ mmol}$



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

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

At pH = 10.33, the system is a buffer in which the ratio of [A²⁻] and [HA⁻] is equal to 1.

Thus

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

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

$$n(\text{Na}_2\text{A}) = \underline{3.00 \text{ mmol}}$$

$$n(\text{NaHA}) = \underline{2.40 \text{ mmol}}$$

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

PART B

- 2.6 Solution III is the indicator solution at $1 \times 10^{-5} \text{ M}$ in a solution containing 1.0 M CH₃COOH.

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.

$$[H^+] \text{ of solution III} = \sqrt{K_a c} = \sqrt{1.75 \times 10^{-5} \times 1.0} = 4.18 \times 10^{-3}$$

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

$$\frac{[In^-]}{[HIn]} = \frac{K_{in}}{[H^+]} = \frac{1 \times 10^{-3.38}}{1 \times 10^{-2.38}} = 0.100$$

$$\text{Since } [HIn] + [In^-] = 1 \times 10^{-5}$$

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

$$[In^-] = 0.091 \times 10^{-5}$$

$$\text{Absorbance of solution III} = \frac{0.091 \times 10^{-5}}{1.00 \times 10^{-5}} \times 0.300 = 0.027$$

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.

$$[H^+] \text{ of the mixture solution} = K_a \frac{[CH_3COOH]}{[CH_3COO^-]} = 1.75 \times 10^{-5} \times \frac{0.45}{0.05} = 15.75 \times 10^{-5}$$

$$\frac{[In^-]}{[HIn]} = \frac{K_{in}}{[H^+]} = \frac{1 \times 10^{-3.38}}{15.75 \times 10^{-5}} = 2.65$$

$$\text{Since } [HIn] + [In^-] = 1 \times 10^{-5}$$

$$\frac{[In^-]}{2.65} + [In^-] = 1 \times 10^{-5}$$

$$[In^-] = 0.726 \times 10^{-5}$$

$$\text{Absorbance of solution} = \frac{0.726 \times 10^{-5}}{1.00 \times 10^{-5}} \times 0.300 = 0.218$$

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

PROBLEM 3

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

- 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 ($1 \text{ W} = \text{J s}^{-1}$) produced by 1.00 kilogram of ${}^{232}\text{Th}$ ($t_{1/2} = 1.40 \times 10^{10}$ years).
- 3.4 ${}^{228}\text{Th}$ 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 ${}^{228}\text{Th}$ ($t_{1/2} = 1.91$ 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 ${}^{228}\text{Th}$.
- 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 :

$${}^4_2\text{He} = 4.00260 \text{ u}, \quad {}^{208}_{82}\text{Pb} = 207.97664 \text{ u}, \quad {}^{232}_{90}\text{Th} = 232.03805 \text{ u}; \text{ and } 1 \text{ u} = 931.5 \text{ MeV}$$

$$1 \text{ MeV} = 1.602 \times 10^{-13} \text{ J}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

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

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

$$12 - 8 = 4 \beta^- \text{ emitted.}$$

$$\text{Number of beta decays} = 4$$

- 3.2 ${}^{232}_{90}\text{Th} \rightarrow {}^{208}_{82}\text{Pb} + 6 {}^4_2\text{He} + 4 \beta^-$

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)

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

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

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

$$1.00 \text{ kg contains} = \frac{1000 \text{ g} \times 6.022 \times 10^{23} \text{ mol}^{-1}}{232 \text{ g mol}^{-1}} = 2.60 \times 10^{24} \text{ atoms}$$

Decay constant for ^{232}Th :

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

For activity: $A = N \lambda = 2.60 \times 10^{24} \times 1.57 \times 10^{-18} = 4.08 \times 10^6 \text{ dis s}^{-1}$
(disintegrations s^{-1})

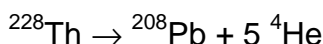
Each decay liberates 42.67 MeV

Rate of production of energy (power):

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

$$= 2.79 \times 10^{-5} \text{ J s}^{-1} = 2.79 \times 10^{-5} \text{ W}$$

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

$$A = \lambda N = \frac{0.693}{1.91 \text{ y}} \times \frac{1.000 \text{ g} \times 6.022 \times 10^{23} \text{ mol}^{-1}}{228 \text{ g mol}^{-1}} = 9.58 \times 10^{20} \text{ y}^{-1}$$

Number of He collected:

$$N_{\text{He}} = 9.58 \times 10^{20} \text{ y}^{-1} \times 20.0 \text{ y} \times 5 \text{ particles} = 9.58 \times 10^{22} \text{ particles of He}$$

$$V_{\text{He}} = \frac{9.58 \times 10^{22} \times 22.4 \text{ dm}^3 \text{ mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 3.56 \text{ dm}^3 = 3.56 \times 10^3 \text{ cm}^3$$

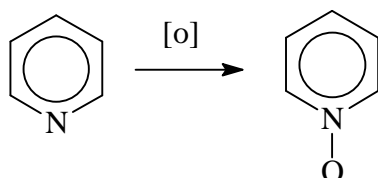
3.5 The half-life:

$$A = \lambda N$$

$$t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693 N}{A} = \frac{0.693 \times 510 \times 10^{10} \text{ atoms}}{3440 \text{ atoms min}^{-1}} = 3.02 \times 10^6 \text{ min} = 5.75 \text{ years}$$

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 $\text{FeL}_m(\text{ClO}_4)_n \cdot 3 \text{H}_2\text{O}$ (**A**) and $\text{CrL}_x\text{Cl}_y(\text{ClO}_4)_z \cdot \text{H}_2\text{O}$ (**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 , $\mu \text{ B.M.}$	Colour
A	6.13	Yellow
B	Not measured	Purple

Table 4c Relationship of wavelength to colour.

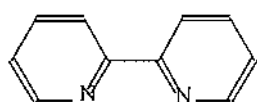
Wavelength (nm) and colour absorbed	Complementary colour
400 (violet)	Yellow Green
450 (blue)	Yellow
490 (blue green)	Orange
500 (green)	Red
570 (yellow green)	Violet
580 (yellow)	Blue
600 (orange)	Blue green
650 (red)	Green

- 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 $\text{FeL}_m(\text{ClO}_4)_n \cdot 3 \text{H}_2\text{O}$? 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 $\text{CrL}_x\text{Cl}_y(\text{ClO}_4)_z \cdot \text{H}_2\text{O}$.

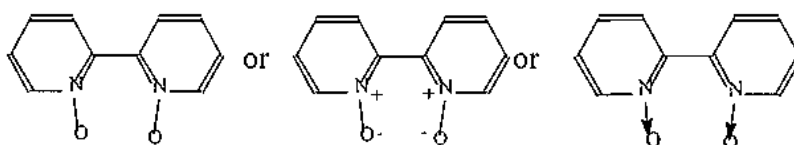
SOLUTION

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:



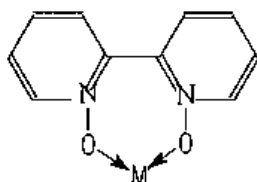
Structure of bipyridine



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 $FeL_m(C_{104})_n \cdot 3 H_2O$:

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 $[\text{FeL}_3](\text{ClO}_4)_3 \cdot 3 \text{H}_2\text{O}$

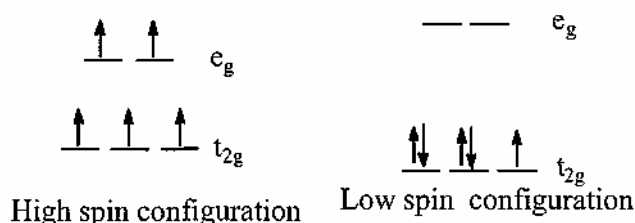
The ratio of cation to anion is equal to 1 : 3.

The three ClO_4^- groups will dissociate as free ion in solution. So the entire complex will be in the ion forms as $[\text{FeL}_3]^{3+}$ 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, $\mu = \sqrt{3(3 + 2)} = \sqrt{15} = 3.87 \text{ B.M.}$

4.9 The empirical formula of B is $\text{Cr}_{20}\text{H}_{18}\text{N}_4\text{Cl}_3\text{O}_9$, i.e. $x = 2, y = 2, z = 1$.

PROBLEM 5

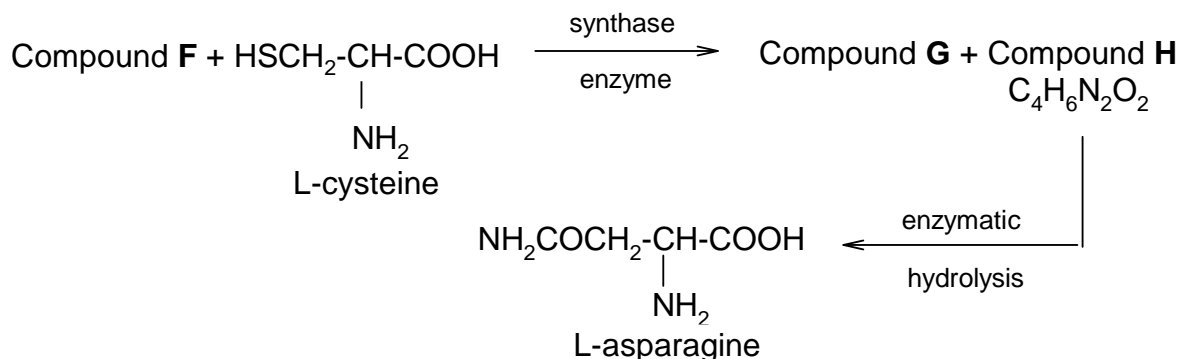
Glycoside **A** ($C_{20}H_{27}NO_{11}$), found in seeds of *Rosaceae* gives a negative test with Benedict's or Fehling's solutions. Enzymatic hydrolysis of **A** yields (-) **B**, C_8H_7NO and **C**, $C_{12}H_{22}O_{11}$, but complete acid hydrolysis gives as organic products, (+) **D**, $C_6H_{12}O_6$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

C has a β -glycosidic linkage and gives positive test with Benedict's 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.

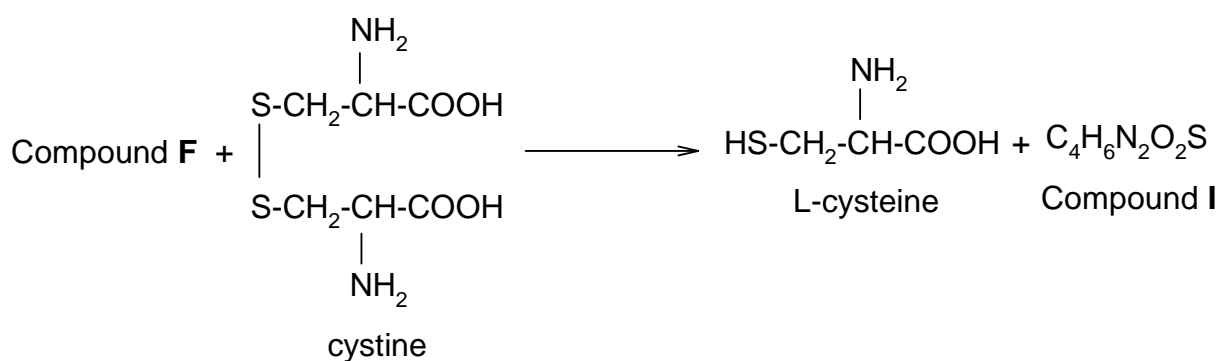
(\pm)**B** can be prepared from benzaldehyde and $NaHSO_3$ followed by $NaCN$. Acidic hydrolysis of (\pm)**B** gives (\pm)**E**, $C_8H_8O_3$.

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).



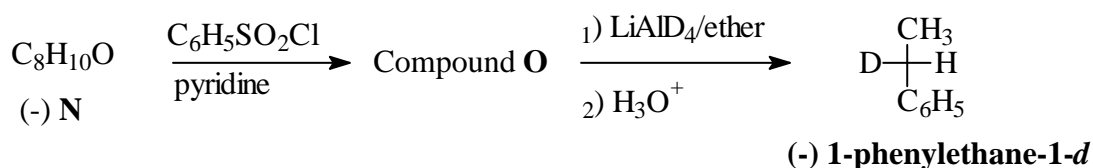
A small amount of compound **F** in human being is believed to be detoxified by a direct reaction with cystine giving L-cysteine and compound **I**, $C_4H_6N_2O_2S$ which is excreted in urine (stereochemistry not shown).



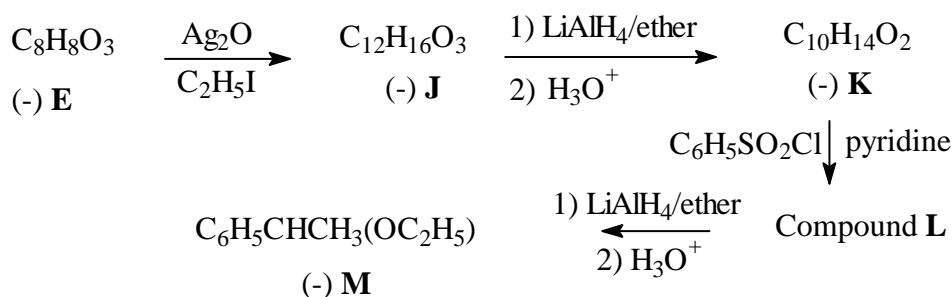
Compound **I** shows no absorption at 2150-2250 cm^{-1} in its IR spectrum but a band at 1640 cm^{-1} and the bands of carboxyl group are observed.

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.)

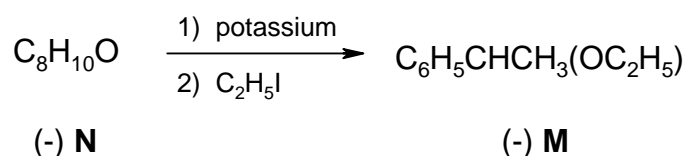
(-)-1-Phenylethane-1-*d*, $\text{C}_6\text{H}_5\text{CHDCH}_3$ can be prepared in optically active form and the magnitude of its rotation has the relatively high value, $[\alpha]_{\text{D}}$ is equal to -0.6.



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.

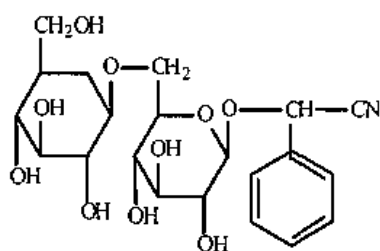
5.4 Choose the mechanism involved in the conversion of compound **O** to 1-phenylethane-1-d.

Table 5.1 Characteristic Infrared Absorption

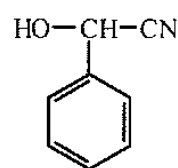
Stretching Vibration	Region (cm ⁻¹)	Stretching Vibration	Region (cm ⁻¹)
C-H (alkane)	2850-2960	O-H (free alcohol)	3400-3600
C-H (alkene)	3020-3100	O-H (H-bonded alcohol)	3300-3500
C=C	1650-1670	O-H (acid)	2500-3100
C-H (alkyne)	3300	C-O	1030-1150
C≡C	2100-2260	NH, NH ₂	3310-3550
C-H (aromatics)	3030	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

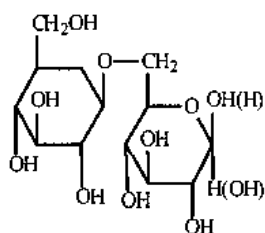
5.1



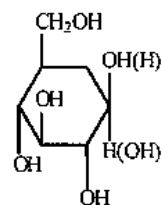
A



B



C

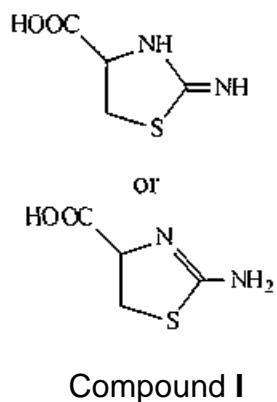
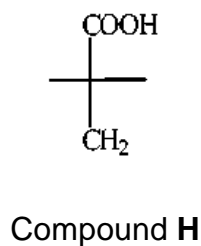


D

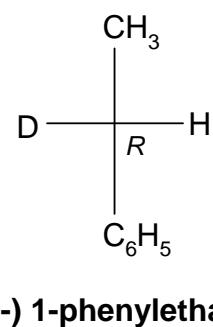
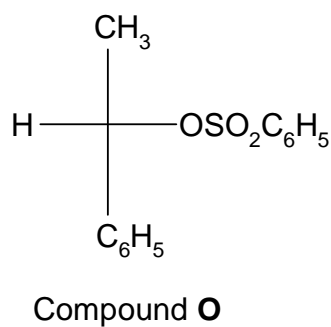
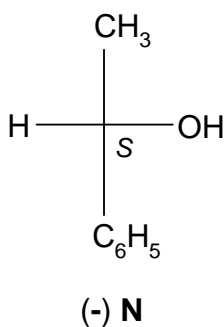
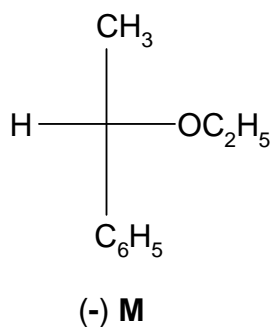
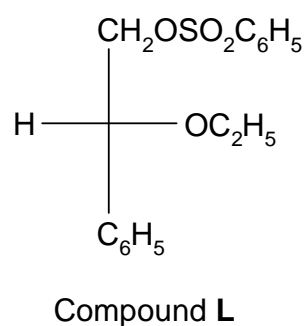
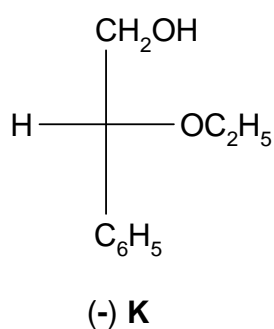
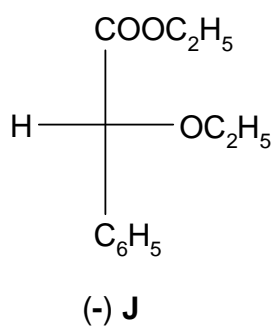
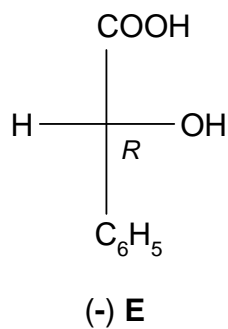
5.2

Molecular formula of compound **F** = HCN

Molecular formula of compound **G** = H₂S



5.3



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 complete 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

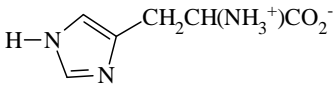
Name	Formula	Three-letter symbol
Alanine	$\text{CH}_3\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Ala
Arginine	$\text{H}_2\text{NC}(=\text{NH})\text{NH}(\text{CH}_2)_3\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Arg
Asparagine	$\text{H}_2\text{NCOCH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Asn
Aspartic Acid	$\text{HO}_2\text{CCH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Asp
Cysteine	$\text{HSCH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Cys
Cystine	$[\text{SCH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-]_2$	-
Glutamic Acid	$\text{HO}_2\text{CCH}_2\text{CH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Glu
Glutamine	$\text{H}_2\text{NCOCH}_2\text{CH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Gln
Glycine	$^+\text{H}_3\text{NCH}_2\text{CO}_2^-$	Gly
Histidine		His
Isoleucine	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Ile
Leucine	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Leu
Lysine	$\text{H}_2\text{N}(\text{CH}_2)_4\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Lys

Table 1 (continued)

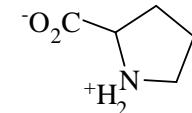
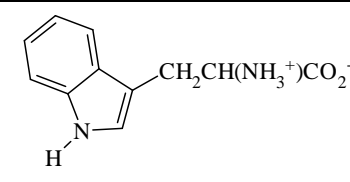
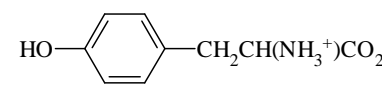
Methionine	$\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Met
Phenylalanine	$\text{PhCH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Phe
Proline		Pro
Serine	$\text{HOCH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Ser
Threonine	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{NH}_3^+)\text{CO}_2^-$	Thr
Tryptophan		Trp
Tyrosine		Tyr
Valine	$(\text{CH}_3)_2\text{CHCH}(\text{NH}_3^+)\text{CO}_2^-$	Val

Table 2: pK_a of some important groups in amino acids

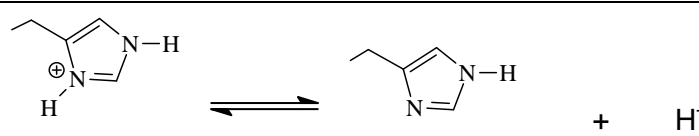
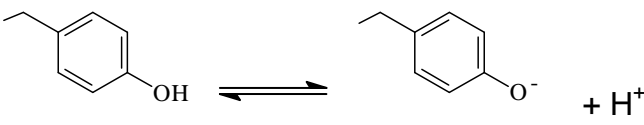
Groups	Equilibrium	pK _a
Terminal carboxyl	$-\text{CO}_2\text{H} \rightleftharpoons -\text{CO}_2^- + \text{H}^+$	3.1
Asp /or Glu side- chain carboxyl	$-\text{CO}_2\text{H} \rightleftharpoons -\text{CO}_2^- + \text{H}^+$	4.4
His side-chain		6.5
Terminal amino	$-\text{NH}_3^+ \rightleftharpoons -\text{NH}_2 + \text{H}^+$	8.0
Cys side-chain	$-\text{SH} \rightleftharpoons -\text{S}^- + \text{H}^+$	8.5

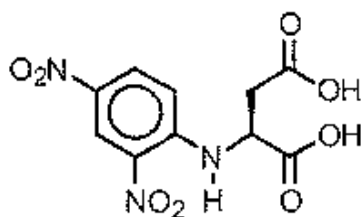
Table 2 (continued)

Tyr side-chain		10.0
Lys side-chain amino	$-\text{NH}_3^+ \rightleftharpoons -\text{NH}_2 + \text{H}^+$	10.0
Arg side-chain	$-\text{NH}(\text{NH}_2)\text{C}=\text{NH}_2^+ \rightleftharpoons -\text{NH}(\text{NH}_2)\text{C}=\text{NH} + \text{H}^+$	12.0

SOLUTION

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

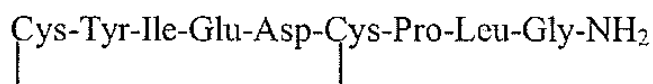
6.2 Complete structure of DNP-Asp at its isoelectric point is



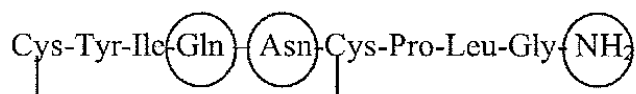
6.3 The sequence of B8 is: Cys-Tyr-Ile-Glu

6.4 The sequence of B9 is: Asp-Cys-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



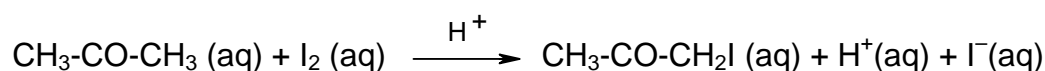
6.7 The isoelectric point of A is 9.

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⁺.



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 I₂(aq) has been shown to have the form

$$\text{Rate} = -\frac{d[\text{I}_2]}{dt} = k[\text{CH}_3\text{COCH}_3]^x [\text{I}_2]^y [\text{H}^+]^z$$

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.

$$\text{Initial rate} = k[\text{CH}_3\text{COCH}_3]_0^x [\text{I}_2]_0^y [\text{H}^+]_0^z$$

where []₀ are the initial concentrations of acetone, I₂ 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 I₂(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 I₂ (aq) is determined by titration with sodium thiosulphate, Na₂S₂O₃. 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 cm³
2. 0.100 M aq. HCl 50 cm³
3. 0.50 M aq. CH₃COONa 80 cm³
4. Standard 0.02 M Na₂S₂O₃(aq) solution 200 cm³
(the exact concentration will be announced at the beginning of practical part)
5. Aqueous acetone (50% by volume) 50 cm³
(Density of pure acetone; 0.787 g cm⁻³, MW. = 58.08)
6. Starch indicator 7 cm³

Procedure**A. Standardization of Iodine Solution**

1. Pipet 5.00 cm³ of aqueous iodine into a clean 125 cm³ Erlenmeyer flask.
2. Add 10 cm³ 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.

- Measure out 10 cm³ of 0.50 M aq. CH₃COONa into the graduated cylinder.
- Set the stop-watch to 0.0000 display.
- Pipet 5.00 cm³ of iodine solution into the stoppered Flask No. I.
Start the stop-watch as soon as the first drop of iodine solution is added.
- Stopper the flask and swirl continuously.
- Just before 7.0 min, remove the stopper, at 7.0 min, immediately pour 10 cm³ of sodium acetate solution (from step 3) into the reaction flask. Shake well.
- Titrate the remaining iodine with standard thiosulphate solution.
- Record the volume of the thiosulphate solution.
- Repeat the above steps (Steps 3 to 9) for Flask II, III and IV but add in step 5 the I₂(aq) solution to each flask as indicated:

Flask II: 10.00 cm³ I₂ solution

Flask III: 5.00 cm³ I₂ solution

Flask IV: 5.00 cm³ I₂ solution

Calculations

- Calculate the initial concentrations (M) of iodine, acetone and HCl solutions in Flasks I to IV, assuming volumes are additive.
- Calculate concentrations of iodine (M) remaining in Flasks I to IV at 7.0 minutes.
- Calculate the initial reaction rate for Flasks I to IV in M s⁻¹.
- The rate of reaction has the form

$$\text{Rate} = -\frac{d[\text{I}_2]}{dt} = k [\text{CH}_3\text{COCH}_3]^x [\text{I}_2]^y [\text{H}^+]^z$$

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 $\text{Na}_2\text{S}_2\text{O}_3$ 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.*

$$\text{Rate of disappearance of iodine (M s}^{-1}\text{)} = -\frac{d[\text{I}_2]}{dt} = \frac{c(\text{I}_2)_{\text{initial}} - c(\text{I}_2)_{7 \text{ min}}}{7 \times 60 \text{ s}}$$

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

$$\text{rate} = -\frac{d[\text{I}_2]}{dt} = k[\text{CH}_3\text{COCH}_3]^x [\text{I}_2]^y [\text{H}^+]^z$$

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

$$x = 1; \quad y = 0; \quad z = 1$$

The rate equation has the form: $\text{rate} = k [\text{CH}_3\text{COCH}_3] [\text{H}^+]$

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 Na₂SO₄ (in a plastic vial), dichloromethane, ceric ammonium nitrate solution, 2,4-Dinitrophenylhydrazine (labelled as 2,4-DNP), 2 % aq. NH₃, 5 % aq. AgNO₃, 5 % aq. HCl, 5 % aq. NaOH, 5 % aq. NaHCO₃, 1 % FeCl₃ in EtOH, 0.2 % aq. KMnO₄, decolourised with easily oxidised functional groups, acetone (for washing).

Procedure:

1. Apparatus: Assemble a distillation apparatus using a 25 cm³ round bottomed flask for distillation and a 10 cm³ 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 cm³ of water in the 25 cm³ 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 cm³ 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 cm³ capped centrifuge tube and add 1 cm³ 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 cm³ test tube. Repeat this extraction with fresh 1 cm³ dichloromethane twice and combine with the first extract.

Drying: Dry the dichloromethane extract by adding anhydrous Na₂SO₄ and stir occasionally for 10 minutes.

Evaporation: With a clean, dry cotton plugged Pasteur pipette transfer the organic layer to a dry 5 cm³ conical vial. Use approximately 1 cm³ of clean dichloromethane to wash Na₂SO₄ using the dry cotton plugged Pasteur pipette, then transfer into the vial. Be careful not to transfer any of the Na₂SO₄ into the vial. Use Hickman still head and dry condenser to distil the dichloromethane from the solution until the volume is reduced to 1 cm³. 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 cm³) by using the appropriate reagents at your station. (Note: dichloromethane is immiscible with water.)

Tollen's Reagent: add 1 drop of 5 % aq. AgNO₃ in a small test tube followed by 1 drop of 5 % aq. NaOH, brown precipitate will appear. Add 2 % aq NH₃ 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 CH₃I in the presence of K₂CO₃ gives compound **X** (C₁₁H₁₄O₂). Oxidation of **X** gives unknown **Y** (C₁₀H₁₂O₄) as the main product and CO₂.

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 ^1H NMR spectra. ^1H NMR spectra will be given only when the functional group analysis is completed.

- 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 ^1H NMR spectra by labelling the peak number on the proton in the structure in the answer sheet.
- Draw the structures of compound X and unknown Y. Assign each proton of unknown Y from the provided ^1H NMR spectra in the same manner as in (4).

SOLUTION

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

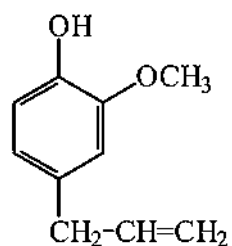
Functional groups in S	Present	Not present
-C=C-	✓	
-OH (alcoholic)		✓
-OH (phenolic)	✓	
-CHO		✓
-CO-		✓
-COOH		✓

- Functional 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		✓

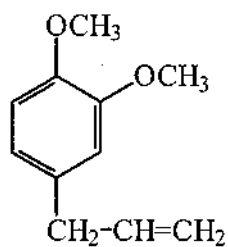
Functional groups in Unknown Y	Present	Not present
-C=C-		✓
-OH (alcoholic)		✓
-OH (phenolic)		✓
-CHO		✓
-CO-		✓
-COOH	✓	

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

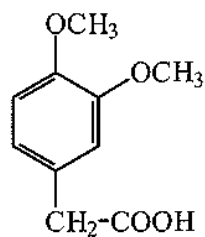


5. The structure of compound **X** and unknown **Y**:

Compound **X**



Compound **Y**

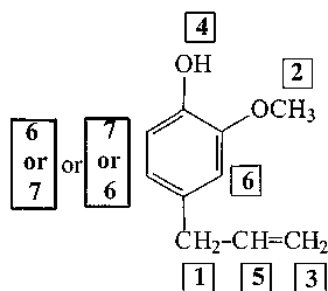


NMR spectrum of the main essential oil (S):

(See peak number in the given ¹H 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):

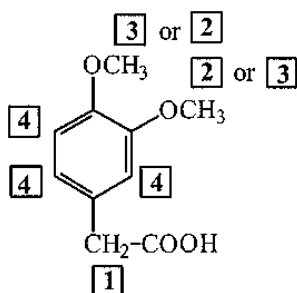


NMR spectrum of the unknown Y:

(See peak number in the given ¹H 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

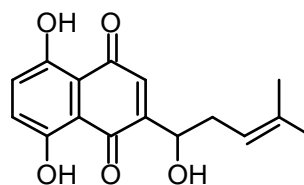
THEORETICAL PROBLEMS

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.

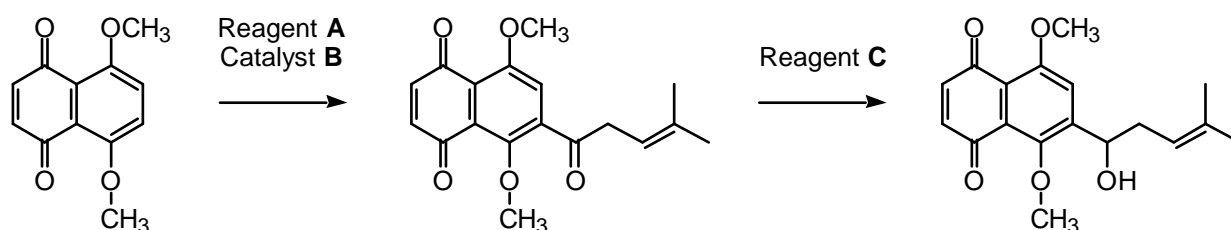


Shikonin

- 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:



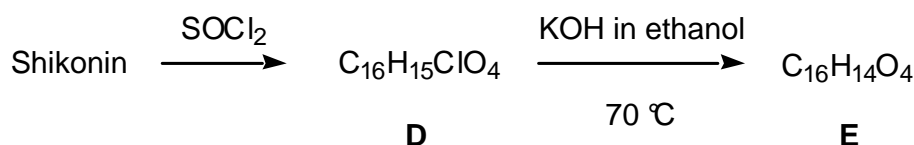
1.3 Draw the structural formula of reagent **A**.

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**.

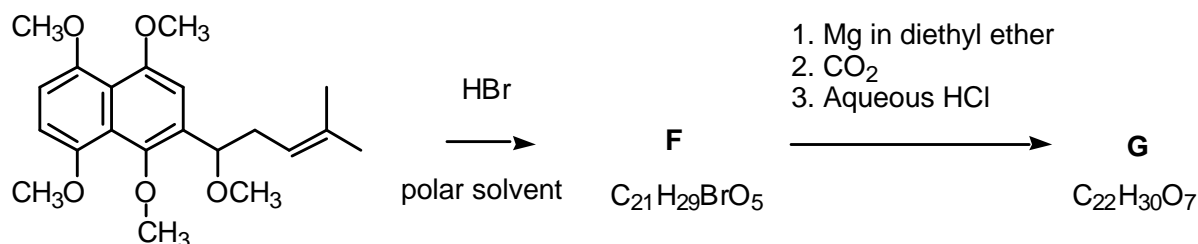
Numerous Shikonin analogues have been synthesized with a view to obtaining more potent compounds. One reaction sequence is shown below:



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**.

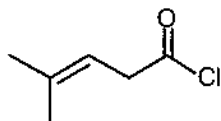
1.9 Draw the structural formula of compound **G**.

SOLUTION

1.1 2 stereoisomers.

1.2 Stereoisomers of Shikonin have the same melting point.

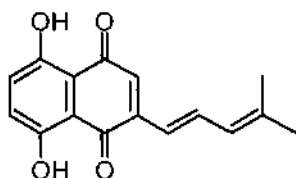
1.3 The structural formula of reagent **A**:



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

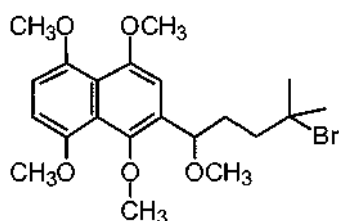
1.5 NaBH_4 (LiAlH_4 will be accepted)

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

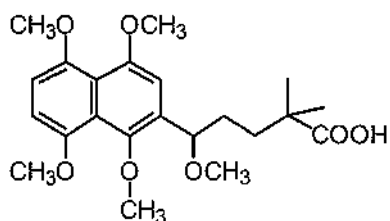


1.7 2 stereoisomers

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, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, 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, $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$. Consider the following reaction:



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

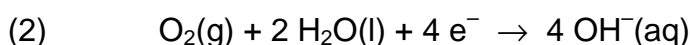
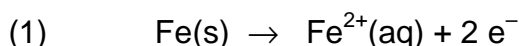
Compound	$\Delta_f H$ (kJ mol ⁻¹)	S (J K ⁻¹ mol ⁻¹)
CaSO ₄ · 2 H ₂ O(s)	-2021.0	194.0
CaSO ₄ · ½ H ₂ O(s)	-1575.0	130.5
H ₂ O(g)	-241.8	188.6

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

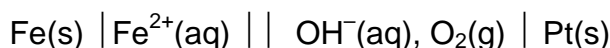
0 °C = 273.15 K.

- 2.1** Calculate ΔH (in kJ) for transformation of 1.00 kg of CaSO₄ · 2 H₂O(s) to hemihydrate CaSO₄ · ½ H₂O(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 CaSO₄ · 2 H₂O(s), CaSO₄ · ½ H₂O(s) and H₂O(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.

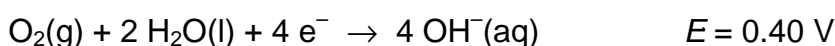
Corrosion of metals is associated with electrochemical reactions. This also applies for the formation of rust on iron surfaces, where the initial electrode reactions usually are:



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



Standard electrode potentials (at 25 °C):



Nernst factor: $RT \ln 10 / F = 0.05916 \text{ volt (at 25 °C)}$

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

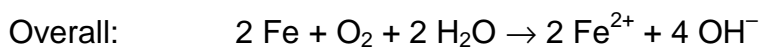
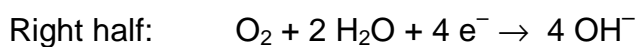
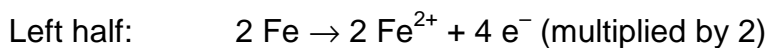
- 2.4** Calculate the standard electromotive force (the standard cell voltage), E , at 25 °C.

- 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 °C for the 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 Fe²⁺ after 24 hours. Oxygen and water may be assumed to be present in excess.
- 2.8 Calculate E for the cell at 25 °C for the following conditions :
 $[\text{Fe}^{2+}] = 0.015 \text{ M}$, $pH_{\text{right-hand half-cell}} = 9.00$, $p(\text{O}_2) = 0.700 \text{ bar}$.

SOLUTION

- 2.1 $\Delta H^{\circ} = -1575.0 \text{ kJ mol}^{-1} + 1.5 \times (-241.8) \text{ kJ mol}^{-1} - (-2021.0 \text{ kJ mol}^{-1}) = 83.3 \text{ kJ mol}^{-1}$
 $n = m / M = 1000 \text{ g} / 172.18 \text{ g mol}^{-1} = 5.808 \text{ mol}$
 $\Delta H^{\circ} = 484 \text{ kJ}$
 The reaction is endothermic.
- 2.2 $\Delta S^{\circ} = 130.5 \text{ J K}^{-1} \text{ mol}^{-1} + 3/2 \times 188.6 \text{ J K}^{-1} \text{ mol}^{-1} - 194.0 \text{ J K}^{-1} \text{ mol}^{-1}$
 $= 219.4 \text{ J K}^{-1} \text{ mol}^{-1}$
 $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = 17886 \text{ J mol}^{-1}$
 $\Delta G^{\circ} = -RT \ln K$
 $K = (p(\text{H}_2\text{O}))^{3/2} = 7.35 \times 10^{-4}$ (pressure in bar)
 $p(\text{H}_2\text{O}) = 8.15 \times 10^{-3} \text{ bar}$
- 2.3 $p(\text{H}_2\text{O}) = 1.00 \text{ bar}$ implies $K = 1.00$ and $\Delta G^{\circ} = -RT \ln K = 0$
 $\Delta G = \Delta H - T\Delta S$
 $0 = 83300 \text{ J K}^{-1} - T 219.4 \text{ J K}^{-1} \text{ mol}^{-1}$
 $T = 380 \text{ K}$ or $107 \text{ }^{\circ}\text{C}$
- 2.4 $E^{\circ}(\text{cell}) = E^{\circ}(\text{right}) - E^{\circ}(\text{left}) = 0.40 \text{ V} - (-0.44 \text{ V}) = 0.84 \text{ V}$

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



2.6 $K = [\text{Fe}^{2+}]^2 [\text{OH}^-]^4 / p(\text{O}_2)$ (conc. in M and pressure in bar)

$$\Delta G = -nFE(\text{cell}) = -RT \ln K$$

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

2.7 $Q = It = 0.12 \text{ A} \times 24 \times 60 \times 60 \text{ s} = 10\,368 \text{ C}$

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

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

2.8 $E(\text{cell}) = E^0(\text{cell}) - \frac{0.05916 \text{ V}}{n} \log \frac{[\text{Fe}^{2+}]^2 [\text{OH}^-]^4}{p(\text{O}_2)}$

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

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

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 $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$.

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

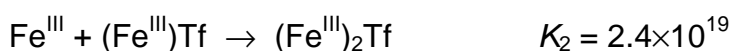
- 1) empirical formula $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$,
- 2) an anion and a cation and is composed of discrete, monomeric square planar platinum(II) complex,
- 3) only one type of cation and one type of anion. The answer must clearly reveal the composition of each discrete platinum(II) complex 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 °C corresponding to the reactions:



In the diferric protein, $(\text{Fe}^{\text{III}})_2\text{Tf}$, the two iron(III) ions are bound at two similar, but non-identical sites, and the two possible monoferric protein products, $(\text{Fe}^{\text{III}})\text{Tf}$, can be denoted $\{\text{Fe}^{\text{III}} \cdot \text{Tf}\}$ and $\{\text{Tf} \cdot \text{Fe}^{\text{III}}\}$. Their relative abundance at equilibrium is given by the constant

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

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

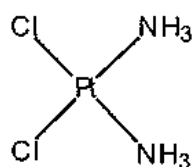
3.6 Calculate the values of the two constants $K_2' = \frac{[(\text{Fe}^{\text{III}})_2\text{Tf}][\text{Fe}^{\text{III}}]^{-1}[\{\text{Fe}^{\text{III}} \cdot \text{Tf}\}^{-1}]}{[(\text{Fe}^{\text{III}})_2\text{Tf}][\text{Fe}^{\text{III}}]^{-1}[\{\text{Tf} \cdot \text{Fe}^{\text{III}}\}^{-1}]}$ and $K_2'' = \frac{[(\text{Fe}^{\text{III}})_2\text{Tf}][\text{Fe}^{\text{III}}]^{-1}[\{\text{Tf} \cdot \text{Fe}^{\text{III}}\}^{-1}]}{[(\text{Fe}^{\text{III}})_2\text{Tf}][\text{Fe}^{\text{III}}]^{-1}[\{\text{Fe}^{\text{III}} \cdot \text{Tf}\}^{-1}]}$ 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.

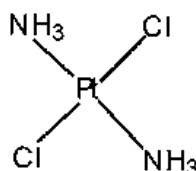
3.7 What is the total number of oxygen donor atoms that surround a 6-coordinate iron(III) ion in transferrin?

SOLUTION

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



cis



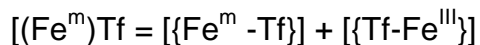
trans

3.2 $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$
 $[\text{Pt}(\text{NH}_3)_3\text{Cl}][\text{Pt}(\text{NH}_3)\text{Cl}_3]$
 $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2[\text{PtCl}_4]$
 $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{NH}_3)\text{Cl}_3]_2$

3.3 Eight *d*-electrons.

3.4 Orbital $5d_{x^2-y^2}$. 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



$$K_1' + K_1'' = K_1 \quad K_1' K_1'' = K_1$$

$$K_1' = \frac{K_1}{1 + K_1''} = \frac{4.7 \times 10^{20}}{1 + 5.9} = 6.8 \times 10^{19}$$

$$K_1'' = K_1 - K_1' = (4.7 - 0.68) \times 10^{20} = 4.0 \times 10^{20}$$

3.6 $K_1' K_2' = K_1'' K_2'' = K_1 K_2$

$$K_1' = \frac{K_1 K_2}{K_1''} = \frac{4.7 \times 10^{20} \times 2.19 \times 10^{19}}{6.8 \times 10^{19}} = 1.7 \times 10^{20}$$

$$K_1'' K_2'' = K_1 K_2$$

$$K_2'' = \frac{K_1 K_2}{K_1''} = \frac{4.7 \times 10^{20} \times 2.4 \times 10^{19}}{4.0 \times 10^{20}} = 2.8 \times 10^{19}$$

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

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**.

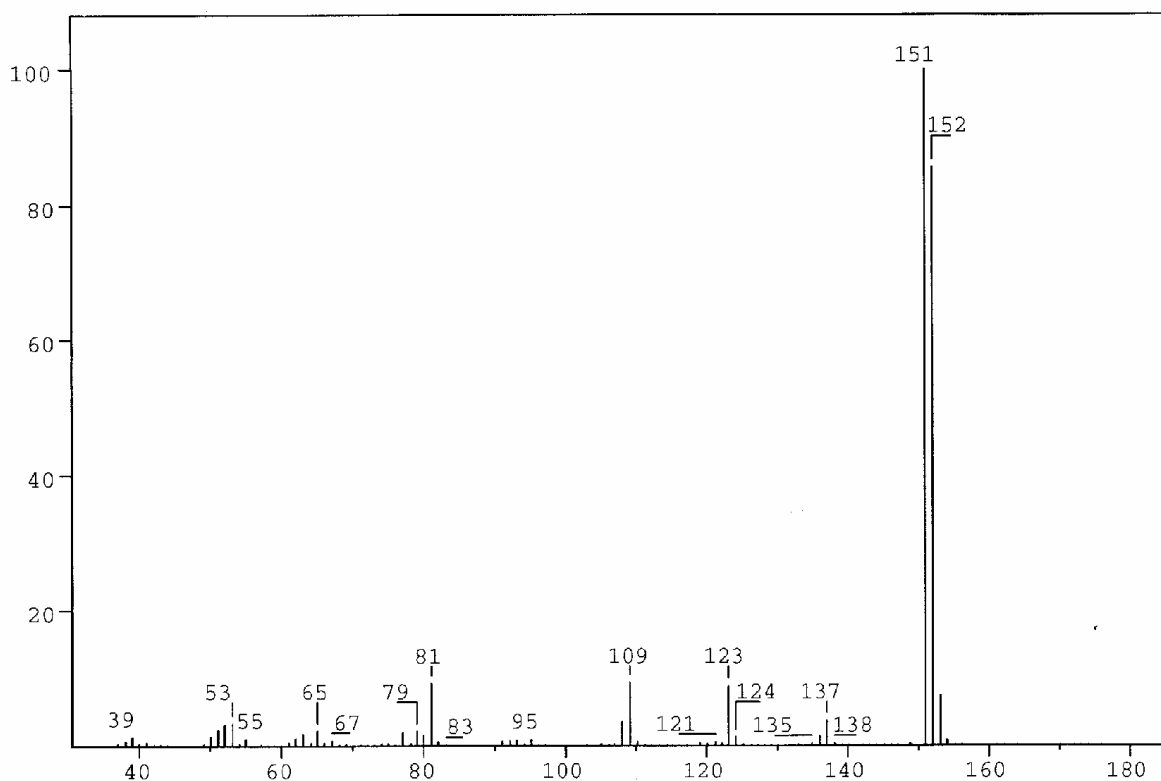


Figure 1

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 NaHCO₃. **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 ($\text{Ag}(\text{NH}_3)_2^+$).

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

Table of Integrals

FROM	TO	VALUE
10.00 PPM	9.69 PPM	0.94
7.56 PPM	7.32 PPM	1.91
7.15 PPM	6.92 PPM	0.93
6.41 PPM	6.20 PPM	0.94
4.02 PPM	3.89 PPM	3.10

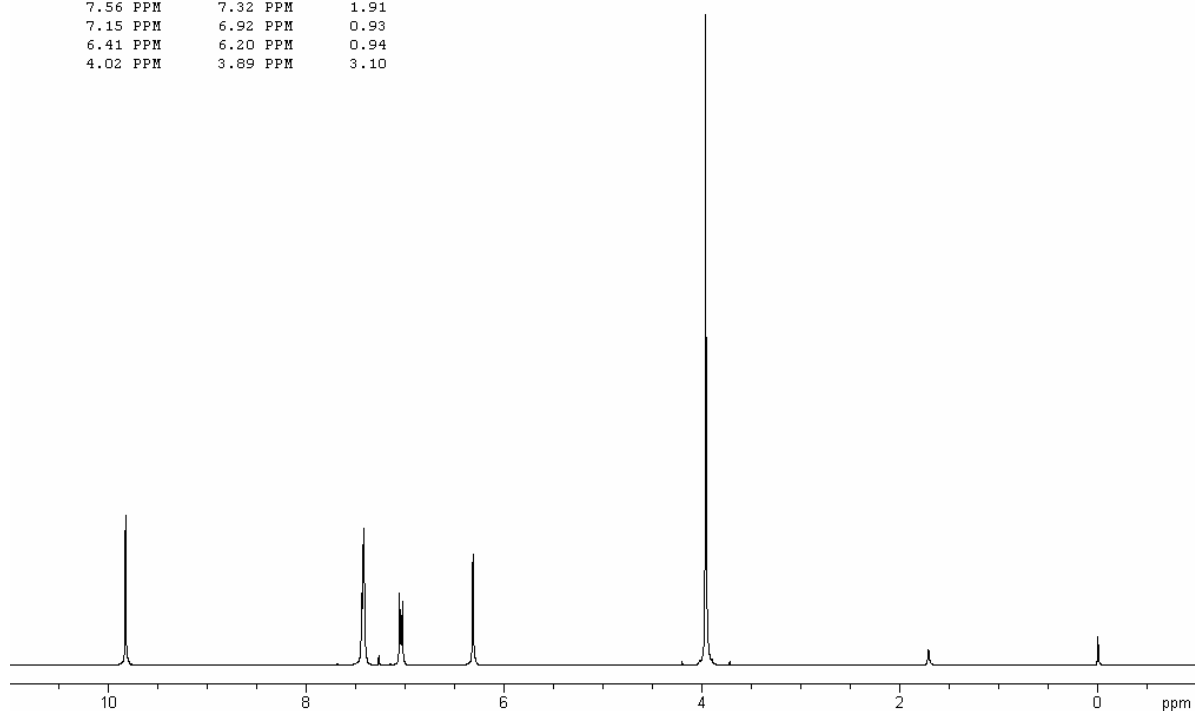


Figure 2a

The ^1H 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.

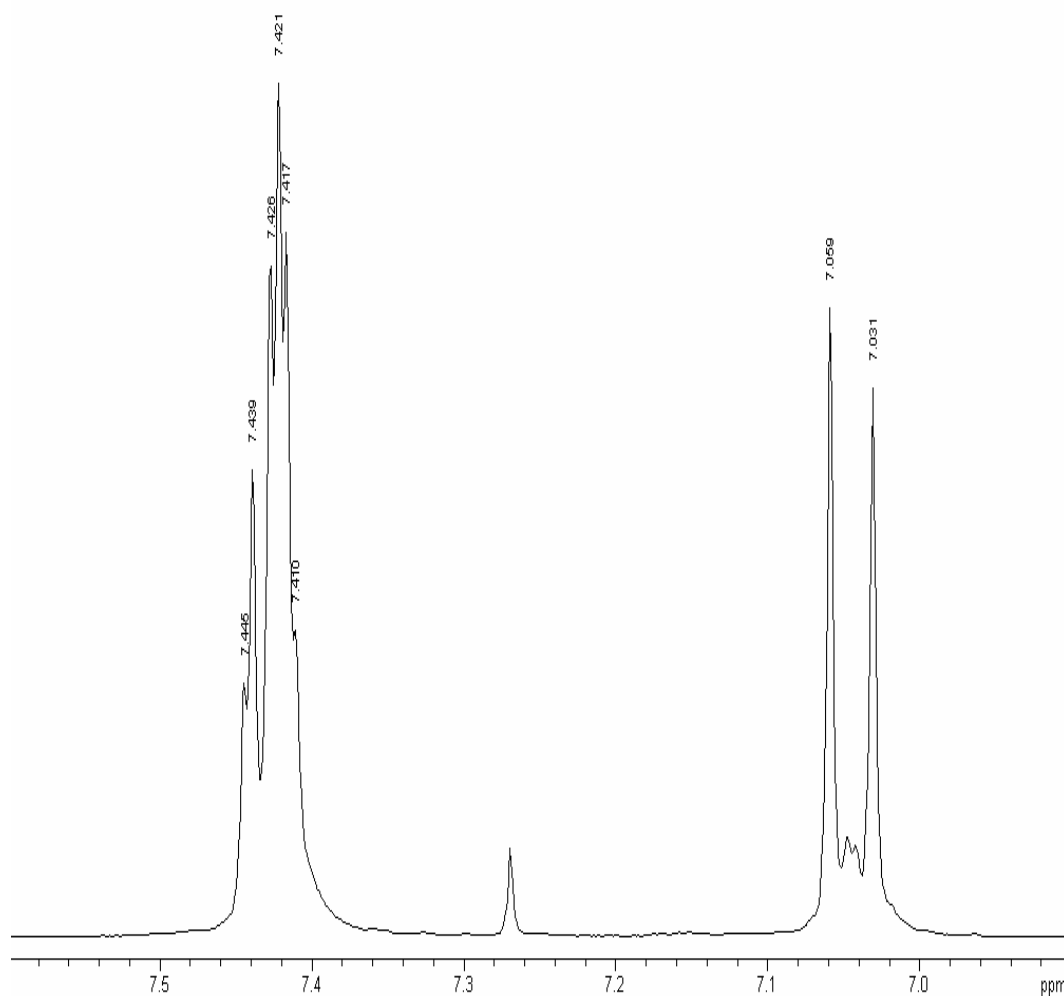


Figure 2b

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. ^1H Chemical Shift δ

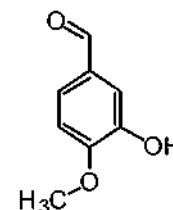
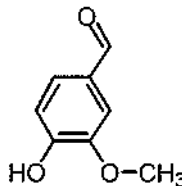
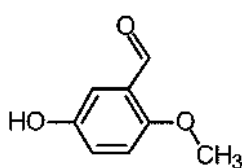
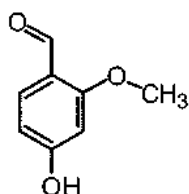
Hydrogens attached to carbon		
<i>Methyl</i>	$\text{CH}_3\text{-C-}$ $\text{CH}_3\text{-C=O-}$ $\text{CH}_3\text{-O-R}$ $\text{CH}_3\text{-OCOR}$	0.9 – 1.6 ppm 2.0 – 2.4 ppm 3.3 – 3.8 ppm 3.7 – 4.0 ppm
<i>Methylene</i>	$\text{CH}_2\text{-C-}$ $\text{CH}_2\text{-C=O-}$ $\text{CH}_2\text{-OR}$ $\text{CH}_2\text{-OCOR}$	1.4 – 2.7 ppm 2.2 – 2.9 ppm 3.4 – 4.1 ppm 4.3 – 4.4 ppm
<i>Methine</i>	CH-	1.5 – 5.0 ppm depending on the substituents. Generally higher than for methyl and methylene
<i>Alkene</i>		4.0 – 7.3 ppm depending on the substituent
<i>Aldehyde</i>	R-CHO	9.0 – 10.0 ppm

Table 1 (continued) ¹H Chemical Shift δ

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

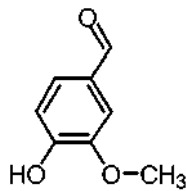
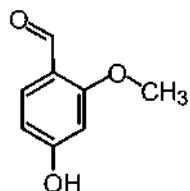
SOLUTION

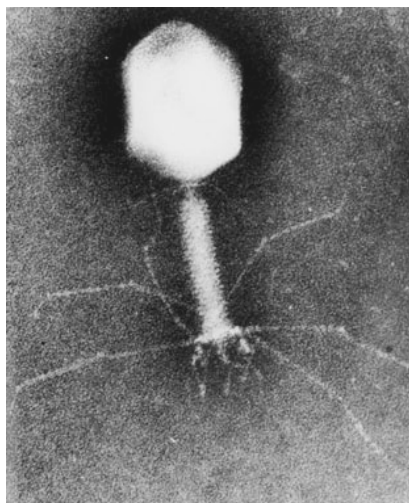
- 4.1 The empirical formula of **A** is C₈H₈O₃.
- 4.2 The molecular formula of compound **A**: C₈H₈O₃.
- 4.3 The compound **A** is a phenol.
- 4.4 Compound **A** forms a mirror with Tollen's reagent. This indicates the presence of carbonyl group of an aldehyde.
- 4.5 It indicates exchange of oxygen-bonded 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

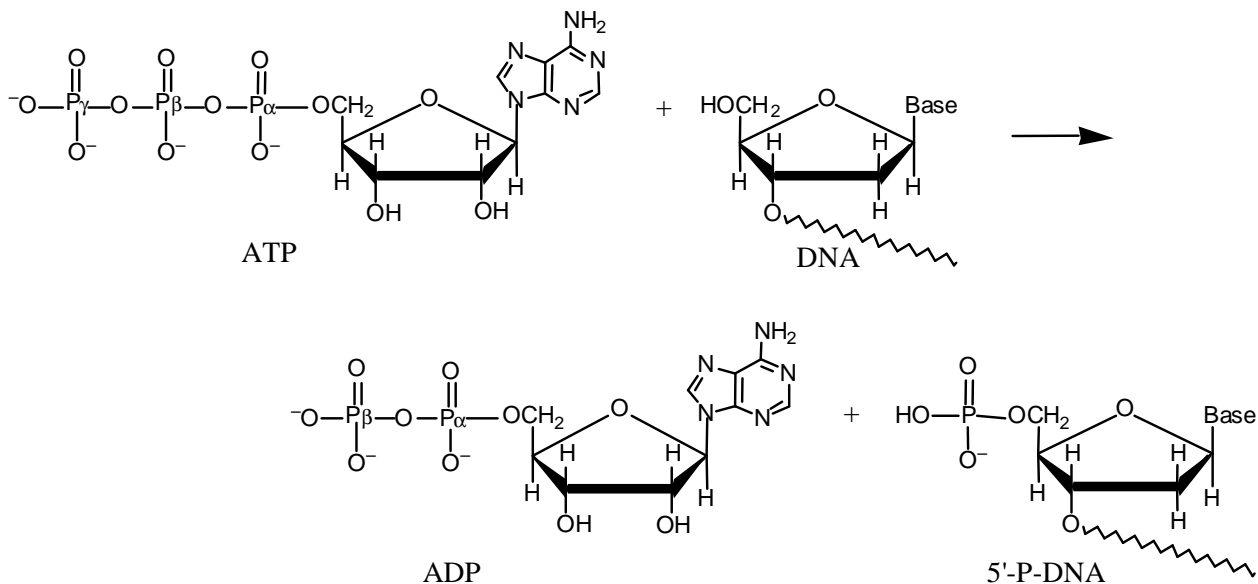
dNTP	Molar mass /g mol ⁻¹
dATP	487
dGTP	503
dCTP	464
dTTP	478

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 $[\gamma\text{-}^{32}\text{P}]\text{ATP}$ by PNK. 37 days ago, the specific activity of $[\gamma\text{-}^{32}\text{P}]\text{ATP}$ 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 $[\gamma\text{-}^{32}\text{P}]\text{ATP}$ 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/cm^3) 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 $\Sigma \epsilon_{\text{amino acid}}$, is approximately equal to the molar absorptivity, $\epsilon_{\text{protein}}$, for the protein. The molar absorptivity, $\epsilon_{\text{amino acid}}$, at 280 nm for tyrosine, tryptophan and phenylalanine is $1400 \text{ M}^{-1} \text{ cm}^{-1}$, $5600 \text{ M}^{-1} \text{ cm}^{-1}$ and $5 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. The absorbance of a $10 \mu\text{M}$ 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.

($M = \text{mol dm}^{-3}$)

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

1000 bp double stranded DNA $M(\text{DNA}) = ((483 - 175) \times 2 \times 1000 + 2 \times 17) \text{ g mol}^{-1} = 616034 \text{ g mol}^{-1}$.

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: $m(\text{DNA}) = 1073741824 / N_A \times 616350 \text{ g mol}^{-1} = 1.1 \text{ ng}$

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 $\frac{243464}{370} \text{ pmol } 5' -^{32} \text{ P-DNA} = 658 \text{ pmol } 5' -^{32} \text{ P-DNA}$.

Since volume of the labelled DNA is $10 \mu\text{L}$, the concentration of the DNA is thus approx. $66 \mu\text{M}$.

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:

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

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

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

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

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

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

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

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

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

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

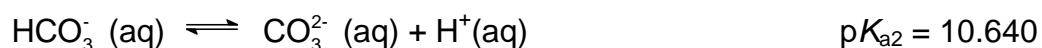
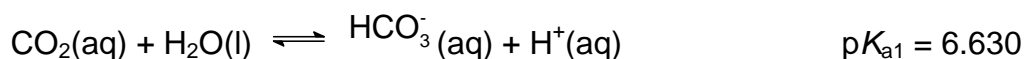
The number of tryptophan residues in a PNK molecule is thus:

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

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, CO₂, is a diprotic acid in aqueous solution. The pK_a-values at 0 °C are:



The liquid volume change associated with dissolution of CO₂ may be neglected for all of the following problems. The temperature is to be taken as being 0 °C.

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 $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$

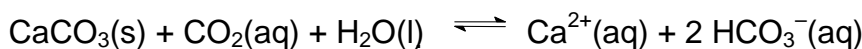
6.2 Calculate the equilibrium concentration of hydrogen ions and the equilibrium concentration of CO₂ in water saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar.

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:



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.

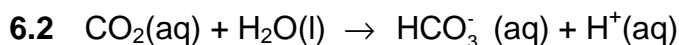
SOLUTION

6.1 $c(\text{CO}_2) = 0.0752 \text{ M}$ $n(\text{CO}_2) = 0.0752 \text{ mol}$

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

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

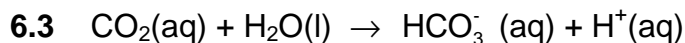
$$V = 1.71 \text{ dm}^3$$



$$[\text{H}^{+}] = [\text{HCO}_3^{-}] = x \quad \text{and} \quad [\text{CO}_2] + [\text{HCO}_3^{-}] = 0.0752$$

$$K_a = 10^{-6.63} = \frac{[\text{H}^{+}][\text{HCO}_3^{-}]}{[\text{CO}_2]} = \frac{x^2}{0.0752 - x}$$

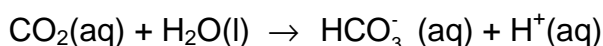
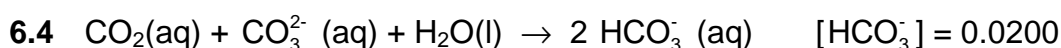
$$[\text{H}^{+}] = 0.000133 \quad \text{and} \quad [\text{CO}_2] = 0.0751$$



$$[\text{CO}_2] = 0.0751 \quad \text{and} \quad [\text{HCO}_3^-] = 0.0100$$

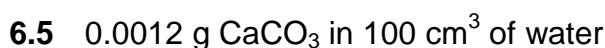
$$K_a = 10^{-6.63} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = \frac{x \cdot 0.0100}{0.0751}$$

$$x = [\text{H}^+] = \underline{1.76 \times 10^{-6}}$$



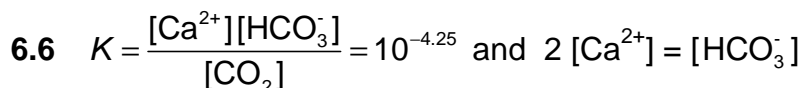
$$K_a = 10^{-6.63} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = \frac{x \cdot 0.0200}{0.0751}$$

$$x = [\text{H}^+] = 8.8 \times 10^{-7}$$

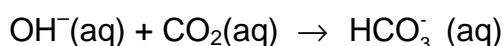
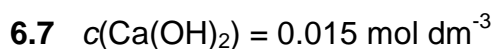


$$0.0012 \text{ g} / 100 \times 0.872 \text{ g mol}^{-1} = 0.000012 \text{ mol } \text{CaCO}_3 \text{ in } 100 \text{ cm}^3 \text{ of water}$$

$$[\text{Ca}^{2+}] = 1.2 \times 10^{-4} \quad c(\text{Ca}^{2+}) = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$$



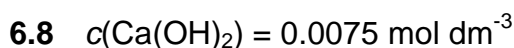
$$\frac{4 [\text{Ca}^{2+}]}{0.0751} = 10^{-4.25} \quad [\text{Ca}^{2+}] = 1.02 \times 10^{-2} \quad c(\text{Ca}^{2+}) = 1.02 \times 10^{-2} \text{ mol dm}^{-3}$$



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

$$[\text{Ca}^{2+}] = 1.02 \times 10^{-2} \quad c(\text{Ca}^{2+}) = 1.02 \times 10^{-2} \text{ mol dm}^{-3}$$



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

$$[\text{Ca}^{2+}] = 0.75 \times 10^{-2} \quad c(\text{Ca}^{2+}) = 0.75 \times 10^{-2} \text{ mol dm}^{-3}$$

6.9

$$K = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]}{[\text{CO}_2]} = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]}{[\text{CO}_2]} \times \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{CO}_3^{2-}][\text{H}^+]} = \frac{K_{sp} K_{a1}}{K_{a2}}$$

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

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

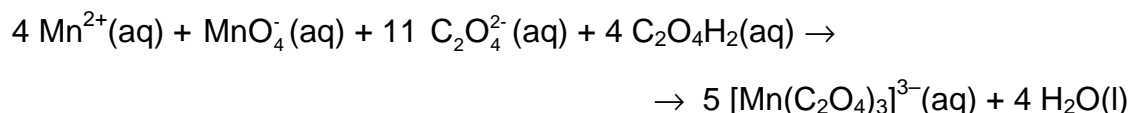
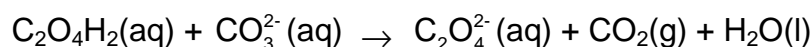
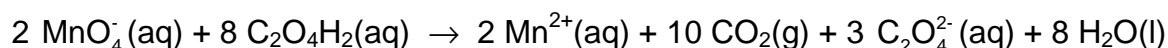
This experiment includes one preparation of a metal complex salt and two analyses of a provided sample of the same compound. The compound is a “classic” within inorganic photo chemistry.

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 sufficient 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.



Dissolve 5.00 g of $C_2O_4H_2 \cdot 2 H_2O$ in 35 cm³ of water in a 150 cm³ 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 °C 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 cm^3 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.

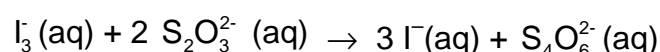
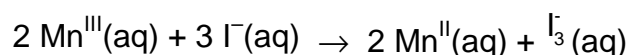
1.1 Record the yield in grams.

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

Analysis of the Provided Sample of $\text{K}_3[\text{Mn}(\text{C}_2\text{O}_4)_3] \cdot x \text{H}_2\text{O}$ 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.



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

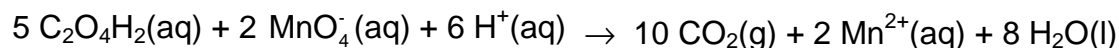
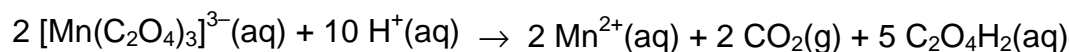
liquid in small portions before the residue is washed down) quantitatively with demineralized water to the flask. Titrate the I_3^- formed with the standardized, approx. 0.025 M $Na_2S_2O_3$ solution. When the brown colour has faded to light yellow, add 2 cm³ of starch indicator solution and continue 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.



Transfer an accurately preweighed sample (approx. 200 mg) of the provided complex quantitatively with demineralized water to a 250 cm³ conical flask. Add 25 cm³ 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.

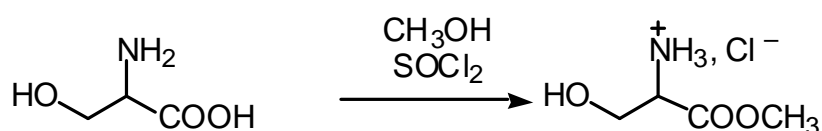
The results of the two types of analysis may differ by up to 10 %. Use only the result from the titration with $KMnO_4$ for the following calculation.

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 cm³) 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 cm³) is drawn up into a 1 cm³ 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 °C 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 cm³) 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 cm³ beaker.

The crystals are washed two times on the filter, each time with 1 cm³ 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.

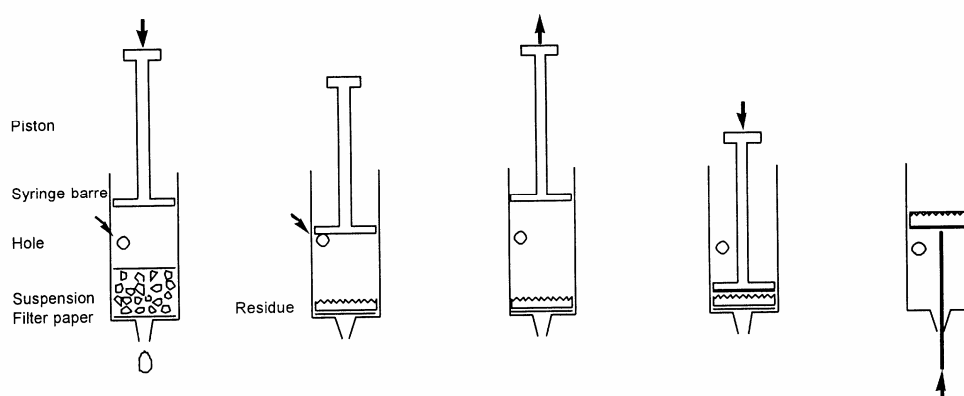
The solid is then collected on a piece of filter paper in order to absorb residual solvent. When dry, the residue is placed in a tarred plastic sample tube with lid (Eppendorf tube) found in the box. The sample tube is then closed and weighed.

PROCEDURE A

Filtration procedures

Modified syringes are used for filtration in the laboratory tasks. A 60 cm³ syringe with a disc of porous polypropylene is used in task 1, while a 10 cm³ 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 cm³ standard medical polypropylene syringe from which the piston has been temporarily removed and a 3 mm hole drilled at the 35 cm³ 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.

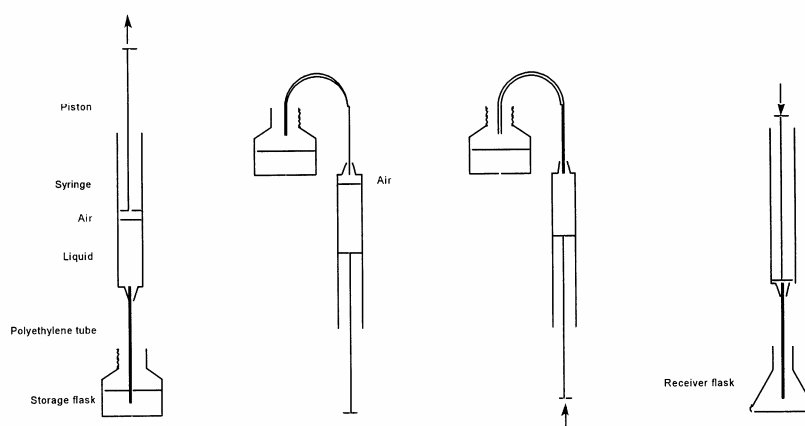
Filtration procedure for practical problem 2

The provided filter syringe to be used in this experiment is made from a 10 cm³ standard medical polypropylene syringe from which the piston has been temporarily removed and a 3 mm hole drilled at the 5.5 cm³ 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.
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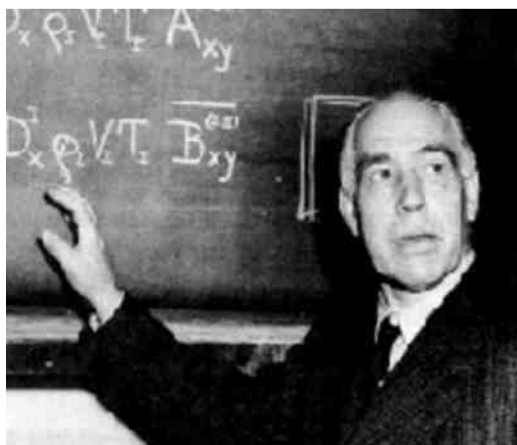
**7 theoretical problems
3 practical problems**

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

THEORETICAL PROBLEMS

PROBLEM 1

Hydrogen Atom and Hydrogen Molecule



Niels Bohr (1885-1962)

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

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

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

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

1.1 Calculate the longest wavelength in Å ($1 \text{ Å} = 10^{-10} \text{ m}$) 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, $a_0 = \frac{\epsilon_0 h^2}{m_e e^2 \pi}$) 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 $\psi_{1s}(r)$ 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 H₂ molecule can dissociate through two different channels:

- (i) H₂ → H + H (two separate hydrogen atoms)
- (ii) H₂ → H⁺ + H⁻ (a proton and a hydride ion)

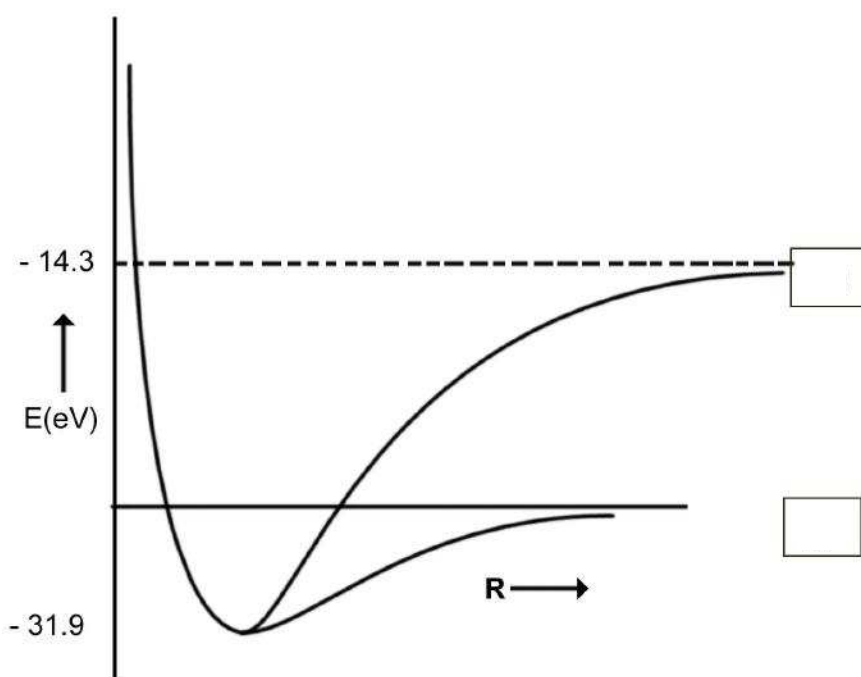
The graph of energy (E) vs internuclear distance (R) for H₂ is shown schematically in the figure. The atomic and molecular energies are given in the same scale.

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

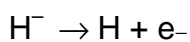
1.6 Determine the values of the dissociation energies (D_e in eV) of the H_2 molecule corresponding to

channel (i)

channel (ii)



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



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 λ_L corresponds to $n = 3$

For He^+

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

$$\lambda_L = 1641.1 \text{ \AA}$$

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

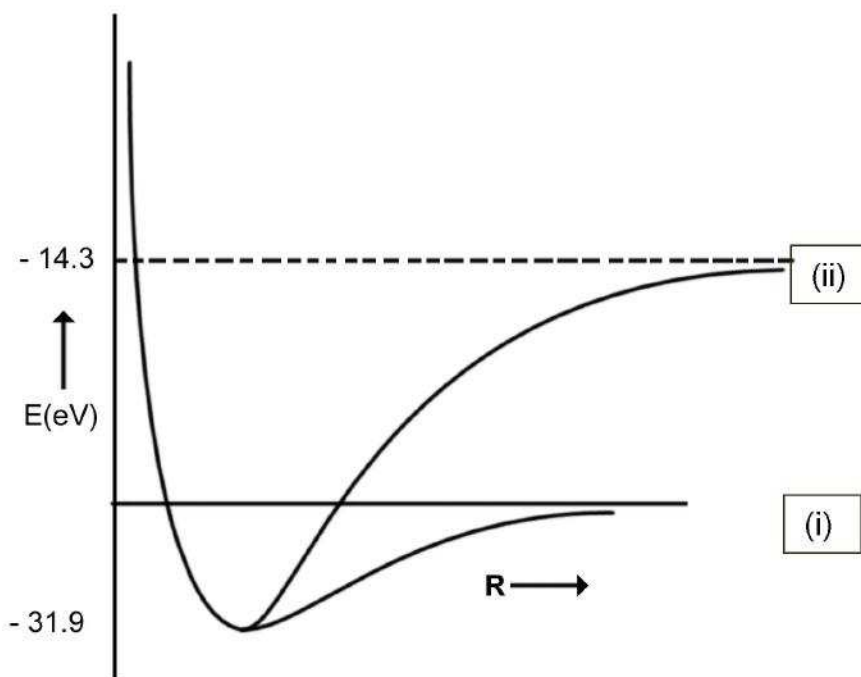
$$E = -hcR_H = -13.6 \text{ eV}$$

$$1.3 \quad \text{Lowest energy} = -207 \times 13.6 = -2.82 \text{ keV}$$

$$\text{Radius of the first Bohr orbit} = 0.53 / 207 = 2.6 \times 10^{-3} \text{ \AA}$$

$$1.4 \quad \text{Probability} = |\psi(a_0)|^2 4\pi a_0^2 \times 0.001 a_0 = 0.004 e^{-2} = 5.41 \times 10^{-4}$$

1.5



$$1.6 \quad \text{Channel (i):} \quad 4.7 \text{ eV}$$

$$\text{Channel (ii):} \quad 17.6 \text{ eV}$$

$$1.7 \quad \text{Electron affinity} = -13.6 - (-14.3) = 0.7 \text{ eV}$$

$$1.8 \quad Z_{\text{eff}} = -13.6 + 27.2 Z_{\text{eff}}^2 = 0.7$$

PROBLEM 2

Phosphoric Acid

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

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

$$pK_{1a} = 2.12$$

$$pK_{2a} = 7.21$$

$$pK_{3a} = 12.32$$

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

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

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

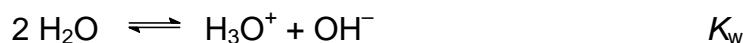
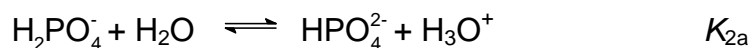
2.3 Phosphoric acid is used as a fertiliser for agriculture. 1.00×10^{-3} M phosphoric acid is added to an aqueous soil suspension and the pH is found to be 7.00.

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

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

SOLUTION

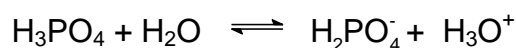
2.1 The conjugate base of dihydrogen phosphate (H_2PO_4^-) is monohydrogen phosphate (HPO_4^{2-}):



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

$$pK_{2b} = 6.79$$

2.2 Concentration of $\text{H}_3\text{PO}_4 = \frac{0.5}{98} = 0.0051 \text{ M}$



$$0.0051 - x \qquad \qquad \qquad x \quad + \quad x$$

$$pK_{1a} = 2.12 \quad \text{gives} \quad K_{1a} = 7.59 \times 10^{-3}$$

$$7.59 \times 10^{-3} = \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]} = \frac{x^2}{0.0051 - x}$$

$$x = [\text{H}_3\text{O}^+] = 3.49 \times 10^{-3}$$

$$pH = 2.46$$

2.3 Let $f_0 = \frac{[\text{H}_3\text{X}]}{C}$, $f_1 = \frac{[\text{H}_2\text{X}^-]}{C}$,

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

denote the fractional concentrations of different phosphate species. C is the total initial concentration of H_3X . ($X = \text{PO}_4$)

$$f_0 + f_1 + f_2 + f_3 = 1$$

$$K_{1a} = \frac{[\text{H}_2\text{X}^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{X}]} = \frac{f_1}{f_0} [\text{H}_3\text{O}^+]$$

$$K_{2a} = \frac{[\text{HX}^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{X}^-]} = \frac{f_2}{f_1} [\text{H}_3\text{O}^+]$$

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

These equations lead to

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

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

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

$$K_{1a} = 7.59 \times 10^{-3}; \quad K_{2a} = 6.17 \times 10^{-8}; \quad K_{3a} = 4.79 \times 10^{-13}; \quad [H_3O^+] = 1 \times 10^{-7}$$

The fractional concentrations of different phosphate species are:

$$H_3PO_4 \quad (f_0) = 8.10 \times 10^{-6}$$

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

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

$$PO_4^{3-} \quad (f_3) = 1.83 \times 10^{-6}$$

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

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

Total concentration of different phosphate species = $2S$

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

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

$$\text{For } pH = 7, \quad f_3 = 1.83 \times 10^{-6}$$

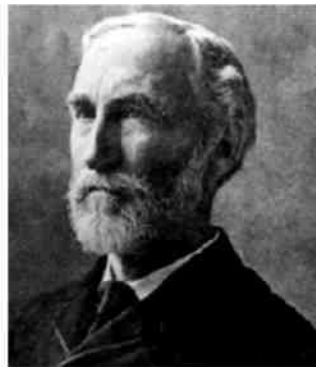
$$K_{sp} = [Zn^{2+}]^3 [PO_4^{3-}]^2$$

$$9.1 \times 10^{-33} = (3S)^3 (f_3 \times 2S)^2$$

$$[Zn^{2+}] = 9 \times 10^{-5}$$

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

$$\text{Solubility of } Zn_3(PO_4)_2 = 3.0 \times 10^{-5} \text{ mol dm}^{-3}$$

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 CO₂ gas expands isothermally (in thermal contact with the surroundings; temperature = 15 °C) against a fixed external pressure of 1.00 bar. The initial and final volumes of the gas are 10.0 dm³ and 30.0 dm³, respectively.

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

- | | | | |
|-----|-----------------------------|-----------------------------|--------------------------|
| (a) | $\Delta S_{\text{sys}} > 0$ | $\Delta S_{\text{sur}} = 0$ | <input type="checkbox"/> |
| (b) | $\Delta S_{\text{sys}} < 0$ | $\Delta S_{\text{sur}} > 0$ | <input type="checkbox"/> |
| (c) | $\Delta S_{\text{sys}} > 0$ | $\Delta S_{\text{sur}} < 0$ | <input type="checkbox"/> |
| (d) | $\Delta S_{\text{sys}} = 0$ | $\Delta S_{\text{sur}} = 0$ | <input type="checkbox"/> |

(Mark X in the correct box.)

3.2 Calculate ΔS_{sys} assuming CO₂ to be an ideal gas.

3.3 Calculate ΔS_{sur} .

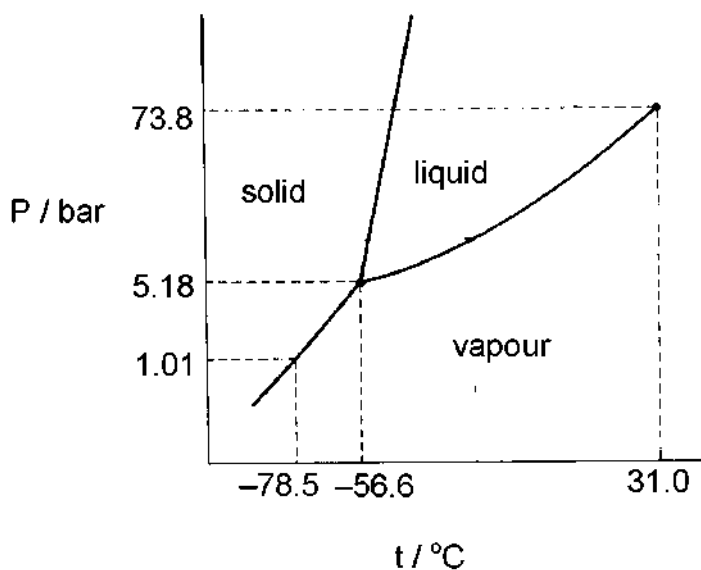
3.4 Calculate the change in entropy of the universe.

Does your answer agree with the Second Law of Thermodynamics?

(Mark X in the correct box.)

Yes No

The pressure – temperature phase diagram of CO₂ is given below schematically. The diagram is not to scale.



Phase diagram of CO₂

3.5 CO₂ gas, initially at a pressure of 4.0 bar and temperature of 10.0 °C is cooled at constant pressure. In this process,

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

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

3.6 Starting with the same pressure and temperature as above (in 3.5), CO₂ is compressed isothermatically. In this process,

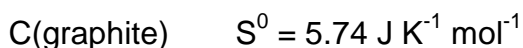
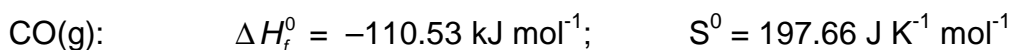
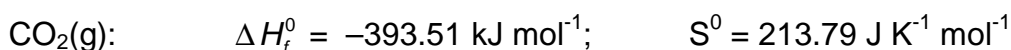
(a) it goes first to the liquid phase and then to the solid phase.

(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 CO₂. Write down the formula used.

3.8 CO gas, used extensively in organic synthesis, can be obtained by reacting CO₂ 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



- 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 CO₂ and excess hot graphite in a reactor maintained at about 800 °C and a total pressure of 5.0 bar. The equilibrium constant K_p under these conditions is 10.0. Calculate the partial pressure of CO at equilibrium.

SOLUTION

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

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

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

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

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

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

The answer agrees with the second law of thermodynamics (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.

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

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

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

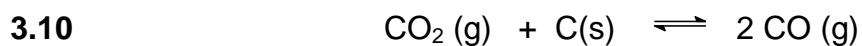
$\Delta S^0 = 176 \text{ J K}^{-1}\text{mol}^{-1}$

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

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

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

$T = 980 \text{ K}$



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

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

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

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

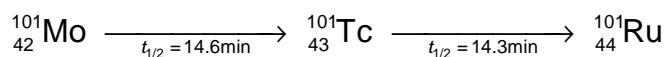
PROBLEM 4**Beach Sand Mineral in Kerala**

Beach sand mineral, monazite, is a rich source of thorium, available in large quantities in the state of Kerala in India. A typical monazite sample contains about 9 % ThO₂ and 0.35 % U₃O₈. ²⁰⁸Pb and ²⁰⁶Pb are the stable end-products in the radioactive decay series of ²³²Th and ²³⁸U, respectively. All the lead (Pb) found in monazite is of radiogenic origin.

The isotopic atom ratio ²⁰⁸Pb/²³²Th, measured mass spectrometrically, in a monazite sample was found to be 0.104. The half-lives of ²³²Th and ²³⁸U are 1.41×10¹⁰ years and 4.47×10⁹ years, respectively. Assume that ²⁰⁸Pb, ²⁰⁶Pb, ²³²Th and ²³⁸U 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 ²⁰⁶Pb/²³⁸U 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 ²³³U by successive β⁻ decays. Write the nuclear reactions for the formation of ²³³U from ²³²Th.

In nuclear fission of ²³⁵U a complex mixture of radioactive fission products is formed. The fission product ¹⁰¹Mo initially undergoes radioactive decay as shown below:



- 4.4 A freshly prepared radiochemically pure sample of ¹⁰¹Mo contains 5000 atoms of ¹⁰¹Mo initially. How many atoms of
 - i) ¹⁰¹Mo
 - ii) ¹⁰¹Tc
 - iii) ¹⁰¹Ru
 will be present in the sample after 14.6 min?

SOLUTION

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

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

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

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

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

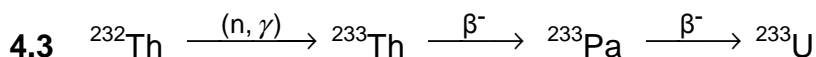
$$t = 2.01 \times 10^9 \text{ years.}$$

4.2 Let x be the required ratio.

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

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

$$x = 0.366$$



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 :

$$N_3 = N_0 - N_1 - N_2 = 790 \text{ atoms}$$

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 Cl₂, Br₂ and I₂ 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.

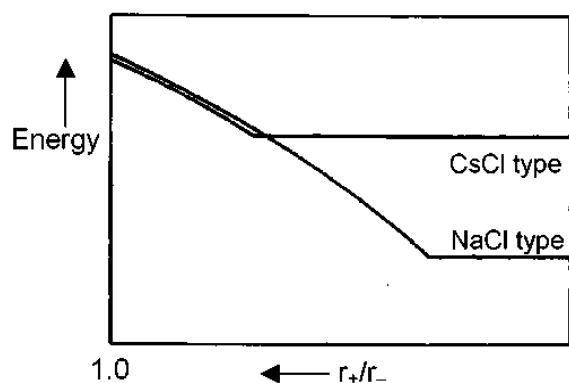
5.8 Chlorine dioxide reacts with sodium hydroxide as shown below. Identify the products X and Y (both containing chlorine) and balance the equation.

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.

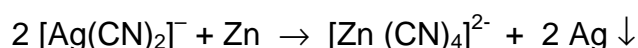
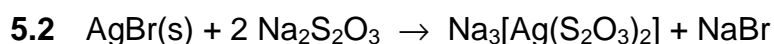
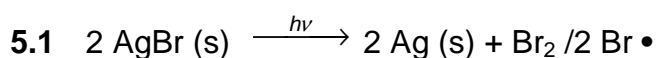
(Mark X in the correct box.)

- 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 $\text{CuK}\alpha$ X-rays ($\lambda = 154 \text{ nm}$), 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.

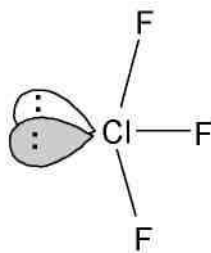
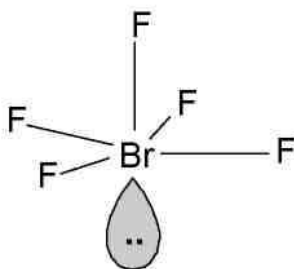
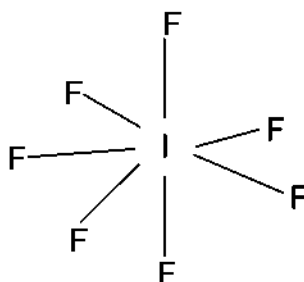
2 nd nearest neighbours			3 rd nearest neighbours		
number	sign of the charge	distance (pm)	number	sign of the charge	distance (pm)

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

SOLUTION

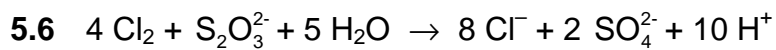


5.4

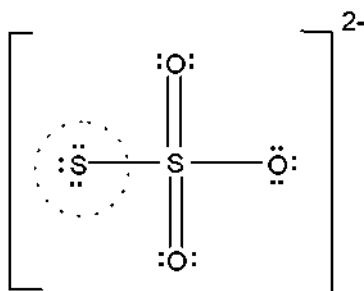
ClF₃BrF₅IF₇

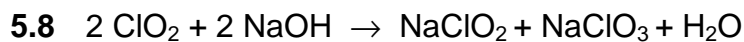
5.5.

Mass:	162	164	466	476
Species:	I ³⁵ Cl	I ³⁷ Cl	I ₂ ³⁵ Cl ₅ ³⁷ Cl	I ₂ ³⁷ Cl ₆

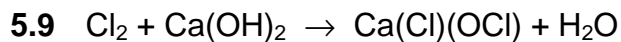


5.7

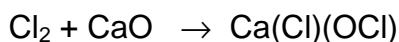




X Y



or



or



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

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

5.12 RbBr

5.13 In CsCl-type structure,

Cell edge, $a = 2r$

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

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

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

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

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

$$a = 628 \text{ pm}$$

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

2 nd nearest neighbours			3 rd 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 ailments. 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: $C_{17}H_{24}O_4$

Shogaol: $C_{17}H_{24}O_3$

6.1 Zingerone gives positive $FeCl_3$ 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 | <input type="checkbox"/> | (e) ester | <input type="checkbox"/> |
| (b) aldehydic carbonyl | <input type="checkbox"/> | (f) alkoxy | <input type="checkbox"/> |
| (c) ketonic carbonyl | <input type="checkbox"/> | (g) unsaturation | <input type="checkbox"/> |
| (d) phenolic hydroxyl | <input type="checkbox"/> | | |

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

Table 1: ¹H 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 ₂ O 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	$\begin{array}{c} \text{O} & & \text{O} \\ & & \\ -\text{C}- & \text{CH}- & \text{C}- \\ & & \end{array}$	3.4 - 3.6
$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{CH} \\ \diagup \quad \diagdown \end{array}$	2.0 - 2.7	$\begin{array}{c} & \text{H} \\ & / \\ \diagdown \text{C}=\text{C} \diagup \\ / \quad \backslash \end{array}$	4.0 - 7.0
Ph - CH	2.3 - 2.9	Ph - H	6.0 - 8.0
- O - CH	3.3 - 3.9	Ar - OH	4.0 - 11.0

Spin-spin coupling constants (J)

Alkenes	<i>cis</i>	5 – 14 Hz (commonly around 6 – 8 Hz)
	<i>trans</i>	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 weak *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.

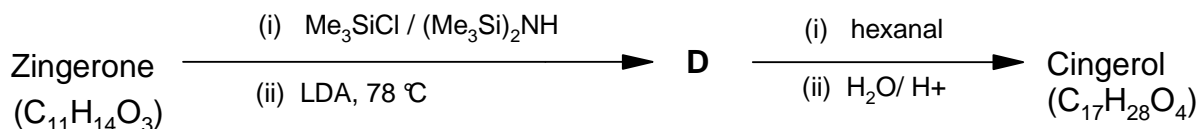


A + **B** (C₃H₆O)



C

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



Notes: (1) Me₃SiCl / (Me₃Si)₂NH is used to convert OH into –OSiMe₃; the group –SiMe₃ can be removed by acid hydrolysis.

(2) LDA is lithium diisopropylamine, 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 enantiomers? | <input type="checkbox"/> |
| (b) a mixture of diastereomers? | <input type="checkbox"/> |
| (c) a mixture of an enantiomeric pair and a meso isomer? | <input type="checkbox"/> |
- (Mark X in the correct box.)
- vi) Gingerol (C₁₇H₂₆O₄) when heated with a mild acid (such as KHSO₄) gives Shogaol (C₁₇H₂₄O₃). 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. Curcumin (C₂₁H₂₀O₆), 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 | <input type="checkbox"/> |
| (b) a carbonyl group | <input type="checkbox"/> |
| (c) an extended conjugation | <input type="checkbox"/> |
| (d) a hydroxyl group | <input type="checkbox"/> |
- (Mark X in the correct box.)

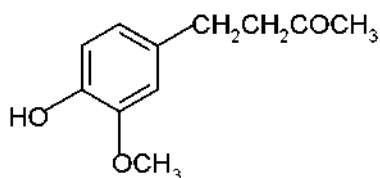
SOLUTION

6.1 Zingerone contains the following functional groups:

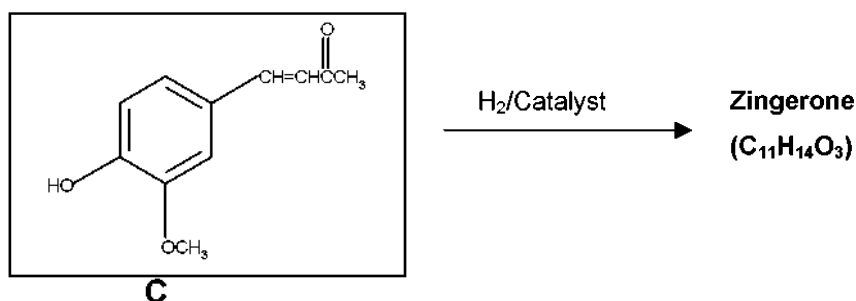
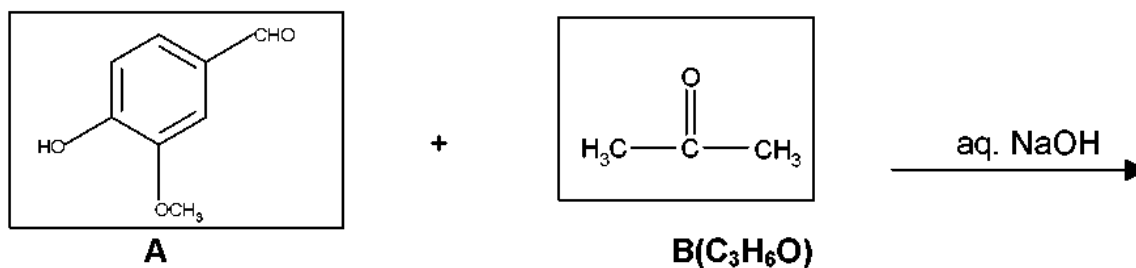
- (c) ketonic carbonyl
- (d) phenolic hydroxyl

- 6.2 i) side chain in Zingerone: $\text{CH}_2\text{CH}_2\text{COCH}_3$
 ii) substituents on the aromatic ring: OH , OCH_3
 iii) relative positions of the substituents on the ring: 1, 2, 4

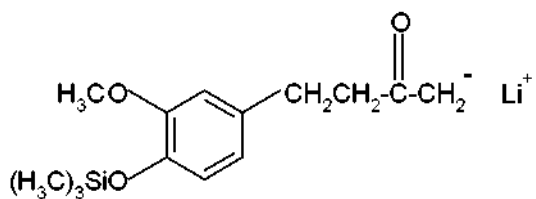
6.3



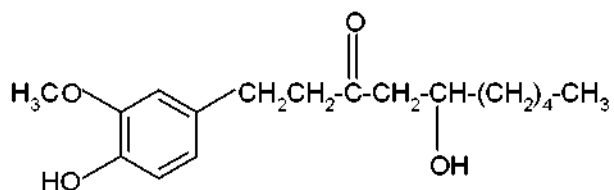
6.4



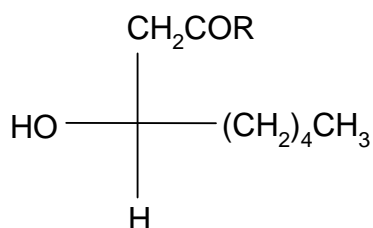
6.5 i)



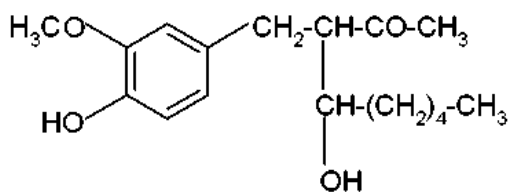
ii)



iii)

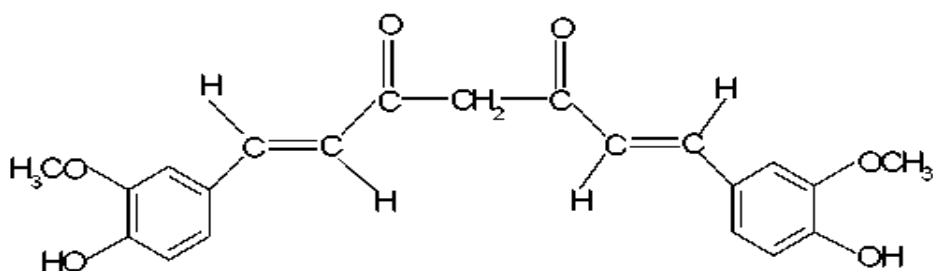


iv)

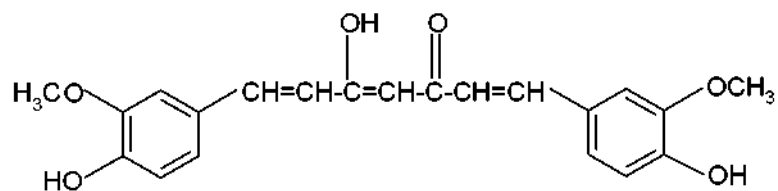


v) Compound E will be formed as: (b) a mixture of diastereomers

6.6 i)



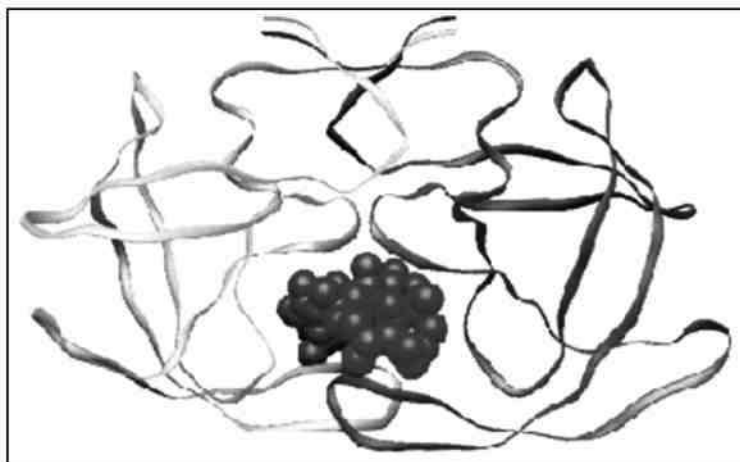
ii)



- iii) Curcumin is yellow in colour 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

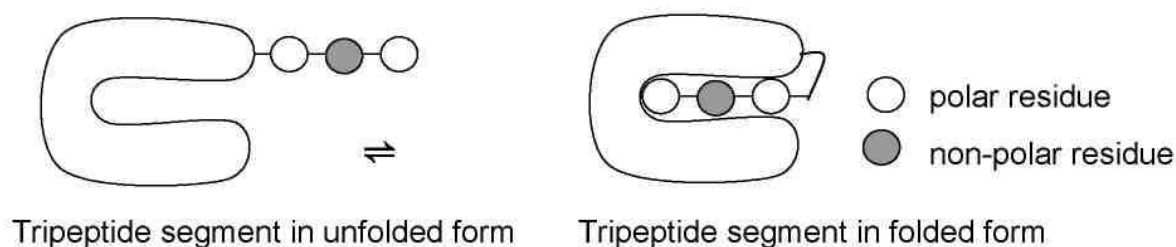
(Mark X in the correct box.)

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 disordered 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 (ΔG) 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): $\Delta G = +8 \text{ kJ mol}^{-1}$
 (b) a non-polar residue and the rest of the protein: $\Delta G = -4 \text{ kJ mol}^{-1}$
 (c) a polar residue and the solvent (water): $\Delta G = -16 \text{ kJ mol}^{-1}$
 (d) a polar residue and the rest of the protein: $\Delta G = -14 \text{ kJ mol}^{-1}$

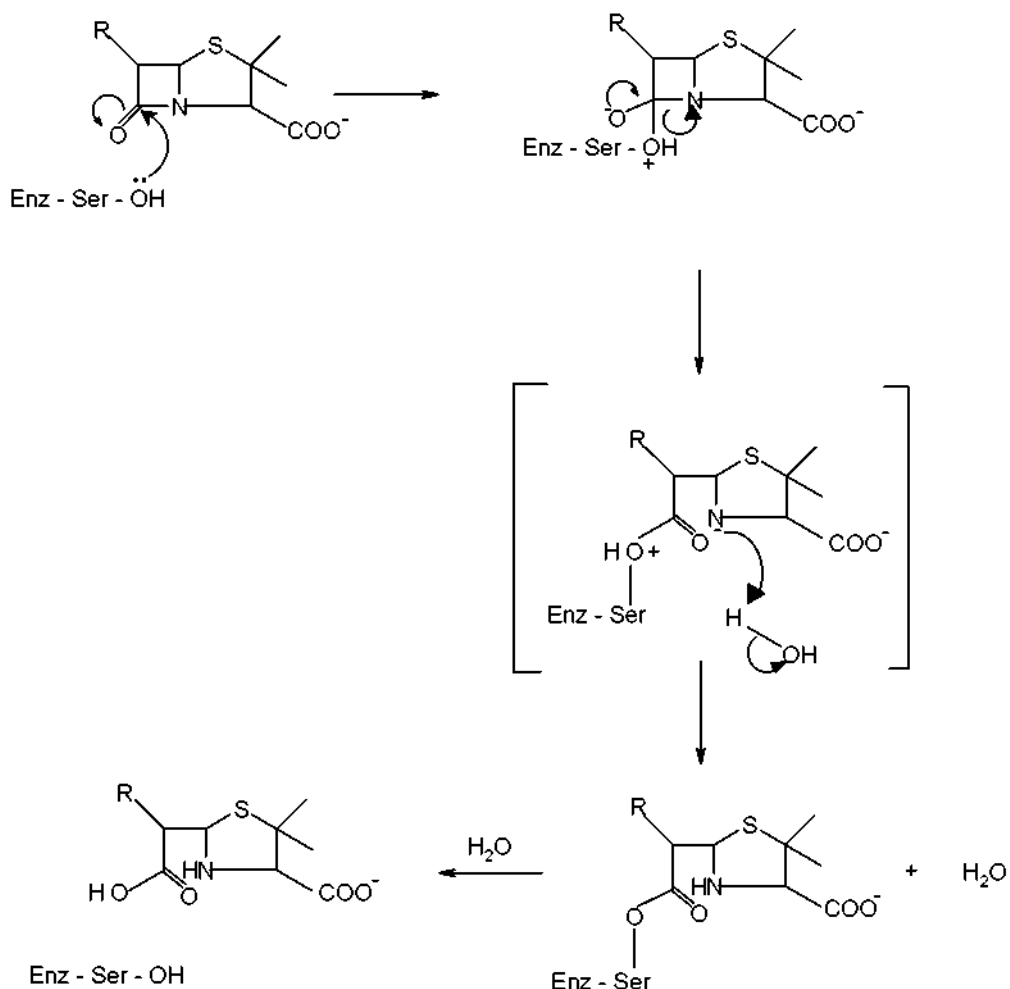


7.4 Calculate ΔG for the folding of the tripeptide segment.

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 enzyme called β -lactamase (also known as penicillinase), which inactivates penicillin by opening its β -lactam ring. The mechanism for this β -lactam ring opening involves the nucleophilic attack by serine-OH at the active site of the enzyme as shown below.



An attempt was made to characterize the β -lactamase from *Staphylococcus aureus*. When the pure enzyme was treated with a radiolabelled [³²P] 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 β -lactamase.

7.6 Estimate the minimal molecular mass of this β -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 β -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 phenylalanine 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 β -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	$\begin{array}{c} \text{COO}^- \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{COOH} \\ \\ \text{H} \end{array}$	147
Hms – Homoserine	$\begin{array}{c} \text{COO}^- \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{OH} \\ \\ \text{H} \end{array}$	119
Leu – Leucine	$\begin{array}{c} \text{COO}^- \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{CH}_2 - \text{CH} \\ \quad \diagup \quad \diagdown \\ \text{H} \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	131
Met – Methionine	$\begin{array}{c} \text{COO}^- \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{S} - \text{CH}_3 \\ \\ \text{H} \end{array}$	149
Lys – Lysine	$\begin{array}{c} \text{COO}^- \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH}_2 \\ \\ \text{H} \end{array}$	146
Phe – Phenylalanine	$\begin{array}{c} \text{COO}^- \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{CH}_2 - \text{C}_6\text{H}_5 \\ \\ \text{H} \end{array}$	165

Table (continued)

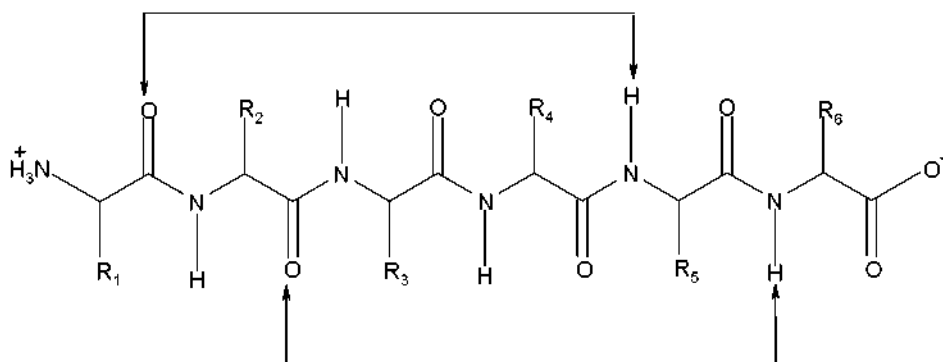
Arg – Arginine	$\begin{array}{c} \text{COO}^- \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{NH} - \text{C} \begin{array}{l} / \text{NH}_2 \\ \backslash \text{NH} \end{array} \\ \\ \text{H} \end{array}$	174
Ser – Serine	$\begin{array}{c} \text{COO}^- \\ \\ \text{H}_3\text{N}^+ - \text{C} - \text{CH}_2 - \text{OH} \\ \\ \text{H} \end{array}$	105

SOLUTION

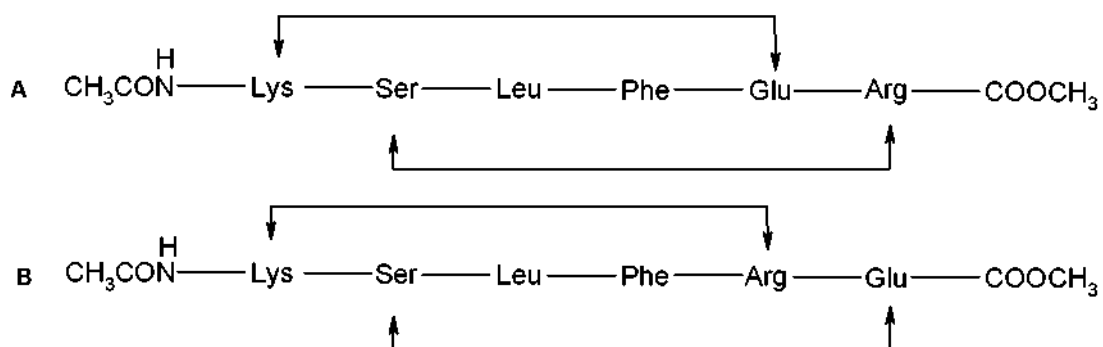
7.1 The end-to-end distance in a hexapeptide when it is in a fully extended conformation is approximately :

(c) 20 Å

7.2



7.3



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

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

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

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

(c) 275

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

P2: Glu – Ser – Met – Leu – Lys

P3: Phe – Glu – Ser – Hms/Met

P4: Leu – Lys

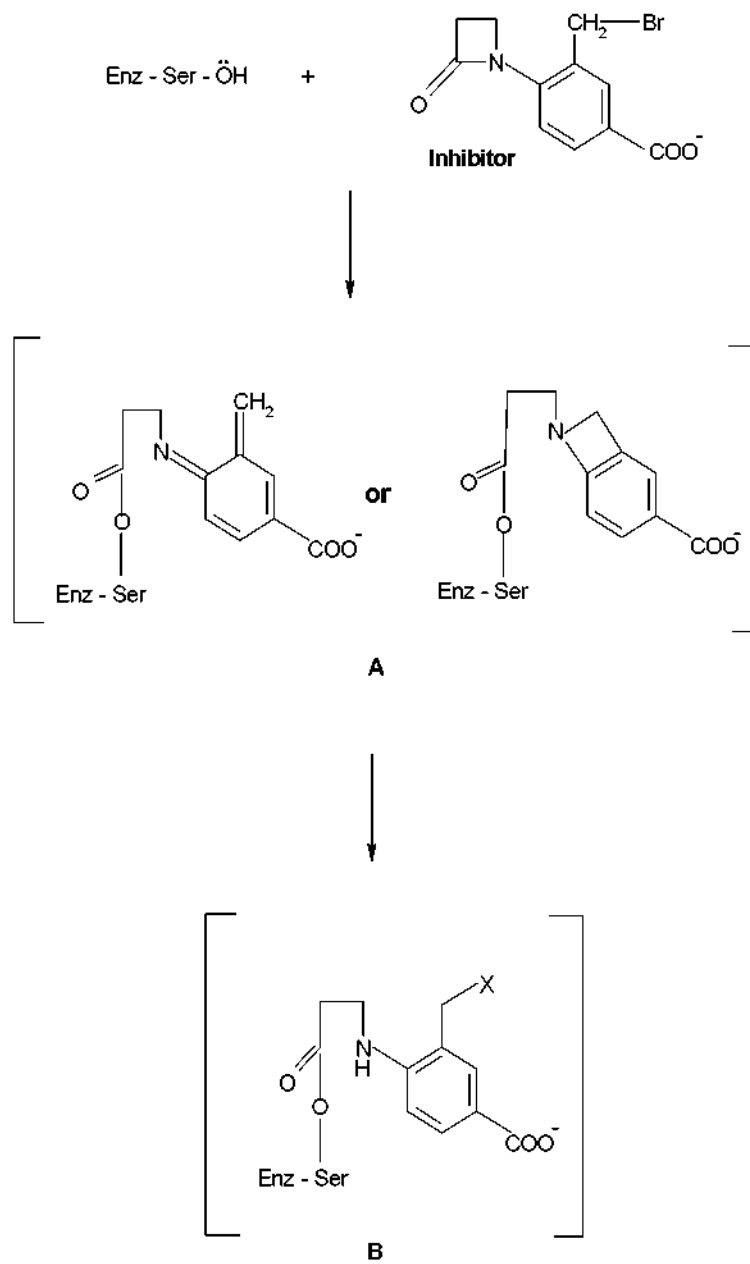
7.9 Phe - Glu - Ser - Hms

$$(165 + 147 + 105 + 119) - 3 \text{ H}_2\text{O} = 536 - 54 = 482 \text{ Da}$$

7.10 700 M

7.11 The most effective inhibitor is C.

7.12



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 H₂SO₄).

Procedure

- 1) Quantitatively transfer the given sample of solid 2-aminobenzoic acid into a 100 cm³ beaker placed in the ice-bath. Add 7.2 cm³ of H₂SO₄ (2.6 M) (labelled H₂SO₄) 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 cm³ of supplied cooled NaNO₂ solution from the vial placed in the ice-bath.
- 3) With the help of a dropper, slowly add the cooled NaNO₂ 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 cm³ 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 cm³). Collect the washings along with the main filtrate.
- 7) Neutralize the combined filtrate by gradually adding the given solid Na₂CO₃ 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 cm³ conical flask. Pour about 15 to 20 cm³ of the supplied NaHCO₃ solution (using test tube) over the filter paper so as to dissolve the precipitate completely.

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

- 9) Add dilute H_2SO_4 gradually to the filtrate till effervescence ceases. Filter the purified product. Use 10 -15 cm^3 distilled water to wash the precipitate. Keep the filter paper with the product on a watch glass.
- 10) Cover the product with the same funnel and hand over the product to the laboratory expert for drying (for a minimum of one hour).

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

SOLUTION

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

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

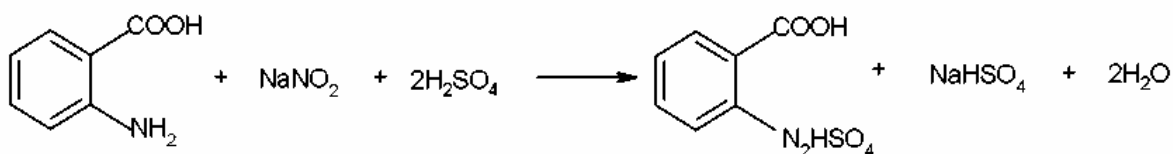
Tasks:

Write down the balanced chemical equations for:

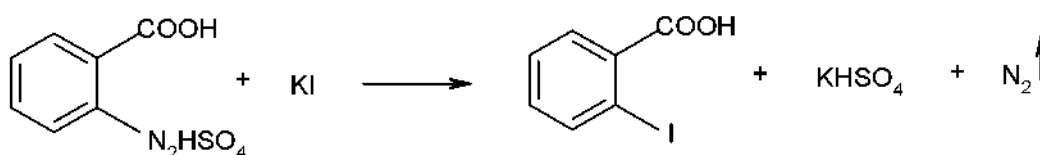
- (a) diazotization of 2-aminobenzoic acid using NaNO_2 and H_2SO_4 .
- (b) the reaction of KI with the diazotized product.

Solutions of the tasks:

a)



b)



PROBLEM 2 (Practical)

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

In this experiment, estimation of the amounts of Mn (II) and Mg (II) present in the given sample is carried out by complexometric titration using standard Na₂EDTA 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 Na₂EDTA 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 cm³ 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 cm³) are supplied to you. Fill one with the given standard Na₂EDTA solution and the other with the given standard Mn (II) solution.

Titration 1

To the sample solution (supplied in the 250 cm³ conical flask), add all of the solid hydroxylamine hydrochloride given in one vial followed by 50 cm³ of distilled water. With the help of a measuring cylinder, add 10 cm³ 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 Na₂EDTA solution until the colour changes from wine red to blue. Record your burette reading (**A** cm³). 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 cm³ 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 cm³) 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 Na₂EDTA solution till the colour changes from wine red to blue. Record your burette reading (**B** cm³).

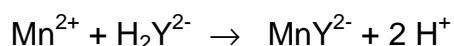
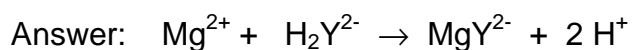
Repeat the same procedure for Trial II.

SOLUTION

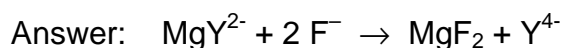
The results of the titration (volumes) were required to be written on the Answer Sheet.

The other tasks to be solved:

2.2 Give the balanced chemical equation for the reactions of Mg(II) and Mn(II) with Na₂EDTA . (Use the symbol Na₂HY for Na₂EDTA.)



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



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 cm³ 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 cm³ of this solution to a clean conical flask containing 4 cm³ 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 cm³ 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 $\text{CH}_3\text{CH}_2\text{OH}$.

Solution: Acetic acid, CH_3COOH
Acetaldehyde, CH_3CHO

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

Solution: $2 \text{HCrO}_4^- + 6 \text{I}^- + 14 \text{H}^+ \rightarrow 3 \text{I}_2 + 2 \text{Cr}^{3+} + 8 \text{H}_2\text{O}$

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

Solution: $\text{I}_2 + 2 \text{S}_2\text{O}_3^{2-} \rightarrow 2 \text{I}^- + \text{S}_4\text{O}_6^{2-}$

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

3.5 Give concentrations of HCrO_4^- at different times (in a table attached).

3.6 Plot the graph of $\log [\text{HCrO}_4^-]$ 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

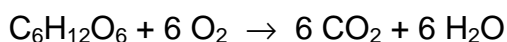
Theme 1 - Chemistry of Life

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:

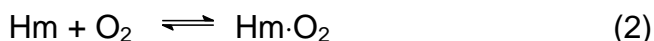


This reaction releases 400 kJ of energy per mol of oxygen. O₂ uptake by blood is at four heme (Hm) groups in the protein hemoglobin (Hb).

Free Hm consists of an Fe²⁺ ion attached to four N atoms of a porphyrin²⁻ ligand. Oxygen can bind at the coordination site of Fe²⁺ giving a Hm·O₂ complex. Carbon monoxide can be complexed similarly, giving a Hm·CO complex. CO is a poison as it binds more strongly to Hm than O₂ does. The equilibrium constant K_1 for the reaction:



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



Each Hb molecule can take up four molecules of O₂. Blood in contact with O₂ 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: O₂ pressure in lungs is 15 kPa; in the muscles it is 2 kPa. The maximum

flow of blood through heart and lungs is $4 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}$. 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} . $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. $T = 298 \text{ K}$.

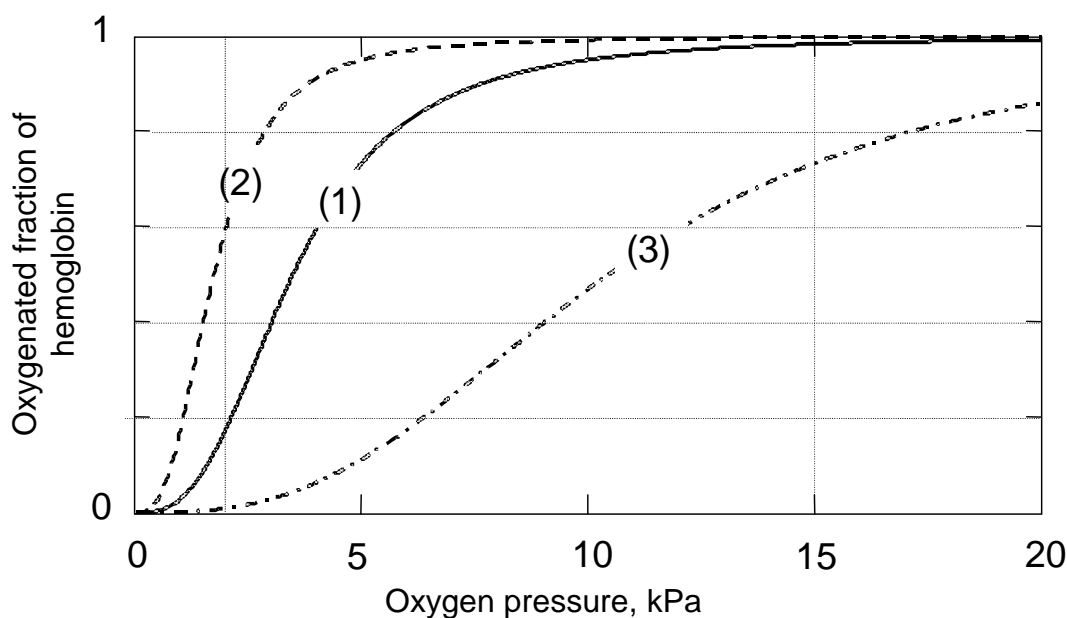


Figure 1

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

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

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

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 O₂ is too strong.

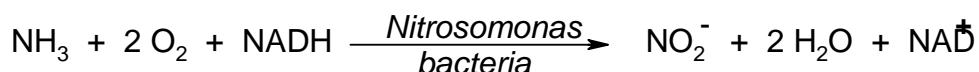
1.4 $(4 \times 10^{-4} \text{ m}^3 \text{ s}^{-1}) \times 0.4 \times (340 \text{ kg m}^{-3}) \times (3.2 \text{ mol O}_2 / \text{mol Hb}) / (64 \text{ kg mol}^{-1}) =$
 $= 2.72 \times 10^{-3} \text{ mol s}^{-1}$

1.5 $(2.72 \times 10^{-3} \text{ mol s}^{-1}) \times (400 \text{ kJ mol}^{-1}) = 1088 \text{ W}$

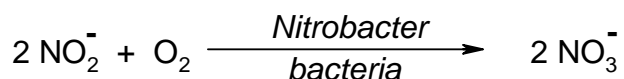
PROBLEM 2

Nitrogen Cycle in Nature

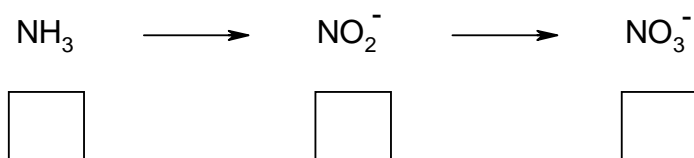
Ammonia is a toxic substance to marine animals at levels exceeding 1 ppm. Nitrifying bacteria play an important role in the conversion of NH_3 first to nitrite and then to nitrate, the storage form of nitrogen in the soil.



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



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 $\lambda = 543 \text{ nm}$. For quantitative analyses a calibration curve has to be made, in which absorbance at the maximum absorbance wavelength $\lambda = 543 \text{ nm}$ 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).

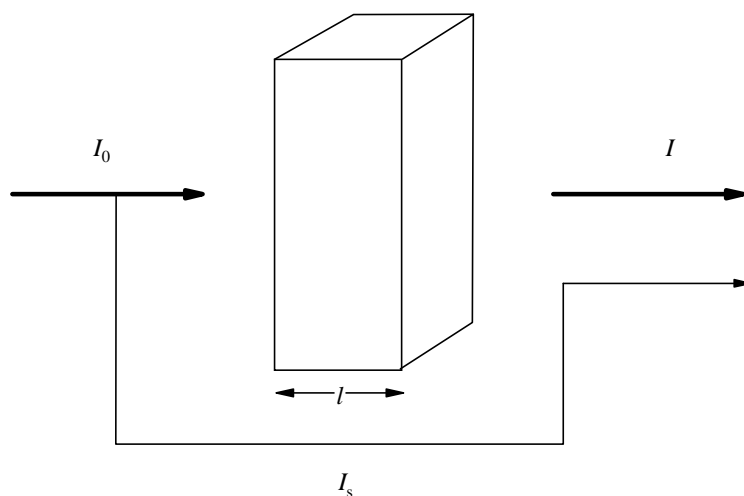


Figure 2

- 2.3** Calculate the value of the absorbance A shown by the spectrophotometer if $\varepsilon = 6000 \text{ M}^{-1} \text{ cm}^{-1}$, $l = 1 \text{ cm}$ and $c = 1 \times 10^{-4} \text{ M}$

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

$$\text{corrected absorbance} = 0.1769 c + 0.0015 \quad (\text{a})$$

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

2.5 Calculate the average nitrite nitrogen concentration in ppm and $\mu\text{g cm}^{-3}$.

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:

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

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

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

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

Slope m of the calibration curve:

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

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:

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

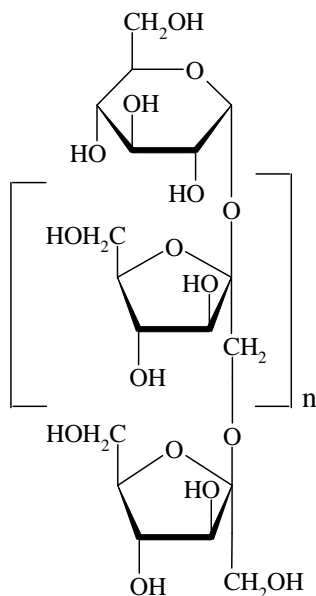
$$c = 1.55 \text{ ppm} = 1.55 \mu\text{g cm}^{-3}$$

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.

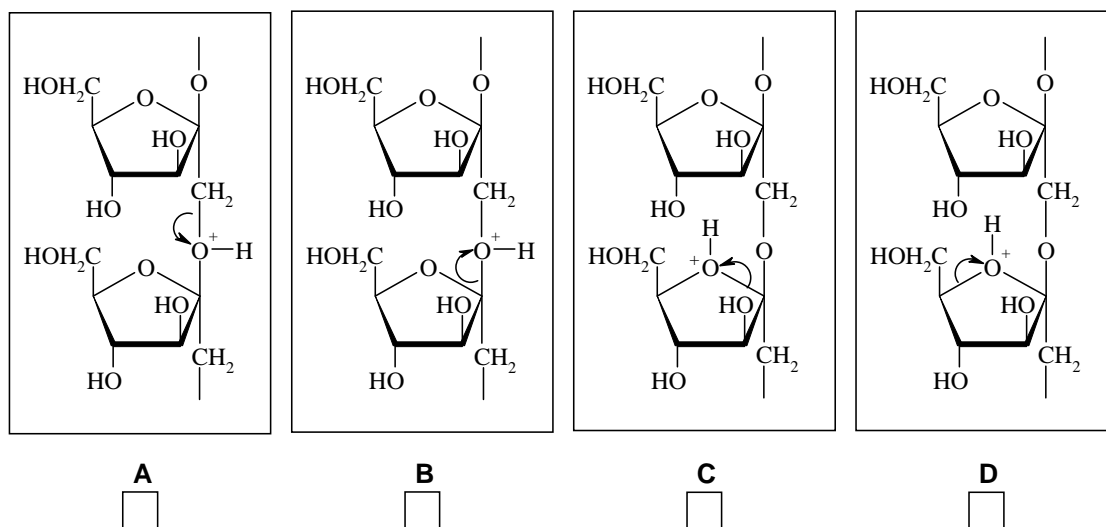
PROBLEM 3

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.



Mark the correct cleavage mechanism for the most efficient hydrolysis.

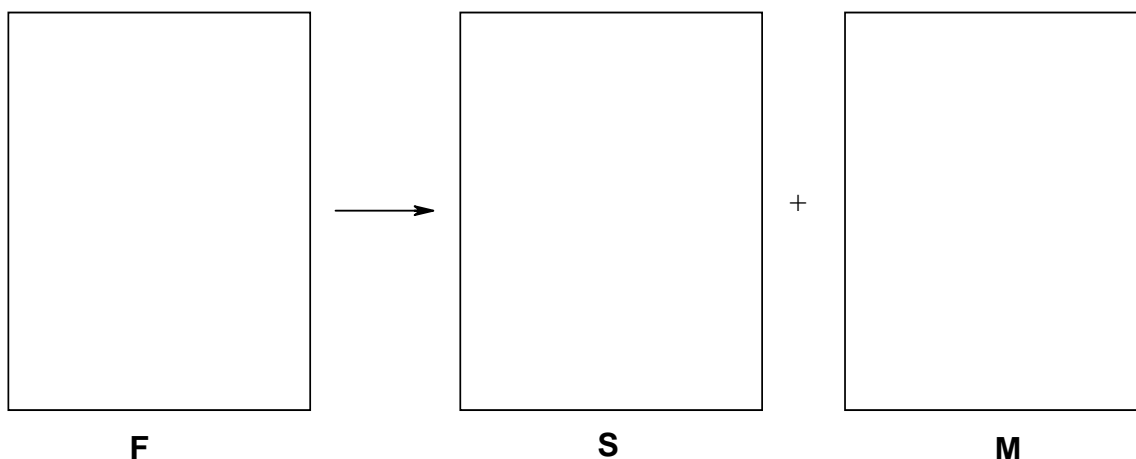
Hydrolysis with isotopically labelled water can provide information about the mechanism of hydrolysis using modern NMR techniques, which can “see” deuterium (^2H) and the oxygen isotope ^{17}O .

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

- $^2\text{H}_2\text{O}$
 H_2^{17}O
 $^2\text{H}_2^{17}\text{O}$
 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**).



1.00 mol of inulin in 2.00 kg of water with added catalysts, is subjected to hydrolysis and hydrogenation at 95 °C 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 °C. The solubility of **M** is 0.40 mol kg⁻¹ in water at 25 °C and the solubility of **S** is so high that it will not precipitate.

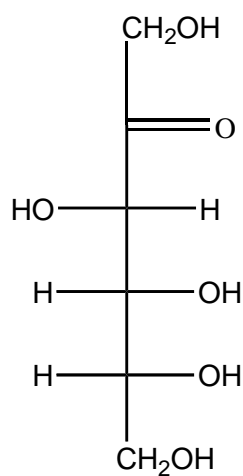
3.5 Calculate how many moles of **M** will precipitate.

SOLUTION

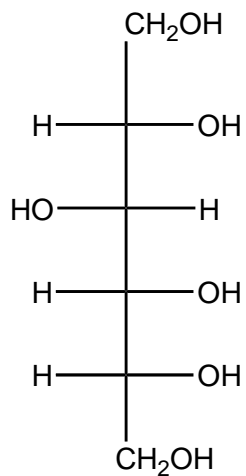
3.1 B is correct.

3.2 H_2^{17}O

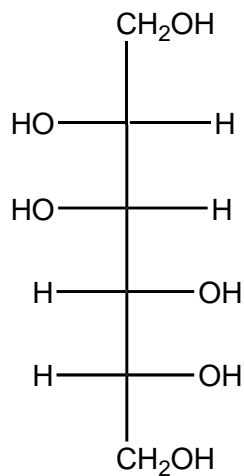
3.3



F



S



M

3.4 $n(\text{M}): 7 \text{ mol}$ $n(\text{S}): 4 \text{ mol}$

3.5 Remaining amount of water:

$$m(\text{H}_2\text{O}) = 2 \text{ kg} - (10 \times 0.018 \text{ kg}) = 1.82 \text{ kg}$$

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

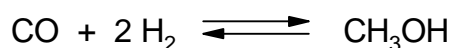
$$n(\text{M})_{\text{dissolved}} = 1.82 \times 0.4 \text{ mol} = 0.73 \text{ mol}$$

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

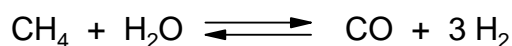
PROBLEM 4

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:



Hydrogen and CO are obtained by the reaction:



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 .

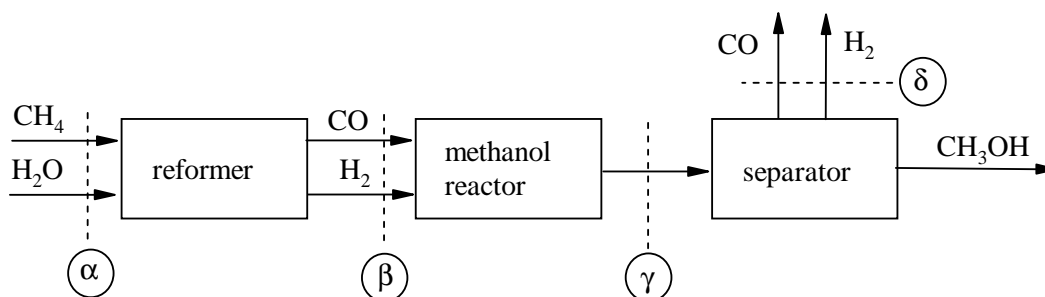


Figure 1

The flow of methanol at position γ is $\eta[\text{CH}_3\text{OH}, \gamma] = 1000 \text{ mol s}^{-1}$. 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:

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

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:

$$K_p = \frac{p_{\text{CH}_3\text{OH}} p_0^2}{p_{\text{CO}} p_{\text{H}_2}^2}$$

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).

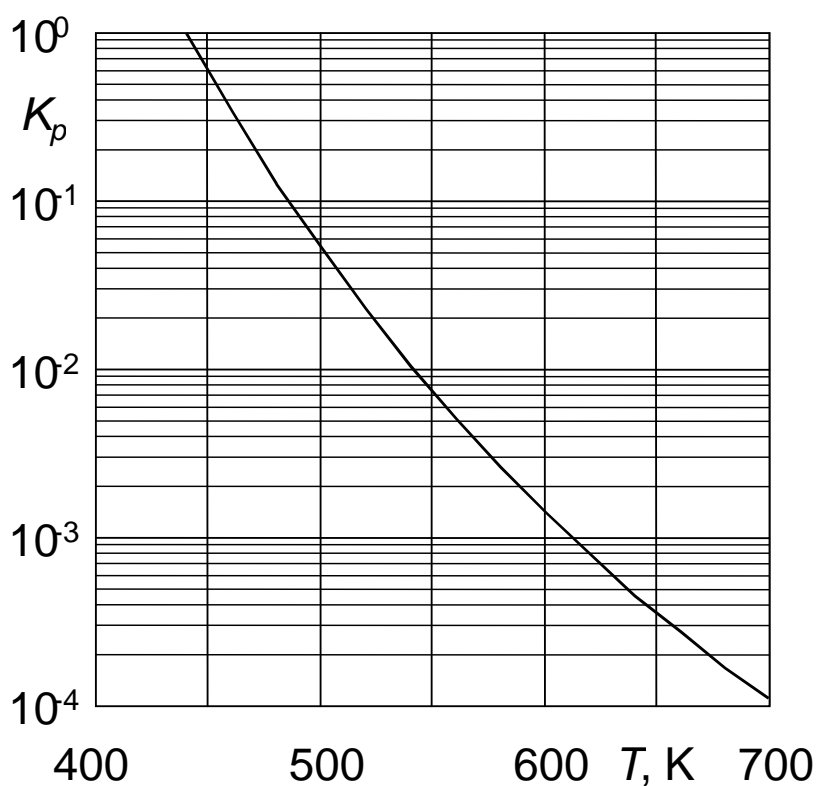


Figure 2

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

SOLUTION

$$4.1 \quad n(\text{CO}, \beta) = 3/2 \times n(\text{CH}_3\text{OH}, \gamma) = 1500 \text{ mol s}^{-1}$$

$$n(\text{H}_2, \beta) = 3 \times n(\text{CO}, \beta) = 4500 \text{ mol s}^{-1}$$

4.2 $n(\text{CO}, \gamma) = n(\text{CO}, \beta) - n(\text{CH}_3\text{OH}, \gamma) = (1500 - 1000) \text{ mol s}^{-1} = 500 \text{ mol s}^{-1}$
 $n(\text{H}_2, \gamma) = n(\text{H}_2, \beta) - 2 \times n(\text{CH}_3\text{OH}, \gamma) = (4500 - 2 \times 1000) \text{ mol s}^{-1} = 2500 \text{ mol s}^{-1}$

4.3 $n(\text{CH}_4, \alpha) = n(\text{CO}, \beta) = 1500 \text{ mol s}^{-1}$
 $n(\text{H}_2\text{O}, \alpha) = n(\text{CO}, \beta) = 1500 \text{ mol s}^{-1}$

4.4 $n_{\text{tot}} = (1000 + 500 + 2500) \text{ mol s}^{-1} = 4000 \text{ mol s}^{-1}$
 $p_i = p_{\text{tot}} \cdot (n_i/n_{\text{tot}})$
 $p(\text{CO}, \gamma) = 10 \text{ MPa} \times (500/4000) = 1,25 \text{ MPa}$
 $p(\text{H}_2, \gamma) = 10 \text{ MPa} \times (2500/4000) = 6,25 \text{ MPa}$
 $p(\text{CH}_3\text{OH}, \gamma) = 10 \text{ MPa} \times (1000/4000) = 2,50 \text{ MPa}$

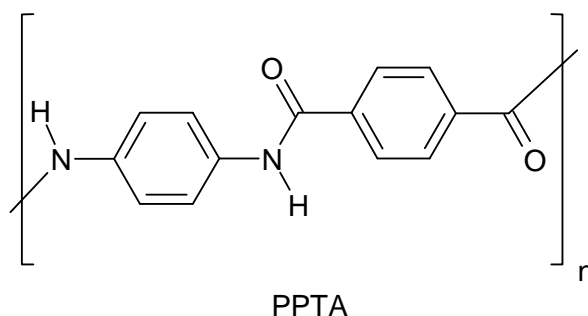
4.5 Calculation of K_p : $K_p = (2.5 \times 0.1^2) / (1.25 \times 6.25^2) = 5.12 \times 10^{-4}$.

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

PROBLEM 5

Aramids, High-performance Polymeric Materials

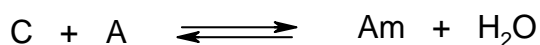
Aromatic polyamides (aramids) are high strength, high performance polymer fibers that find use in composite materials, bullet-proof vests, high quality skis, safety helmets, etc. Aramid PPTA is marketed under the names Kevlar® (DuPont) and Twaron® (Teijin), and amongst others manufactured in the north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



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 \bar{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 .

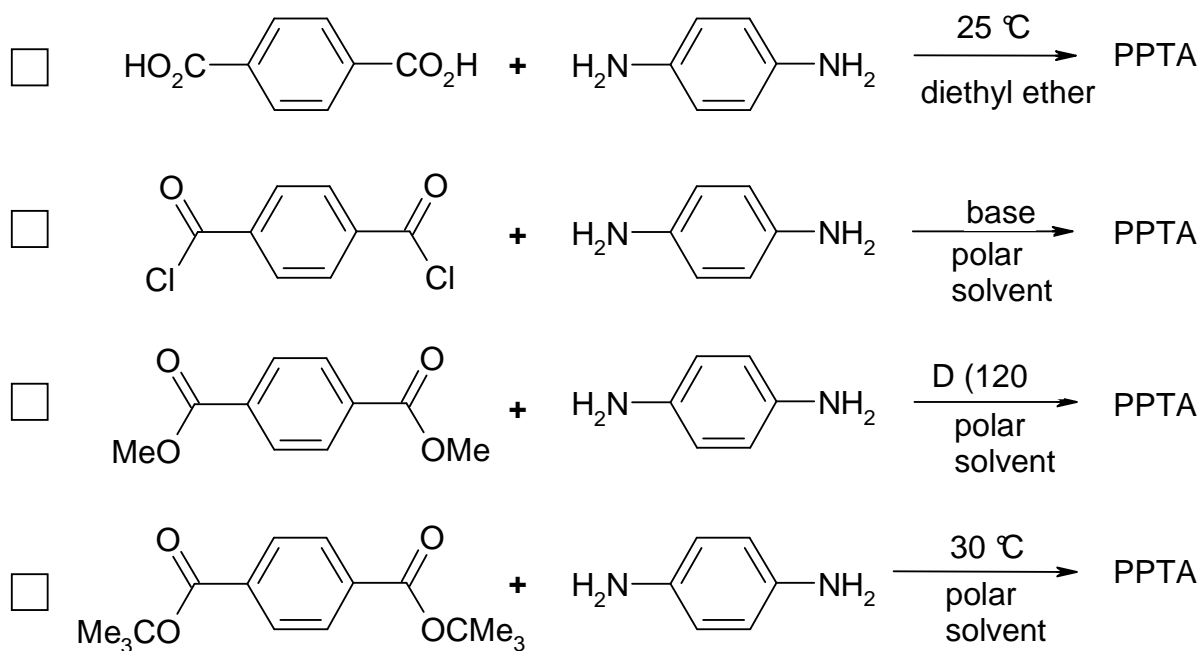
Assuming that the polymerization equilibrium can fully be described by:



where C stands for any $-\text{CO}_2$ group, A stands for any $-\text{NH}_2$ 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).

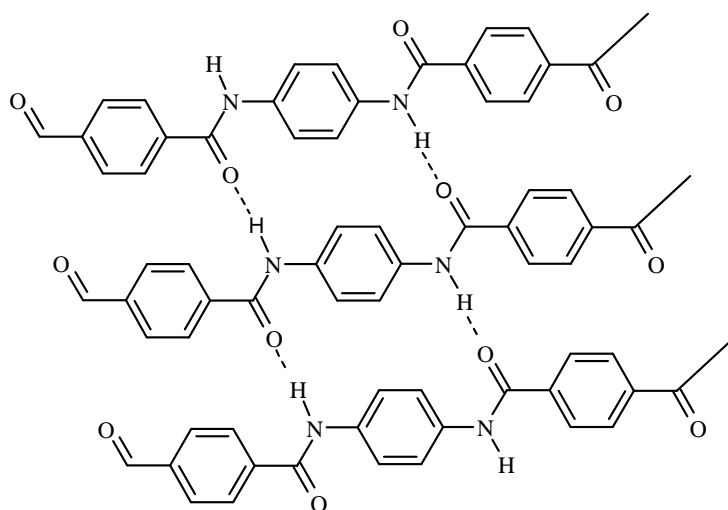


5.4 Another type of aramid can be produced from 4-aminobenzoic acid (4-aminobenzene-carboxylic acid) by heating.

- Give the structure of this aramid ($n = 4$)
- Calculate the average chain length at equilibrium (reaction is carried out in a closed vessel). The equilibrium constant $K = 576$.

SOLUTION

5.1



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

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

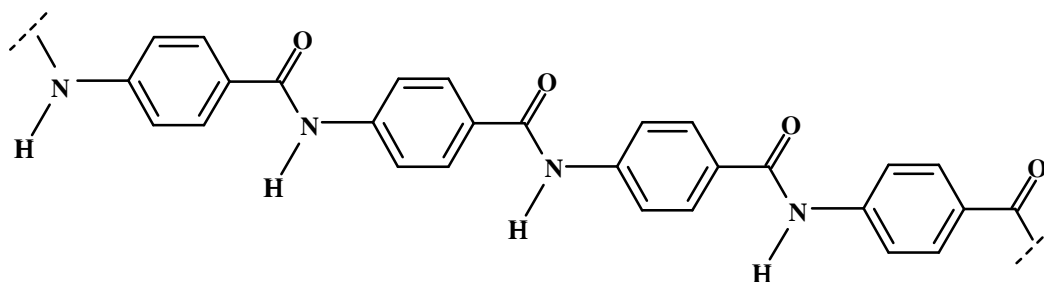
$$500 = \frac{1}{1-p} \quad p = \frac{499}{500} = 0.998$$

5.3

2 and 3

5.4

a)



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

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

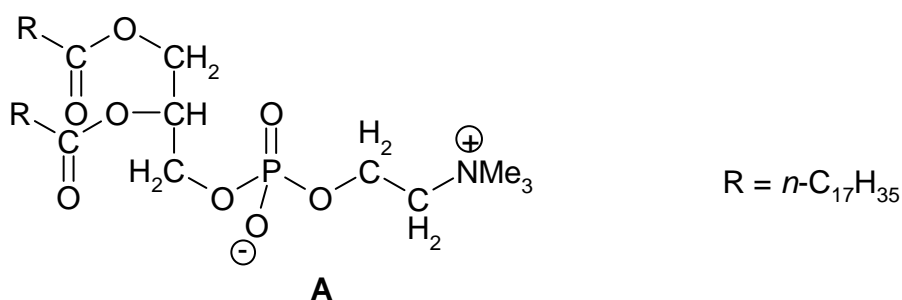
Theme III - Chemistry of Functional Molecules in Nature

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

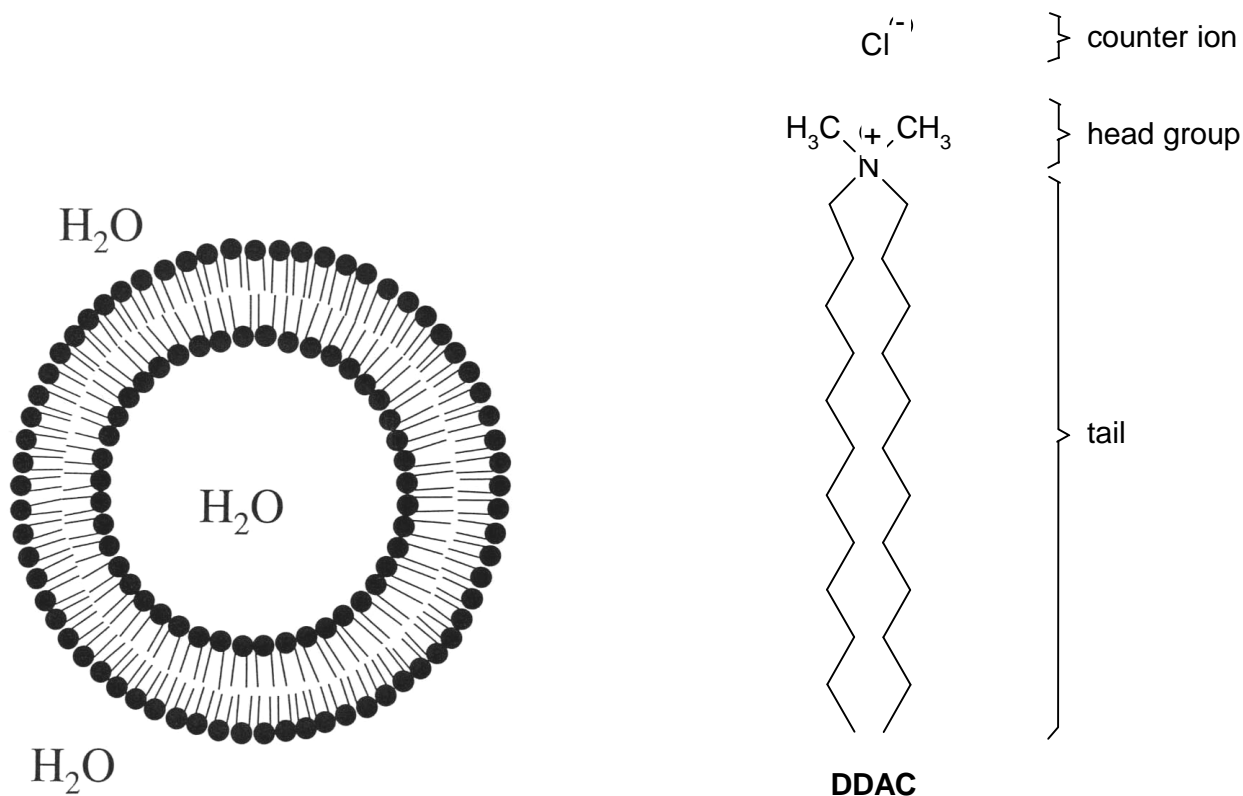
Phospholipids in Membranes

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**.

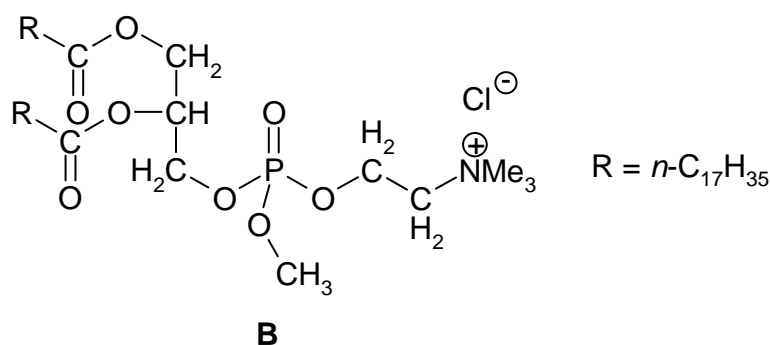


Upon dispersion in water (above a low critical concentration) compound **A** forms closed bilayer structures, called liposomes, which are employed as model compounds for aspects of the chemistry of the structurally much more complex cell membranes. Liposomes are globular aggregates with the polar or 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**).

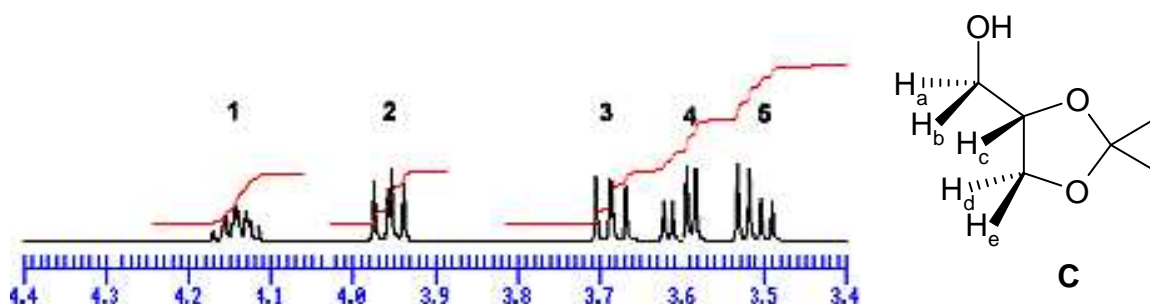


- 6.1 (a)** How many stereoisomers are possible for compound **A**?
- (b)** How many stereoisomers are possible for the trialkylphosphate **B**?



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

- 6.2** Which signal number in the ¹H-NMR spectrum corresponds to proton **H_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:

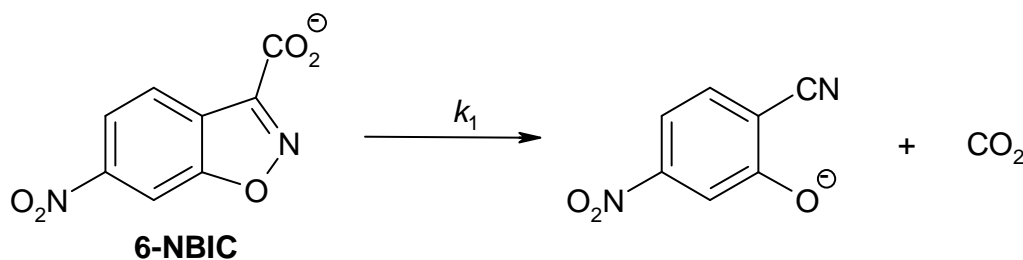
$$V = (27.4 + 26.99 n) \times 10^{-3} \text{ nm}^3$$

$$l_c = (0.154 + 0.1265 n) \text{ nm}$$

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, c_{vc}) catalyse the unimolecular decarboxylation of 6-nitro-benzisoxazole-3-carboxylate (**6-NBIC**).



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

6.4 Sketch a plot of k_1 vs. $[\text{DDAC}]$ for $[\text{DDAC}] = 0 \rightarrow 3 c_1$.

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

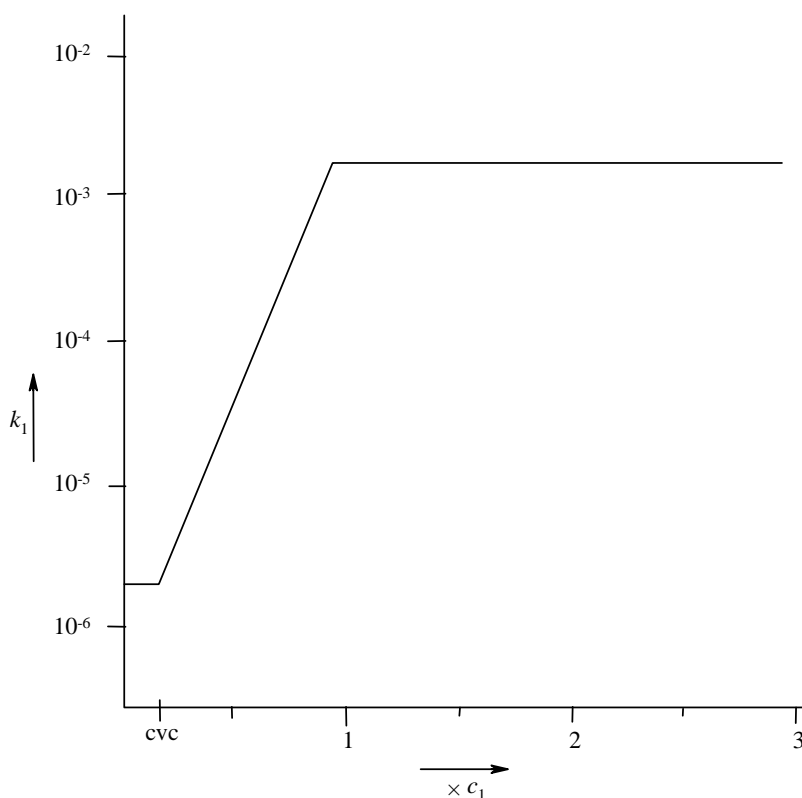
6.2 Signal No 1.

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

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

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

6.4



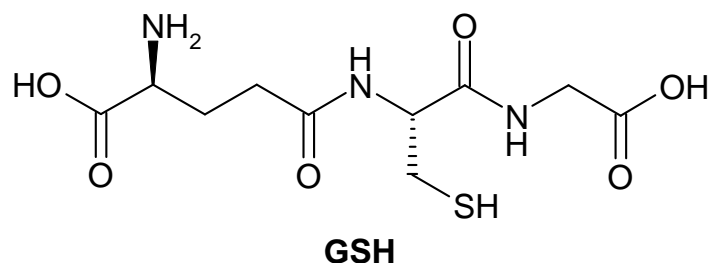
We expect curved bends in the graph, however, sharp corners (see the Figure) are also accepted.

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

PROBLEM 7

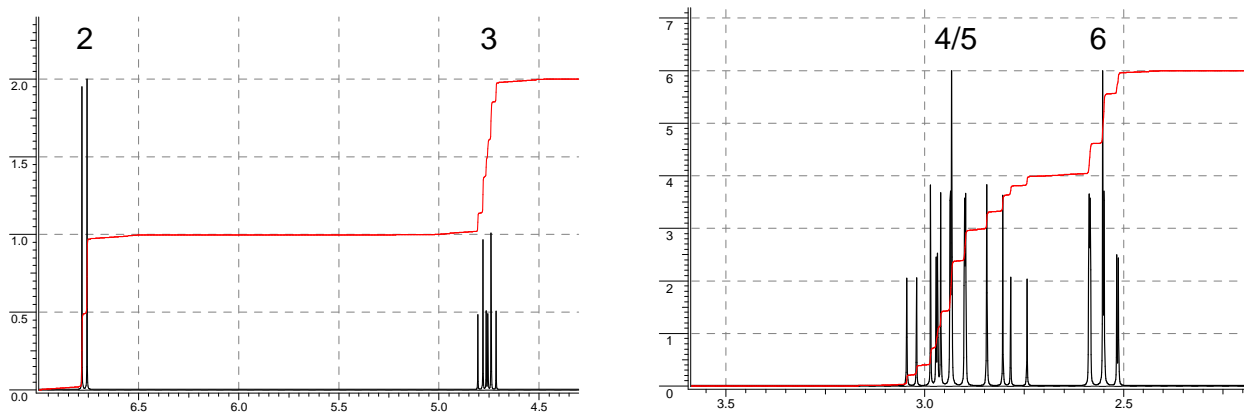
Glutathione, an Essential Mini-Peptide

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 .



- 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 ($\text{H}_2\text{C}=\text{CH}-\text{CN}$) has the molecular formula $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_3\text{S}$. The ^1H -NMR spectrum of **A** in $(\text{CD}_3)_2\text{SO}$ 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.



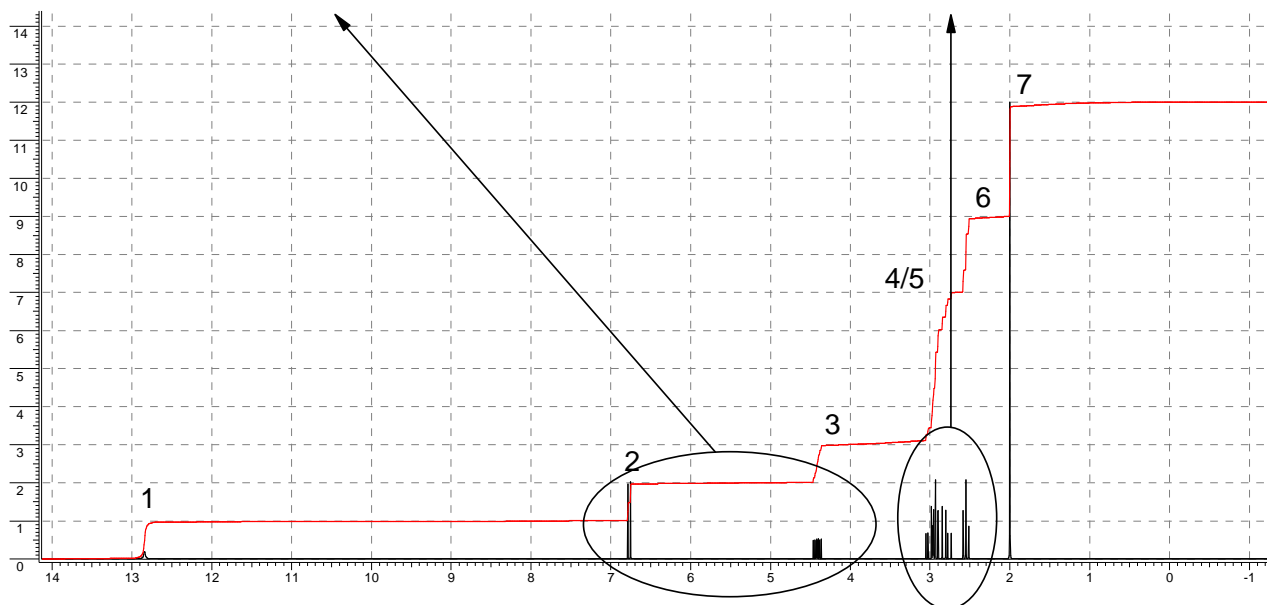


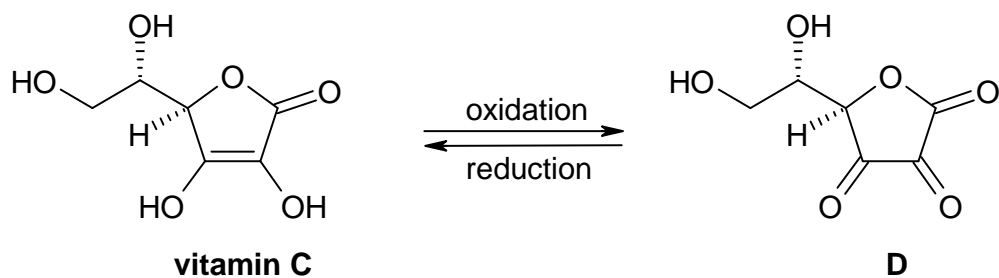
Figure 1

7.2 (a) The NMR-signals correspond with protons in the following groups: CH, CH₂, CH₃, 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	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>

- (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**



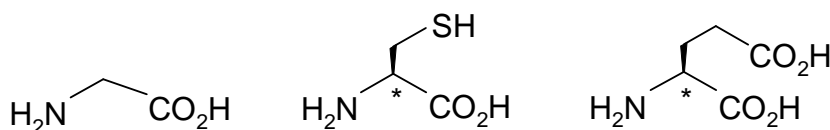
7.3 Eating fresh fruit and vegetables is healthy

- 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)

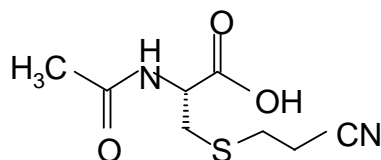


7.2 a)

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.

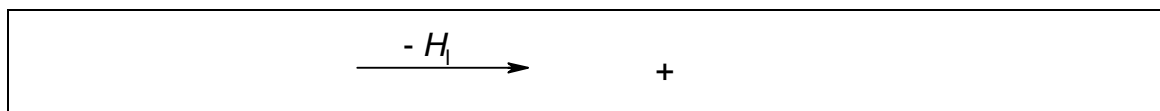
Theme IV - Chemistry Related to Light and Energy

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. ($H_l = H_{\text{lattice}}$; $H_e = H_{\text{electrostatic}}$; $H_s = H_{\text{sublimation}}$; H is not absolute, H means ΔH)



+



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

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

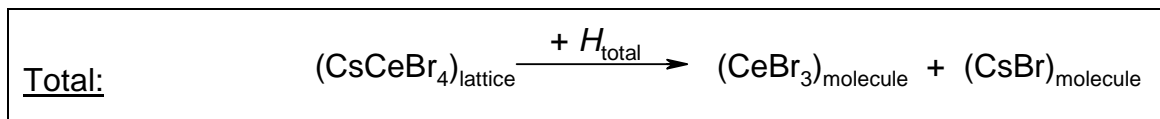
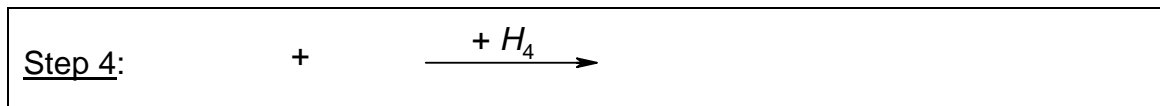
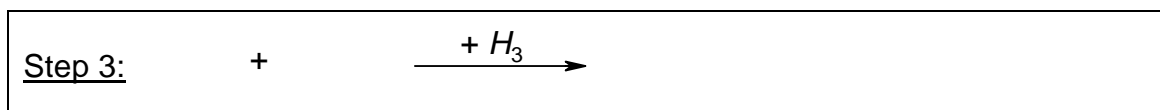
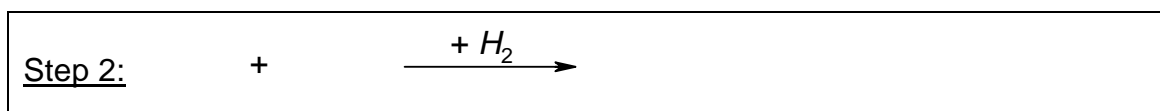
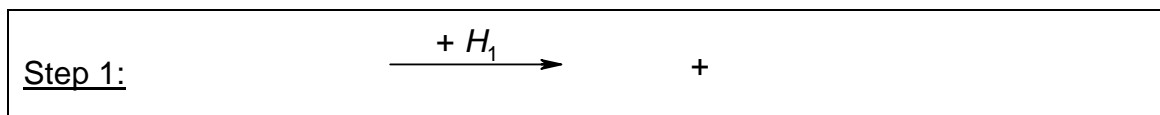
The factor $f e^2$ (necessary in order to calculate the lattice energy in kJ mol^{-1}) amounts to 139 when the ionic radii are substituted in nm. The Madelung constant A for the lattice is

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.



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

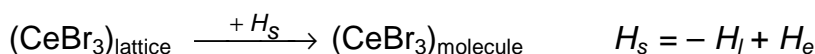
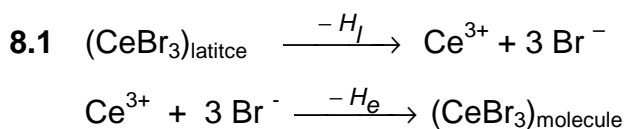
Use the Born–Landé formula for all steps in the process and report the separate energies also (be aware of the signs!). The Madelung constant for NaCl is 1.75. The

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.

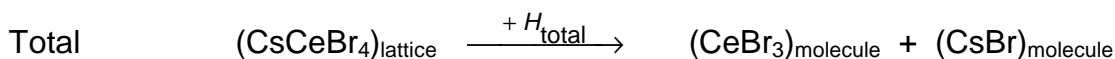
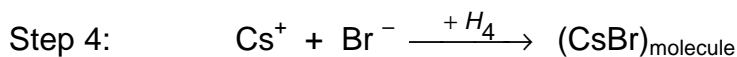
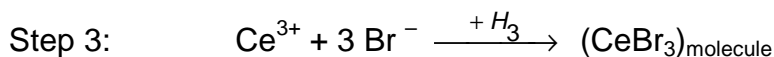
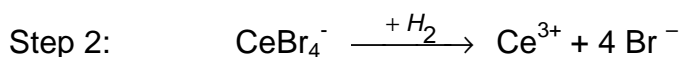
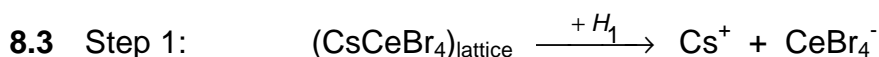
SOLUTION



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

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

$$H_s = 718 \text{ kJ mol}^{-1}$$



8.4 Step 1: The lattice energy of CsCeBr₄ 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 CeBr₃ 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:

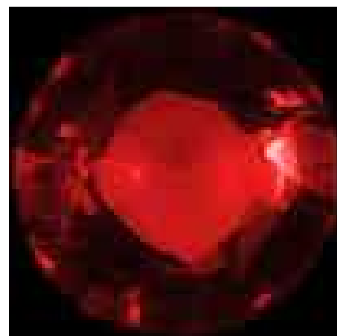
$$H_{\text{total}} = H_1 + H_2 + H_3 + H_4 = 461 \text{ kJ mol}^{-1}$$

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 3d shell and the absorption of light is due to electronic transitions between 3d orbitals of lower and higher energy.



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

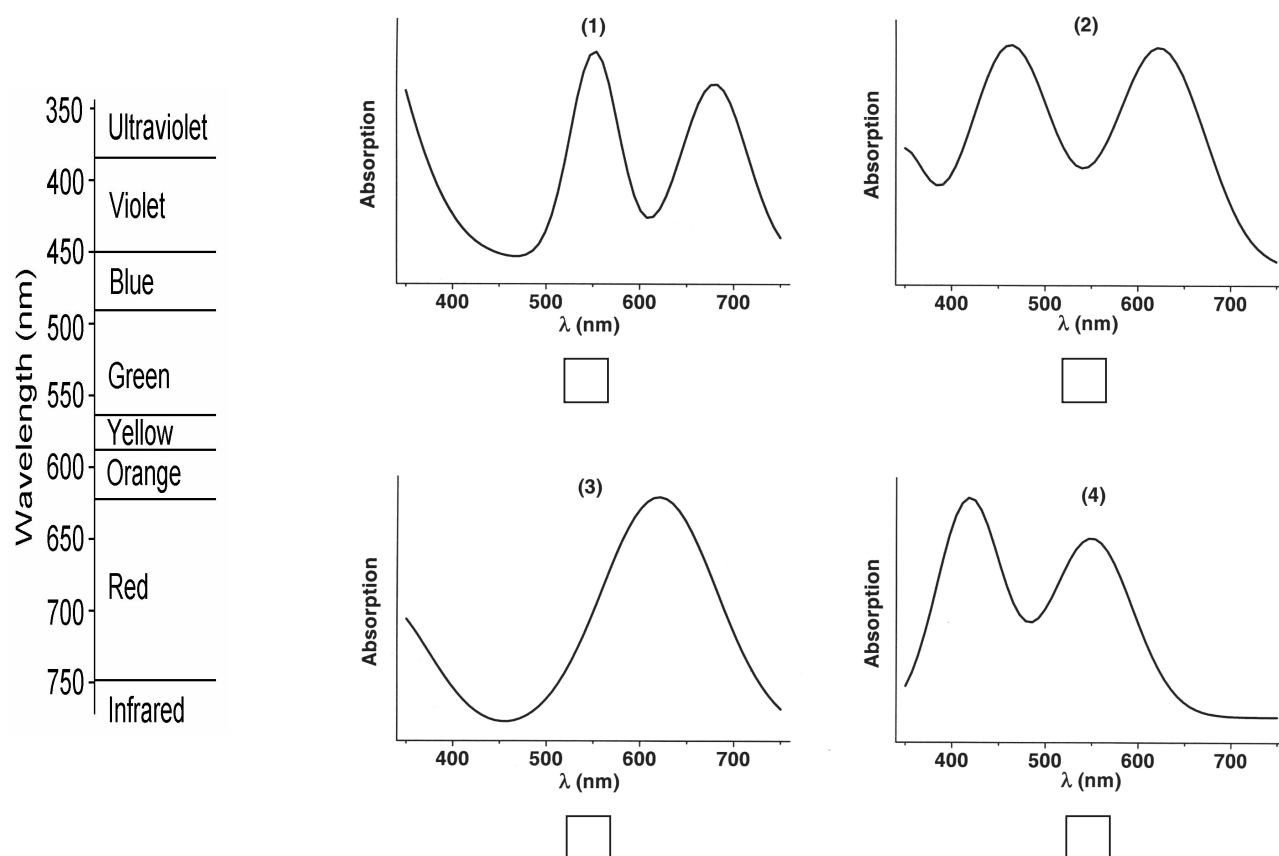


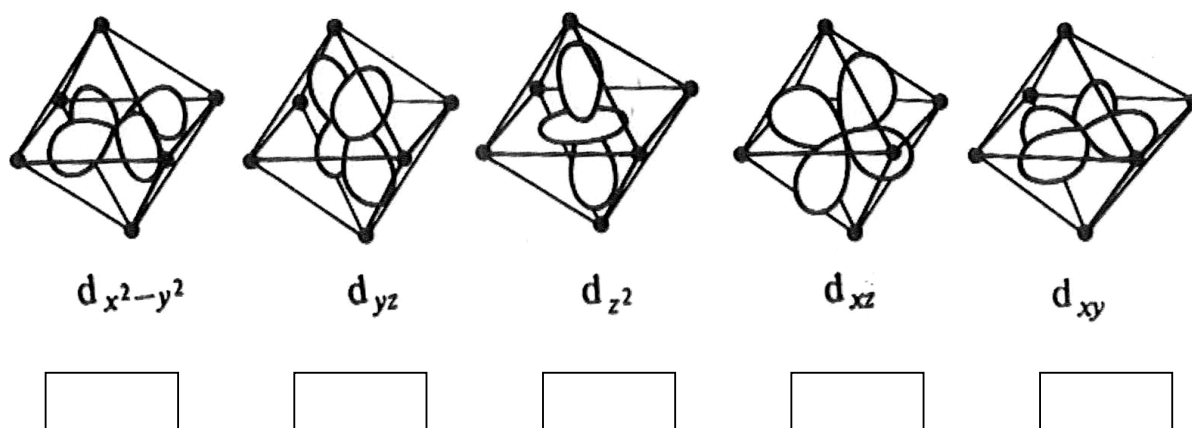
Figure 1

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 $\text{Cr} = 52\text{u}$. ($1\text{u} = 1.67 \times 10^{-27} \text{ kg}$).

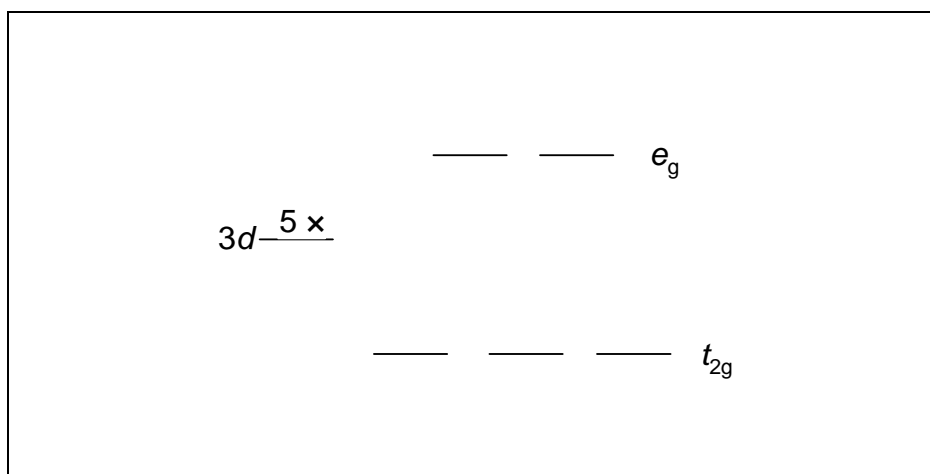
9.2 Calculate how many Cr^{3+} ions are in this laser rod.

In rubies the Cr^{3+} ions are coordinated by an octahedron of 6 oxygen ions. The shape of the five $3d$ orbitals is shown below. The box below shows the splitting of the five $3d$ 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 $3d$ 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 $3d$ 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.

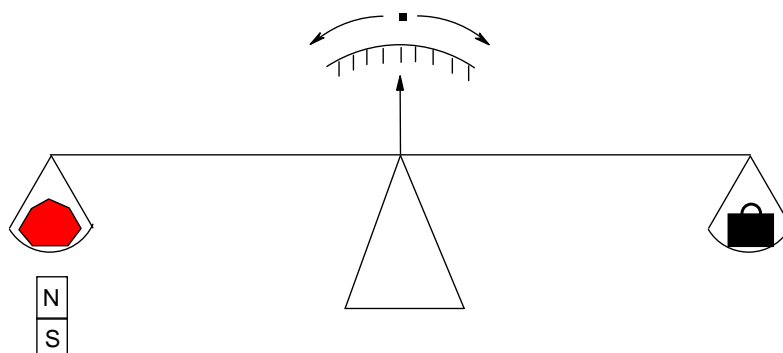


Figure 2

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 = $\pi \times r^2 \times l$

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

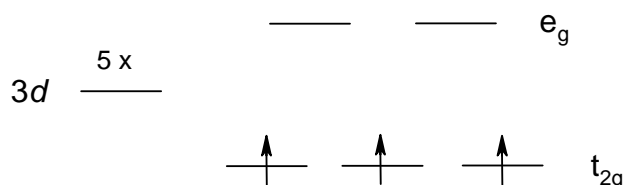
Mass of the rod: $m = 15.79 \times 4.05 \text{ g} = 63.94 \text{ g}$

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

Number of 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

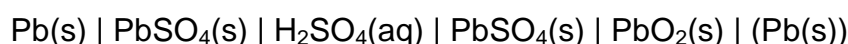
Vehicle Traction Batteries

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.

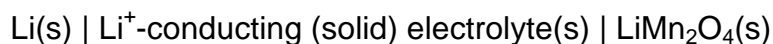
Lead-acid batteries are extensively used as portable power sources for vehicles and traction. A lead-acid battery capable of efficient recharging has an energy density of 45 Wh/kg.

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:



A lithium battery is represented by:



Upon discharge the insertion product $\text{Li}_2\text{Mn}_2\text{O}_4$ 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 .

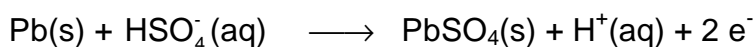
A typical family car of 1000 kg requires at least 5 kWh of energy to move 50 km, which corresponds with the consumption of about 5.0 litres or 3.78 kg of petrol. This conventional car has a petrol tank volume of 50 L. The weight of the tank is 10 kg. The fuel consumption is 10 km L^{-1} .

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:

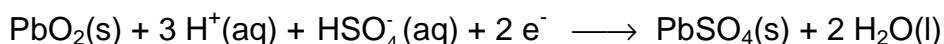
- (a) Extra weight of a lead-acid battery car.
 (b) Extra weight of a lithium battery car.

SOLUTION

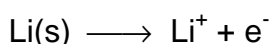
10.1 Reaction at the negative electrode:



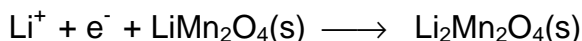
Reaction at the positive electrode:



10.2 Reaction at the negative electrode:



Reaction at the positive electrode:



10.3 Li – ions: coordination number = 4 Mn – ions: coordination 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

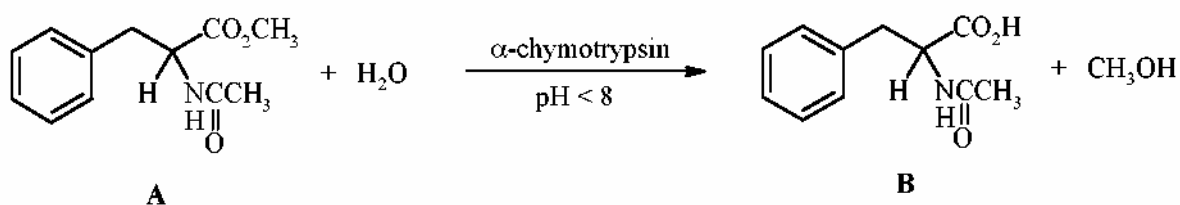
Extra weight of a lithium battery car = 1111.1 kg / 3 – 47.8 kg = 322.6 kg.

PRACTICAL PROBLEMS

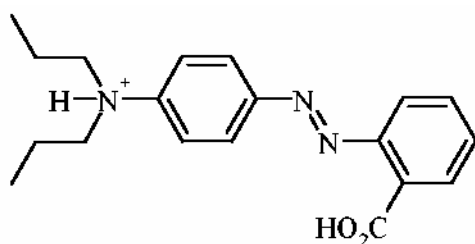
PROBLEM 1 (Practical)

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).



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 cm³ Erlenmeyer flask and dissolved in methanol (~ 2.5 cm³). Subsequently, propyl red (0.02 % solution in ethanol; 4 drops) is added. The kinetic experiment is started by adding α -chymotrypsin (10.0 cm³ 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 cm³ 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 cm³.
 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 %.
-
-

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 cm³) is added. A stirring bar is introduced and the suspension is stirred thoroughly whilst heating at 80 °C 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 benzyldantoin that you have prepared by determining its melting point using an automatic melting point apparatus.

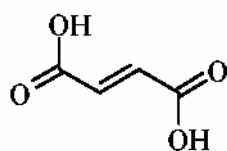
SOLUTION

The competitors were expected to show the following data, tables, graphs or calculations on the answer sheet:

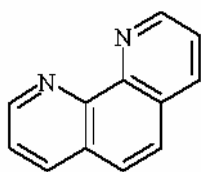
1. Mass of your starting material **A** (see label on the vial) in mg.
 2. Amount of benzyhydantoin **C** obtained.
 3. Calculation of the yield of benzyhydantoin **C** in %.
 4. R_f value of urea derivative **B**.
 5. R_f value of benzyhydantoin **C**.
 6. A copy of the TLC diagram with indication of 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 benzyhydantoin **C**: white colour, yellowish colour, sticky, crystalline, powder.
 9. Melting point of benzyhydantoin **C** was determined by the examination committee.
 10. The TLC plate was necessary to pack in an envelope and leave it to a laboratory supervisor.
-
-

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:

**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 cm³ beaker with the aid of a small amount of distilled water. Hydrochloric acid (5 cm³, 4 M) is added. The content of the beaker is heated up to approximately 60 °C 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 cm³) and the final volume adjusted by adding distilled water and with regular mixing. An amount of 10 cm³ is pipetted from this solution and transferred into a volumetric flask of 100 cm³. Again the volume is adjusted with distilled water while mixing the content of the flask.

From this solution, 10 cm³ is pipetted and transferred into a volumetric flask of 100 cm³. Subsequently, 1,10-phenanthroline solution (10 cm³) and hydroxylammonium chloride solution (1 cm³) 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⁻¹cm⁻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



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 $\text{Th}(\text{IO}_3)_4$ 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 $[\text{H}^+]$ of an aqueous HCl solution at any concentration c_{HCl} ? ($K_w = 1 \times 10^{-14}$).

- (a) $[\text{H}^+] = c_{\text{HCl}}$
- (b) $[\text{H}^+] = c_{\text{HCl}} + K_w / [\text{H}^+]$
- (c) $[\text{H}^+] = c_{\text{HCl}} + K_w$
- (d) $[\text{H}^+] = c_{\text{HCl}} - K_w / [\text{H}^+]$

QUESTION 3

The molar mass of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is 180 g mol^{-1} and N_A is the Avogadro constant. Which one of the following statements is not correct?

- (a) An aqueous 0.5 M solution of glucose is prepared by dissolving 90 g of glucose to give 1000 cm³ of solution.
- (b) 1.00 mmol amount of glucose has a mass of 180 mg.
- (c) 0.0100 mol of glucose comprises of 0.0100×24×N_A atoms.
- (d) 90.0 g glucose contain 3×N_A atoms of carbon.
- (e) 100 cm³ of a 0.10 M solution contain 18 g of glucose.

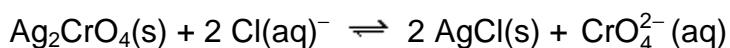
QUESTION 4

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 dm³ 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:



is given by the equation:

- (a) $K = K_{sp}(\text{Ag}_2\text{CrO}_4) / K_{sp}(\text{AgCl})^2$
- (b) $K = K_{sp}(\text{Ag}_2\text{CrO}_4) \times K_{sp}(\text{AgCl})^2$
- (c) $K = K_{sp}(\text{AgCl}) / K_{sp}(\text{Ag}_2\text{CrO}_4)$
- (d) $K = K_{sp}(\text{AgCl})^2 / K_{sp}(\text{Ag}_2\text{CrO}_4)$
- (e) $K = K_{sp}(\text{Ag}_2\text{CrO}_4) / K_{sp}(\text{AgCl})$

QUESTION 6

How many cm³ of 1.00 M NaOH solution must be added to 100.0 cm³ of 0.100 M H₃PO₄ solution to obtain a phosphate buffer solution with pH of about 7.2? (The pK values for H₃PO₄ are pK₁ = 2.1, pK₂ = 7.2, pK₃ = 12.0)

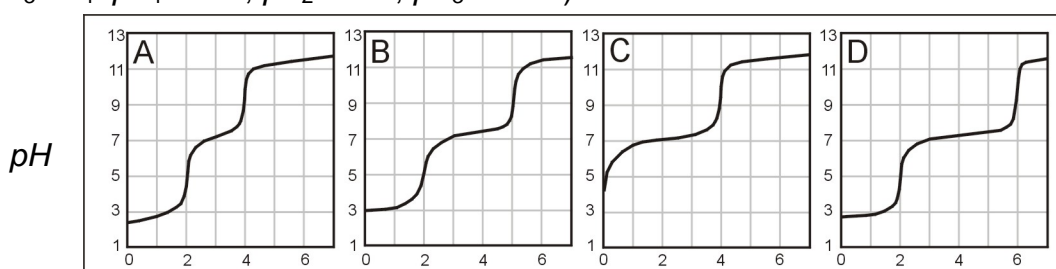
- (a) 5.0 cm³

- (b) 10.0 cm³
- (c) 15.0 mL
- (d) 20.0 mL

QUESTION 7

Solutions containing H₃PO₄ and/or NaH₂PO₄ 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 H₃PO₄: $pK_1 = 2.1$, $pK_2 = 7.2$, $pK_3 = 12.0$)



Volume of titrant (cm³)

- a) The sample contains H₃PO₄ only.

Curve A (), Curve B (), Curve C (), Curve D ()

- b) The sample contains both in a mole ratio H₃PO₄ : NaH₂PO₄ = 2 : 1.

Curve A (), Curve B (), Curve C (), Curve D ()

- c) The sample contains both in a mole ratio H₃PO₄ : NaH₂PO₄ = 1 : 1.

Curve A (), Curve B (), Curve C (), Curve D ()

QUESTION 8

A fuel/oxidant system consisting of N,N-dimethylhydrazine (CH₃)₂NNH₂ and N₂O₄ (both liquids) is commonly used in space vehicle propulsion. Components are mixed stoichiometrically so that N₂, CO₂ and H₂O are the only products (all gases under the same reaction conditions). How many moles of gases are produced from 1 mol of (CH₃)₂NNH₂?

- (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) ${}_{30}^{68}\text{Zn} + {}_0^1\text{n} \rightarrow {}_{28}^{65}\text{Ni} + \text{X}$
- b) ${}_{52}^{130}\text{Te} + {}_1^2\text{H} \rightarrow {}_{53}^{131}\text{I} + \text{X}$
- c) ${}_{82}^{214}\text{Pb} \rightarrow {}_{83}^{214}\text{Bi} + \text{X}$
- d) ${}_{11}^{23}\text{Na} + {}_0^1\text{n} \rightarrow {}_{11}^{24}\text{Na} + \text{X}$
- e) ${}_{9}^{19}\text{F} + {}_0^1\text{n} \rightarrow {}_{9}^{20}\text{F} + \text{X}$

QUESTION 11

10.0 cm³ of 0.50 M HCl and 10.0 cm³ 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 cm³ of 0.50 M NaOH were used instead of 10.0 cm³. Thermal losses 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: ^1H , ^2H . 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

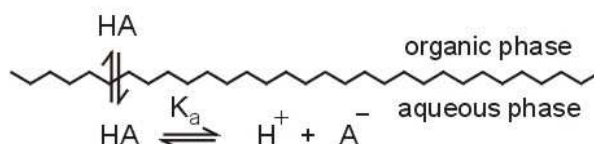
QUESTION 13

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)

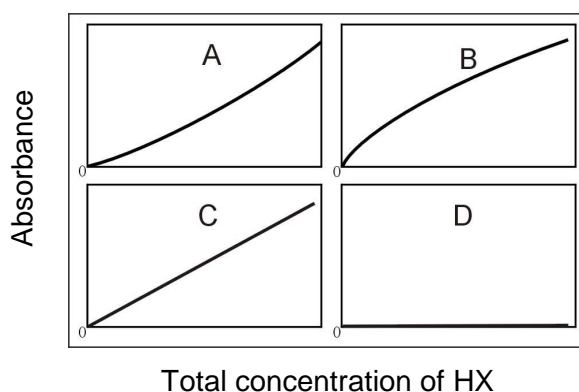
QUESTION 16

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?

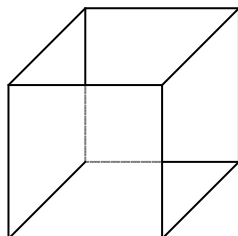
IE_1	IE_2	IE_3	IE_4	IE_5	IE_6
11	24	48	64	392	490

- 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 $\text{NH}_3 - \text{NH}_4^+$. (Y) (N)
 e) Pure water at $80 \text{ }^\circ\text{C}$ 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 | <input type="checkbox"/> | d) | 2.8 | <input type="checkbox"/> |
| b) | 2.4 | <input type="checkbox"/> | e) | 3.0 | <input type="checkbox"/> |
| c) | 2.6 | <input type="checkbox"/> | f) | 3.2 | <input type="checkbox"/> |

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);

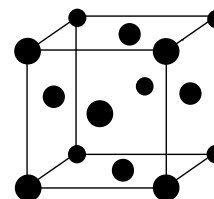
19: (b);

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;

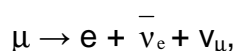
f) N;

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:



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 ^1H 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:

$$E_\mu = m_\mu c^2 = E_e + E_{\nu,\nu}$$

$$m_\mu c^2 = m_e c^2 + (T_e + E_{\nu,\nu})$$

$$m_\mu = \frac{m_e + (T_e + E_{\nu,\nu})}{c^2} = \frac{9.109 \times 10^{-31} + (1.4846 \times 10^{-11} + 2.000 \times 10^{-12})}{(2.998 \times 10^8)^2} = 1.883 \times 10^{-28} \text{ kg}$$

- b) From Bohr theory:

$$E_n = -\frac{me^4}{2n^2 h^2} = -109700 \text{ cm}^{-1} \times \frac{1}{n^2} \times \left(\frac{m}{m_e}\right),$$

where

$$m = \frac{m_{\mu} m_{\text{H}}}{m_{\mu} + m_{\text{H}}}$$

$$\lambda = \frac{1}{E_4 - E_2} = \frac{1}{109700 \left(\frac{m}{m_{\text{e}}} \right) \left(\frac{1}{4} - \frac{1}{16} \right)} = 2.615 \times 10^{-7} \text{ cm}$$

$$\frac{m}{m_{\text{e}}} = 185.9$$

$$m = 185.9 \times 9.109 \times 10^{-31} = 1.693 \times 10^{-28} \text{ kg}$$

The mass of a proton from Tables attached :

$$m_{\text{H}} = 1.673 \times 10^{-27} \text{ kg}$$

$$m_{\mu} = \frac{m m_{\text{H}}}{m_{\text{H}} - m} = \frac{1.693 \times 10^{-28} \times 1.673 \times 10^{-27}}{1.673 \times 10^{-27} - 1.693 \times 10^{-28}} = 1.884 \times 10^{-28} \text{ kg}$$

PROBLEM 26 **Spectrum of CO**

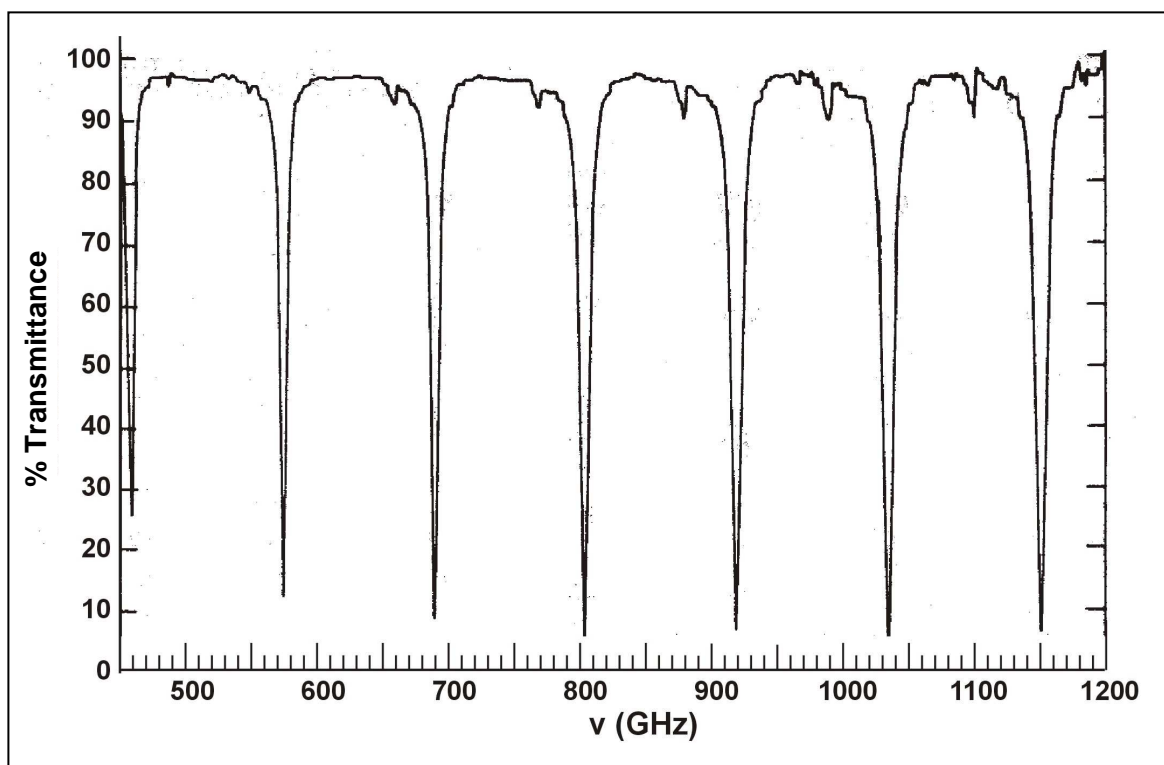
Rotational energy levels of diatomic molecules are well described by the formula $E_J = B J(J+1)$, where J is the rotational quantum number of the molecule and B its rotational constant. Constant B is related to the reduced mass μ and the bond length R of the molecule through the equation

$$B = \frac{h^2}{8\pi^2 \mu R^2}$$

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 $^{12}\text{C}^{16}\text{O}$ with appropriate units:

- $\Delta \nu$
- B
- R



SOLUTION

a) For example: $\Delta\nu = 1150 - 1035 = 115 \text{ GHz}$

b)
$$B = \frac{h \Delta\nu}{2} = \frac{6.63 \times 10^{-34} \times 115 \times 10^9}{2} = 3.81 \times 10^{-23} \text{ J}$$

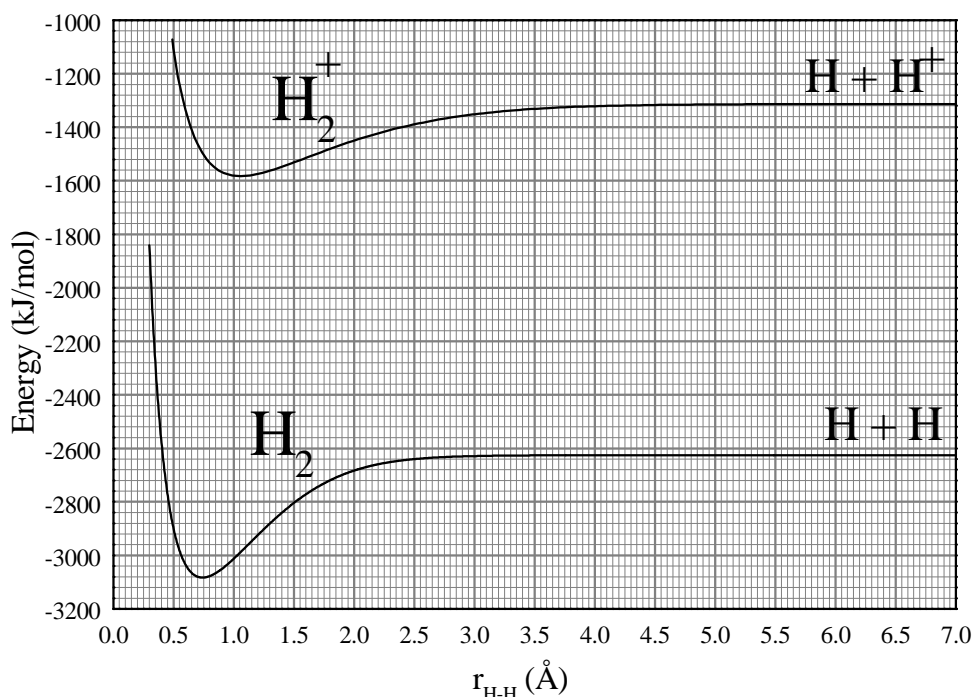
c)
$$\mu = \frac{m(\text{C}) \times m(\text{O})}{m(\text{CO})} = \frac{12 \times 16}{28} = 6.86 \text{ a.u.} = 1.14 \times 10^{-26} \text{ kg}$$

For interatomic distance R :

$$R = \frac{h}{2\pi \sqrt{2\mu B}} = \frac{6.63 \times 10^{-34}}{2 \times 3.14 \sqrt{2 \times 1.14 \times 10^{-26} \times 3.81 \times 10^{-23}}} = 1.13 \times 10^{-10} \text{ m} = 1.13 \text{ \AA}$$

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 H₂ and H₂⁺?
2. What are the binding energies of H₂ and H₂⁺?
3. What is the ionisation energy of the H₂ 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 H₂, what will be the velocity of the extracted electrons? (Ignore molecular vibrational energy.)

SOLUTION

1. The equilibrium bond lengths of H₂ and H₂⁺ can be read from the minimum of the curves: $r(\text{H}_2) = 0.75 \text{ \AA}$; $r(\text{H}_2^+) = 1.05 \text{ \AA}$
2. The binding energies of H₂ and H₂⁺ can be calculated as the differences in the values for infinitive bond lengths and those for minima of the particular curves:

$$E_{\text{bond}}(\text{H}_2) = -2620 - (-3080) = 460 \text{ kJ mol}^{-1}$$

$$E_{\text{bond}}(\text{H}_2^+) = -1310 - (-1580) = 270 \text{ kJ mol}^{-1}$$

3. The ionization energy $E_{\text{ion}}(\text{H}_2)$:

$$E_{\text{ion}}(\text{H}_2) = -1580 - (-3080) = 1500 \text{ kJ mol}^{-1}$$

4. $E_{\text{ion}}(\text{H}) = -1310 - (-2620) = 1310 \text{ kJ mol}^{-1}$

5. $\text{H}_2 + h\nu \rightarrow \text{H}_2^+ + \text{e}^-$

$$E(\text{H}_2) + h\nu \rightarrow E(\text{H}_2^+) + \frac{m_e v_e^2}{2}$$

$$v_e = \sqrt{\frac{2(E(\text{H}_2) - E(\text{H}_2^+) + h\nu)}{m_e}} =$$

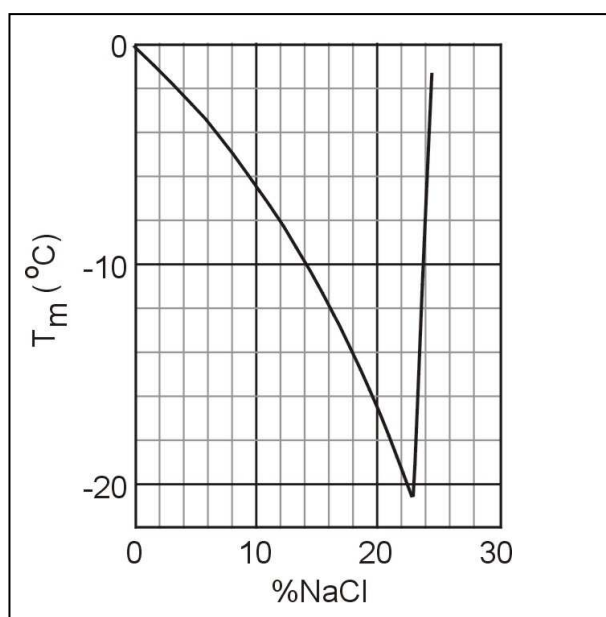
$$= \sqrt{\frac{2\left(\frac{-3080 \times 10^3 - (-1510 \times 10^3)}{6.02 \times 10^{23}}\right) + 6.63 \times 10^{-34} \times 4.1 \times 10^{15}}{9.11 \times 10^{-31}}} = 492 \times 10^3 \text{ ms}^{-1}$$

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 CO₂ 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 the freezing point of the bath based on the diagram?



- d) If an equal mass of MgCl₂ 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 °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:

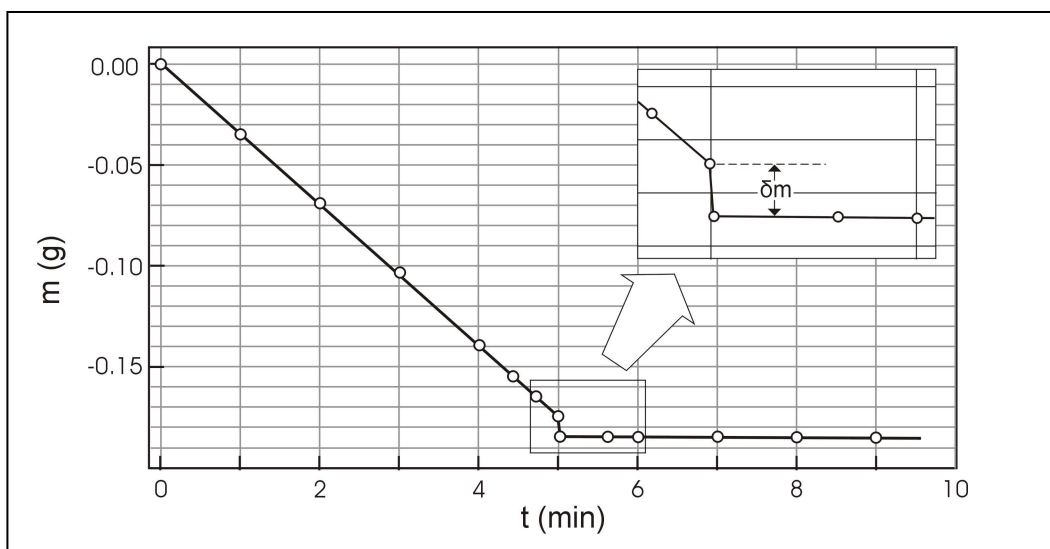
- a) The heat delivered to the water.
- b) Is the change of entropy of the resistor positive, negative, or zero?
- (i) $\Delta S_{\text{res}} > 0$
- (ii) $\Delta S_{\text{res}} = 0$
- (iii) $\Delta S_{\text{res}} < 0$
- c) Is the change of entropy of the water positive, negative, or zero?
- i) $\Delta S_{\text{pool}} > 0$
- (ii) $\Delta S_{\text{pool}} = 0$
- (iii) $\Delta S_{\text{pool}} < 0$
- d) Is the change of entropy of the system positive, negative, or zero?
- (i) $\Delta S_{\text{total}} > 0$
- (ii) $\Delta S_{\text{total}} = 0$
- (iii) $\Delta S_{\text{total}} < 0$
- e) Is the process reversible? (Y) (N)

SOLUTION

- a) $Q = 500 \text{ W} \times 20 \text{ min} \times 60 = 600 \text{ kJ}$
- b) $\Delta S_{\text{res}} = 0$
- c) $\Delta S_{\text{pool}} > 0$
- d) $\Delta S_{\text{total}} > 0$
- 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., $f = \frac{1}{2} u \frac{dm}{dt}$. Using the data provided determine the mean velocity of ethanol molecules at 290 K. Assume $g = 9.8 \text{ m s}^{-2}$.

SOLUTION

$$\frac{dm}{dt} = \frac{\Delta m}{\Delta t} = \frac{0.14 \text{ g}}{4 \text{ min}} = 0.035 \text{ g min}^{-1} = 5.8 \times 10^{-4} \text{ g s}^{-1}$$

$$\delta m g = \frac{1}{2} u \frac{dm}{dt}$$

$$u = \frac{0.01 \times 9.81 \times 2}{5.8 \times 10^{-4}} = 338 \text{ m s}^{-1}$$

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 cm³ of a 1.00 M NaOH solution. Following the saponification, the solution required 6.00 cm³ 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 I₂/NaOH to give a yellow precipitate and C₆H₅COONa. The diacid **B** reacted with Br₂ in CCl₄ to give a single, optically inactive product (compound **D**). Ozonolysis of **B** gave only one product.

- Determine the molecular mass of compound **A**.
- Give the structural formulas of **A**, **B**, and **C** without stereochemical information.
- Give the possible stereochemical formulas (with bold and dashed bonds) for **C**.
- Give the stereochemical formula for **D**, using a Fischer projection.
- Give the stereochemical formula for **B**.

The diester **A** also reacted with Br₂ in CCl₄ and was converted to a mixture of two compounds (**E**, **F**) both optically active.

- 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.

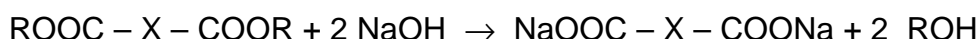
If we use Na¹⁸OH for the saponification of compound **A**, would the oxygen isotope be incorporated in (either or both of) the products **B** and **C**?

- Mark the correct answer:
 - Only **B**
 - Only **C**
 - Both **B** and **C**

SOLUTION

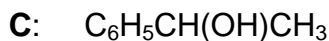
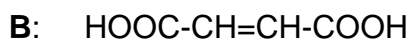
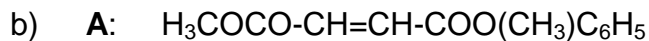
- For reaction with diester **A** $30 - 6 = 24$ cm³ of 1.00 M NaOH (0.024 mol NaOH)

Reaction:

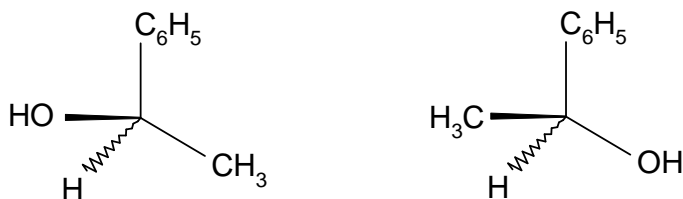


The amount of diester: $0.024 \text{ mol} / 2 = 0.012 \text{ mol}$

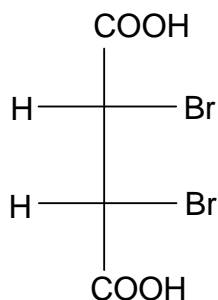
$$M(A) = 2.81 \text{ g} / 0.012 \text{ mol} = 234 \text{ g mol}^{-1}$$



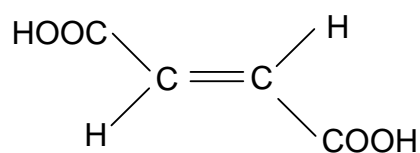
c) Possible stereochemical formulas for **C**:



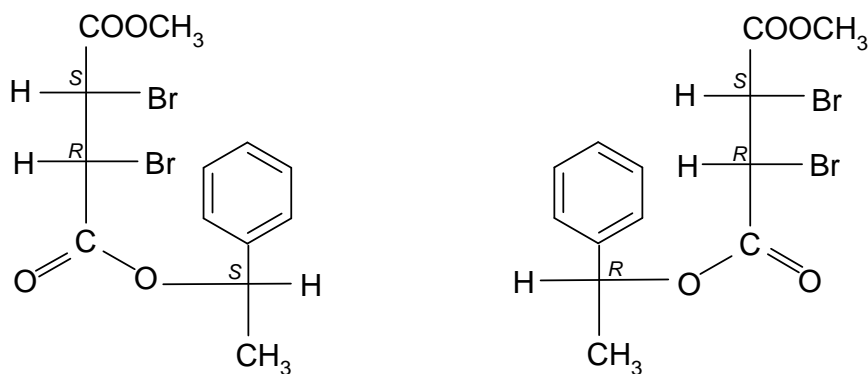
d) Stereochemical formula for **D**:



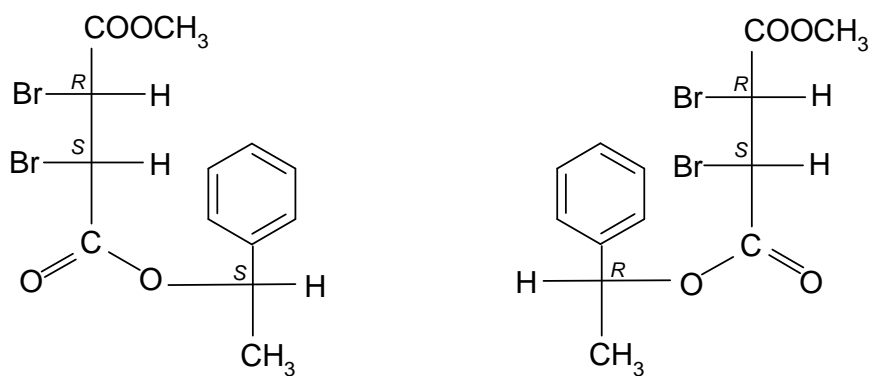
e) Stereochemical formula for **B**:



f) Possible stereochemical formula(s) for **E**:



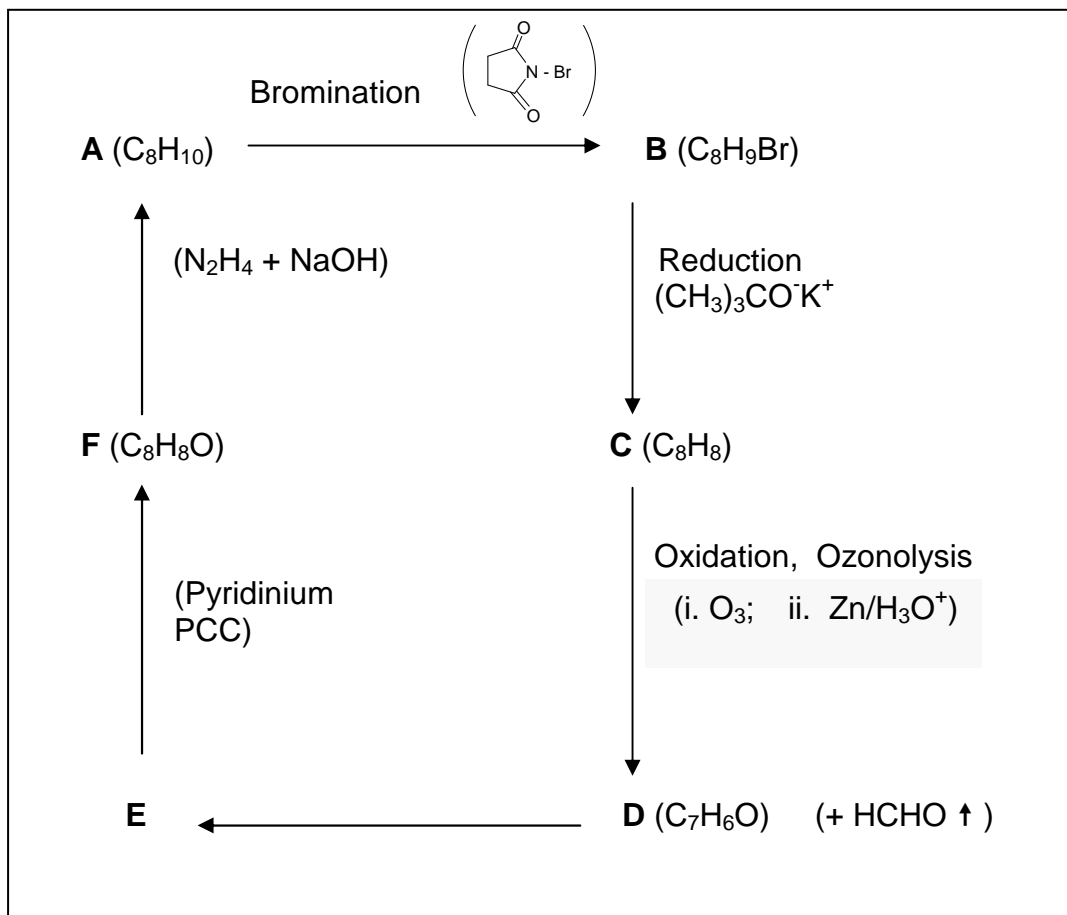
Possible stereochemical formula(s) for F:



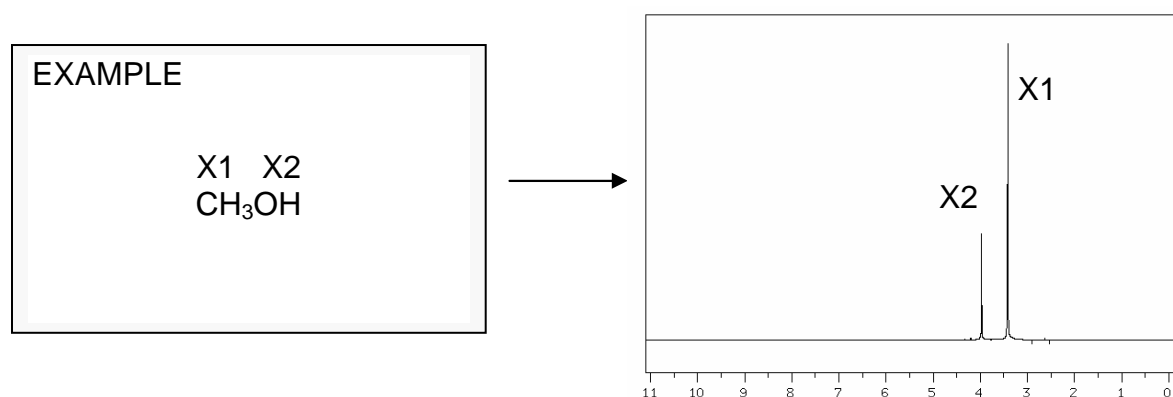
g) Correct answer is ii).

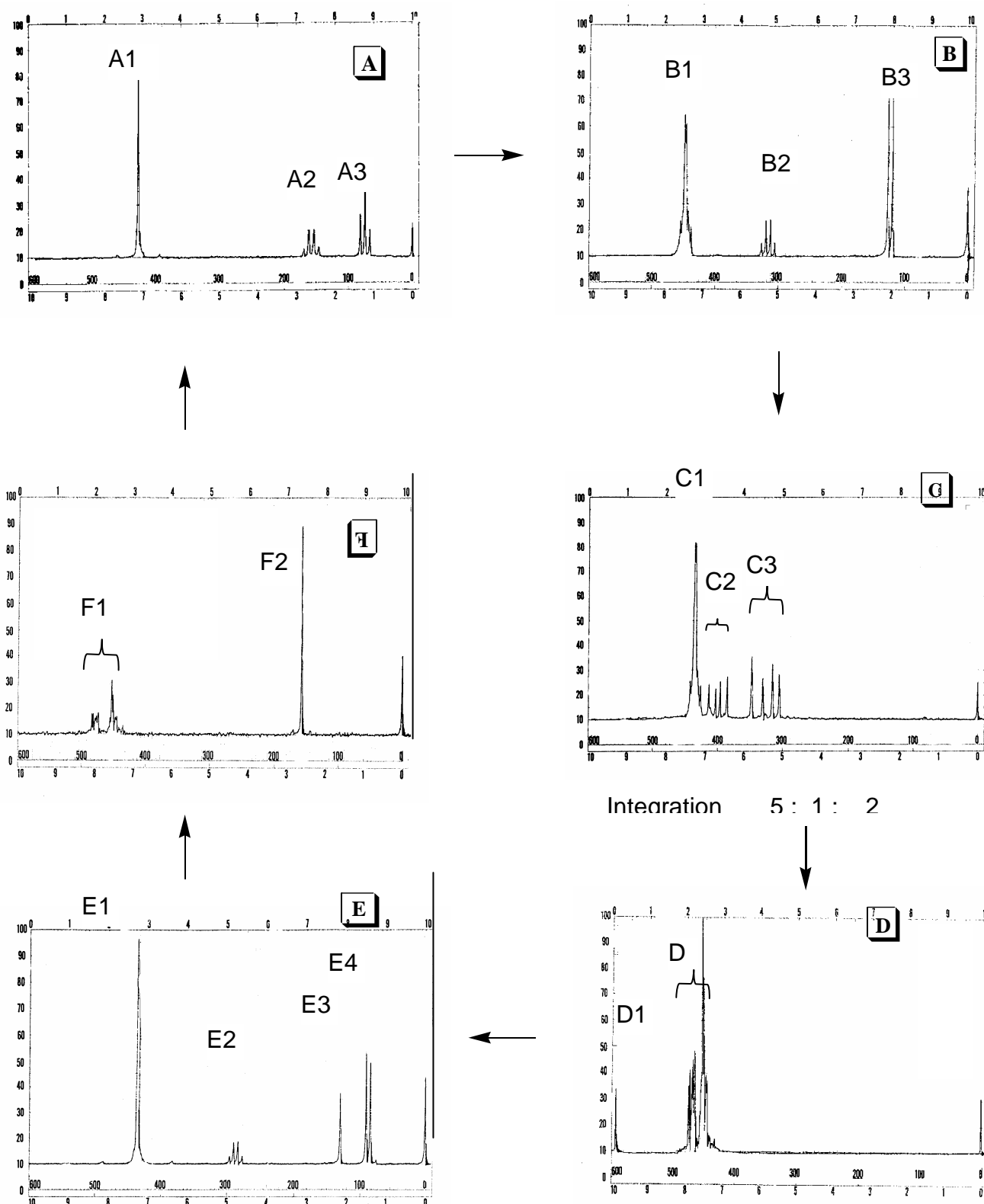
PROBLEM 32 NMR puzzle

An organic compound **A** (C_8H_{10}) gives the following chain of reactions:

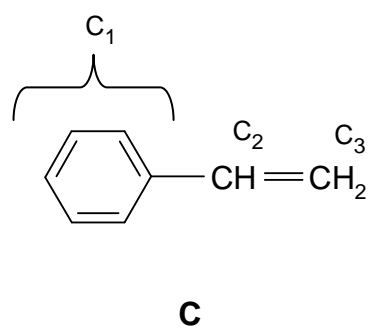
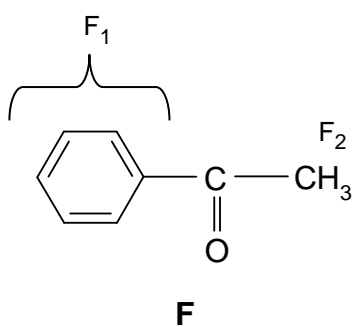
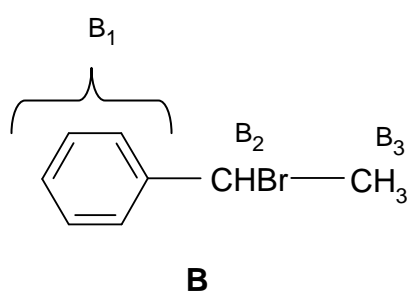
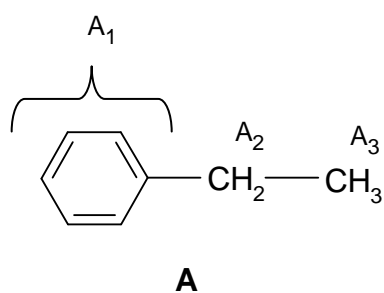
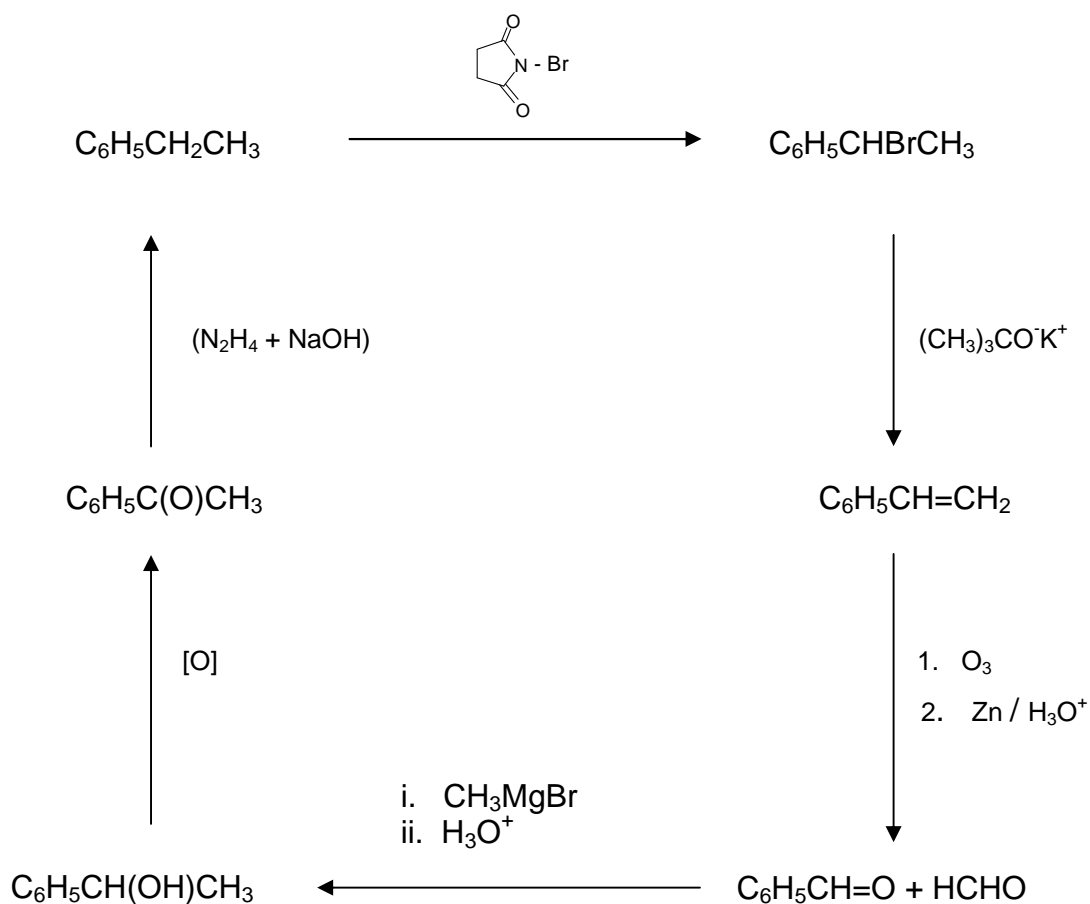


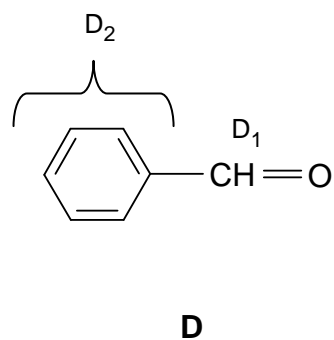
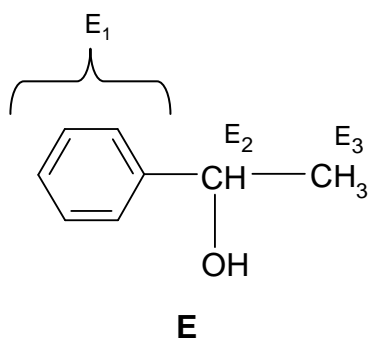
Based on the $^1\text{H-NMR}$ spectra given, draw the structures of compounds **A**, **B**, **C**, **D**, **E** and **F**, and match the groups of the hydrogen atoms of each compound to the corresponding $^1\text{H-NMR}$ peaks, as shown in the example.





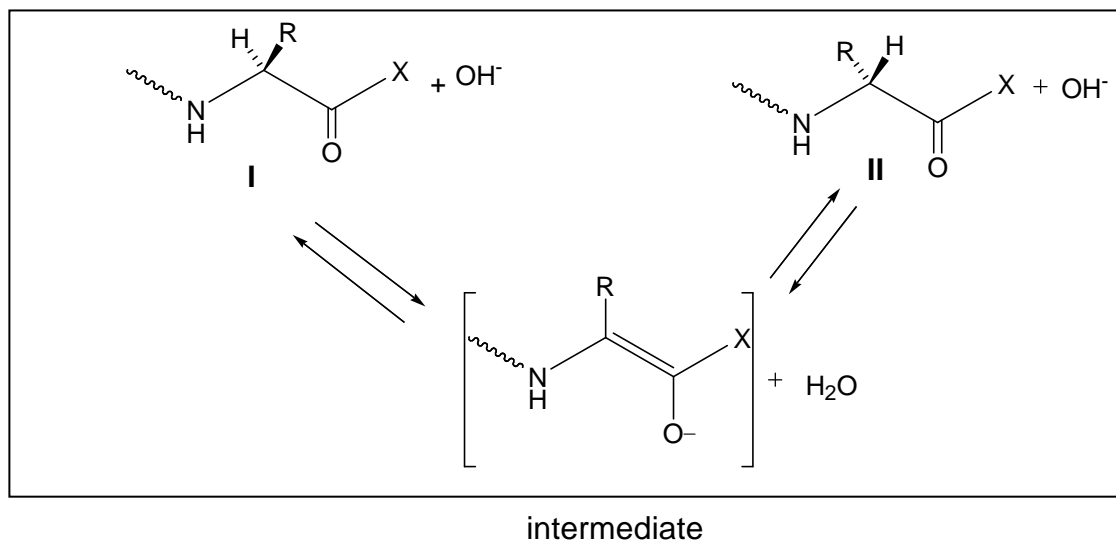
General remarks: NMR spectra were recorded in CDCl_3 on a 60 MHz Perkin Elmer Spectrometer. Under ordinary conditions (exposure to air, light and water vapour) acidic impurities may develop in CDCl_3 solutions and catalyse rapid exchange of some particular protons.

SOLUTION




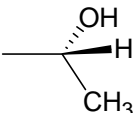
PROBLEM 33 Peptides

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:



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 ($R = -\text{CH}_2\text{OH}$)

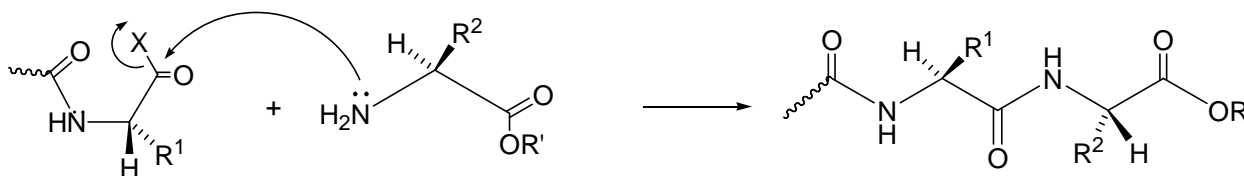
B: ($2S,3R$)-threonine ($R =$ )

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.

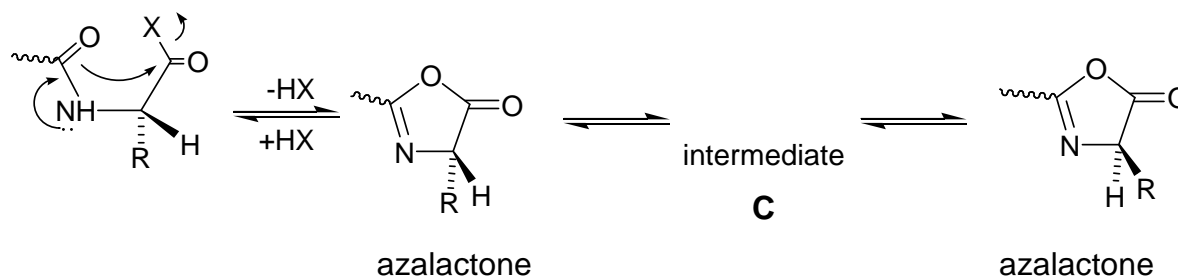
	enantiomers	diastereomers
A _{I, II}	<input type="checkbox"/>	<input type="checkbox"/>

	enantiomers	diastereomers
B _{I, II}	<input type="checkbox"/>	<input type="checkbox"/>

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:



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 amino acid. Therefore, the coupling reaction can proceed to completion albeit affording racemized or epimerized products.

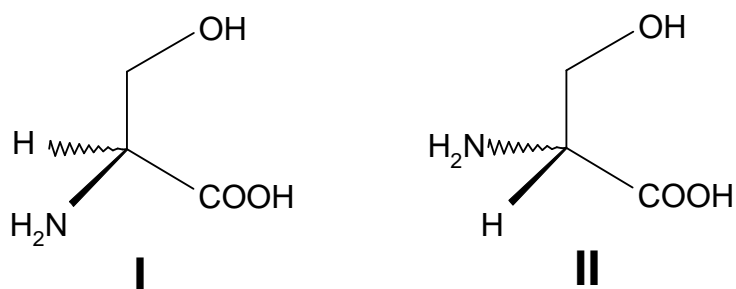
4. If *N*-benzoyl glycine, $C_9H_9NO_3$, is warmed to 40 °C with acetic anhydride it is converted into a highly reactive substance, $C_9H_7NO_2$ (**P**₁).
- Propose a structure for substance **P**₁.
 - Write the reaction product(s) of the substance **P**₁ with *S*-alanine ethyl ester (**P**₂) (the side chain R of the amino acid alanine is a methyl group) using

stereochemical formulas (with bold and dashed bonds) for both reactants and product.

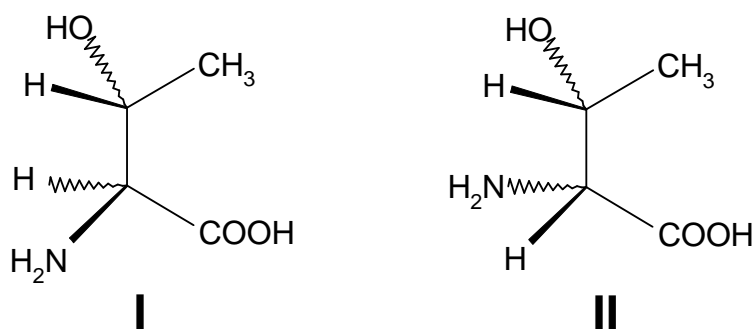
SOLUTION

1.

A:

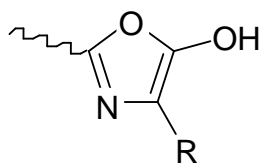


B:

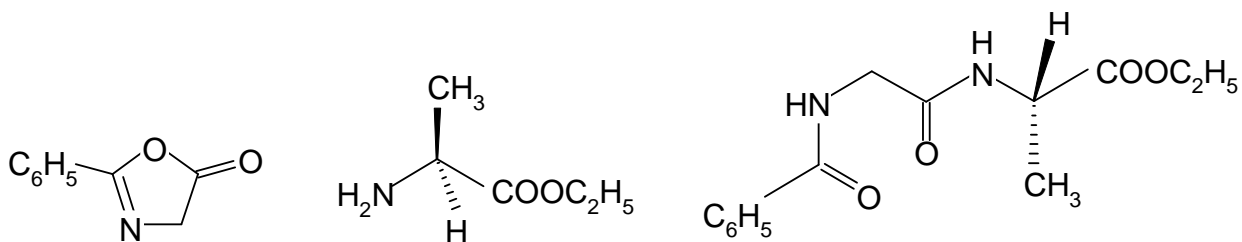


2. **A(I)** and **A(II)** are enantiomers.
B(I) and **B(II)** are diastereomers.

3. Intermediate **C**



4.

Substance P₁Ester P₂

Product

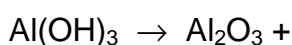
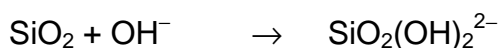
SECTION D: Inorganic Chemistry**PROBLEM 34 Aluminium**

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 – $\text{AlO}_x(\text{OH})_{3-2x}$ where $0 < x < 1$.

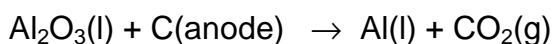
Production of Al metal follows a two-stage process:

- (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 °C.

Complete and balance the following chemical reactions:



- ii) Hérault-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°C, under constant pressure of 1 atm, in a carbon-lined steel cell (cathode) with carbon anodes. Balance the main reaction of the electrolysis:



Since cryolite is a rather rare mineral, it is prepared according to the following reaction.

Complete and balance this reaction:



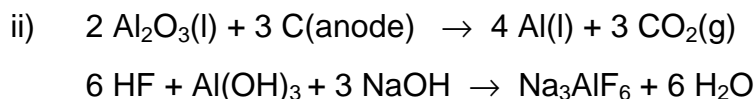
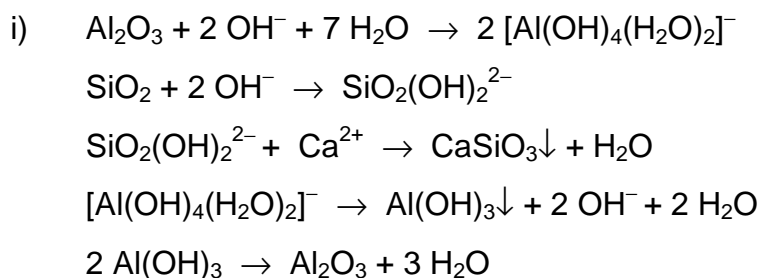
During the electrolysis process several parallel reactions take place that degrade the graphite (C) anodes or reduce the yield.

- 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 °C for the reaction:



	Al(s)	Al ₂ O ₃ (s)	C (graphite)	CO(g)	CO ₂ (g)	O ₂ (g)
$\Delta_f H^\circ$ (kJ mol ⁻¹)	0	-1676	0	-111	-394	
S° (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
- $$2 \text{Al}(\text{l}) + 3 \text{CO}_2(\text{g}) \rightarrow \text{Al}_2\text{O}_3(\text{l}) + 3 \text{CO}(\text{g})$$
- given that $\Delta S = -126 \text{ J K}^{-1} \text{ mol}^{-1}$. (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 $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, as well as in strong bases at room temperature producing hydrated tetrahydroxyaluminate anion, $[\text{Al}(\text{OH})_4]^{-}(\text{aq})$. In both cases liberation of H₂ occurs. AlF₃ is made by treating Al₂O₃ with HF gas at 700 °C, while the other trihalides, AlX₃, are made by the direct exothermic reaction of Al with the corresponding dihalogen. Write all 4 chemical reactions described above.
- vi) The AlCl₃ is a crystalline solid having a layer lattice with 6-coordinate Al(III), but at the melting point (192.4°C) the structure changes to a 4-coordinate molecular dimer, Al₂Cl₆. The covalently bonded molecular dimer, in the gas phase and at high temperature, dissociates into trigonal planar AlCl₃ molecules.
- For the molecular dimer Al₂Cl₆, 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 Al₂Cl₆ and AlCl₃?

SOLUTION

iii) $\Delta_r H_{1213}^0 = 2\Delta_f H_{1213}^0(\text{CO}) - \Delta_f H_{1213}^0(\text{CO}_2) = 2 \times (-111) - (-394) = 172 \text{ kJ}$
 $\Delta_r S_{1213}^0 = 2S_{1213}^0(\text{CO}) - S_{1213}^0(\text{CO}_2) - S_{1213}^0(\text{C}) = 2 \times (-198) - 214 - 6 = 176 \text{ JK}^{-1}$
 $\Delta_r G_{1213}^0 = \Delta_r H_{1213}^0 - T\Delta_r S_{1213}^0 = 172 - 1213 \times 0.176 = -41.5 \text{ kJ K}^{-1}$

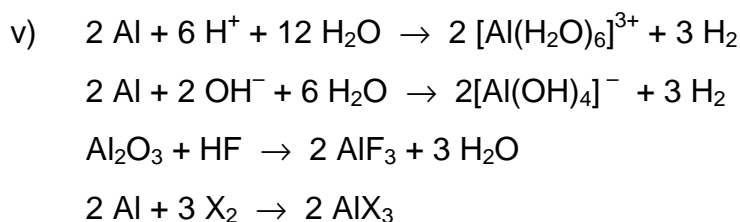
iv)

$$\Delta_r H_{1213}^0 = 3\Delta_f H_{1213}^0(\text{CO}) + \Delta_f H_{298}^0(\text{Al}_2\text{O}_3) + \Delta_{\text{melt}} H(\text{Al}_2\text{O}_3) - 3\Delta_f H_{1213}^0(\text{CO}_2) - 2\Delta H_{\text{melt}} H(\text{Al}) =$$

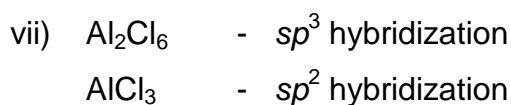
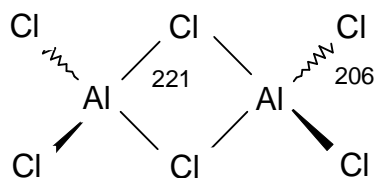
$$= 3 \times (-111) - (-1676) + 109 - 3 \times (-394) - 2 \times 11 = -740 \text{ kJ}$$

$$\Delta_r H_{1213}^0 = 3\Delta_f H_{1213}^0(\text{CO}) + \Delta_f H_{298}^0(\text{Al}_2\text{O}_3) + \Delta_{\text{melt}} H(\text{Al}_2\text{O}_3) - 3\Delta_f H_{1213}^0(\text{CO}_2) - 2\Delta H_{\text{melt}} H(\text{Al}) =$$

$$= 3 \times (-111) - (-1676) + 109 - 3 \times (-394) - 2 \times 11 = -740 \text{ kJ}$$



vi)



PROBLEM 35 Kinetics

The acid-catalyzed reaction $\text{CH}_3\text{COCH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{I} + \text{HI}$ 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 $0.010 \text{ mol dm}^{-3}$ was measured under various concentrations of the reactants.

Based on the information provided in the table, answer fulfil the following tasks:

$[\text{CH}_3\text{COCH}_3]$ (mol dm^{-3})	$[\text{I}_2]$ (mol dm^{-3})	Time (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

- Derive the rate law for the reaction and calculate the rate constant.
- Calculate the time needed for 75 % of CH_3COCH_3 to react in excess I_2 .
- Show graphically the dependence of the rate on $[\text{CH}_3\text{COCH}_3]$ and on $[\text{I}_2]$, for fixed initial concentration of the other reagents.
- If the rate is doubled by raising the temperature by 10°C from 298 K, calculate the activation energy for this reaction.

SOLUTION

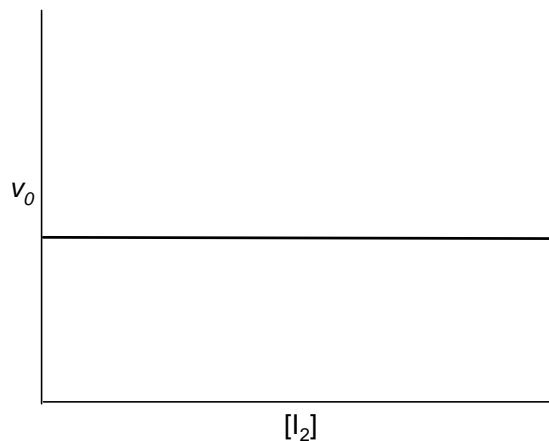
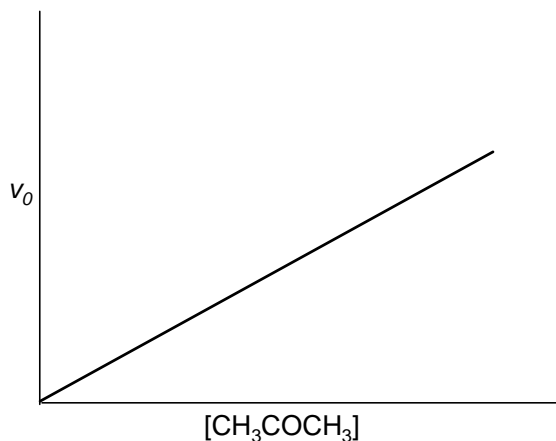
a) $v = k [\text{CH}_3\text{COCH}_3]$

$$k = \frac{v}{[\text{CH}_3\text{COCH}_3]} = \frac{0.010}{0.25 \times 7.2} = 5.56 \times 10^{-3} \text{ min}^{-1} = 9.26 \times 10^{-5} \text{ s}^{-1}$$

b) $\tau = \ln 2 / k = 125 \text{ min}$

$$t = 2 \tau = 250 \text{ min}$$

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-OCH₃)

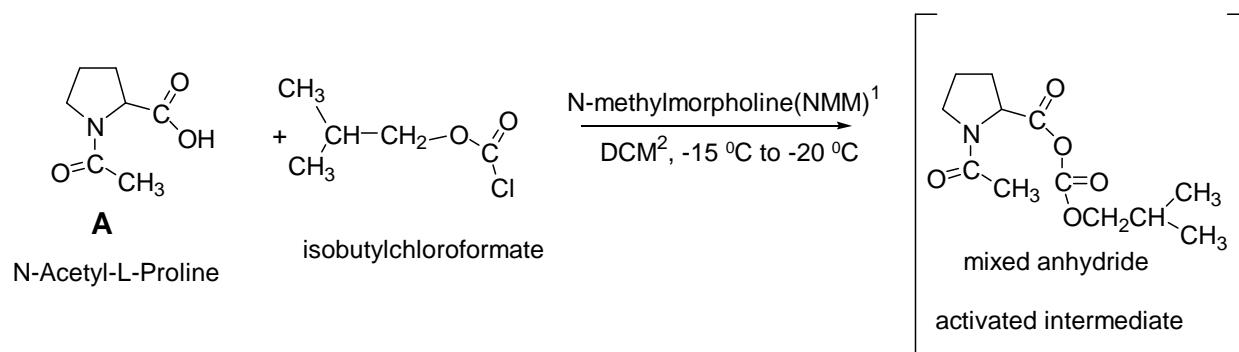
Introduction

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.

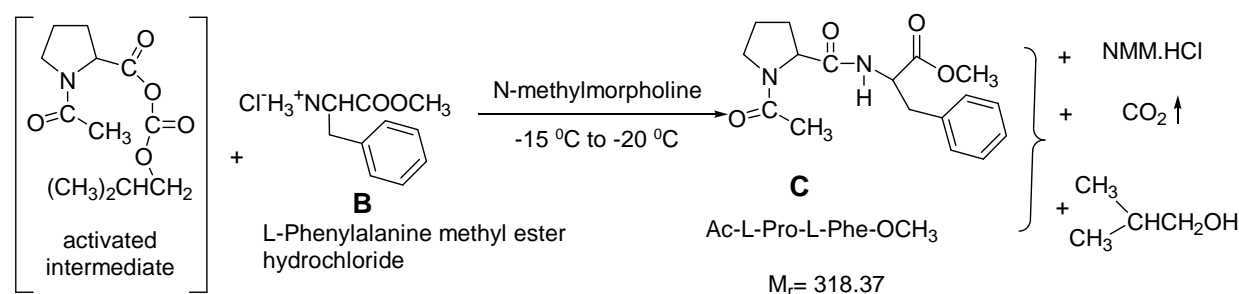
In this experiment the one-pot procedure for synthesizing the title dipeptide from its components, suitably protected amino acids, is described.

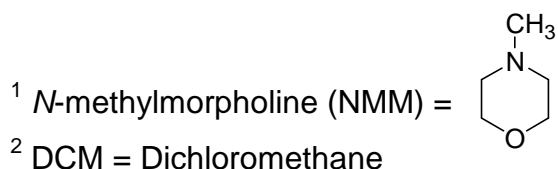
Reactions

STEP 1



STEP 2





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-cm³ round-bottom flask. Add 20 cm³ dichloromethane (labelled DCM) in the graduated cylinder. Use some of the 20 cm³ 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 $-15\text{ }^{\circ}\text{C}$ to $-20\text{ }^{\circ}\text{C}$ in the ice/sodium chloride cold bath provided by the supervisor. Allow approximately 5 minutes for cooling. Add 1.2 cm³ (0.0109 mol) of *N*-methylmorpholine (labelled NMM) to the flask, by means of a syringe. Then, slowly add 1.5 cm³ (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 ° to $-15\text{ }^{\circ}\text{C}$.

STEP 2

Remove the septum and quickly add all the *L*-phenylalanine methyl ester hydrochloride (2.15 g, 0.0100 mol), (labelled HCl-H₂NPheOCH₃) using the polypropylene powder funnel. Plug the flask again with the septum. Immediately add 1.2 cm³ (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 $-15\text{ }^{\circ}\text{C}$ to $-20\text{ }^{\circ}\text{C}$, swirling periodically by hand.

During this waiting period you are highly advised to start working on the Analytical Chemistry experiment.

After 60 min at $-20\text{ }^{\circ}\text{C}$ to $-15\text{ }^{\circ}\text{C}$, remove the 50 cm³ round-bottomed flask from the ice/sodium chloride bath and place the flask in the 250 cm³ beaker and let it warm up to

room temperature. Transfer the contents of the flask into the 50 cm³ separating funnel by means of the glass funnel. Rinse the flask with a small amount of dichloromethane (3 – 5 cm³), which is in a vial (labelled DCM). Wash the organic layer successively with two 20 cm³ portions of 0.2 M aqueous HCl solution, two 20 cm³ portions of 1 % aqueous

NaHCO₃ solution (read caution comment in next paragraph) and finally one 10 cm³ 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).

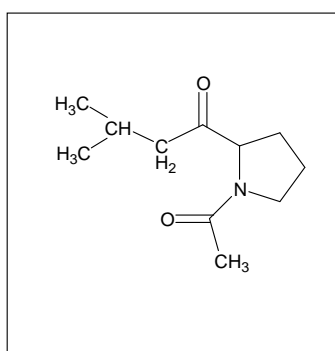
CAUTION: Keep in mind, also, that during washing with 1 % NaHCO₃, the CO₂ liberated is exerting pressure on the separating funnel stopper, so be sure to let the gas out through the stopcock before and after each shaking, while holding the funnel upside down.

Before continuing, wash the glass funnel, the 50 cm³ cylinder and the 50 cm³ 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.

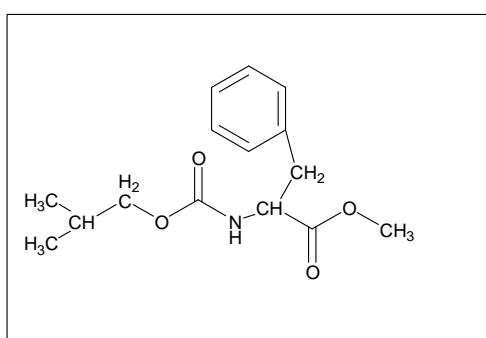
Pour the organic layer into a clean 50 cm³ Erlenmeyer flask. Add the anhydrous sodium sulphate, which is in a vial labelled Na₂SO₄, to the Erlenmeyer flask containing the organic layer. The organic phase should become clear. Filter it through the cleaned and dried funnel, whose stem you have previously stuffed with a small piece of cotton to trap any solids, into the cleaned and dried 50 cm³ round-bottom flask. Rinse the Erlenmeyer flask with a small amount of dichloromethane (3 – 5 cm³). 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 cm³ 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 cm³ 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).

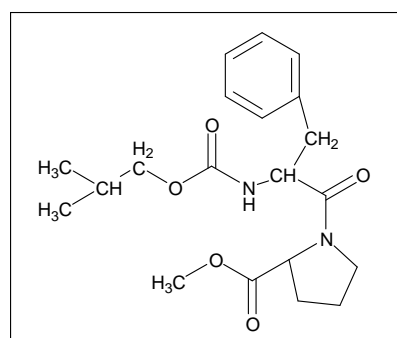
During the reaction between the phenylalanine methylester **B** and the activated mixed anhydride intermediate (step 2) the formation of the desired dipeptide product **C** is usually accompanied by a by-product the correct structure of which is one of the three structures **I**, **II**, **III** given 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, $[\alpha]_D^t$, using an accurate polarimeter apparatus.

SOLUTION

The following values were required to be written in the Answer Sheet

- Mass of Ac-L-Pro-L-Phe-OCH₃ obtained (product **C**).
 - The yield of Ac-L-Pro-L-Phe-OCH₃ **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-OCH₃ (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-OCH₃ C (to be measured later by the examination committee)
$$[\alpha]_D^{25} = 45^\circ$$

 - The correct structure of the by-product: **II**.
-
-

36th



International Chemistry Olympiad

**8 theoretical problems
2 practical problems**

THE THIRTY-SIXTH INTERNATIONAL CHEMISTRY OLYMPIAD 18–27 JULY 2004, KIEL, GERMANY

THEORETICAL PROBLEMS

PROBLEM 1

Thermodynamics

For his 18th birthday party in February Peter plans to turn a hut in the garden of his parents into a swimming pool with an artificial beach. In order to estimate the costs for heating the water and the house, Peter obtains the data for the natural gas composition and its price.

1.1 Write down the chemical equations for the complete combustion of the main components of natural gas, methane and ethane, given in Table 1. Assume that nitrogen is inert under the chosen conditions.

Calculate the reaction enthalpy, the reaction entropy, and the Gibbs energy under standard conditions ($1.013 \cdot 10^5$ Pa, 25.0 °C) for the combustion of methane and ethane according to the equations above assuming that all products are gaseous.

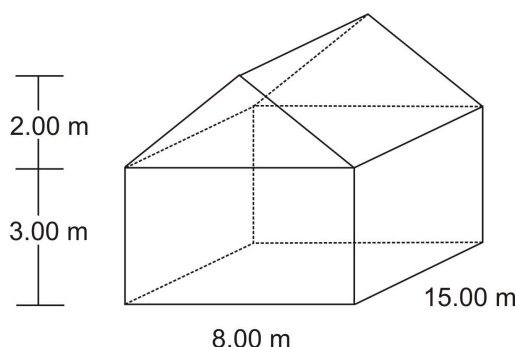
The thermodynamic properties and the composition of natural gas can be found in Table 1.

1.2 The density of natural gas is 0.740 g dm^{-3} (1.013×10^5 Pa, 25.0 °C) specified by PUC, the public utility company.

- Calculate the amount of methane and ethane (in moles) in 1.00 m^3 of natural gas (natural gas, methane, and ethane are not ideal gases!).
- Calculate the combustion energy which is released as thermal energy during the burning of 1.00 m^3 of natural gas under standard conditions assuming that all products are gaseous. (If you do not have the amount from 1.2a) assume that 1.00 m^3 natural gas corresponds to 40.00 mol natural gas.)

According to the PUC the combustion energy will be 9.981 kWh per m³ of natural gas if all products are gaseous. How large is the deviation (in percent) from the value you obtained in b)

The swimming pool inside the house is 3.00 m wide, 5.00 m long and 1.50 m deep (below the floor). The tap water temperature is 8.00 °C and the air temperature in the house (dimensions given in the figure below) is 10.0 °C. Assume a water density of $\rho = 1.00 \text{ kg dm}^{-3}$ and air behaving like an ideal gas.



- 1.3** Calculate the energy (in MJ) which is required to heat the water in the pool to 22.0 °C and the energy which is required to heat the initial amount of air (21.0 % of O₂, 79.0 % of N₂) to 30.0 °C at a pressure of $1.013 \times 10^5 \text{ Pa}$.

In February, the outside temperature is about 5 °C in Northern Germany. Since the concrete walls and the roof of the house are relatively thin (20.0 cm) there will be a loss of energy. This energy is released to the surroundings (heat loss released to water and/or ground should be neglected). The heat conductivity of the wall and roof is $1.00 \text{ W K}^{-1} \text{ m}^{-1}$.

- 1.4** Calculate the energy (in MJ) which is needed to maintain the temperature inside the house at 30.0 °C during the party (12 hours).

1.00 m³ of natural gas as delivered by PUC costs 0.40 € and 1.00 kWh of electricity costs 0.137 €. The rent for the equipment for gas heating will cost him about 150.00 € while the corresponding electrical heaters will only cost 100.00 €.

- 1.5** What is the total energy (in MJ) needed for Peter's "winter swimming pool" calculated in 1.3 and 1.4? How much natural gas will he need, if the gas heater has an efficiency of 90.0 %? What are the different costs for the use of either natural gas or electricity? Use the values given by PUC for your calculations and assume 100 % efficiency for the electric heater.

Table 1: Composition of natural gas

Chemical Substance	mol fraction x	$\Delta_f H^0$ (kJ mol ⁻¹) ⁻¹	S^0 (J mol ⁻¹ K ⁻¹) ⁻¹	C_p^0 (J mol ⁻¹ K ⁻¹) ⁻¹
CO ₂ (g)	0.0024	-393.5	213.8	37.1
N ₂ (g)	0.0134	0.0	191.6	29.1
CH ₄ (g)	0.9732	-74.6	186.3	35.7
C ₂ H ₆ (g)	0.0110	-84.0	229.2	52.5
H ₂ O (l)	-	-285.8	70.0	75.3
H ₂ O (g)	-	-241.8	188.8	33.6
O ₂ (g)	-	0.0	205.2	29.4

Equation:

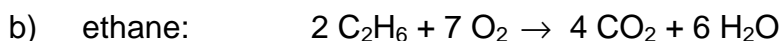
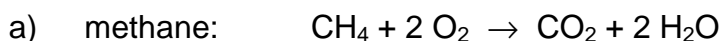
$$J = E \times (A \times \Delta t)^{-1} = \lambda_{\text{wall}} \times \Delta T \times d^{-1}$$

J energy flow E along a temperature gradient (wall direction z) per area A and time Δt

d wall thickness

λ_{wall} heat conductivity

ΔT difference in temperature between the inside and the outside of the house

SOLUTION**1.1** Chemical equations:

Thermodynamic data for the equations:

$$\Delta H^0 = [2 \times (-241.8) - 393.5 - (-74.6)] \text{ kJ mol}^{-1} = -802.5 \text{ kJ mol}^{-1}$$

$$\Delta S^0 = [2 \times (188.8) + 213.8 - 186.3 - 2 \times 205.2] \text{ J mol}^{-1} \text{ K}^{-1} = -5.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G^{\circ} = -802.5 \text{ kJ mol}^{-1} - 298.15 \text{ K} \times (-5.3 \text{ J mol}^{-1} \text{ K}^{-1}) = -800.9 \text{ kJ mol}^{-1}$$

$$\text{Methane: } \Delta H^{\circ} = -802.5 \text{ kJ mol}^{-1}; \Delta S^{\circ} = -5.3 \text{ J mol}^{-1} \text{ K}^{-1}; \Delta G^{\circ} = -800.9 \text{ kJ mol}^{-1}$$

$$\Delta H^{\circ} = [6 \times (-241.8) - 4 \times 393.5 - 2 \times (-84.0)] \text{ kJ mol}^{-1} = -2856.8 \text{ kJ mol}^{-1}$$

$$\Delta S^{\circ} = [6 \times 188.8 + 4 \times 213.8 - 2 \times 229.2 - 7 \times 205.2] \text{ J mol}^{-1} \text{ K}^{-1} = +93.2 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G^{\circ} = -2856.8 \text{ kJ mol}^{-1} - 298.15 \text{ K} \times (93.2 \text{ J mol}^{-1} \text{ K}^{-1}) = -2884.6 \text{ kJ mol}^{-1}$$

$$\text{Ethane: } \Delta H^{\circ} = -2856.8 \text{ kJ mol}^{-1}; \Delta S^{\circ} = +93.2 \text{ J mol}^{-1} \text{ K}^{-1}; \Delta G^{\circ} = -2884.6 \text{ kJ mol}^{-1}$$

1.2 a) Amount of methane and ethane in 1 m³ natural gas:

$$m = \rho \times V = 0.740 \text{ g dm}^{-3} \times 1000 \text{ dm}^3 = 740 \text{ g}$$

$$M_{\text{av}} = \sum_i x(i)M(i) = (0.0024 \times 44.01 \text{ g mol}^{-1}) + (0.0134 \times 28.02 \text{ g mol}^{-1}) \\ + (0.9732 \times 16.05 \text{ g mol}^{-1}) + (0.011 \times 30.08 \text{ g mol}^{-1}) = 16.43 \text{ g mol}^{-1}$$

$$n_{\text{tot}} = m (M_{\text{av}})^{-1} = 740 \text{ g} \times (16.43 \text{ g/mol})^{-1} = 45.04 \text{ mol}$$

$$n(i) = x(i) \cdot n_{\text{tot}}$$

$$n(\text{CH}_4) = x(\text{CH}_4) \times n_{\text{tot}} = 0.9732 \times 45.04 \text{ mol} = 43.83 \text{ mol}$$

$$n(\text{C}_2\text{H}_6) = x(\text{C}_2\text{H}_6) \times n_{\text{tot}} = 0.0110 \times 45.04 \text{ mol} = 0.495 \text{ mol}$$

b) Energy of combustion, deviation:

$$E_{\text{comb.}}(\text{H}_2\text{O}(\text{g})) = \sum_i n(i)\Delta_c H^{\circ}(i) = \\ = 43.83 \text{ mol} \times (-802.5 \text{ kJ mol}^{-1}) + 0.495 \text{ mol} \times 0.5 \times (-2856.8 \text{ kJ mol}^{-1}) \\ = -35881 \text{ kJ}$$

$$E_{\text{comb.}}(\text{H}_2\text{O}(\text{g})) = -35881 \text{ kJ}$$

Deviation from PUC

$$E_{\text{PUC}}(\text{H}_2\text{O}(\text{g})) = 9.981 \text{ kWh m}^{-3} \times 1 \text{ m}^3 \times 3600 \text{ kJ (kWh)}^{-1} = 35932 \text{ kJ}$$

$$\text{Deviation: } \Delta^E = (E_{\text{comb.}}(\text{H}_2\text{O}(\text{g})) - E_{\text{PUC}}(\text{H}_2\text{O}(\text{g})) \times 100 \% \times [E_{\text{comb.}}(\text{H}_2\text{O}(\text{g}))]^{-1} \\ = (35881 \text{ kJ} - 35932 \text{ kJ}) \times 100 \% \times (35881 \text{ kJ})^{-1} = -0.14\%$$

1.3 Energy for heating the water:

$$\text{Volume of water: } V_{\text{water}} = 22.5 \text{ m}^3$$

$$n_{\text{water}} = V_{\text{water}} \rho_{\text{water}} (M_{\text{water}})^{-1} = 22.5 \text{ m}^3 \times 10^6 \text{ g m}^{-3} \times (18.02 \text{ g mol}^{-1})^{-1} = 1.249 \times 10^6 \text{ mol}$$

$$E_{\text{water}} = n_{\text{water}} \times C_p \times \Delta T = 1.249 \times 10^6 \text{ mol} \times 75.30 \text{ J K}^{-1} \text{ mol}^{-1} \times 14 \text{ K} = 1316 \text{ MJ}$$

Energy for heating the air:

Volume of the house is:

$$V_{\text{air}} = (15 \text{ m} \times 8 \text{ m} \times 3 \text{ m}) + 0.5 \times (15 \text{ m} \times 8 \text{ m} \times 2 \text{ m}) = 480 \text{ m}^3$$

$$n_{\text{air}} = pV(RT)^{-1} = 1.013 \times 10^5 \text{ Pa} \times 480 \text{ m}^3 \times (8.314 \text{ J (K mol)}^{-1} \times 283.15 \text{ K})^{-1} = \\ = 2.065 \times 10^4 \text{ mol}$$

$$C_p(\text{air}) = 0.21 \times 29.4 \text{ J (K mol)}^{-1} + 0.79 \times 29.1 \text{ J (K mol)}^{-1} = 29.16 \text{ J (K mol)}^{-1}$$

$$E_{\text{air}} = n_{\text{air}} \times C_p(\text{air}) \times \Delta T = 2.065 \times 10^4 \text{ mol} \times 29.17 \text{ J (K mol)}^{-1} \times 20 \text{ K} = 12.05 \text{ MJ}$$

1.4 Energy for maintaining the temperature:

Surface area of the house:

$$A_{\text{house}} = 3 \text{ m} \times 46 \text{ m} + 8 \text{ m} \times 2 \text{ m} + ((2 \text{ m})^2 + (4 \text{ m})^2)^{1/2} \times 2 \times 15 \text{ m} = 288.16 \text{ m}^2$$

Heat conductivity: $\lambda_{\text{wall}} = 1 \text{ J (s K m)}^{-1}$

Energy flux along a temperature gradient (wall thickness $d = 0.2 \text{ m}$)

$$J = E_{\text{loss}} (A \times \Delta t)^{-1} = \lambda_{\text{wall}} \Delta T d^{-1}$$

$$E_{\text{loss}} = 288.16 \text{ m}^2 \times (12 \cdot 60 \cdot 60 \text{ s}) \times 1 \text{ J (s K m)}^{-1} \times 25 \text{ K} \times (0.2 \text{ m})^{-1} = 1556 \text{ MJ}$$

$$E_{\text{loss}} = 1556 \text{ MJ}$$

1.5 Total energy and costs:

$$\text{Total energy: } E_{\text{tot}} = E_{\text{water}} + E_{\text{air}} + E_{\text{loss}} = 1316 \text{ MJ} + 12 \text{ MJ} + 1556 \text{ MJ} = 2884 \text{ MJ}$$

$$2884 \text{ MJ corresponds to } 2.884 \times 10^6 \text{ kJ} \times (3600 \text{ s h}^{-1} \times 9.981 \text{ kJ s}^{-1} \text{ m}^{-3} \times 0.9)^{-1} = \\ 89.18 \text{ m}^3$$

$$\text{Volume of gas: } V = 89.18 \text{ m}^3$$

2884 MJ correspond to a cost of:

$$0.40 \text{ € m}^{-3} \times 89.18 \text{ m}^3 = 35.67 \text{ €}$$

Rent for equipment: 150.00 €

Total cost of gas heating = 185.67 €

2884 MJ correspond to a cost of

$$2.884 \cdot 10^6 \text{ kJ} \times 0.137 \text{ €} \times (3600 \text{ s h}^{-1} \times 1 \text{ kJ s}^{-1} \text{ h})^{-1} = 109.75 \text{ €}$$

Rent for equipment: 100.00 €

Total cost of electric heating: 209.75 €

PROBLEM 2

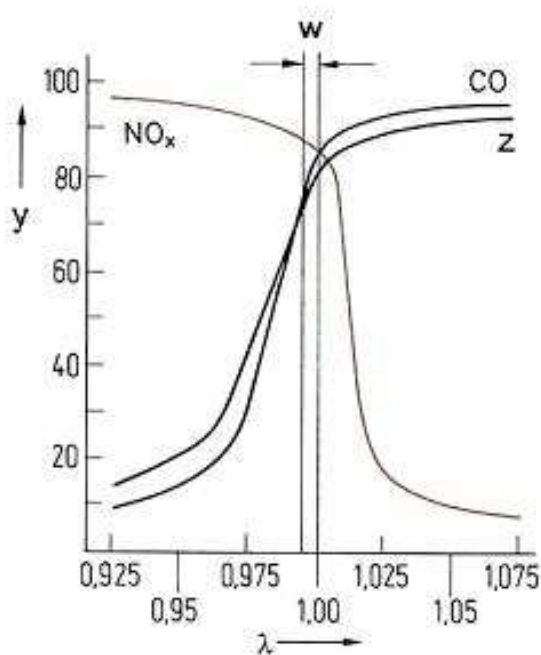
Kinetics at catalyst surfaces

Apart from other compounds the exhaust gases of an Otto engine are the main pollutants carbon monoxide, nitrogen monoxide and uncombusted hydrocarbons, as, for example, octane. To minimize them they are converted to carbon dioxide, nitrogen and water in a regulated three-way catalytic converter.

2.1 Complete the chemical reaction equations for the reactions of the main pollutants in the catalyst.

To remove the main pollutants from the exhaust gas of an Otto engine optimally, the λ -value is determined by an electro-chemical element, the so called lambda probe. It is located in the exhaust gas stream between engine and the three-way catalytic converter.

The lambda value is defined as $\lambda = \frac{\text{amount of air at the inlet}}{\text{amount of air necessary for complete combustion}}$.



w: λ -window

y: conversion efficiency (%)

z: Hydrocarbons

2.2 Decide the questions on the answer sheet concerning the λ probe.

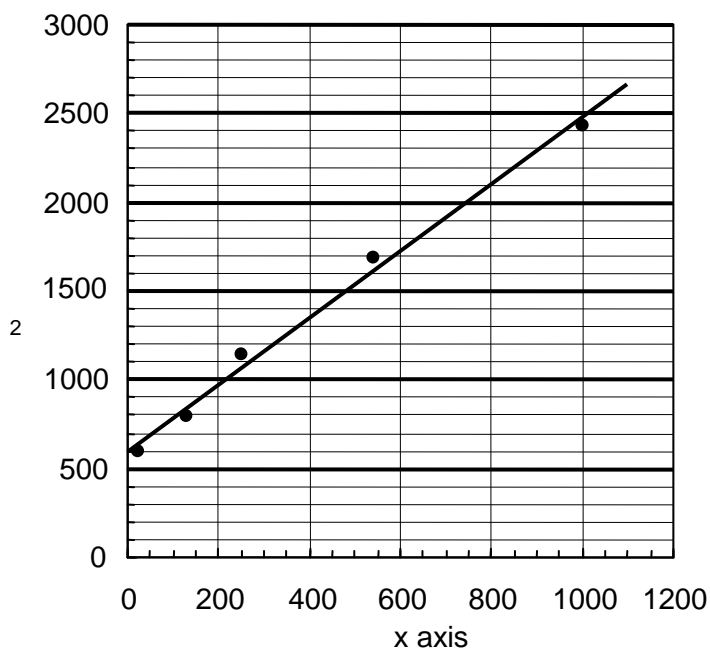
The adsorption of gas molecules on a solid surface can be described in a simple model by using the Langmuir isotherm:

$$\theta = \frac{K \times p}{1 + K \times p}$$

where θ is the fraction of surface sites that are occupied by the gas molecules, p is the gas pressure and K is a constant.

The adsorption of a gas at 25 °C may be described by using the Langmuir isotherm with $K = 0.85 \text{ kPa}^{-1}$.

- 2.3** a) Determine the surface coverage θ at a pressure of 0.65 kPa.
 b) Determine the pressure p at which 15 % of the surface is covered.
 c) The rate r of the decomposition of gas molecules at a solid surface depends on the surface coverage θ (reverse reaction neglected): $r = k \theta$
 Give the order of the decomposition reaction at low and at high gas pressures assuming the validity of the Langmuir isotherm given above (products to be neglected).
 d) Data for the adsorption of another gas on a metal surface (at 25 °C)



x axis: $p \cdot (\text{Pa})^{-1}$

y axis: $p \cdot V_a^{-1} \cdot (\text{Pa cm}^{-3})^{-1}$

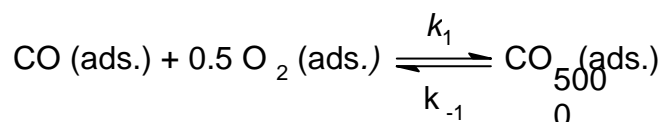
V_a is the gas volume that has been adsorbed.

If the Langmuir isotherm can be applied, determine the gas volume $V_{a,\text{max}}$ needed for a complete coverage of the metal surface and the product $K V_{a,\text{max}}$.

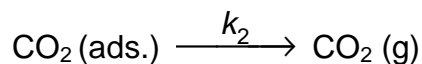
Hint: Set $\theta = V_a / V_{a,\text{max}}$.

Assume that the catalytic oxidation of CO on a Pd surface with equal surface sites proceeds in the following way:

In a first step adsorbed CO and adsorbed O_2 form adsorbed CO_2 in a fast equilibrium,



In a slow second step, CO₂ is then desorbed from the surface:



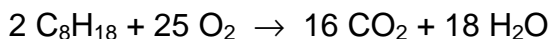
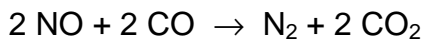
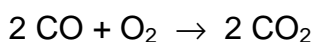
2.4 Derive the formula for the reaction rate of the CO₂(g) - formation as a function of the partial pressures of the reaction components.

Hint: Use the Langmuir isotherm with the proper number of gas components

$$\theta_i = \frac{K_j \times p_j}{1 + \sum_j K_j \times p_j} \quad \text{j: relevant gas components}$$

SOLUTION

2.1 Reaction equations:



2.2 Questions concerning the λ probe:

true false no decision

possible

If the λ -value is in the range of the λ -window, carbon monoxide and hydrocarbons can be oxidised at the three-way catalytic converter.

With $\lambda > 1$, carbon monoxide and hydrocarbons can be oxidised at the three-way catalytic converter.

With $\lambda < 0.975$, nitrogen oxides can be reduced poorly.

2.3 a) Surface coverage:

$$\theta = \frac{0.85 \text{ kPa}^{-1} \times 0.65 \text{ kPa}}{1 + 0.85 \times 0.65}$$

$$\theta = 0.356 \text{ or } 35.6 \%$$

b) Pressure at which 15 % of the surface is covered:

$$\theta = \frac{K \times p}{1 + K \times p} \Leftrightarrow K \times p = \theta + \theta \times K \times p \Leftrightarrow p \cdot (K - \theta \times K) = \theta \Leftrightarrow$$

$$p = \frac{\theta}{K - \theta \times K}$$

$$\theta = 0.15$$

$$p = 0.21 \text{ kPa}$$

c) Orders of decomposition:

Order of the decomposition reaction at low gas pressures 1

Order of the decomposition reaction at high gas pressures 0

Notes:

$$r = k \times \theta = k \frac{K \times p}{1 + K \times p},$$

$$p \text{ low} \Rightarrow p \ll \frac{1}{K} \Rightarrow r = k K p \quad \text{reaction order } 1.$$

$$p \text{ high} \Rightarrow p \gg \frac{1}{K} \Rightarrow r = k \quad \text{reaction order } 0.$$

d) Gas volume $V_{a,\max}$ and product $K \cdot V_{a,\max}$:

$$\frac{1}{\theta} = \frac{1}{K p} + 1 = \frac{V_{a,\max}}{V_a} \Rightarrow \frac{1}{K V_{a,\max}} + \frac{p}{V_{a,\max}} = \frac{p}{V_a}$$

$$\text{Slope: } \frac{1}{V_{a,\max}} = 1.9 \text{ cm}^{-3} \Rightarrow V_{a,\max} = 0.53 \text{ cm}^3$$

$$\text{Intercept: } \frac{1}{K V_{a,\max}} = 6 \times 10^2 \text{ Pa cm}^{-3} \Rightarrow K V_{a,\max} = 1.7 \times 10^{-3} \text{ Pa}^{-1} \text{ cm}^3$$

2.4 Equation for reaction rate:

The information given in the text leads directly to $r = k_2 \theta_{\text{CO}_2}$

The law of mass action for the first step of the mechanism is given by

$$\theta_{\text{CO}_2} = \frac{k_1}{k_{-1}} \cdot \theta_{\text{CO}} \theta_{\text{O}_2}^{\frac{1}{2}}, \Rightarrow r = k_2 \frac{k_1}{k_{-1}} \theta_{\text{CO}} \theta_{\text{O}_2}^{\frac{1}{2}}.$$

The Langmuir isotherm gives:

$$\theta_{\text{CO}} = \frac{K_{\text{CO}} p_{\text{CO}}}{1 + K_{\text{CO}_2} p_{\text{CO}_2} + K_{\text{CO}} p_{\text{CO}} + K_{\text{O}_2} p_{\text{O}_2}} \quad \text{and} \quad \theta_{\text{O}_2} = \frac{K_{\text{O}_2} p_{\text{O}_2}}{1 + K_{\text{CO}_2} p_{\text{CO}_2} + K_{\text{CO}} p_{\text{CO}} + K_{\text{O}_2} p_{\text{O}_2}}$$

$$r = k_2 \frac{k_1}{k_{-1}} \frac{K_{\text{CO}} p_{\text{CO}} (K_{\text{O}_2} p_{\text{O}_2})^{\frac{1}{2}}}{(1 + K_{\text{CO}_2} p_{\text{CO}_2} + K_{\text{CO}} p_{\text{CO}} + K_{\text{O}_2} p_{\text{O}_2})^{\frac{3}{2}}}$$

PROBLEM 3

Monovalent alkaline earth compounds?

In the past there have been several reports on compounds of monovalent calcium. Until recently the nature of these “compounds” was not known but they are still of great interest to solid state chemists.

Attempts to reduce CaCl_2 to CaCl have been made with

- (a) Calcium (b) Hydrogen (c) Carbon

3.1 Give the corresponding reaction equations that could potentially lead to the formation of CaCl .

After an attempt to reduce CaCl_2 with the stoichiometric 1 : 1 molar amount of Ca one obtains an inhomogeneous grey substance. A closer look under the microscope reveals silvery metallic particles and colourless crystals.

3.2 What substance are the metallic particles and the colourless crystals?

When CaCl_2 is attempted to be reduced with elemental hydrogen a white product forms. Elemental analysis shows that the sample contains 52.36 % (by mass) of calcium and 46.32 mass % of chlorine.

3.3 Determine the empirical formula of the compound formed.

When CaCl_2 is attempted to be reduced with elemental carbon a red crystalline product forms. The molar ratio of Ca and Cl determined by elemental analysis is $n(\text{Ca}) : n(\text{Cl}) = 1.5 : 1$. During the hydrolysis of the red crystalline substance the same gas is evolved as during the hydrolysis of Mg_2C_3 .

- 3.4** a) Show the two acyclic constitutional isomers of the gas that are formed by hydrolysis.
b) What compound is formed by the reaction of CaCl_2 with carbon?
(Provided that monovalent calcium does not exist.)

As none of these attempts lead to the formation of CaCl more consideration has to be given as to the hypothetical structure of CaCl . One can assume that CaCl is likely to crystallize in a simple crystal structure.

It is the radius ratio of cation $r(M^{m+})$ and anion $r(X^{x-})$ of salts that often determines the crystal structure of a particular compound as shown for MX compounds in the table below.

Coordination number of M	Surrounding of X	Radius ratio r_M/r_X	Structure type	estimated $\Delta_L H^\circ$ for CaCl
3	Triangular	0.155 – 0.225	BN	$-663.8 \text{ kJ mol}^{-1}$
4	Tetrahedral	0.225 – 0.414	ZnS	$-704.8 \text{ kJ mol}^{-1}$
6	Octahedral	0.414 – 0.732	NaCl	$-751.9 \text{ kJ mol}^{-1}$
8	Cubic	0.732 – 1.000	CsCl	$-758.4 \text{ kJ mol}^{-1}$

$\Delta_L H^\circ(\text{CaCl})$ is defined for the reaction $\text{Ca}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{CaCl}(\text{s})$

3.5 a) What type of structure is CaCl likely to have?

$[r(\text{Ca}^+) \approx 120 \text{ pm (estimated)}, r(\text{Cl}^-) \approx 167 \text{ pm}]$

Not only the lattice energy $\Delta_L H^\circ$ for CaCl is important for the decision whether CaCl is thermodynamically stable or not. In order to decide whether it is stable against decomposition into its elements, the standard enthalpy of formation $\Delta_f H^\circ$ of CaCl has to be known.

b) Calculate the value of $\Delta_f H^\circ(\text{CaCl})$ with the aid of a Born-Haber-cycle.

heat of fusion	$\Delta_{\text{fusion}} H^\circ(\text{Ca})$		9.3 kJ mol^{-1}
ionization enthalpy	$\Delta_{1. \text{IE}} H(\text{Ca})$	$\text{Ca} \rightarrow \text{Ca}^+$	$589.7 \text{ kJ mol}^{-1}$
ionization enthalpy	$\Delta_{2. \text{IE}} H(\text{Ca})$	$\text{Ca}^+ \rightarrow \text{Ca}^{2+}$	$1145.0 \text{ kJ mol}^{-1}$
heat of vaporization	$\Delta_{\text{vap}} H^\circ(\text{Ca})$		$150.0 \text{ kJ mol}^{-1}$
dissociation energy	$\Delta_{\text{diss}} H(\text{Cl}_2)$	$\text{Cl}_2 \rightarrow 2 \text{ Cl}$	$240.0 \text{ kJ mol}^{-1}$

enthalpy of formation	$\Delta_f H^\ominus(\text{CaCl}_2)$		$-796.0 \text{ kJ mol}^{-1}$
electron affinity	$\Delta_{\text{EA}} H(\text{Cl})$	$\text{Cl} + \text{e}^- \rightarrow \text{Cl}^-$	$-349.0 \text{ kJ mol}^{-1}$

To decide whether CaCl is thermodynamically stable to disproportionation into Ca and CaCl₂ the standard enthalpy of this process has to be calculated. (The change of the entropy ΔS is very small in this case, so its influence is negligible.)

3.6 Does the disproportionation of CaCl take place from a thermodynamic point of view? Base your decision on a calculation!

SOLUTION

3.1 Chemical equations:

- (a) $\text{CaCl}_2 + \text{Ca} \rightarrow 2 \text{CaCl}$
 (b) $2 \text{CaCl}_2 + \text{H}_2 \rightarrow 2 \text{CaCl} + 2 \text{HCl}$
 (c) $4 \text{CaCl}_2 + \text{C} \rightarrow 4 \text{CaCl} + \text{CCl}_4$

3.2

Silvery metallic particles: Ca

Colourless crystals: CaCl₂

Note: CaCl cannot be obtained by a conventional solid state reaction of Ca and CaCl₂

3.3 Empirical formula:

$$100 \% - (\text{mass \% Ca} + \text{mass \% Cl}) = \text{mass \% X}$$

$$100 \% - (52.36 \% + 46.32 \%) = 1.32 \% \text{ X}$$

$$\text{mol \% of Ca} = 52.36 \text{ mass \%} / M(\text{Ca})$$

$$= 52.36 \text{ mass \%} / 40.08 \text{ g mol}^{-1} = 1.31 \text{ mol \%}$$

$$\text{mol \% of Cl} = 46.32 \text{ mass \%} / M(\text{Cl})$$

$$= 46.32 \text{ mass \%} / 35.45 \text{ g mol}^{-1} = 1.31 \text{ mol \%}$$

$$\text{mol \% of X} = 1.32 \% \text{ X} / M(\text{H})$$

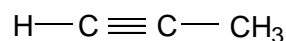
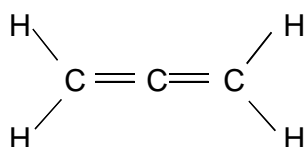
$$= 1.32 \% \text{ X} / 1.01 \text{ g mol}^{-1} = 1.31 \text{ mol \%}$$

$$n(\text{Ca}) : n(\text{Cl}) : n(\text{H}) = 1 : 1 : 1$$

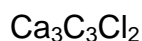
Empirical formula: CaClH

Notes: The reaction of CaCl_2 with hydrogen does not lead to CaCl . The hydride CaClH is formed instead. The structure of this compound was determined by X-ray structure analysis which is not a suitable method to determine the position of light elements like hydrogen. Thus, the presence of hydrogen was missed and CaClH was thought to be CaCl for quite a long time.

3.4 a) Structures only:



b) Empirical formula of the compound formed:



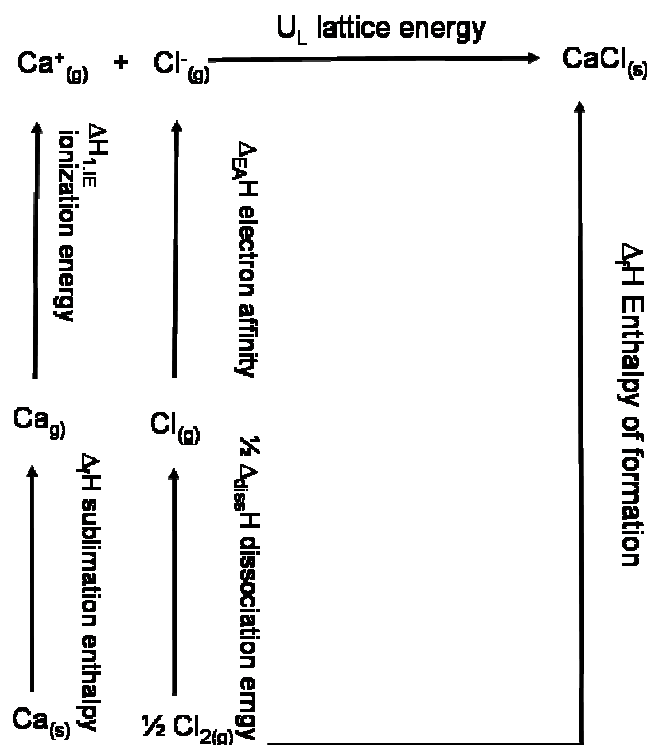
Notes: If the ratio of $n(\text{Ca}) : n(\text{Cl}) = 1.5 : 1$ [or better = $3 : 2$ which can be rewritten as $\text{CaCl}_2 \cdot 2 \text{Ca}^{2+} = \text{Ca}_3\text{Cl}_2^{4+}$] is given and the reduction product must contain a C_3^{4-} anion which needs two Ca^{2+} cations for electroneutrality, the composition $\text{Ca}_3\text{C}_3\text{Cl}_2$ will follow.

3.5 a) Structure type CaCl likely to have:

$$r(\text{Ca}^+)/r(\text{Cl}^-) = 120 \text{ pm} / 167 \text{ pm} = 0.719$$

NaCl	CsCl	ZnS	BN	no decision possible
<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

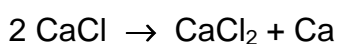
b) $\Delta_f H^\circ(\text{CaCl})$ with a Born-Haber-cycle:



Summing up of all the single steps of the Born-Haber-cycle:

$$\begin{aligned}\Delta_f H^0(\text{CaCl}) &= \Delta_{\text{subl}} H^0(\text{Ca}) + \Delta_{1, \text{IE}} H(\text{Ca}) + \frac{1}{2} \Delta_{\text{diss}} H(\text{Cl}_2) + \Delta_{\text{EA}} H(\text{Cl}) + \Delta_{\text{L}} H(\text{CaCl}) \\ &= (159.3 + 589.7 + 120 - 349.0 - 751.9) \text{ kJ mol}^{-1} \\ &= -231.9 \text{ kJ mol}^{-1}\end{aligned}$$

3.6 Stability to disproportionation:



$$\Delta H = \Delta_f H^0(\text{CaCl}_2) - 2 \Delta_f H^0(\text{CaCl}) = -796.0 \text{ kJ mol}^{-1} + 463.8 \text{ kJ mol}^{-1} = -332.2 \text{ kJ mol}^{-1}$$

Disproportionation:	yes	no	no decision possible, more information needed
	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>

PROBLEM 4**Determining atomic masses**

The reaction of the element X with hydrogen leads to a class of compounds that is analogous to hydrocarbons. 5.000 g of X form 5.628 g of a molar 2 : 1 mixture of the stoichiometric X-analogues of methane and ethane, respectively.

- 4.1** Determine the molar mass of X from this information. Give the chemical symbol of X, and the 3D-structure of the two products.

The following more complex case is of great historical interest.

The mineral Argyrodite is a stoichiometric compound that contains silver (oxidation state +1), sulphur (oxidation state -2) and an unknown element Y (oxidation state +4). The ratio between the masses of silver and Y in Argyrodite is $m(\text{Ag}) : m(\text{Y}) = 11.88 : 1$. Y forms a reddish brown lower sulfide (oxidation state of Y is +2) and a higher white sulfide (oxidation state of Y is +4). The coloured lower sulfide is the sublimate obtained by heating Argyrodite in a flow of hydrogen. The residues are Ag_2S and H_2S . To convert 10.0 g of Argyrodite completely, 0.295 dm^3 of hydrogen are needed at 400 K and 100 kPa.

- 4.2** Determine the molar mass of Y from this information. Give the chemical symbol of Y, and the empirical formula of Argyrodite.

The atomic masses are correlated with spectroscopic properties. To determine the vibrational frequency $\tilde{\nu}$ expressed in wave numbers of chemical bonds in IR spectra chemists use Hooke's law which focuses on the frequency of the vibration (attention to units!):

$$\tilde{\nu} = \frac{1}{2\pi c} \cdot \sqrt{\frac{k}{\mu}}$$

$\tilde{\nu}$ - vibrational frequency of the bond, in wavenumbers (cm^{-1})

c - speed of light

k - force constant, indicating the strength of the bond ($\text{N m}^{-1} = \text{kg s}^{-2}$)

μ reduced mass in AB_4 , which is given by $\mu = \frac{3 m(\text{A}) m(\text{B})}{3 m(\text{A}) + 4 m(\text{B})}$

$m(\text{A}), m(\text{B})$ - the masses of the two bond atoms

The vibrational frequency of the C-H bond of methane is known to be 3030.00 cm^{-1} . The vibrational frequency of the Z-analogue of methane is known to be 2938.45 cm^{-1} . The bond enthalpy of a C-H bond in methane is $438.4 \text{ kJ mol}^{-1}$. The bond enthalpy of a Z-H bond in the Z-analogue of methane is known to be $450.2 \text{ kJ mol}^{-1}$.

4.3 Determine the force constant k of a C-H bond using Hooke's law.

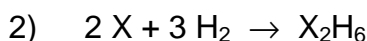
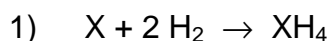
Estimate the force constant k of a Z-H bond, assuming that there is a linear proportionality between force constant and bond enthalpy.

Determine the atomic mass of Z from this information.

Give the chemical symbol of Z.

SOLUTION

4.1 Atomic mass of X, symbol of X, structures:



i) $5.0 \text{ g} = [n_1(X) + n_2(X)] \cdot M(X)$

ii) $5.628 \text{ g} =$

$$= n_1(\text{XH}_4) \times [M(X) + 4 \times 1.01 \text{ g mol}^{-1}] + n_2(\text{X}_2\text{H}_6) \times [2 M(X) + 6 \times 1.01 \text{ g mol}^{-1}]$$

iii) $n_1(\text{XH}_4) = 2 n_2(\text{X}_2\text{H}_6)$

iii,i) \rightarrow i') $2 n_1(X) \times M(X) = 5.0 \text{ g}$

iii,ii) \rightarrow ii') $n_1(X) \times [2M(X) + 7.07 \text{ g mol}^{-1}] = 5.628 \text{ g}$

i',ii') \rightarrow vi) $(5.0 \text{ g}) \times [2 M(X)]^{-1} = (5.628 \text{ g}) \times [2 M(X) + 7.07 \text{ g mol}^{-1}]^{-1}$

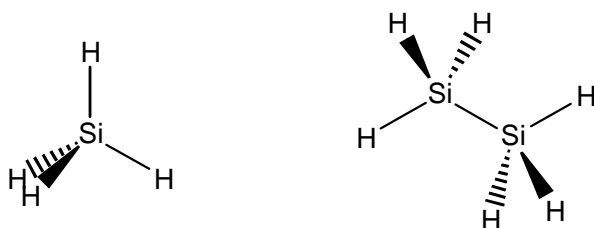
$$M(X) = 3.535 \text{ g mol}^{-1} \times (5.628 \text{ g})^{-1} \times [(5.0 \text{ g})^{-1} - (5.628 \text{ g})^{-1}]^{-1}$$

$$M(X) = 28.14 \text{ g mol}^{-1}$$

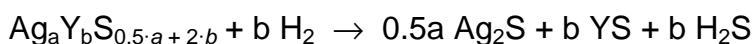
Atomic mass of X: $M(X) = 28.14 \text{ g mol}^{-1}$

Chemical symbol of X: Si

3D structures of the two products:



4.2 Atomic mass of Y and empirical formula of Argyrodite:



$$\text{i) } 10 \text{ g} = n(\text{Ag}_a\text{Y}_b\text{S}_{0.5\cdot a+2\cdot b}) \times [a \cdot 107.87 \text{ g mol}^{-1} + b M(\text{Y}) + (0.5 a + 2 b) \times 32.07 \text{ g mol}^{-1}]$$

$$\text{ii) } n(\text{H}_2) = \frac{p V(\text{H}_2)}{RT} \qquad n(\text{H}_2) = \frac{100 \text{ kPa} \times 0.295 \times 10^{-3} \text{ m}^3}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 400 \text{ K}}$$

$$n(\text{H}_2) = 8.871 \times 10^{-3} \text{ mol} \qquad n(\text{Ag}_a\text{Y}_b\text{S}_{0.5\cdot a+2\cdot b}) = b^{-1} \times 8.871 \cdot 10^{-3} \text{ mol}$$

$$\text{iii) } 11.88 = \frac{a \times 107.87 \text{ g mol}^{-1}}{b \times M(\text{Y})} \qquad a \cdot 107.87 \text{ g mol}^{-1} = 11.88 \times b \times M(\text{Y})$$

ii,i) \rightarrow ii')

$$b \times 10 \text{ g} \times (8.871 \cdot 10^{-3} \text{ mol})^{-1} =$$

$$= a \cdot 107.87 \text{ g mol}^{-1} + b M(\text{Y}) + (0.5 a + 2 b) \times 32.07 \text{ g mol}^{-1}$$

$$b \cdot 1127 \text{ g mol}^{-1} = a \cdot 107.87 \text{ g mol}^{-1} + b M(\text{Y}) + (0.5 a + 2 b) \times 32.07 \text{ g mol}^{-1}$$

iii,ii') \rightarrow iv)

$$b \cdot 1127 \text{ g mol}^{-1} = 11.88 \cdot b \cdot M(\text{Y}) + b \cdot M(\text{Y}) + (0.5 \cdot a + 2b) \cdot 32.07 \text{ g mol}^{-1}$$

$$b \cdot 1127 \text{ g mol}^{-1} =$$

$$= 11.88 b M(\text{Y}) + b M(\text{Y}) + (0.5 \frac{11.88 \times b \times M(\text{Y})}{107.87 \text{ g mol}^{-1}} + 2 b) \times 32.07 \text{ g mol}^{-1}$$

$$M(\text{Y}) = 72.57 \text{ g mol}^{-1} \rightarrow \text{iii} \qquad a : b = 8 : 1$$

Chemical symbol of Y: Ge

Empirical formula of Argyrodite: Ag_8GeS_6

4.3 The force constants of a C-H bond:

$$k(\text{C-H}) = [2\pi c \tilde{\nu}(\text{C-H})]^2 \cdot \frac{1}{N_A} \cdot \frac{3 M(\text{C}) \times M(\text{H})}{3 M(\text{C}) + 4 M(\text{H})}$$

$$= [2\pi \times 3 \cdot 10^{10} \text{ cm s}^{-1} \times 3030 \text{ cm}^{-1}]^2 \frac{1}{6.022 \times 10^{23} \text{ mol}^{-1}} \times \frac{3 \times 12.01 \times 1.01}{3 \times 12.01 + 4 \times 1.01} \text{ g mol}^{-1}$$

$$k(\text{C-H}) = 491.94 \text{ N m}^{-1}$$

The force constants of a Z-H bond:

 $k(\text{Z-H})$

$$k(\text{Z-H}) = k(\text{C-H}) \cdot \frac{\Delta_b H(\text{Z-H})}{\Delta_b H(\text{C-H})}$$

$$= 491.94 \text{ N m}^{-1} \cdot 450.2 \text{ kJ mol}^{-1} \cdot [438.4 \text{ kJ mol}^{-1}]^{-1} = 505.18 \text{ N m}^{-1}$$

The atomic mass and symbol of Z:

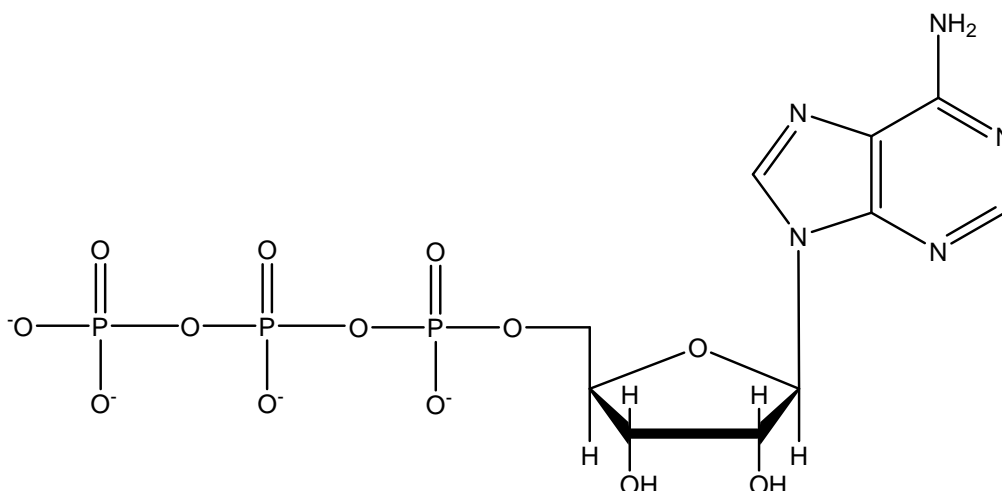
$$\frac{3 M(\text{Z}) \times M(\text{H})}{3 M(\text{Z}) + 4 M(\text{H})} = \frac{k(\text{Z-H}) \times N_A}{[2\pi c \tilde{\nu}(\text{Z-H})]^2}$$

$$M(\text{Z}) = \frac{4}{3} \left(\frac{[2\pi c \tilde{\nu}(\text{Z-H})]^2}{k(\text{Z-H}) \cdot N_A} - \frac{1}{M(\text{H})} \right)^{-1}$$

$$M(\text{Z}) = \frac{4}{3} \left(\frac{[2\pi \times 3 \cdot 10^{10} \times 2938.45]^2}{505180 \times 6.022 \cdot 10^{23}} - \frac{1}{1.01} \right)^{-1} \text{ g mol}^{-1}$$

Atomic mass of Z: $M(\text{Z}) = 72.68 \text{ g mol}^{-1}$

Chemical symbol of Z: Ge

PROBLEM 5**Biochemistry with Thermodynamics**Structure of ATP⁴⁻

Shifting chemical equilibria with ATP:

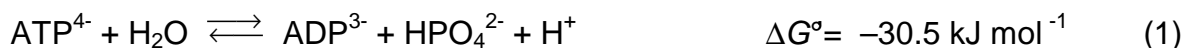
Animals use free energy from the oxidation of their food to maintain concentrations of ATP, ADP, and phosphate far from equilibrium. In red blood cells the following concentrations have been measured:

$$c(\text{ATP}^{4-}) = 2.25 \text{ mmol dm}^{-3}$$

$$c(\text{ADP}^{3-}) = 0.25 \text{ mmol dm}^{-3}$$

$$c(\text{HPO}_4^{2-}) = 1.65 \text{ mmol dm}^{-3}$$

Free energy stored in ATP can be released according to the following reaction:



As the pH is close to 7 in most living cells, biochemists use ΔG° instead of ΔG° . The standard state of ΔG° is defined as having a constant pH of 7. In equations with ΔG° and K for reactions at $pH = 7$ the concentration of H^+ is therefore omitted. Standard concentration is 1 mol dm^{-3} .

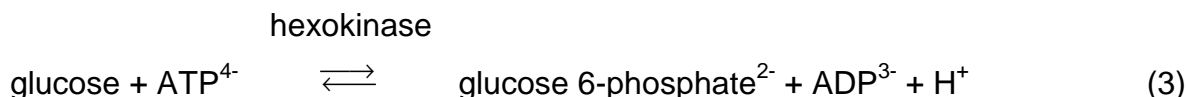
5.1 Calculate the actual $\Delta G'$ of reaction (1) in the red blood cell at 25 °C and $pH = 7$.

In living cells many so-called “anabolic” reactions take place, which are at first sight thermodynamically unfavourable because of a positive ΔG . The phosphorylation of glucose is an example:



5.2 Calculate first the equilibrium constant K of reaction (2) and then the ratio $c(\text{glucose 6-phosphate}) / c(\text{glucose})$ in the red blood cell in chemical equilibrium at 25 °C and $pH = 7$.

To shift the equilibrium to a higher concentration of glucose 6-phosphate, reaction (2) is coupled with hydrolysis of ATP:



5.3 Calculate ΔG° and K of reaction (3).

What is now the ratio $c(\text{glucose 6-phosphate}) / c(\text{glucose})$ in the red blood cell in chemical equilibrium at 25 °C and $pH = 7$?

ATP synthesis:

An adult person ingests about 8000 kJ of energy ($\Delta G'$) per day with the food.

- 5.4** a) What will be the mass of ATP that is produced per day if half of this energy is used for ATP synthesis? Assume a $\Delta G'$ of -52 kJ mol^{-1} for reaction (1), and a molecular weight of 503 g mol^{-1} for ATP.
- b) What mass of ATP does the human body contain on average if the mean lifetime of an ATP molecule until its hydrolysis is 1 min?
- c) What happens to the rest of the free energy, which is not used for ATP synthesis? Mark on the answer sheet.

In animals the energy obtained by the oxidation of food is used to pump protons out of specialized membrane vesicles, the mitochondria. ATP-synthase, an enzyme, will allow protons to re-enter the mitochondria if ATP is simultaneously synthesized from ADP and phosphate.

- 5.5 a) How many protons (H^+) are in a spherical mitochondrion with a diameter of 1 μm at $pH = 7$?
- b) How many protons have to enter into each of the 1000 mitochondria of a liver cell via the ATP-synthase to allow the production of a mass of 0.2 fg of ATP per cell? Assume that 3 protons have to enter for the synthesis of 1 molecule of ATP.

SOLUTION

5.1 Actual $\Delta G'$ of reaction (1):

$$\begin{aligned}\Delta G' &= \Delta G^{\circ'} + R T \ln \frac{[ADP^{3-}][HPO_4^{2-}]}{[ATP^{4-}]} \\ &= -30500 \text{ J mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times \ln \frac{0.00025 \times 0.00165}{0.00225} \\ &= -30.5 \text{ kJ mol}^{-1} - 21.3 \text{ kJ mol}^{-1} = -51.8 \text{ kJ mol}^{-1}\end{aligned}$$

5.2 Equilibrium constant K' of reaction (2), ratio $c(\text{glucose 6-phosphate}) / c(\text{glucose})$:

$$\begin{aligned}\Delta G^{\circ'} &= -R T \ln K' \\ K' &= e^{-\Delta G^{\circ'}/RT} = e^{-13800 \text{ J/mol} / (8.314 \text{ J/(mol K)} \cdot 298.15 \text{ K})} = 0.0038 \\ K' &= \frac{[\text{glucose 6-phosphate}]}{[\text{glucose}][HPO_4^{2-}]} \\ \frac{[\text{glucose 6-phosphate}]}{[\text{glucose}]} &= K' \cdot [HPO_4^{2-}] \\ &= 0.0038 \cdot 0.00165 \\ &= 6.3 \cdot 10^{-6}\end{aligned}$$

5.3 ΔG° and K' of reaction (3), ratio $c(\text{glucose 6-phosphate}) / c(\text{glucose})$:

$$\begin{aligned}\Delta G^{\circ}(3) &= \Delta G^{\circ}(1) + \Delta G^{\circ}(2) = -30.5 \text{ kJ mol}^{-1} + 13.8 \text{ kJ mol}^{-1} = -16.7 \text{ kJ mol}^{-1} \\ \Delta G^{\circ} &= -R T \ln K' \\ K' &= e^{-\Delta G^{\circ}/RT} = e^{16700 \text{ J/mol} / (8.314 \text{ J/(mol K)} \cdot 298.15 \text{ K})} = 843\end{aligned}$$

$$K' = \frac{c(\text{glucose 6-phosphate}) \times c(\text{ADP}^{3-})}{c(\text{glucose}) \times c(\text{ATP}^{4-})}$$

$$\frac{c(\text{glucose 6-phosphate})}{c(\text{glucose})} = K' \frac{c(\text{ATP}^{4-})}{c(\text{ADP}^{3-})}$$

$$= 843 \times (2.25 \text{ mmol dm}^{-3} / 0.25 \text{ mmol dm}^{-3}) = 7587$$

5.4 a) Mass of ATP produced per day:

Energy available for ATP synthesis: $8000 \text{ kJ day}^{-1} \times 0.5 = 4000 \text{ kJ day}^{-1}$

Energy required for synthesis of ATP: 52 kJ mol^{-1}

Amount of ATP produced: $4000 \text{ kJ day}^{-1} / 52 \text{ kJ mol}^{-1} = 76.9 \text{ mol day}^{-1}$

Mass of ATP produced: $76.9 \text{ mol day}^{-1} \times 503 \text{ g mol}^{-1} = 38700 \text{ g day}^{-1}$

$$\underline{m_{\text{day-1}} = 38.7 \text{ kg day}^{-1}}$$

b) Mass of ATP in the human body:

Average lifetime: 1 day = 1440 min 1 min = 1440^{-1} day

Mass of ATP in the body: $38.7 \text{ kg day}^{-1} / (1440 \text{ min day}^{-1}) \cdot 1 \text{ min} = 26.9 \text{ g}$

$$m_{\text{body}} = 26.9 \text{ g}$$

c) What happens to the rest of the free energy? Mark one correct answer:

- It is used to reduce the entropy of the body.
- It is released from the body in the O-H bonds of the water molecule and the C=O bonds of the carbon dioxide molecule.
- It is used to regenerate the state of the enzymes which act as catalysts in the production of ATP.
- It heats the body of the person.

5.5 a) How many protons are in a spherical mitochondrion with a diameter of 1 μm at $\text{pH} = 7$?

$$V = 4/3 \pi r^3 = 4/3 \pi (0.5 \times 10^{-6} \text{ m})^3 = 5.2 \times 10^{-19} \text{ m}^3 = 5.2 \times 10^{-16} \text{ dm}^3$$

$$c = 1 \times 10^{-7} \text{ mol dm}^{-3}$$

$$n = V c \cdot N_A = 5.2 \times 10^{-16} \text{ dm}^3 \times 1 \times 10^{-7} \text{ mol dm}^{-3} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 31$$

b) How many protons have to enter a mitochondrion?

Number of ATP molecules:

$$n(\text{ATP}) = \frac{m(\text{ATP}) N_A}{M(\text{ATP})} = \frac{0.2 \times 10^{-15} \text{ g} \times 6.022 \times 10^{23} \text{ mol}^{-1}}{503 \text{ g mol}^{-1}} = 239400$$

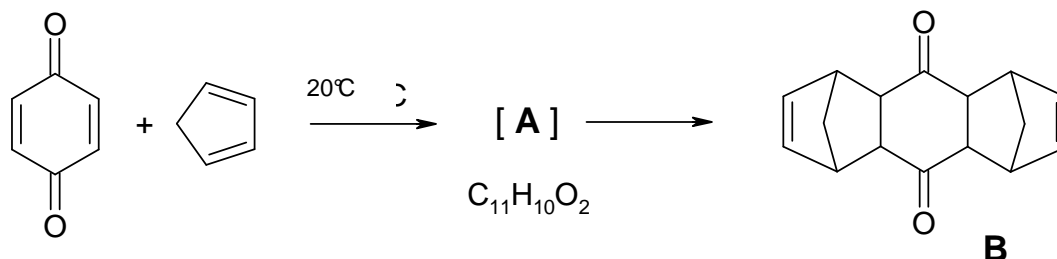
$$\text{Number of H}^+ \text{ per cell: } n(\text{H}^+_{\text{per cell}}) = n(\text{ATP}) \times 3 = 718300$$

$$\text{Number of H}^+ \text{ per mitochondrion: } n(\text{H}^+_{\text{mit}}) = n(\text{H}^+_{\text{per cell}}) / 1000 = 718$$

PROBLEM 6

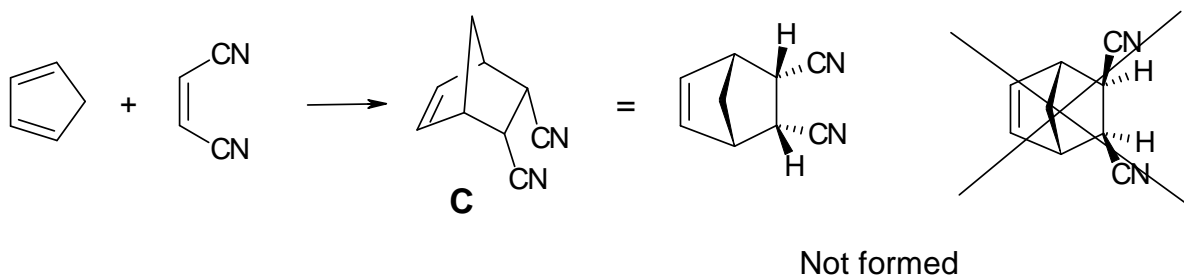
Diels-Alder Reactions

The Diels-Alder reaction, a concerted [4+2]-cycloaddition between a diene and an olefin to yield a cyclohexene, was discovered in 1928 here in Kiel. Prof. Otto Diels and his coworker Kurt Alder mixed *p*-benzoquinone with an excess of cyclopentadiene and obtained the following result:



6.1 Draw the structure of **A** (without stereochemical information).

The Diels-Alder reaction is a concerted, one-step reaction that proceeds with high stereospecificity. For example, only a single stereoisomer **C** is formed in the following reaction



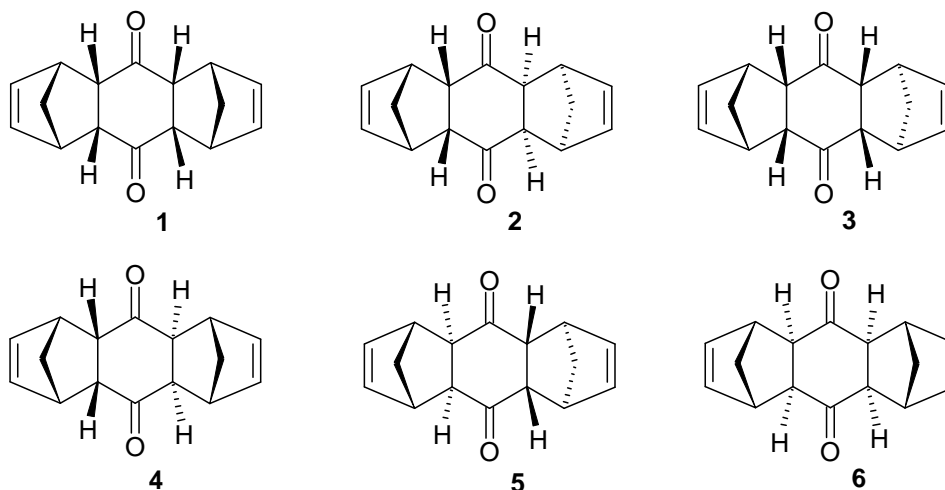
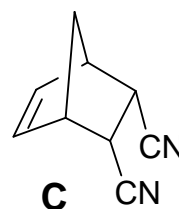
If you use the *E*-isomer of the alkene instead, you will obtain two other stereoisomers **D1** and **D2**.

6.2 Give the structures of **D1** and **D2**.

Accordingly, in the original reaction (formation of **B** from cyclopentadiene and benzoquinone) Diels and Alder found only one of the following six conceivable stereoisomers of **B** (see next page).

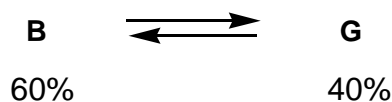
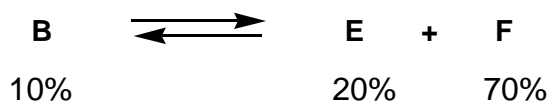
Hints:

- keep the stereospecific formation of **C** in mind and
- the sterically less hindered isomer forms.



6.3 Which single isomer of the six stereoisomers 1-6 of **B** shown above did they isolate?

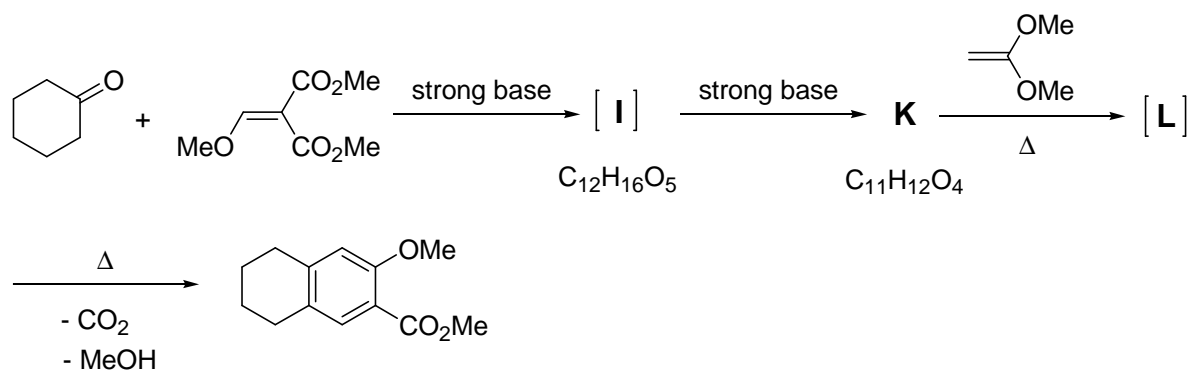
After prolonged heating (15h, 120 °C) of the originally isolated stereoisomer **B** (melting point mp: 157 °C), Diels and Alder obtained two new stereoisomers **E** (mp: 153 °C) and **F** (mp: 163 °C). Equilibration of **B** with a catalytic amount of a strong base at 25 °C gave a further stereoisomer **G** (mp: 184 °C).



6.4 Decide the questions on the answer sheet concerning the Diels-Alder reaction.

Hint: You do not need to know, which of the six stereoisomers 1 – 6 (shown above) corresponds to either **E**, **F** or **G** in order to answer this question.

The Diels-Alder reaction plays also an important role in the following reaction sequence.



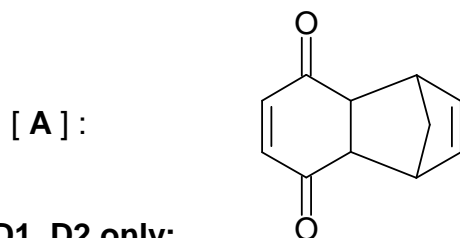
6.5 Draw the structures for I, K and L.

Hints: - K has only one methyl group.

- L is the Diels-Alder adduct of K and the alkene shown.

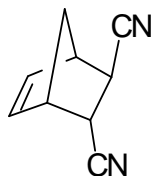
SOLUTION

6.1 Structure of A only:

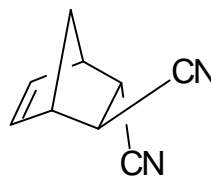


6.2 Structures of D1, D2 only:

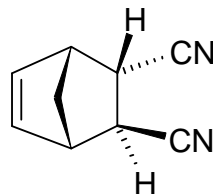
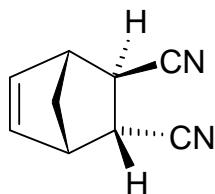
D1:



D2:



alternatively, the following structures are also correct:



Note: The two compounds are enantiomers

6.3 Correct structure of **B** (circle only one):

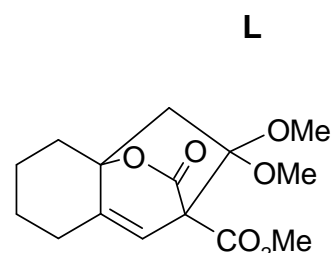
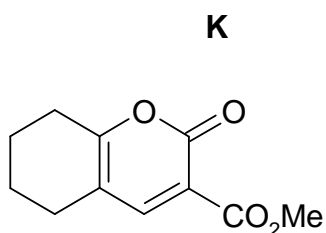
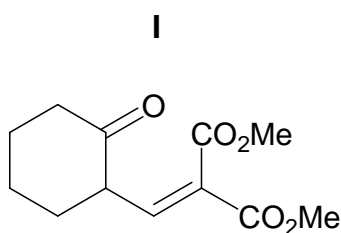
1 2 3 4 5 6

Notes: The Diels-Alder reaction gives products with an endo-stereochemistry. The preference of this configuration was outlined in problem 6.2, structure **C**. As shown in structure **C** this endo- configuration is characterized by the two H atoms and the CH₂-bridge of the bicyclic system being on the same side of the ring. Only structures **1** and **2** of the six stereoisomers have an endo,endo stereochemistry. All other isomers have at least one exo configuration. In structure **1** the three rings form a U-shaped molecule which is sterically more hindered than structure **2** which has a zig-zag structure.

6.4 Decide the questions concerning the Diels-Alder reaction.

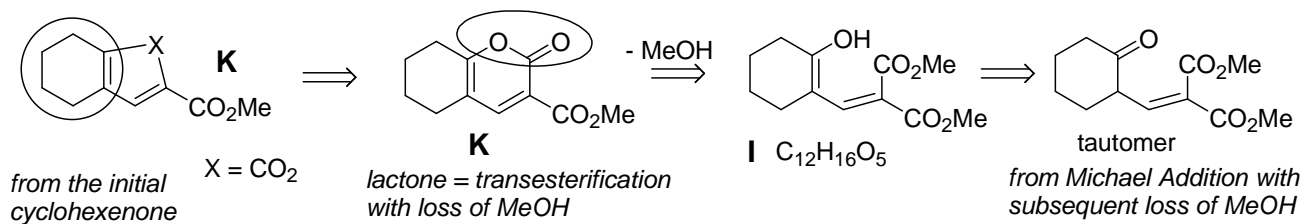
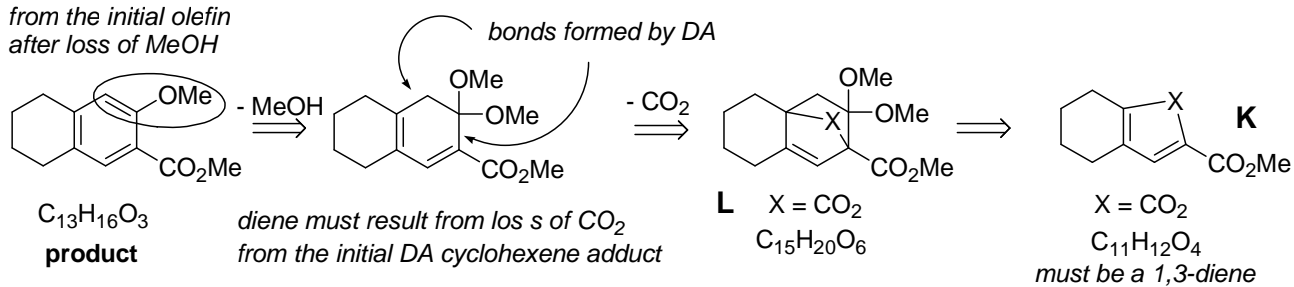
	true	false	no decision possible
• The Diels-Alder reaction is reversible	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
• The formation of B in the original reaction is thermodynamically controlled	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
• B is thermodynamically more stable than E	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
• E is thermodynamically less stable than F	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
• G is an enantiomer of B	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
• G is thermodynamically more stable than F	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>

6.5 Structures of **I**, **K**, **L** only:



Notes:

from the initial olefin
after loss of MeOH

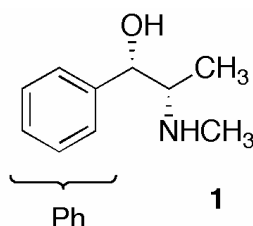


PROBLEM 7**Stereochemistry in Drugs**

The Cahn-Ingold-Prelog rules are used to specify the stereochemistry of molecules.

- 7.1 Order the groups on the answer sheet according to their priority in the Cahn-Ingold-Prelog (CIP)-system.

Pseudoephedrine (**1**) is a constituent in many common drugs against colds, e.g. in nasal sprays.



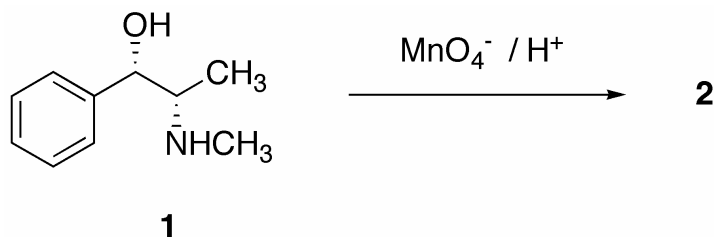
- 7.2 Mark the stereocenters in **1** with an asterisk * on the answer sheet.

Order the substituents on each stereocenter in **1** according to their priority and determine their absolute configuration (*R* or *S*).

- 7.3 Draw a Newman or a sawhorse representation of **1**.

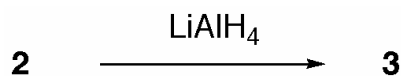
Draw a Fischer representation of **1**.

Treatment of **1** with acidic permanganate solutions under mild conditions yields the stimulant Methcathinone **2**:



- 7.4 Draw the stereochemically correct structure of compound **2** and a balanced redox equation of the reaction. Indicate in your equation the particular oxidation number on all atoms which undergo a change in their formal oxidation numbers.

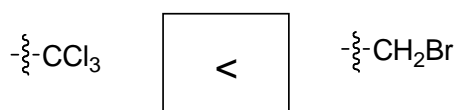
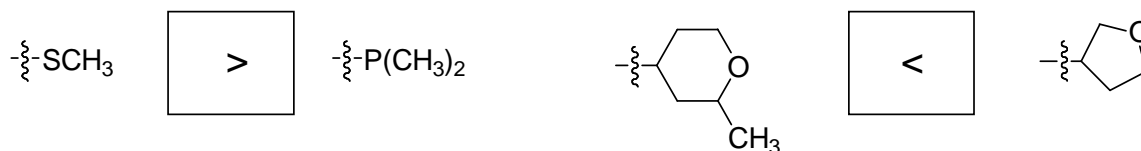
The treatment of **2** with LiAlH_4 results exclusively in compound **3**, which differs from **1** in its melting point.



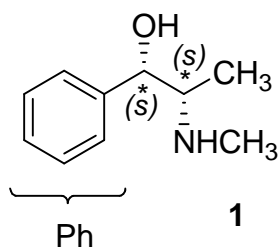
- 7.5 a) Draw the stereochemically correct structure of **3**.
 b) Decide the statements on the answer sheet concerning isomers.
 c) Draw a structural model to rationalize the exclusive formation of **3** from **2**.

SOLUTION

7.1 Fill in < or > (A < B means A has a priority lower than B) :

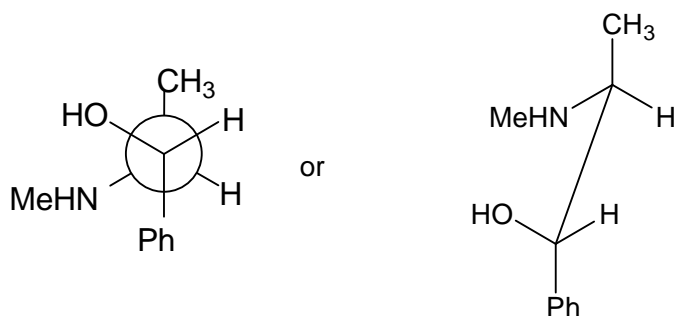


7.2



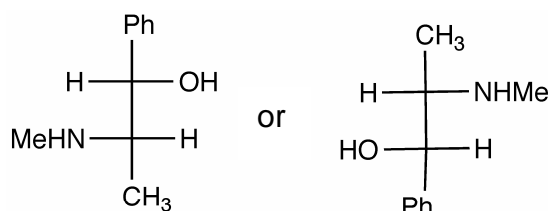
highest priority				lowest priority
OH	CH(NHCH ₃)CH ₃	Ph	H	
NHCH ₃	CH(OH)Ph	CH ₃	H	

7.3 Newman projection or sawhorse projection of **1**:



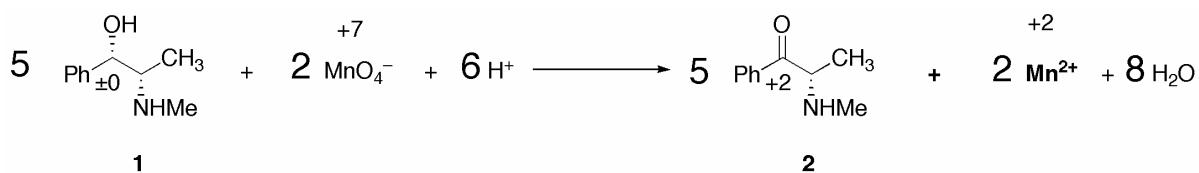
(Me = CH₃)

Fischer projection of **1**:

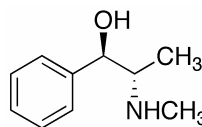


(Me = CH₃)

7.4 Equation with oxidation numbers and stereochemically correct structure of **2**:



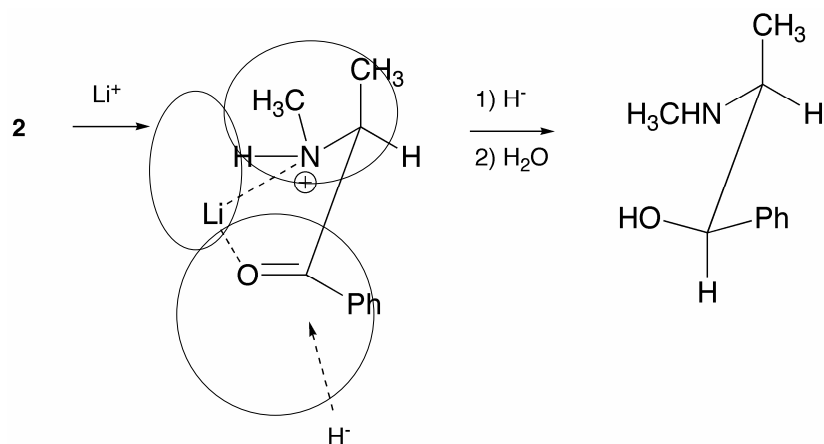
7.5 a) Structure of **3** (correct stereochemistry):



b) Statements concerning isomers:

	true	false
1 and 3 are stereo-isomers	<input checked="" type="checkbox"/>	<input type="checkbox"/>
1 and 3 are enantiomers	<input type="checkbox"/>	<input checked="" type="checkbox"/>
1 and 3 are diastereomers	<input checked="" type="checkbox"/>	<input type="checkbox"/>
1 and 3 are conformational isomers	<input type="checkbox"/>	<input checked="" type="checkbox"/>

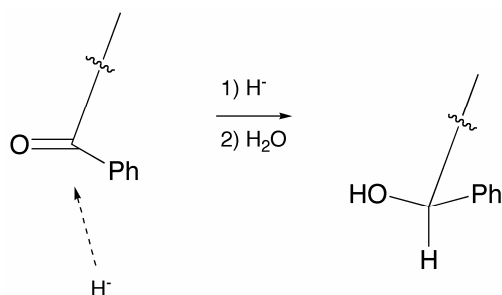
- c) Draw a structural model to rationalize the exclusive formation of **3** from **2**



Notes: Attack of hydride occurs from the sterically least hindered side.

Full points will also be given for an explanation using the formation of a hydrogen bond.

1 point will be given for any representation indicating the attack of hydride on the correct face of the carbonyl group, i.e.



PROBLEM 8

Colloids

The combination of an inorganic and an organic component on a nanometer scale yields materials with excellent properties. Thus the synthesis of hybrid nanoparticles is of interest.

($T = 298.15$ K throughout whole problem)

Solution **A** is an aqueous solution of CaCl_2 with a concentration of 1.780 g dm^{-3} .

Solution **B** is an aqueous solution of Na_2CO_3 with a concentration of 1.700 g dm^{-3} .

$$pK_{a1}(\text{H}_2\text{CO}_3) = 6.37$$

$$pK_{a2}(\text{HCO}_3^-) = 10.33$$

8.1 Calculate the pH of solution **B** using reasonable assumptions.

100 cm^3 of solution **A** and 100 cm^3 of solution **B** are mixed to form solution **C**.

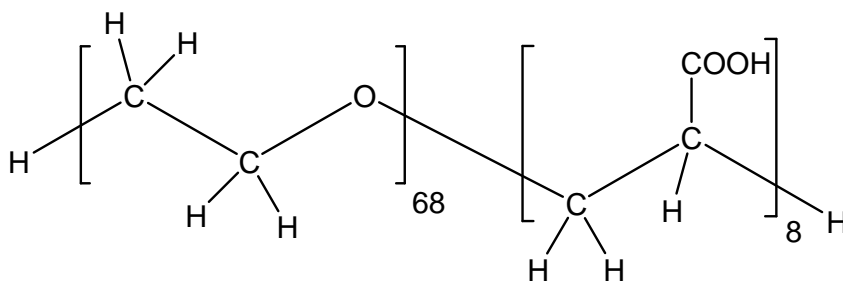
Solution **C** is adjusted to pH 10. A precipitate forms.

$$K_{sp}(\text{Ca}(\text{OH})_2) = 6.46 \times 10^{-6}$$

$$K_{sp}(\text{CaCO}_3) = 3.31 \times 10^{-9}$$

8.2 Show by calculation for each of the compounds $\text{Ca}(\text{OH})_2$ and CaCO_3 whether it can be found in the precipitate or not.

In a similar experiment 100 cm^3 of solution **A** additionally contain 2 g of a copolymer consisting of two water soluble blocks: a poly(ethylene oxide) block and a poly(acrylic acid) block:



The polymer does not undergo any chemical reaction (except protolysis of the acid) and yet has a strong effect: after mixing of the two solutions (**A+B**) no precipitate can be observed. Small calcium carbonate particles with the polymer chains attached to their surface form. The attached polymers prevent further crystal growth and the hybrid particles remain in solution.

8.3 Circle the block of the polymer (on the answer sheet) that attaches to the surface of the growing calcium carbonate crystal.

To characterize the hybrid particles they are separated from the preparation solution and transferred into 50 cm³ of an aqueous NaOH solution ($c(\text{NaOH}) = 0.19 \text{ mol dm}^{-3}$). The solution is diluted by the addition of 200 cm³ of water. Assume that the new solution contains only the hybrid particles and no additional calcium or carbonate ions. All acidic groups participate in the acid-base equilibrium.

- For the new solution, a pH of 12.30 is measured.
- In electron microscopy you only can see the inorganic particles (not the polymer): Spherical particles of 100 nm diameter are observed.
- The molar mass of the hybrid particles (inorganic and organic part together) is determined to be $M = 8.01 \cdot 10^8 \text{ g mol}^{-1}$
- The charge of the particles is found to be $Z = -800$ (number of unit charges). ($pK_a(\text{COOH}, \text{copolymer}) = 4.88$)

8.4 How much of the initial amount of polymer (2 g) can still be found in the hybrid particles?

8.5 Calculate which modification of calcium carbonate has been formed.

Modification	density
Calcite	2.71 g cm ⁻³
Vaterite	2.54 g cm ⁻³
Aragonite	2.95 g cm ⁻³

SOLUTION

8.1 pH of solution B:

$$K_{b2} = \frac{c(\text{HCO}_3^-)/(1 \text{ mol dm}^{-3}) \times c(\text{OH}^-)/(1 \text{ mol dm}^{-3})}{c(\text{CO}_3^{2-})/(1 \text{ mol dm}^{-3})} \quad K_{b2} = \frac{10^{-14}}{10^{-10.33}}$$

$$K_{b2} = 2.14 \times 10^{-4}$$

$$K_{b1} = 2.34 \times 10^{-8}$$

Since $K_{b2} \gg K_{b1}$, only one protonation step of the CO_3^{2-} has to be considered.

$$c(\text{HCO}_3^-) = c(\text{OH}^-) = x \quad \text{and} \quad c(\text{CO}_3^{2-}) = c_0(\text{CO}_3^{2-}) - x$$

$$c_0(\text{Na}_2\text{CO}_3) = \frac{1.700 \text{ g dm}^{-3}}{105.99 \text{ g mol}^{-1}}$$

$$c_0(\text{Na}_2\text{CO}_3) = c_0(\text{CO}_3^{2-}) = 0.016 \text{ mol dm}^{-3}$$

$$K_{b2} = \frac{x^2 / (1 \text{ mol dm}^{-3})}{(c_0(\text{CO}_3^{2-}) - x)} \quad x = c(\text{OH}^-) = 1.75 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pH = 11.2$$

8.2 Ca(OH)₂, CaCO₃ in the precipitate?

$$M(\text{CaCl}_2) = 110.98 \text{ g mol}^{-1} \quad pH = 10, \quad c(\text{OH}^-) = 1 \times 10^{-4} \text{ mol dm}^{-3}$$

$$c_0(\text{Na}_2\text{CO}_3) = \frac{1.700 \text{ g cm}^{-3}}{105.99 \text{ g mol}^{-1} \times 2} \quad c(\text{CaCl}_2) = \frac{1.780 \text{ g dm}^{-3}}{110.98 \text{ g mol}^{-1} \times 2}$$

$$c_0(\text{Na}_2\text{CO}_3) = 8.0 \times 10^{-3} \text{ mol dm}^{-3} \quad c(\text{CaCl}_2) = c_0(\text{Ca}^{2+}) = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$$

Calculations for Ca(OH)₂:

$$c(\text{OH}^-)^2 \times c_0(\text{Ca}^{2+}) = 8 \times 10^{-11} < 6.46 \times 10^{-6} = K_{sp}(\text{Ca(OH)}_2) \quad \text{no precipitate}$$

Calculations for CaCO₃:

$$K_{b2} = \frac{c(\text{HCO}_3^-) \times c(\text{OH}^-)}{c(\text{CO}_3^{2-})}, \quad c(\text{HCO}_3^-) = \frac{K_{b2}}{c(\text{OH}^-)} \times c(\text{CO}_3^{2-})$$

$$c(\text{HCO}_3^-) = 2.14 \times c(\text{CO}_3^{2-}) \quad \text{and} \quad c(\text{HCO}_3^-) + c(\text{CO}_3^{2-}) = c_0(\text{Na}_2\text{CO}_3)$$

$$2.14 \times c(\text{CO}_3^{2-}) + c(\text{CO}_3^{2-}) = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Initial concentration of CO}_3^{2-} \text{ in solution } \mathbf{C}: \quad c(\text{CO}_3^{2-}) = 2.55 \times 10^{-3} \text{ mol dm}^{-3}$$

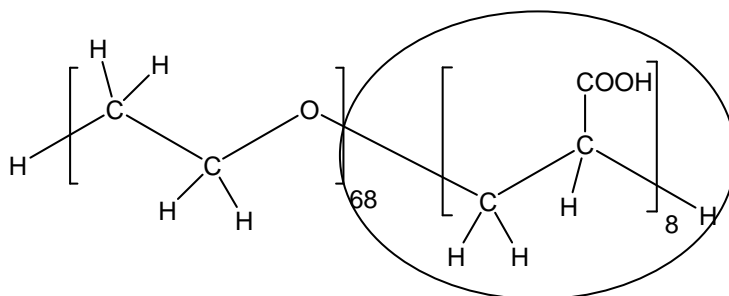
$$\text{Initial concentration of Ca}^{2+} \text{ in solution } \mathbf{C}: \quad c(\text{Ca}^{2+}) = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$$

hence $c(\text{CO}_3^{2-}) \times c(\text{Ca}^{2+}) = 2.04 \times 10^{-5} > 3.3 \times 10^{-9} = K_{sp}(\text{CaCO}_3)$ precipitate

$\text{Ca}(\text{OH})_2$ will be found in the precipitate yes no

CaCO_3 will be found in the precipitate yes no

8.3 Circle the block that attaches to the CaCO_3 crystal:



Notes: Both polymer blocks are hydrophilic. The acrylic acid block will preferably bind to the crystal since it is more polarized and additionally charged. The polymer binds to the surface at positions where there is an excess of calcium ions on the surface of the ionic crystal.

8.4 How much of the initial amount of polymer (2 g) can still be found in the hybrid particles?



pH and pK_a lead to the total concentration of COOH groups in the solution:

$$c(\text{COO}^-) = x \quad c(\text{COOH}) = c_0(\text{COOH}) - x \quad x = c_0(\text{OH}^-) - c(\text{OH}^-)$$

$$c_0(\text{OH}^-) = \frac{50 \text{ cm}^3}{250 \text{ cm}^3} \cdot 0.19 \text{ mol dm}^{-3} \quad c_0(\text{OH}^-) = 0.038 \text{ mol dm}^{-3}$$

$$c(\text{OH}^-) = 10^{-1.7} \text{ mol dm}^{-3} = 0.02 \text{ mol dm}^{-3} \quad x = 0.018 \text{ mol dm}^{-3}$$

$$K_b = \frac{(c_0(\text{COOH}) - x) / (1 \text{ mol dm}^{-3}) \times c(\text{OH}^-) / (1 \text{ mol dm}^{-3})}{x / (1 \text{ mol dm}^{-3})}$$

$$c_0(\text{COOH}) = \frac{K_b \cdot x \times (1 \text{ mol dm}^{-3})}{c(\text{OH}^-)} + x$$

$$c_0(\text{COOH}) = \left(\frac{0.018 \times 10^{-9.12}}{0.02} + 0.018 \right) \text{ mol dm}^{-3}$$

$$c_0(\text{COOH}) = 0.018 \text{ mol dm}^{-3}$$

$$\text{(Or as } \text{pH} \gg \text{p}K_a: \quad c_0(\text{COOH}) = \alpha(\text{COOH}) + x \approx x \text{)}$$

$$\text{Total concentration of polymer chains} \quad c(\text{polymer}) = \frac{c_0(\text{COOH})}{8}$$

$$M(\text{polymer}) = M(\text{C}_{160}\text{O}_{84}\text{H}_{306}) = 3574.66 \text{ g mol}^{-1}$$

$$m(\text{polymer}) = c(\text{polymer}) \times V \times M(\text{polymer})$$

$$m(\text{polymer}) = \frac{c_0(\text{COOH}) \times V \times M(\text{polymer})}{8} = \frac{0.018 \times 0.250 \times 3574.66}{8} \text{ g} = 2.0 \text{ g}$$

8.5 Modification of CaCO_3 :

The charge of the particles is caused by the number of protonized COOH groups per particle.

$$c(\text{COO}^-) \approx c_0(\text{COOH}), \quad \alpha \approx 1$$

$$\text{Number of COOH groups per particle:} \quad N_{\text{COOH}} = \frac{|Z|}{\alpha} \quad N_{\text{COOH}} = 800$$

$$\text{Number of polymer chains per particle:} \quad N_{\text{polymer}} = \frac{N_{\text{COOH}}}{8} = 100$$

The number of polymers per particle indicates the mass of polymer per particle.

Thus, the mass of the calcium carbonate particle can be calculated:

$$M(\text{CaCO}_3 \text{ particle}) = M(\text{total particle}) - N_{\text{polymer}} M(\text{polymer})$$

$$M(\text{CaCO}_3 \text{ particle}) = 8.01 \times 10^8 \text{ g mol}^{-1} - 100 \times 3574.66 \text{ g mol}^{-1}$$

$$M(\text{CaCO}_3 \text{ particle}) = 8.01 \times 10^8 \text{ g mol}^{-1}$$

$$\text{Mass of one } \text{CaCO}_3 \text{ particle:} \quad m(\text{CaCO}_3 \text{ particle}) = M(\text{CaCO}_3 \text{ particle}) \cdot N_A^{-1}$$

and with the volume of the spherical particle ($V = \frac{4}{3} \pi r^3$) the density can be

calculated:

$$\begin{aligned}\rho(\text{CaCO}_3) &= \frac{m(\text{CaCO}_3 \text{ particle})}{V(\text{CaCO}_3 \text{ particle})} = \frac{3 m(\text{CaCO}_3 \text{ particle})}{4 \pi r^3} \\ &= \frac{3 (M (\text{total particle}) - N_{\text{polymer}} M(\text{polymer}))}{N_A 4 \pi r^3} \\ &= \frac{3 \times 8.01 \times 10^8 \text{ g mol}^{-1}}{N_A \cdot 4 \pi (5 \times 10^{-6} \text{ cm})^3} = 2.54 \text{ g cm}^{-3}\end{aligned}$$

The modification of calcium carbonate is Calcite Vaterite Aragonite

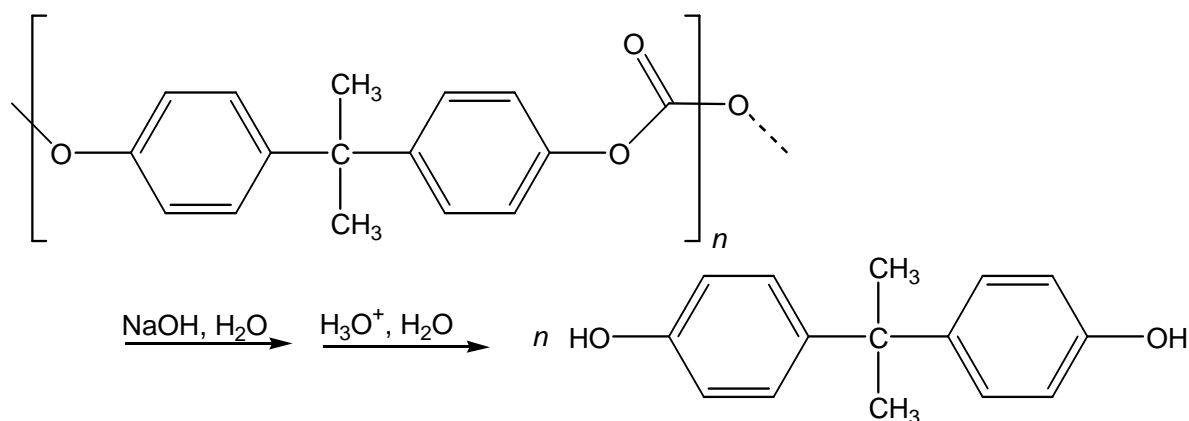
PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

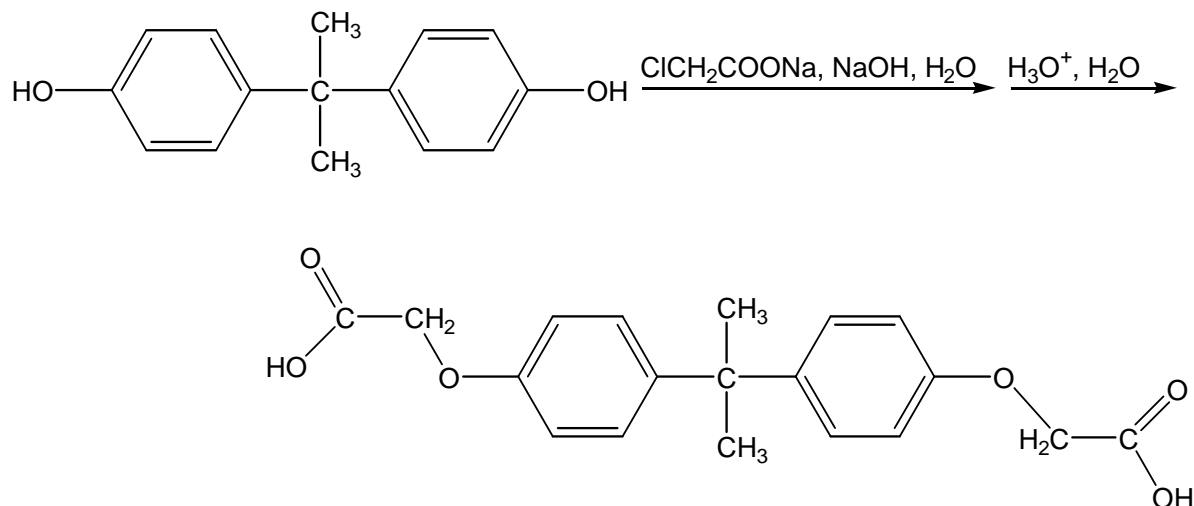
Two-Step Organic Synthesis of 2,2-Bis(*p*-phenyleneoxyacetic acid)propane (Bisphenol A bis(carboxymethyl)ether)

Introduction

In the first step the sodium salt of bisphenol A results as an intermediate from the alkaline hydrolysis of a polycarbonate. By adding an acid this salt is converted into the free 2,2-bis(4-hydroxyphenyl)propane (bisphenol A).



In the second step bisphenol A reacts with sodium chloroacetate to form the phenolic ether, bisphenol A bis(carboxymethyl)ether.



- In each step the product has to be isolated.
(Drying and weighing will be done by the organizer.)
- For the product of step 2 three melting point tubes have to be filled.
(Filling of the melting point tubes in step 1 will be done by the organizer.)
(The melting points will be determined by the organizer.)
- When the organizer receives your labelled beaker A of step 1 you will get 2.00 g of bisphenol A as starting material for the second step.
- Answer the additional questions on the answer sheet **P1**.
- Do not remove the Ceran plate from the magnetic stirrer.

Procedures

Step 1: Preparation of bisphenol A by alkaline hydrolysis of a polycarbonate

Preparation:

- Put the pre-weighed 2.54 g of polycarbonate (No. 1), 4.0 g of sodium hydroxide (No. 5) and 3 cm³ of demineralized water into a 100 cm³ Erlenmeyer flask with ground-glass joint.
- Close the flask with a plastic plug and swirl it gently so that the solution does not contact the ground-glass joint. For aeration open the plastic plug occasionally. Strong heating can be observed, as the sodium hydroxide partially dissolves.
- Remove the plastic plug after swirling for about 4 minutes, add a magnetic stirring bar and put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Finally, add 20 cm³ of ethanol (No. 2) through the condenser while stirring the reaction mixture.
- Heat the reaction mixture under reflux for 60 minutes. In the beginning adjust the thermostat of the heating plate to maximum. When the mixture starts boiling reduce the heat carefully, so that the mixture is kept under gentle reflux.
- A white precipitate is formed on heating.

During this waiting period you are highly advised to start working on the analytical chemistry experiment.

Isolation:

- Stop heating after one hour, allow the reaction mixture to cool down to ambient temperature, remove the condenser, add 25 cm³ of demineralized water and transfer the reaction mixture into a 400 cm³ beaker. Rinse the Erlenmeyer flask with 25 cm³ of demineralized water and add this to the contents of the beaker.
- Finally, fill up to 150 cm³ with demineralized water.
- If the reaction mixture is not clear, the mixture has to be filtered over fibre glass into an Erlenmeyer flask.
- Add slowly 15 cm³ of hydrochloric acid (No. **3**) stirring the mixture simultaneously with a glass rod. A rather oily or sometimes crystalline precipitate is formed.
- Ask your instructor for some seed crystals of bisphenol A (No. **27**) in order to accelerate the crystallization.
- Stir the reaction mixture thoroughly with the glass rod. For a quantitative crystallisation continue stirring from time to time till the supernatant aqueous solution is nearly clear.
- Collect the crude product by vacuum filtration, wash it twice with 10 cm³ portions of demineralized water and transfer it quantitatively into the tared and labelled beaker A.
- For drying and weighing deliver your labelled beaker A into the instructor room.
- Afterwards you will get a small jar filled with 2.00 g of bisphenol A (No. **28**), your starting material of the second step.
- On delivery of your product and on receipt of the starting material you have to sign. Even if you do not have any bisphenol A, please bring the empty beaker A to the instructors' room in order to get the starting material for step 2.

**Step 2: Reaction of Bisphenol A with Chloroacetic Acid
forming 2,2-Bis(p-phenyleneoxyacetic acid)propane
(Bisphenol A bis(carboxymethyl)ether)**

Preparation:

- Pour all the bisphenol A (No. **28**) you have received from the organizer when you had finished step 1 into a 100 cm³ Erlenmeyer flask with ground-glass joint.
- Add 10 cm³ of an aqueous sodium-hydroxide solution (No. **6**), 1 cm³ of demineralized water and a magnetic stirring bar.

- Put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Heat the reaction mixture with gentle stirring until a clear solution is formed.
- Remove the heating plate and the condenser and add 5.0 g of the sodium salt of chloroacetic acid (No. 4) to the reaction mixture.
- After reconnecting the flask with the reflux condenser, heat the mixture to reflux with vigorous stirring for 30 min.
- Initially a clear solution is formed on heating. In some cases a colorless solid precipitates. If the complete mixture becomes solid in the course of the reaction, heating must be stopped.
- After that, 50 cm³ of ethanol (No. 2) are added carefully through the condenser (beware of sudden boiling!). The mixture is stirred and heated under reflux for 5 minutes. A colourless solid precipitates, or the crystallisation which has already started is completed.

Isolation:

- After leaving it to cool down for 5 minutes, transfer the reaction mixture with another 50 cm³ of ethanol (No. 2) quantitatively to a beaker. The reaction mixture should be stirred vigorously.
- The magnetic stirring bar is removed and the reaction mixture is filtered through a suction filter. Solids which separate in the filtrate are rejected. Rinse the beaker with 10 cm³ of ethanol (No. 2). The precipitate is washed twice with 10 cm³ portions of ethanol (No. 2). (The filtrate must be disposed of in the organic solvent waste!)
- Transfer the precipitate quantitatively into a beaker, add a stirring bar and dissolve it in 150 cm³ of demineralized water. The mixture must be stirred vigorously. Larger lumps of the solid must be crushed with the spatula.
- If the solution is not clear, it has to be filtered over a folded filter paper into an Erlenmeyer flask.
- The slow addition of 5 cm³ of hydrochloric acid (No. 3) to the stirred reaction mixture results in the formation of a white precipitate.
- Collect the crude product by vacuum filtration, wash it twice with 10 cm³ portions of demineralized water and transfer it quantitatively into the tared and labelled beaker B.

- Take a small sample of the product with a micro spatula, crush it and dry it on a shard. Fill three melting point tubes with the homogenized, dried sample. For a close-packed and 5 mm high filling use the 75 cm glass tube and the measure.
- Put all three melting point tubes into the test tube B, which is labelled with your student code, and give it together with your labelled beaker B with the product to the instructor. On delivery you have to sign.

SOLUTION

- 1.1 You started with 2.54 g of polycarbonate. Determine the theoretical yield of bisphenol A in g.

$$M_1(\text{polycarbonate}) = M_1(\text{C}_{16}\text{H}_{14}\text{O}_3)_n\text{H}_2 \approx M_1(\text{C}_{16}\text{H}_{14}\text{O}_3) = 254.30 \text{ g mol}^{-1}$$

$$m_1 = 2.54 \text{ g}$$

$$M_2(\text{C}_{15}\text{H}_{16}\text{O}_2) = 228.31 \text{ g/mol}$$

$$m_2 = m_1 \times M_1^{-1} \times M_2$$

Theoretical yield of bisphenol A: 2.28 g

- 1.2 Determine your theoretical yield of bisphenol A bis(carboxymethyl)ether in g based on 2.00 g bisphenol A.

$$M_2(\text{C}_{15}\text{H}_{16}\text{O}_2) = 228.31 \text{ g/mol}$$

$$m_2 = 2.00 \text{ g}$$

$$M_3(\text{C}_{19}\text{H}_{20}\text{O}_6) = 344.39 \text{ g/mol}$$

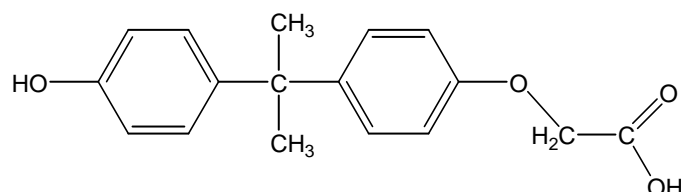
$$m_3 = m_2 \times M_2^{-1} \times M_3$$

Theoretical yield of bisphenol A bis(carboxymethyl)ether: 3.02 g

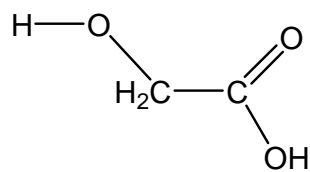
1.3

Unwanted by-products are possible in the second step. Write down the structural formulas of two most probable unwanted by-products.

1. Bisphenol A reacts only once with sodium chloroacetate (monosubstitution):



2. Alkaline hydrolysis of sodium chloroacetate:



PROBLEM 2 (Practical)

Qualitative and Quantitative Analysis of a Superconductor

Introduction

Superconductors based on lanthanum cuprate (La_2CuO_4) have the general composition of $\text{La}_x\text{M}_{(2-x)}\text{CuO}_4$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$).

This problem consists of two parts:

- the qualitative determination of the alkaline earth metal(s)
- the quantitative determination of lanthanum and copper.

Read the burette as accurately as possible. Report your results on the answer sheets.

Answer the additional questions and write the results with adequate accuracy.

The qualitative and quantitative parts of this experiment may be done in any order.

Procedures

2.1 Qualitative determination of the alkaline earth metal(s)

(If the hood is occupied start with the titration 2.2)

In this experiment you have to use the superconductor as a solid ($\text{La}_x\text{M}_{(2-x)}\text{CuO}_4$; No. **14**).

At the beginning, lanthanum has to be separated as an insoluble residue.

All steps must be carried out in the hood!

Dissolve the complete sample in a beaker in about 5 cm^3 of perchloric acid (No. **22**) by heating the mixture. Add 5 cm^3 of demineralized water afterwards.

Cool down the solution until it is lukewarm.

Add about 5 cm^3 of demineralized water and then ammonia solution (No. **17**), until the reaction mixture shows a basic reaction. Lanthanum precipitates as hydroxide and copper forms an intense blue-coloured tetraammine complex. The precipitate is filtered off and washed with a small amount of demineralized water.

An excess of ammonium-carbonate solution (No. **18**) is added to the filtrate and the mixture is being boiled for some minutes. The alkaline earth metal(s) will precipitate as carbonate(s). The precipitate is filtered off and washed a few times with a small amount of demineralized water.

Then, the precipitate is dissolved in acetic acid (No. **16**). Add sodium acetate (No. **9**) and an excess of potassium-dichromate solution (No. **23**). In the presence of barium, yellow BaCrO_4 precipitates. After boiling the mixture for one minute barium chromate is filtered off and washed with demineralized water.

(If there is no barium chromate precipitation, proceed in a way as if there were precipitation.)

Ammonia solution (No. **17**) is added to the clear filtrate until it is basic. Add an excess of ammonium-carbonate solution (No. **18**) and boil the mixture for some minutes. In the presence of strontium and/or calcium, white carbonate(s) precipitate(s).

The precipitate is filtered off and washed a few times with demineralized water.

Then it is dissolved in a mixture of about 2 cm^3 of demineralized water and a few drops of hydrochloric acid (No. **3**). This solution is divided between two test tubes:

- Saturated calcium-sulfate solution (No. **21**) is added to one of the test tubes. In the presence of strontium a small amount of white strontium sulfate precipitates. To accelerate the precipitation, you can grind the inner surface of the test tube with a glass rod for a few minutes.
- Ammonium-sulfate solution (No. **20**) is added to the second test tube. In the presence of strontium and/or calcium, white sulfate(s) precipitate(s). The precipitate is filtered off and washed with a very small amount of demineralized water.

1 cm^3 of ammonium-oxalate solution (No. **19**) is added to the filtrate. In the presence of calcium, white calcium oxalate precipitates after a few minutes.

Preparation of the superconductor parent solution

There is a superconductor solution ($\text{La}_x\text{M}_{(2-x)}\text{CuO}_4$ in perchloric acid; No. 13) in a volumetric flask.

Fill it up with demineralized water to a volume of 250.0 cm^3 . From now on this solution is called "parent solution".

2.2 *Quantitative determination of the total content of lanthanum and copper*

Transfer 25.00 cm^3 of the parent solution into an Erlenmeyer flask. Add about 5-6 piled spatula of sodium acetate (CH_3COONa ; No. **8**) and 2 micro spatula of xylenol orange indicator (No. **15**) to this solution and make up with demineralized water to a volume of

about 75 cm³. The *pH*-value has to be about **pH 6** before the determination, otherwise add more sodium acetate.

Titrate the solution with Na₂-EDTA solution (No. 7). The color of the solution changes from light violet to intensely light-green. (In between, the color changes a few times.)

Repeat this procedure as many times as necessary.

2.3 Quantitative determination of the copper content

Transfer 25.00 cm³ of your parent solution (No. 13) into the 100 cm³ volumetric flask and fill up with demineralized water to a volume of 100.0 cm³. For each titration, transfer 25.00 cm³ of this solution into an Erlenmeyer flask and add sodium hydroxide solution (No. 6), until the solution shows an alkaline reaction. During this procedure, a blue precipitate forms. Add sulfuric acid (No. 12) until the blue precipitate dissolves. The solution has to be acidic (**pH 1-2**) and will contain a small amount of a white precipitate.

Add 10 cm³ of sodium-iodide solution (No. 9), and swirl the Erlenmeyer flask for about 1 minute. Titrate the solution with sodium-thiosulfate solution (No. 10). Add some starch solution (No. 11) as an indicator just before the end of the titration. At the end, the solution has to be colourless for at least 60 seconds.

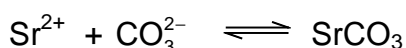
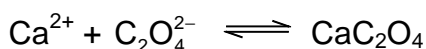
Repeat this procedure as many times as necessary.

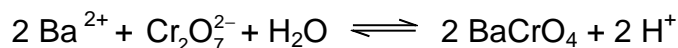
SOLUTION

2.1 Which alkaline earth metal(s) can be found in the superconductor? Mark only one box!

- | | | | | | |
|------------------|--------------------------|-----------|--------------------------|-----------|-------------------------------------|
| Ca | <input type="checkbox"/> | Sr | <input type="checkbox"/> | Ba | <input checked="" type="checkbox"/> |
| Ca and Sr | <input type="checkbox"/> | Ca and Ba | <input type="checkbox"/> | Sr and Ba | <input type="checkbox"/> |
| Ca and Sr and Ba | <input type="checkbox"/> | | | | |

Complete the following reaction equations:





2.2 Quantitative determination of the total content of lanthanum and copper.

Appropriate consumption of 0.1000 mol dm⁻³ EDTA solution: $V = 11.60 \text{ cm}^3$

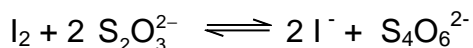
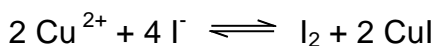
(according to 100 cm³ of superconductor solution)

2.3 Quantitative determination of the copper content.

Appropriate consumption of 0.01000 mol dm⁻³ Na₂S₂O₃ solution: $V = 10.50 \text{ cm}^3$

(according to 100 cm³ of superconductor solution)

Complete the following reaction equations:



2.4 Mass (in mg) of copper in your parent solution,
mass (in mg) of lanthanum in your parent solution.

$$[M(\text{Cu}) = 63.55 \text{ g mol}^{-1}; M(\text{La}) = 138.91 \text{ g mol}^{-1}]$$

Amount of copper:

$$10,50 \text{ cm}^3 \times 0.01 \text{ mol dm}^{-3} \times 4 \times 10 \times 63.55 \text{ g mol}^{-1} = 266.9 \text{ mg}$$

Amount of lanthanum:

$$[11.60 - (10.50 / 10 \times 4)] \text{ cm}^3 \times 0.1 \text{ mol dm}^{-3} \times 10 \times 138.91 \text{ g mol}^{-1} = 1028 \text{ mg}$$

$$\text{Mass Cu: } m(\text{Cu}) = 266.9 \text{ mg}$$

$$\text{Mass La: } m(\text{La}) = 1028 \text{ mg}$$

2.5 Assume a fictive consumption of 39.90 cm³ of 0.1000 mol dm⁻³ EDTA solution and 35.00 cm³ of 0.01000 mol dm⁻³ Na₂S₂O₃ solution. Calculate the coefficient x in the formula La_xM_(2-x)CuO₄ (M = Ca and/or Sr and/or Ba) and give the exact formula of the superconductor

Consumption for lanthanum = $[39.90 - (35.00/10 \times 4)] \text{ cm}^3 = 25.90 \text{ cm}^3$

Consumption for copper = $(39.90 - 25.90) \text{ cm}^3 = 14.00 \text{ cm}^3$

$n(\text{La}) : n(\text{Cu}) = 25.90 : 14.00 = 1.85 : 1$

coefficient x: 1.85

formula: $\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$

37th



International Chemistry Olympiad

**8 theoretical problems
2 practical problems**

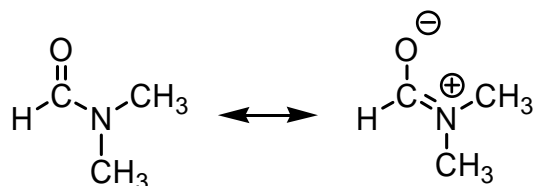
THE THIRTY-SEVENTH INTERNATIONAL CHEMISTRY OLYMPIAD 16–25 JULY 2005, TAIPEI, TAIWAN

THEORETICAL PROBLEMS

PROBLEM 1

Chemistry of Amides and Phenols

Condensation of a carboxylic acid with an amine gives an amide product. For example, condensation of formic acid with dimethylamine forms N,N-dimethylformamide (DMF), which can be described as the following resonance structures.



1.1 Predict the order of melting points among N,N-dimethylformamide (compound **A**), N-methylacetamide ($\text{CH}_3\text{CONHCH}_3$, compound **B**), and propionamide (compound **C**, $\text{CH}_3\text{CH}_2\text{CONH}_2$). Express your answer from high to low melting point as follows:

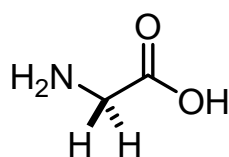
____ > ____ > ____ (Insert compound codes **A**, **B**, **C**)

1.2 Carbonyl groups are usually identified by their characteristic strong absorptions in the infrared spectra. The position of the absorption is dependent on the strength of the C=O bond, which in turn is reflected in their bond lengths. In amides, the strength of the carbonyl groups can be shown by the resonance structure noted above. For example, cyclohexanone shows an absorption at 1715 cm^{-1} for the carbonyl group (C=O). In comparison with cyclohexanone, predict the absorption band for the carbonyl group in propionamide. Select your answer from the following choices.

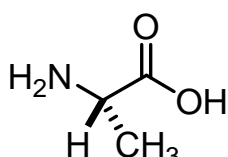
- (a) 1660 cm^{-1} because of the shorter carbonyl bond length.
- (b) 1660 cm^{-1} because of the longer carbonyl bond length.
- (c) 1740 cm^{-1} because of the shorter carbonyl bond length.
- (d) 1740 cm^{-1} because of the longer carbonyl bond length.

1.3 Glycine ($\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$) is an α -amino acid. Three glycine molecules can form a tripeptide Gly-Gly-Gly via amide linkages, accompanied by elimination of two water molecules. Draw the structural formula of this tripeptide.

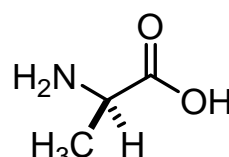
1.4 When an α -amino acid contains a substituent, there is a possibility of optical isomers. For example, L-alanine and D-alanine are two enantiomers. What is the number of all possible linear tripeptides that can be formed from the following three amino acids: glycine, L-alanine and D-alanine as the starting materials in the condensation reaction?



Glycine (Gly)



L-Alanine (L-Ala)



D-Alanine (D-Ala)

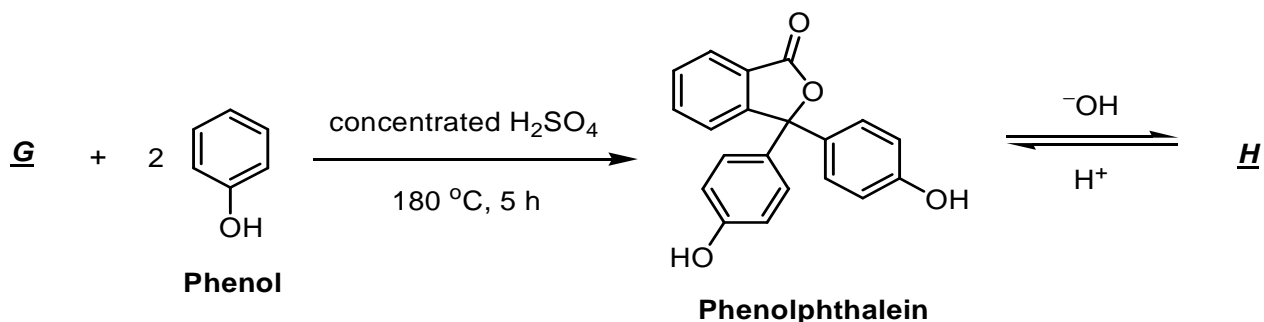
1.5 Among the tripeptides synthesized in 1-4, how many are optically active?

Nowadays, polyacrylamide gel associated with electrophoresis (PAGE) was widely used in analyses of proteins and nucleic acids. However, one of the first applications of polyamide gel is the separation of phenol compounds on thin-layer chromatography. The phenol compounds bearing different substituents have varied acidities. The higher acidity results in stronger binding to PAGE gel.

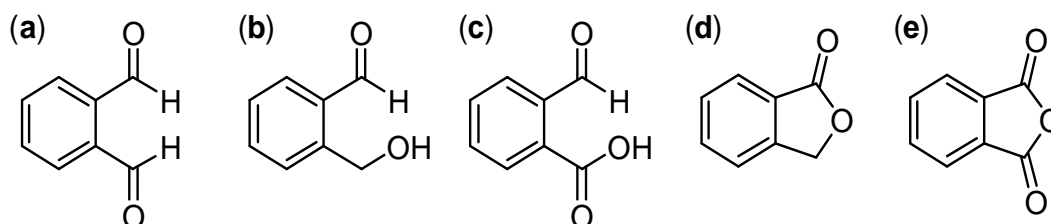
1.6 Predict the binding affinity of phenol (compound **D**), 4-methylphenol (compound **E**) and 4-nitrophenol (compound **F**) with a polyamide gel. Express your answer from high to low binding affinity as follows:

_____ > _____ > _____. (Insert compound codes **D**, **E**, and **F**)

The absorption maximum of a molecule in its ultraviolet and visible spectrum (UV-vis spectrum) is related to the number of conjugated double bonds in a chain. A compound containing more than 5 conjugated double bonds tends to absorb visible light, and hence shows the complementary colour. For example, phenolphthalein is a commonly used acid-base indicator, which is colourless in acidic and neutral solutions, but reddish pink in basic solutions (pH 8.3 – 10.0).



- 1.7 Draw the structural formula of **H** derived from phenolphthalein that is attributable to the reddish pink colour in aqueous NaOH solution.
- 1.8 A simple way to prepare phenolphthalein is via condensation of compound **G** with 2 equivalents of phenol. What is the most effective reagent for **G** to accomplish this transformation? Select your answer from the following compounds.



SOLUTION

- 1.1 The order of the melting points is: **C > B > A**

The resonance structure of amide shows a partial negative charge on oxygen and a partial positive charge on nitrogen. Primary and secondary amides also participate in strong hydrogen bonding, but not tertiary amide.

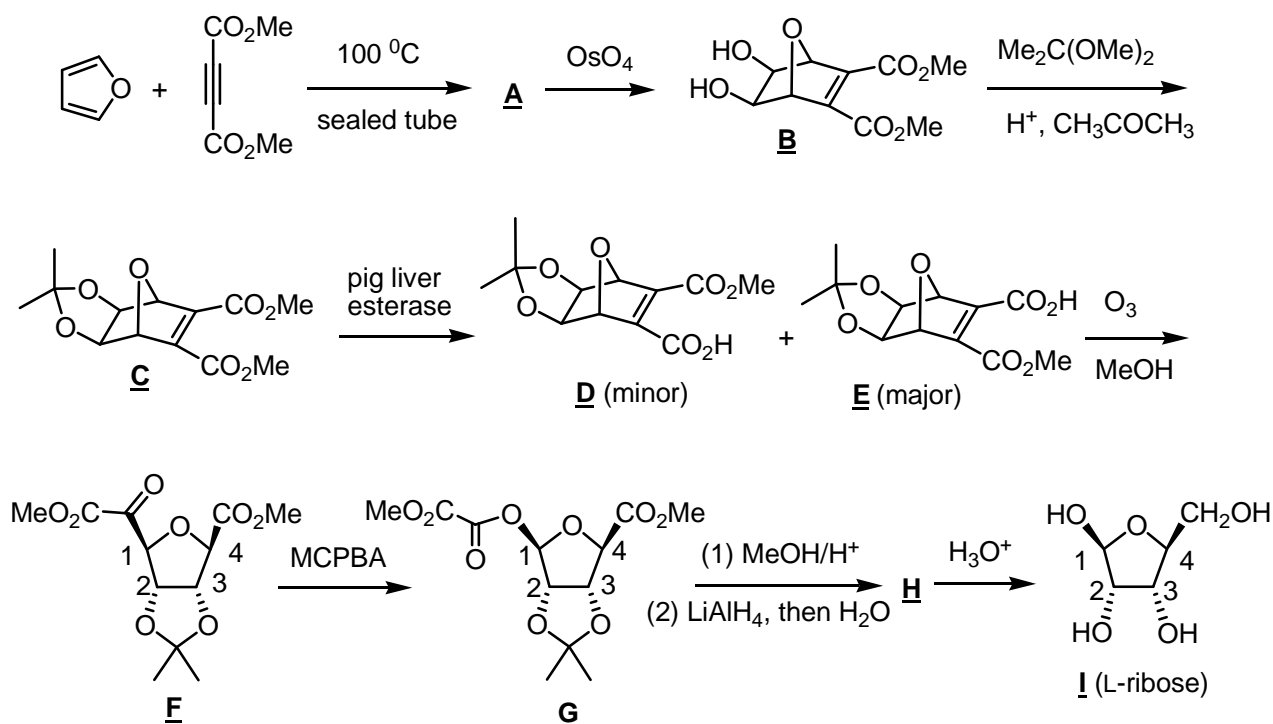
Propionamide, m.p. = 79 °C; *N*-methylacetamide, m.p. = 28 °C;

N,N-dimethylformamide, m.p. = -61 °C.

- 1.2 Correct: (b), 1660 cm⁻¹ due to a longer carbonyl bond length.

PROBLEM 2**Organic Synthesis and Stereochemistry**

Natural carbohydrates are generally produced by photosynthesis in plants. However, unnatural carbohydrates can be prepared by organic synthesis. The following outline is a synthetic scheme for the unnatural L-ribose (compound **I**).



2.1 Compound **A** has the molecular formula of $C_{10}H_{10}O_5$. Draw the structural formula of **A**.

2.2 Given the chemistry described for reaction sequence **A** to **C**, indicate whether the following statements are true or false (Use T to represent true and F to represent false).

- ___ (a) OsO_4 is an oxidizing agent in the reaction of **A** to **B**.
- ___ (b) MeOH is generated as a by-product in the reaction of **B** to **C**.
- ___ (c) Protons act as the catalyst in the transformation of **B** to **C**.
- ___ (d) **C** will still be formed albeit in lower yields in the absence of $Me_2C(OMe)_2$.

Pig liver esterase is an enzyme that can hydrolyze esters to carboxylic acids. Hydrolysis of **C** by the pig liver esterase afforded an enantiomeric mixture of **D** and **E**, in which **E** was the major component. The optical rotation of the mixture was $[\alpha]_D^{20} = -37.1^\circ$. Further purification by recrystallization gave pure **E** with the optical rotation $[\alpha]_D^{20} = -49.0^\circ$.

2.3 What is the molar ratio of **D/E** in the product mixture before the recrystallization?

Show your work.

2.4 Reaction of **F** with meta-chloroperbenzoic acid (MCPBA) afforded **G** as the product. Indicate whether the following statements are true or false (Use T to represent true and F to represent false).

_____ (a) The reaction was to oxidize compound **F**.

_____ (b) The oxygen atom inserted originated from MCPBA.

_____ (c) The *R/S* notation of C-1 remained unchanged before and after the reaction.

The molecular formula of **H** is $C_9H_{16}O_5$. Proton NMR data of **H** are listed as follows:

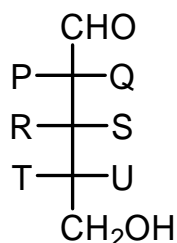
1H NMR ($CDCl_3$) δ 1.24 (s, 3H), 1.40 (s, 3H), 3.24 (m, 1 H), 3.35 (s, 3H), 3.58 (m, 2H), 4.33 (m, 1H); 4.50 (d, $J = 6$ Hz, 1H), 4.74 (d, $J = 6$ Hz, 1H), 4.89 (s, 1H).

2.5 Draw the configurational formula of **H**.

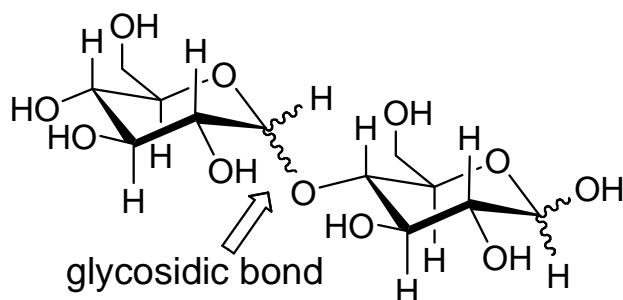
2.6 Assign *R/S* notations for compound **I** at C-1, C-2, C-3 and C-4. Give your answers as follows:

C-1: _____; C-2: _____; C-3: _____; C-4: _____.

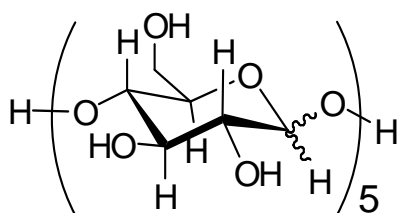
2.7 What are the identities of P, Q, R, S, T and U in the Fischer projection of compound **I** (L-ribose)?



Disaccharides are compounds with two monosaccharide subunits linked together by a glycosidic bond. Polysaccharides contain as few as ten, or as many as thousands, monosaccharide subunits. An example of a disaccharides is as follows:



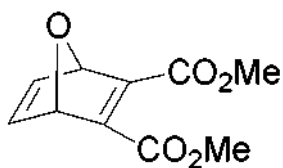
2.8 How many diastereoisomers would be obtained for pentasaccharide **J**, if it is derived from five units of D-glucose?



pentasaccharide **J** derived from D-glucose

SOLUTION

2.1



2.2

T or F

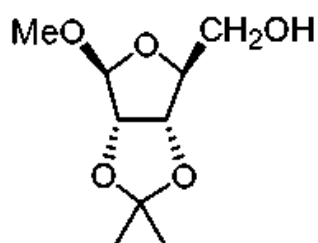
- (a) OsO_4 is an oxidizing agent in the reaction of **A** to **B**.
- (b) MeOH is generated as a by-product in the reaction of **B** to **C**.
- (c) Protons act as the catalyst in the transformation of **B** to **C**.
- (d) **C** will still be formed albeit in lower yields in the absence of $\text{Me}_2\text{C}(\text{OMe})_2$

2.3 12.1 : 87.9 or 12.2 : 87.8

2.4 T or F

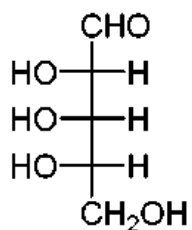
- I (a) The reaction was to oxidize compound **F**.
I (b) The oxygen atom inserted originated from MCPBA.
E (c) The *R/S* notation of C-1 remained unchanged before and after the reaction

2.5



2.6 C-1: S; C-2: S; C-3: R; C-4: S.

2.7



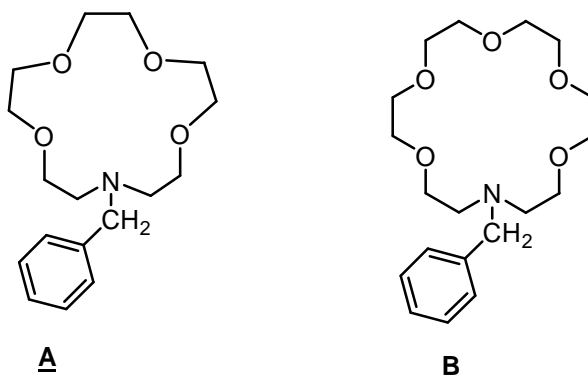
OH group for P, R, and T and H atom for Q, S, and U.

2.8 The number of stereoisomers = 2^5

PROBLEM 3

Organic Photochemistry and Photophysics

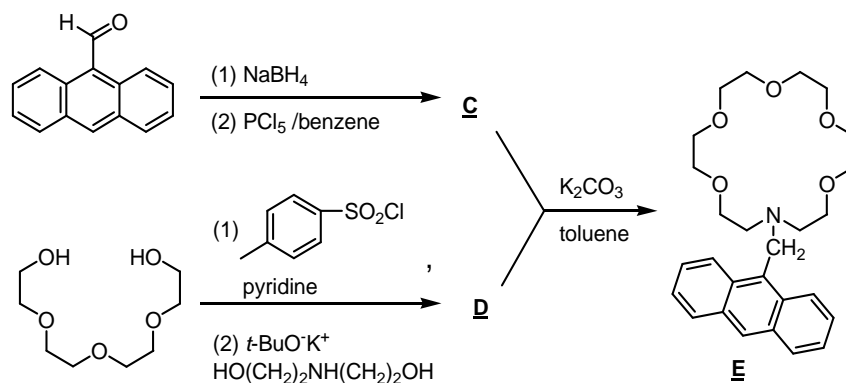
Crown ethers show size-dependent binding capability to alkali metal ions. For example, the azacrowns **A** and **B** exhibit different binding constants for Na^+ , K^+ , and Cs^+ .



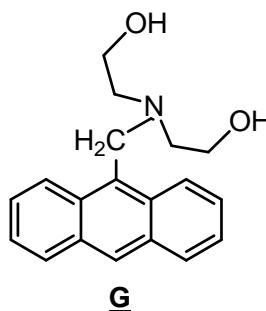
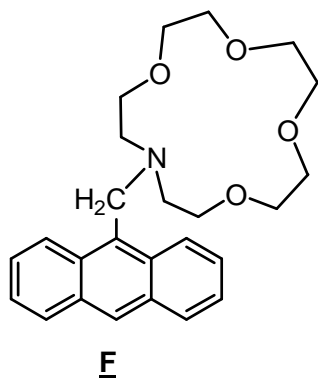
Metal ion	Radius (pm)	Binding constant ($\log_{10} K$)	
		Compound A	Compound B
Na^+	98	2.49	3.57
K^+	133	1.83	5.00
Cs^+	165	1.37	3.39

Anthracene exhibits strong fluorescence with emission wavelength centered at 325 nm. Combining the binding selectivity of azacrowns for alkali metal ions and the highly fluorescent anthracene, a metal ion selective fluorescent sensor **E** has been developed.

3.1 Provide the structural formula of **C** and **D** in the following synthesis.

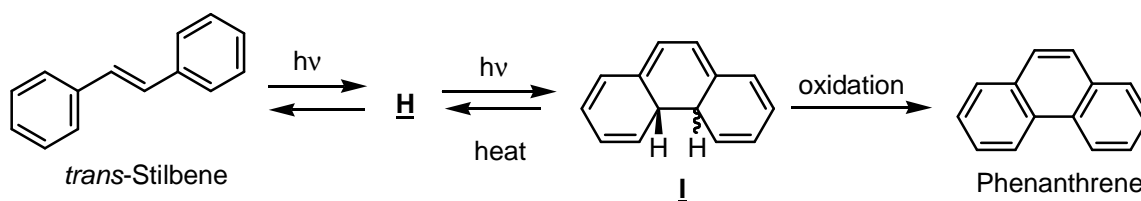


For comparison studies, the anthracene derivatives **F** and **G** shown below were also synthesized. These compounds **E**, **F**, and **G** are almost non-fluorescent in neutral conditions due to the strong photoinduced electron transfer (PET) quenching process arising by donating nitrogen lone-pair electron to the anthracene excited-state.



- 3.2** Upon adding aqueous HCl, which compound will exhibit strong fluorescence? Select your answer from the following choices.
- (a) none of them (b) **E** and **F** only (c) **G** only (d) all of them
- 3.3** By adding one equivalent of potassium acetate into a dilute solution (1×10^{-5} M) of **E**, **F**, and **G** in methanol, respectively, which compound will show the strongest fluorescence? Select your answer from the following choices.
- (a) **E** (b) **F** (c) **G**
- 3.4** Upon adding one equivalent of metal acetate to a dilute solution of **F**, which metal acetate will cause the strongest fluorescence? Select your answer from the following choices.
- (a) sodium acetate (b) potassium acetate (c) cesium acetate (d) doesn't make any difference

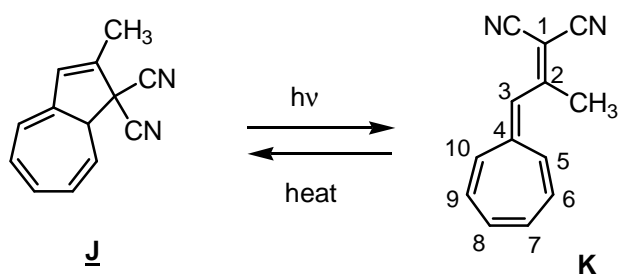
Upon irradiation with ultraviolet light, trans-stilbene is transformed into an intermediate **H**, which undergoes a photocyclization to form dihydrophenanthrene **I**. Further oxidation of **I** gives phenanthrene.



3.5 Draw the structural formula of compound **H**?

3.6 What is the relative stereochemistry of the two H-atoms shown (cis or trans) in compound **I**?

Dihydroazulene derivative **J** exhibits interesting photochromic behavior. Upon irradiation, colorless dihydroazulene **J** undergoes photoinduced rearrangement to the corresponding vinylheptafulvene **K**. The vinylheptafulvene undergoes thermal reversion to dihydroazulene.



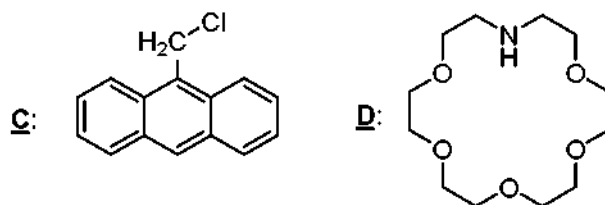
3.7 Which compound will absorb light with longer wavelength? Select your answer from the following choices: (a) **J** (b) **K**

3.8 Compound **K** can react with one equivalent of $\text{CF}_3\text{CO}_2\text{H}$ to generate a stable aromatic salt. Which position of **K** is most likely protonated? Select your answer from the following choices.

- (a) C-2 (b) C-3 (c) C-4 (d) C-5

SOLUTION

3.1

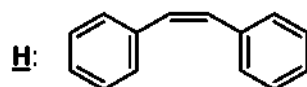


3.2 Correct is (d): All of them

3.3 Correct is (a): **E**

3.4 Correct is (a): sodium acetate

3.5



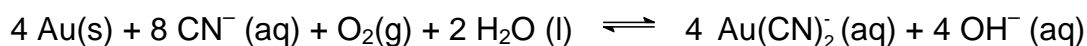
3.6 Trans

3.7 Correct is (b): **K**

3.8 Correct is (b): C-3

PROBLEM 4**A**Gold Capital of Asia

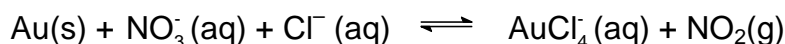
Chiufen, the old mining town located within the hills in the northeast Taiwan, is a place where you can really experience Taiwan's historical legacy. It was the site of one of the largest gold mines in Asia. Accordingly, Chiufen is often referred to as the Gold Capital of Asia. The compound KCN is traditionally used to extract gold from ore. Gold dissolves in cyanide (CN⁻) solutions in the presence of air to form Au(CN)₂⁻, which is stable in aqueous solution.



4.A-1 Draw a structure for Au(CN)₂⁻ showing the spatial arrangements of the atoms.

4.A-2 How many grams of KCN are needed to extract 20 g of gold from ore? Show your work.

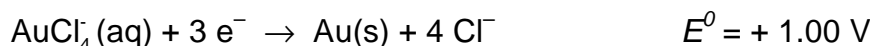
Aqua regia, a 3 : 1 mixture (by volume) of concentrated hydrochloric acid and nitric acid, was developed by the alchemists as a means to "dissolve" gold. The process is actually a redox reaction with the following simplified chemical equation:



4.A-3 Write down the half reactions, and use them to obtain a balanced redox reaction for this process.

4.A-4 What are the oxidizing and reducing agents for 4.A-3 process?

Gold is too noble to react with nitric acid. However, gold does react with aqua regia because the complex ion AuCl₄⁻ forms. Consider the following half-reactions:



An electrochemical cell can be formed from these two redox couples.

4.A-5 Calculate the formation constant for AuCl₄⁻ at 25 °C:

$$K = \frac{[\text{AuCl}_4^{-}]}{[\text{Au}^{3+}][\text{Cl}^{-}]^4}$$

4.A-6 The function of HCl is to provide Cl^- . What is the purpose of the Cl^- for the above reaction. Select your answer from the following choices.

- (a) Cl^- is an oxidizing agent
 - (b) Cl^- is a reducing agent
 - (c) Cl^- is a complexing agent
 - (d) Cl^- is a catalyst
-

B

Gold Nanoparticles

The synthesis and characterization of gold nanoparticles is currently an active research area. The Brust-Schiffrin method for the synthesis of gold nanoparticle (AuNP) allows the facile preparation of thermally stable and air-stable AuNPs of reduced polydispersity with a controlled size distribution ranging in diameter between 1.5 and 5.2 nm. The preparative procedure is briefly described as follows. An aqueous solution of HAuCl_4 is mixed with a toluene solution of tetra-n-octylammonium bromide. The solution is mixed with dodecanethiol and is treated with an excess of NaBH_4 . Formation of the AuNPs is evidenced by the immediate, pronounced darkening of the toluene phase. After ca. 24 h, the toluene solvent is removed with a rotary evaporator and the resulting solid washed on a frit with ethanol and hexane to remove excess thiol. These AuNPs can be repeatedly isolated and re-dissolved in common organic solvents without irreversible aggregation or decomposition.

4.B-1 Is the methodology for this fabrication referred to a top-down or a bottom-up approach? Select your answer from the following choices.

- (a) top-down approach, which entails reducing the size of the smallest structures to the nanoscale
- (b) bottom-up approach, which involves manipulating individual atoms and molecules into nanostructures

4.B-2 The trimethyl-n-octylammonium bromide can also be used as a phase-transfer reagent. It can carry AlCl_4^- from an aqueous phase to an organic phase. Which

property does trimethyl-n-octylammonium bromide possess to function as an efficient phase-transfer reagent? Select your answer from the following choices.

- (a) one side of the molecule is electropositive, the other side is electronegative.
- (b) one side of the molecule is hydrophilic, the other side is hydrophobic.
- (c) one side of the molecule is acidic, the other side is basic.

4.B-3 What is the function of NaBH_4 in this preparation? Select your answer from the following choices.

- (a) reducing agent
- (b) oxidizing agent
- (c) neutralization agent
- (d) complexing agent

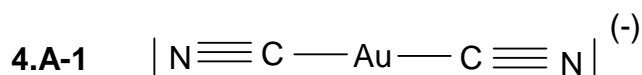
4.B-4 If the average diameter of a gold nanoparticle is 3 nm, what is the estimated number of Au atoms in each nanoparticle? (the atomic radius of Au is 0.144 nm). Select your answer from the following choices and show your work.

- (a) 10^2
- (b) 10^3
- (c) 10^4
- (d) 10^5

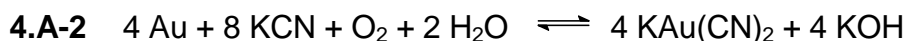
4.B-5 What is the estimated percentage of Au atoms on the surface of a nanoparticle? Select your answer from the following choices and show your work.

- (a) 20 – 30 %
- (b) 40 – 50 %
- (c) 60 – 70 %
- (d) 80 – 90 %

SOLUTION

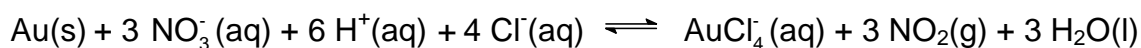
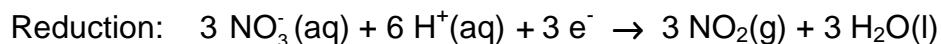
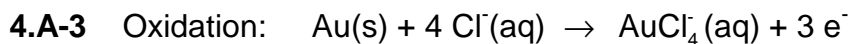


The structure of $\text{Au}(\text{CN})_2^-$ is linear.



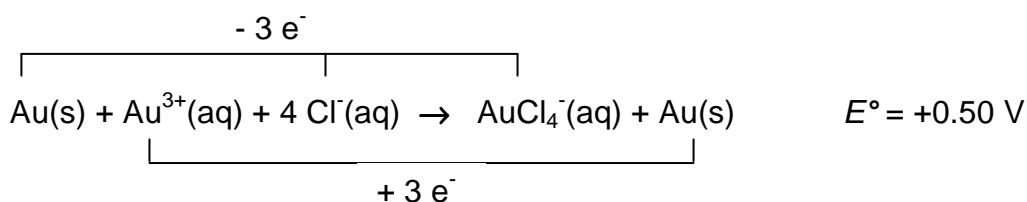
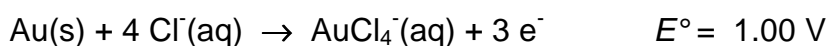
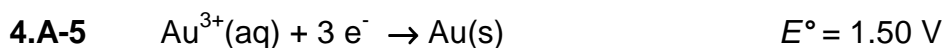
$$20 \text{ g} \div 197 \text{ g mol}^{-1} \approx 0.10 \text{ mol (Au)}$$

$$0.10 \text{ mol} \times (8/4) \times 65.12 \text{ g mol}^{-1} = 13.024 \text{ g KCN}$$



4.A-4 Oxidizing agent: HNO_3 or nitric acid

Reducing agent: Au



$$E = E^\circ - (0.059 / n) \log Q$$

At equilibrium, $Q = K$, $E = 0$, $K = [\text{AuCl}_4^-] / [\text{Au}^{3+}] [\text{Cl}^-]^4$

$$E = (0.059 / n) \log K, \quad 0.50 = (0.059 / 3) \log K, \quad K = 10^{25.42} = 2.6 \times 10^{25}$$

$$\Delta G_1^0 + \Delta G_2^0 = \Delta G_3^0$$

$$(-n F E_1^0) + (-n F E_2^0) = -RT \ln K$$

$$E^\circ = (RT / nF) \ln K = (0.059 / n) \log K,$$

$$0.50 = (0.059 / 3) \log K,$$

$$K = 10^{25.42} = 2.6 \times 10^{25}$$

4.A-6 Answer for multiple choice question: (c)

4.B-1 Answer for multiple choice question: (b)

4.B-2 Answer for multiple choice question: (b)

4.B-3 Answer for multiple choice question: (a)

4.B-4 Answer for multiple choice question: (b)

Calculation:

$$V_{\text{AuNPs}} = \frac{4}{3} \pi r_{\text{AuNPs}}^3$$

$$V_{\text{Au}} = \frac{4}{3} \pi r_{\text{Au}}^3$$

$$N_{\text{Au}} = \frac{V_{\text{AuNPs}}}{V_{\text{Au}}} = \frac{\frac{4}{3} \pi r_{\text{AuNPs}}^3}{\frac{4}{3} \pi r_{\text{Au}}^3} = \left(\frac{r_{\text{AuNPs}}}{r_{\text{Au}}} \right)^3 = \left(\frac{15 \text{ \AA}}{1,44 \text{ \AA}} \right)^3 \approx 1000$$

4B-5 Calculation:

Method 1:

$$4/3 \times \pi \times r_{\text{AuNPs}}^3 = 4/3 \times \pi \times r_{\text{Au}}^3 \times N_{\text{Au}}$$

$$r_{\text{AuNPs}}^3 = r_{\text{Au}}^3 \times N_{\text{Au}}$$

Surface area of a gold nanoparticle: $S_{\text{AuNPs}} = 4 \pi r_{\text{AuNPs}}^2$

$$S_{\text{AuNPs}} = 4 \pi r_{\text{Au}}^2 N_{\text{Au}}^{2/3}$$

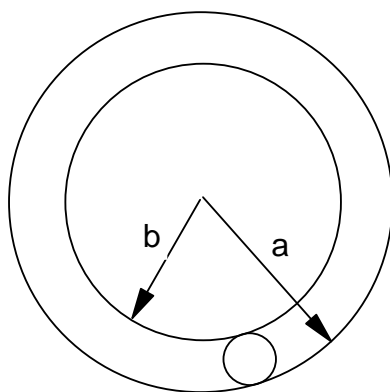
$$N_{\text{S}} \approx S_{\text{AuNPs}} / \pi r_{\text{Au}}^2 = 4 N_{\text{Au}}^{2/3}$$

$$P \approx N_{\text{S}} / N_{\text{Au}} = 4 / N_{\text{Au}}^{1/3}$$

$$N_{\text{Au}} \approx 1000$$

$$P \approx 40 \%$$

or Method 2:



$$a = r_{\text{AuNPs}}$$

$$b = r'_{\text{AuNPs}} = r_{\text{AuNPs}} - 2 r_{\text{Au}}$$

$$P \% = \frac{\frac{V_{\text{AuNPs}}}{V_{\text{Au}}} - \frac{V'_{\text{AuNPs}}}{V_{\text{Au}}}}{\frac{V_{\text{AuNPs}}}{V_{\text{Au}}}} \times 100 \% = \frac{\left(\frac{r_{\text{AuNPs}}}{r_{\text{Au}}}\right)^3 - \left(\frac{r'_{\text{AuNPs}}}{r_{\text{Au}}}\right)^3}{\left(\frac{r_{\text{AuNPs}}}{r_{\text{Au}}}\right)^3} \times 100 \% =$$

$$= \frac{(15 A)^3 - (12.12 A)^3}{(15 A)^3} \times 100 \% = 47 \%$$

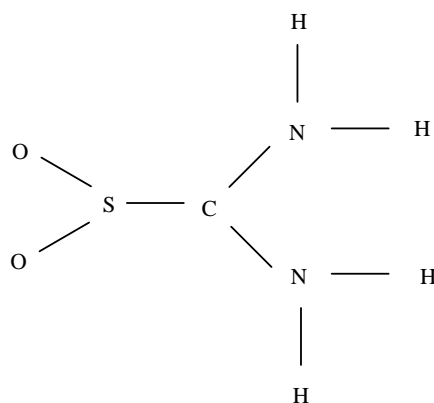
PROBLEM 5**Lewis Structure**

5.1 Draw one Lewis structure for each of the following molecules.

- a) N₂
- b) NH₃
- c) O₃
- d) SO₃

5.2 Draw the Lewis structure of carbon monoxide and assign formal charges and oxidation states to both the carbon and oxygen atoms in carbon monoxide.

Thiourea-S,S-dioxide, O₂SC(NH₂)₂, has the following skeletal structure



5.3 Draw the Lewis structure of thiourea-S,S-dioxide with zero formal charges on all atoms.

5.4 Based on the Valence Shell Electron Pair Repulsion (VSEPR) model, what is the geometry around the sulfur, carbon, and nitrogen according to the Lewis structure you predicted from 5.3?

5.4a What is the geometry around the sulfur atom? Select your answer from the following choices.

- a) trigonal pyramidal
- b) triangular planar
- c) T-shape

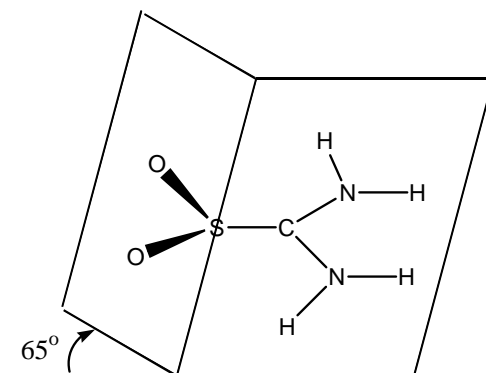
5.4b Similarly, what is the geometry around the C-atom? Select your answer from the following choices.

- a) trigonal pyramidal
- b) triangular planar
- c) T-shape

5.4c Finally, what is the geometry around the N-atom? Select your answer from the following choices.

- a) trigonal pyramidal
- b) triangular planar
- c) T-shape

Molecular structure in the solid state is usually determined by X-ray diffraction analysis. According to this method, the structure of thiourea-S,S-dioxide is shown below:

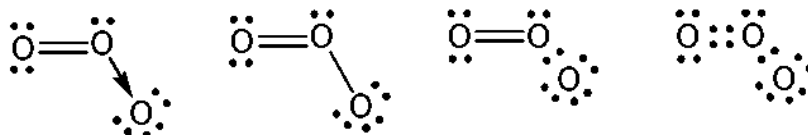
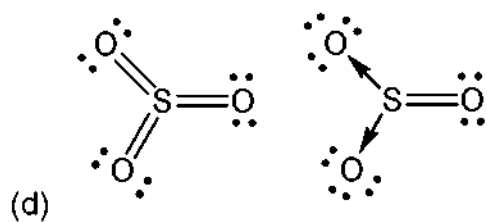
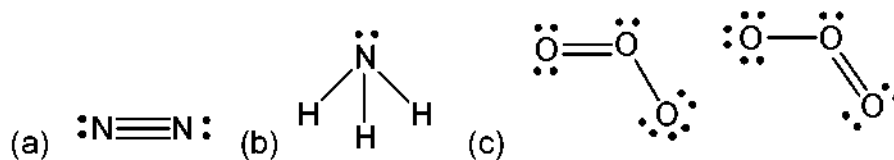


All the N, H atoms are coplanar with S, C atoms, and the dihedral angle between the OSO plane and the SC(NH₂)₂ plane is 65°.

5.5 Draw the Lewis structure and resonance forms that are consistent with the geometry determined.

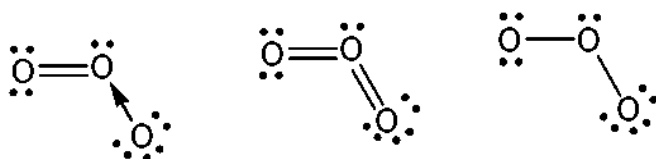
SOLUTION

5.1

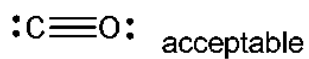
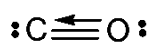


are all correct answers

But



are incorrect answers

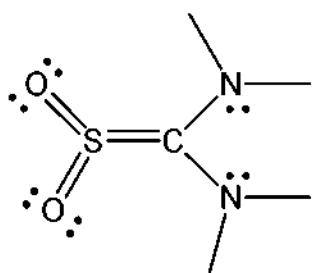


5.2

Formal charge C^{-1} ; O^{+1}

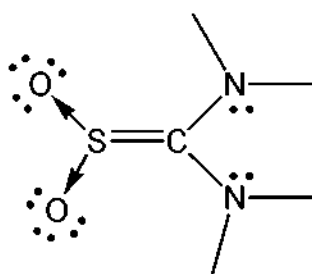
Oxidation state C^{2+} ; O^{2-}

5.3



The structure

is correct.



The structure

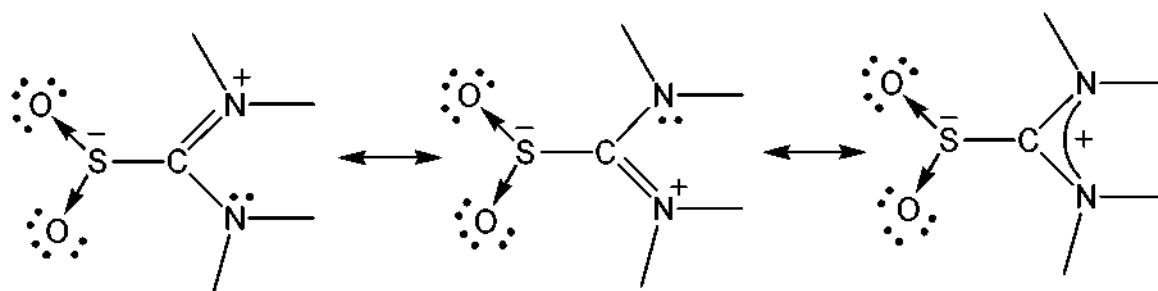
would have a formal charge and is incorrect.

5.4 Sulphur: (b) trigonal planar

Carbon: (b) trigonal planar

Nitrogen: (a) trigonal pyramidal

5.5

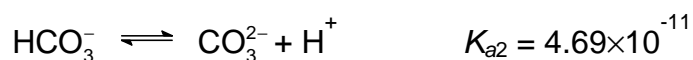
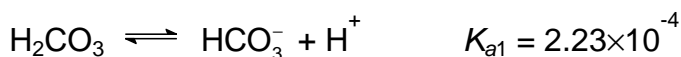
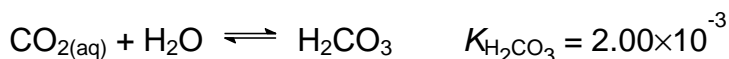
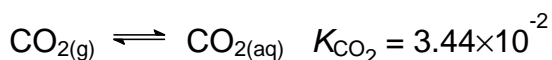


PROBLEM 6**Alkalinity of Water and Solubility of CO₂**

The capacity of water to accept H⁺ ions is called alkalinity. Alkalinity is important in water treatment and in the chemistry and biology of natural waters. Generally, the basic species responsible for alkalinity in water are HCO₃⁻, CO₃²⁻, and OH⁻. At *pH* values below 7, H⁺ in water detracts significantly from alkalinity. Therefore, the complete equation for alkalinity in a medium where HCO₃⁻, CO₃²⁻, and OH⁻ are the only contributors to alkalinity can be expressed as

$$\text{alkalinity} = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

The contributions made by different species to alkalinity depend upon *pH*. Relevant chemical equations and equilibrium constants (at 298 K) are shown below:



Note: Calculations must be shown.

6.1 Natural waters (river or lake water) generally contain dissolved CO₂. The ratio of [H₂CO₃] : [HCO₃⁻] : [CO₃²⁻] in a water at [H⁺] = 1.00 × 10⁻⁷ M will be:

(a) : 1.00 : (b). Calculate (a) and (b).

6.2 Gaseous CO₂ in the atmosphere can be regarded as a contributor to the alkalinity of water in equilibrium with air. Calculate the concentration of CO_{2(aq)} (mol dm⁻³) in pure water that is in equilibrium with the unpolluted air at 1.01 × 10⁵ Pa and 298 K containing 0.0360 % (molar ratio) CO₂. (assuming standard pressure = 1.01 × 10⁵ Pa).

If you are unable to solve this problem, assume that concentration of $\text{CO}_2(\text{aq})$ is equal to 1.11×10^{-5} M for further calculations.

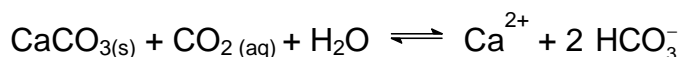
The solubility (S) of CO_2 in water can be defined as

$$S = [\text{CO}_{2(\text{aq})}] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}].$$

The solubility of atmospheric CO_2 in water that is in equilibrium with the unpolluted air at 298 K and 1.01×10^5 Pa will vary with alkalinity.

- 6-3** Find the solubility of atmospheric CO_2 in pure water (mol dm^{-3}). Neglect dissociation of water.
- 6.4** Find the solubility of atmospheric CO_2 (mol dm^{-3}) in a 1.00×10^{-3} mol dm^{-3} NaOH solution.

At 298 K, 1.01×10^5 Pa unpolluted air is in equilibrium with natural water saturated with CaCO_3 . The following main equilibrium may exist:



- 6.5** Calculate the equilibrium constant for the above equation.

If you are unable to solve this problem, assume that equilibrium constant $K_{\text{eq}} = 5.00 \times 10^{-5}$ for further calculations.

- 6.6** Calculate the concentration of Ca^{2+} (mg dm^{-3}) in CaCO_3 -saturated natural water that is in equilibrium with atmospheric CO_2 .

If you are unable to solve this problem, assume that concentration of $\text{Ca}^{2+}_{(\text{aq})} = 40.1$ mg dm^{-3} for further calculations.

- 6.7** Find the alkalinity (mol/L) of the above solution.
- 6.8** In an underground lake saturated with CaCO_3 , the water has a high content of CO_2 . The concentration of Ca^{2+} in this lake was found to be as high as 100 mg dm^{-3} . Assume the lake and the air above is a closed system, calculate the effective pressure of CO_2 (Pa) in air which is in equilibrium with this Ca^{2+} content.

SOLUTION

6.1 $[H^+] = 1.00 \times 10^{-7}$

$$K_{a1} = [HCO_3^-][H^+] / [H_2CO_3] = 2.23 \times 10^{-4},$$

$$[HCO_3^-] / [H_2CO_3] = 2.23 \times 10^3$$

$$K_{a2} = [CO_3^{2-}][H^+] / [HCO_3^-] = 4.69 \times 10^{-11},$$

$$[CO_3^{2-}] / [HCO_3^-] = 4.69 \times 10^{-4}$$

$$[H_2CO_3] : [HCO_3^-] : [CO_3^{2-}] = 4.48 \times 10^{-4} : 1.00 : 4.69 \times 10^{-4}$$

6.2 $p(\text{CO}_2(\text{aq})) = 1.01 \times 10^5 \text{ Pa} \times 3.60 \times 10^{-4} = 36.36 \text{ Pa}$

$$[\text{CO}_2(\text{aq})] = K_{\text{CO}_2} \times p(\text{CO}_2) = 0.0344 \times (36.36 \text{ Pa} / 1.01 \times 10^5 \text{ Pa}) = 1.24 \times 10^{-5}$$

(If you are unable to solve this problem, for further calculations assume that $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$.)

6.3

(a) Solubility = $[\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \approx [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-]$

$$([\text{H}_2\text{CO}_3] = [\text{CO}_2(\text{aq})] \times K_{\text{H}_2\text{CO}_3} = 2.48 \times 10^{-8}$$

$$\text{and } [\text{CO}_3^{2-}] = K_{a2} / ([H^+] / [HCO_3^-]) = K_{a2} = 4.69 \times 10^{-11}$$

both can be neglected.)

$$[H^+][HCO_3^-] / [\text{CO}_2(\text{aq})] = K_{a1} K_{\text{H}_2\text{CO}_3} = (2.23 \times 10^{-4}) (2.00 \times 10^{-3}) = 4.46 \times 10^{-7}$$

From 6-2: $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$,

$$[H^+] = [HCO_3^-] = 2.35 \times 10^{-6}$$

$$\text{Solubility} = [\text{CO}_2(\text{aq})] + [HCO_3^-] = 1.24 \times 10^{-5} + 2.35 \times 10^{-6} = 1.48 \times 10^{-5} \text{ mol dm}^{-3}$$

(b) (Using $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$ for calculation)

$$\text{Solubility} = [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \approx [\text{CO}_2(\text{aq})] + [HCO_3^-]$$

$$([\text{H}_2\text{CO}_3] = [\text{CO}_2(\text{aq})] \times K_{\text{H}_2\text{CO}_3} = 2.22 \times 10^{-8} \text{ and } [\text{CO}_3^{2-}] = K_{a2} / ([H^+] / [HCO_3^-]) =$$

$K_{a2} = 4.69 \times 10^{-11}$ both can be neglected.)

$$[H^+][HCO_3^-] / [\text{CO}_2(\text{aq})] = K_{a1} K_{\text{H}_2\text{CO}_3} = (2.23 \times 10^{-4}) (2.00 \times 10^{-3}) = 4.46 \times 10^{-7}$$

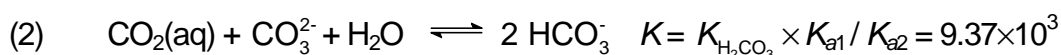
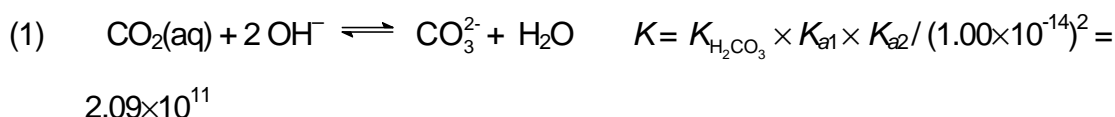
From 6.2: $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$

$[\text{H}^+] = [\text{HCO}_3^-] = 2.225 \times 10^{-6}$

Solubility = $[\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] = 1.11 \times 10^{-5} + 2.225 \times 10^{-6} = 1.34 \times 10^{-5}$

6.4 (Using $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$ for calculation)

In $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ NaOH solution the solubility of CO_2 will be much higher because of the following reactions:



Combining (1) and (2): $\text{CO}_2(\text{aq}) + \text{OH}^- \rightleftharpoons \text{HCO}_3^- \quad K = 4.43 \times 10^7$

With such a large K value all OH^- will finally be converted to HCO_3^- .

$$[\text{HCO}_3^-] = 1.00 \times 10^{-3}$$

$$[\text{OH}^-] = 1.82 \times 10^{-6}$$

$$[\text{H}^+] = 5.49 \times 10^{-9} \quad [\text{CO}_3^{2-}] = 8.54 \times 10^{-6}$$

$$\begin{aligned} \text{Solubility} &= [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \approx [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = \\ &= 1.24 \times 10^{-5} + 1.00 \times 10^{-3} + 8.54 \times 10^{-6} = 1.02 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} \mathbf{6.5} \quad K_{\text{eq}} &= K_{\text{sp}} \times K_{\text{H}_2\text{CO}_3} \times K_{\text{a1}} / K_{\text{a2}} = (4.50 \times 10^{-9}) \times (2.00 \times 10^{-3}) \times (2.23 \times 10^{-4}) / (4.69 \times 10^{-11}) = \\ &= 4.28 \times 10^{-5} \end{aligned}$$

(If you are unable to solve this problem, assume that $K_{\text{eq}} = 5.00 \times 10^{-5}$ for further calculations.)

6.6

(a) (Using $K_{\text{eq}} = 4.28 \times 10^{-5}$ and $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$ for calculation)

$$\text{Mass balance : } [\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$$

$$\text{From 6.5: } K = 4.28 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-] / [\text{CO}_2(\text{aq})] = [\text{Ca}^{2+}] (2 [\text{Ca}^{2+}])^2 / [\text{CO}_2(\text{aq})]$$

$$\text{From 6.2: } [\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$$

$$[\text{Ca}^{2+}] = 0.510 \times 10^{-3} = 20.5 \text{ mg dm}^{-3}$$

- (b) (Using
- $K_{\text{eq}} = 5.00 \times 10^{-5}$
- and
- $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$
- for calculation)

Mass balance : $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

From **6.5**: $K = 5.00 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_2(\text{aq})] = [\text{Ca}^{2+}] (2 [\text{Ca}^{2+}])^2 / [\text{CO}_2(\text{aq})]$

From **6.2**: $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$

$[\text{Ca}^{2+}] =$

$0.5177 \times 10^{-3} = 20.75 \text{ mg dm}^{-3}$

- (c) (Using
- $K_{\text{eq}} = 5.00 \times 10^{-5}$
- and
- $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$
- for calculation)

Mass balance : $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

From **6.5**: $K = 5.00 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_2(\text{aq})] = [\text{Ca}^{2+}] (2 [\text{Ca}^{2+}])^2 / [\text{CO}_2(\text{aq})]$

From **6.2**: $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$

$[\text{Ca}^{2+}] =$

$0.5372 \times 10^{-3} = 21.53 \text{ mg dm}^{-3}$

- (d) (Using
- $K_{\text{eq}} = 4.28 \times 10^{-5}$
- and
- $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$
- for calculation)

Mass balance : $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

From **6.5**: $K = 4.28 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_2(\text{aq})] = [\text{Ca}^{2+}] (2 [\text{Ca}^{2+}])^2 / [\text{CO}_2(\text{aq})]$

From **6.2**: $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$

$[\text{Ca}^{2+}] =$

$0.4916 \times 10^{-3} = 19.70 \text{ mg dm}^{-3}$

(If you are unable to solve this problem, assume that $[\text{Ca}^{2+}]_{(\text{aq})} = 40.1$ for further calculations.)

6.7 HCO_3^- is the major species in solution.

The pH of the solution can be estimated as $pH = (pK_{a1} + pK_{a2})/2 = (3.65 + 10.33) / 2 = 6.99 \approx 7.00$,

where K_{a1} and K_{a2} are the dissociation constants of H_2CO_3 .

At pH 7.00, both $[\text{OH}^-]$ and $[\text{H}^+]$ can be neglected. Besides, $[\text{CO}_3^{2-}] \ll [\text{HCO}_3^-]$

(from **6.1**)

$$\text{Alkalinity} = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \approx [\text{HCO}_3^-]$$

From 6-6, mass balance, $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

- (a) 1.02×10^{-3} (using $[\text{Ca}^{2+}]_{(\text{aq})}$ from 6.6 (a))
- (b) 1.035×10^{-3} (using $[\text{Ca}^{2+}]_{(\text{aq})}$ from 6.6 (b))
- (c) 1.0744×10^{-3} (using $[\text{Ca}^{2+}]_{(\text{aq})}$ from 6-6 (c))
- (d) 0.9831×10^{-3} (using $[\text{Ca}^{2+}]_{(\text{aq})}$ from 6-6 (d))
- (e) 2.00×10^{-3} (assuming $[\text{Ca}^{2+}]_{(\text{aq})} = 40.1$)

Alkalinity = (a) or (b) or (c) or (d) or (e)

6.8

- (a) (Using $K_{\text{eq}} = 4.28 \times 10^{-5}$ for calculation)

Mass balance : $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

$[\text{Ca}^{2+}] = 100 \text{ mg dm}^{-3} = 2.50 \times 10^{-3} \text{ mol dm}^{-3}$

Inserting into $K_{\text{eq}} = 4.28 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_2(\text{aq})] = 4 [\text{Ca}^{2+}]^3 / [\text{CO}_2(\text{aq})]$

$[\text{CO}_2(\text{aq})] = 1.46 \times 10^{-3}$

$p_{\text{CO}_2} = ([\text{CO}_2(\text{aq})] / K_{\text{CO}_2}) \times 1.01 \times 10^5 \text{ Pa} = 4.28 \times 10^3 \text{ Pa}$

- (b) (Using $K_{\text{eq}} = 5.00 \times 10^{-5}$ for calculation)

Mass balance : $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

$[\text{Ca}^{2+}] = 100 \text{ mg dm}^{-3} = 2.50 \times 10^{-3} \text{ mol dm}^{-3}$

Inserting into $K_{\text{eq}} = 5.00 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_2(\text{aq})] = 4 [\text{Ca}^{2+}]^3 / [\text{CO}_2(\text{aq})]$

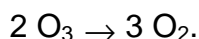
$[\text{CO}_2(\text{aq})] = 1.25 \times 10^{-3}$

$p_{\text{CO}_2} = ([\text{CO}_2(\text{aq})] / K_{\text{CO}_2}) \times 1.01 \times 10^5 \text{ Pa} = 3.67 \times 10^3 \text{ Pa}$

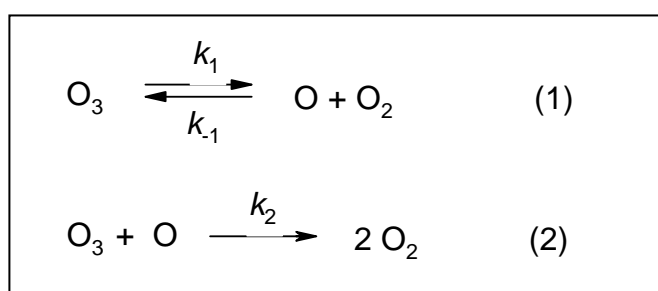
PROBLEM 7**Kinetic Behaviour of Ozone**

Ozone (O_3) is a form of oxygen. It is a natural component of the stratosphere, where it shields the earth from life-destroying ultraviolet radiation. On absorbing light in this region, ozone is converted to dioxygen molecules.

For the overall reaction of ozone decomposition,



One of the proposed mechanisms is expressed as



where k_1 , k_{-1} , and k_2 are the rate constants.

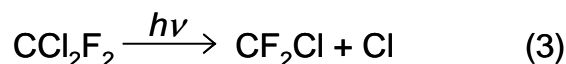
7.1 According to the above mechanism what are the differential rate equations for the formation (or consumption) of O_3 , O_2 , and O at time t , assuming step 2 is irreversible.

7.2 Simplification in obtaining the rate law may be found by making appropriate assumptions. Assuming that the concentration of O atoms reaches equilibrium rapidly, its concentration may be given by the equilibrium constant of the reaction (1). The second step is rate determining. Under this equilibrium approximation, deduce the differential rate equation for the O_3 depletion as a function of O_2 and O_3 concentrations.

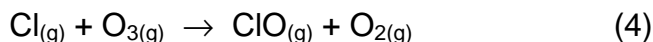
7.3 Another assumption frequently made is that the rates of oxygen atom production and consumption are equal (this is called steady state). Under the steady state approximation, that is $d[O]/dt = 0$, show that the rate equation is:

$$-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]}.$$

One pathway for the destruction of ozone ($2O_3 \rightarrow 3O_2$) in the upper atmosphere is catalyzed by Freons. For instance, when CCl_2F_2 (Freon-12) migrates to the upper atmosphere, the ultraviolet photolysis of CCl_2F_2 may give rise to Cl atoms according to the following reaction:



7.4 Chlorine atom can act as a catalyst for the destruction of ozone. The first slow step of a Cl-catalyzed mechanism is proposed as follows:



Assuming a two-step mechanism, propose the second step in the mechanism.

7.5 The activation energy for Cl-catalyzed destruction of ozone is 2.1 kJ mol^{-1} , while the activation energy for the reaction without the presence of catalyst is 14.0 kJ mol^{-1} . Estimate the ratio of the rate constant for the catalyzed reaction to that for the uncatalyzed reaction at 25°C . Assume the frequency factor is the same for each reaction.

SOLUTION

$$\begin{aligned} 7.1 \quad -\frac{d[\text{O}_3]}{dt} &= k_1 [\text{O}_3] - k_{-1} [\text{O}][\text{O}_2] + k_2 [\text{O}_3][\text{O}] \\ -\frac{d[\text{O}_2]}{dt} &= -k_1 [\text{O}_3] + k_{-1} [\text{O}][\text{O}_2] - 2k_2 [\text{O}_3][\text{O}] \\ -\frac{d[\text{O}]}{dt} &= -k_1 [\text{O}_3] + k_{-1} [\text{O}][\text{O}_2] + k_2 [\text{O}_3][\text{O}] \end{aligned}$$

7.2 Equilibrium constant K is expressed as

$$K = \frac{[\text{O}][\text{O}_2]}{[\text{O}_3]} = \frac{k_1}{k_{-1}}$$

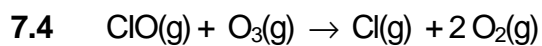
$$[\text{O}] = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]}$$

$$-\frac{d[\text{O}_3]}{dt} = k_2[\text{O}_3][\text{O}] = \frac{k_1 k_2 [\text{O}_3]^2}{k_{-1} [\text{O}_2]}$$

$$7.3 \quad -\frac{d[\text{O}]}{dt} = 0$$

$$-k_1 [\text{O}_3] + k_1 [\text{O}][\text{O}_2] + k_2 [\text{O}_3][\text{O}] = 0$$

$$\text{Thus } -\frac{d[\text{O}_3]}{dt} = 2k_2 [\text{O}_3][\text{O}] = \frac{2k_1 k_2 [\text{O}_3]^2}{k_{-1} [\text{O}_2] + k_2 [\text{O}_3]}$$



7.5 According to equation $k = A \exp(-E_a/RT)$,
the ratio of rate constants yields

$$\text{Ratio} = \exp[(14.0 - 2.1) \times 1000 / (8.314 \times 298)] = 122.$$

PROBLEM 8

Protein Folding

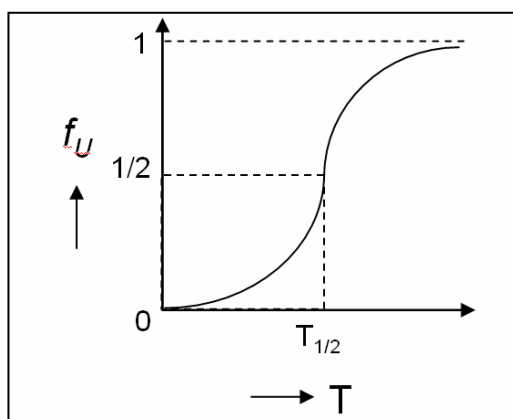
Most proteins exist usually only in two forms, the native form (N) and the unfolded form (U) when they are thermally or chemically denatured, without appreciable concentrations of other stable intermediates in equilibrium with the native and unfolded forms. For these proteins, the folding-unfolding equilibrium can be described by the following simple chemical equation:



where N and U denote the folded state (native state) and the unfolded state (denatured state) of the protein, respectively. $K(T)$ is the equilibrium constant for the process at absolute temperature T .

- 8.1** What is the equilibrium constant for the process when the native and denatured states are present in equal proportions at equilibrium?
- 8.2** What is the standard free energy change of the process ($\Delta G^\circ(T)$) when the native and denatured states are present in equal proportions at equilibrium? Express your answer in SI units.
- 8.3** If $(C_N)_{\text{eq}}$ and $(C_U)_{\text{eq}}$ denote the equilibrium concentrations of N and U in solution, respectively, and C is the total concentration of the protein, the fraction of the total protein that is unfolded under the equilibrium condition is given by $f_U = (C_U)_{\text{eq}}/C$. Deduce an expression for f_U in terms of the equilibrium constant K . Show all work on the answer sheet.

When a protein is denatured by increasing the temperature of the solution, the fraction of the unfolded protein increases with temperature, as shown in the following Figure.



The mid-point of the denaturation curve is given by $f_U = \frac{1}{2}$ and $T = T_{\frac{1}{2}}$. The latter is often referred to as the denaturation temperature. At temperatures higher than $T_{\frac{1}{2}}$, f_U increases above $\frac{1}{2}$, but at temperatures lower than $T_{\frac{1}{2}}$, f_U decreases below $\frac{1}{2}$.

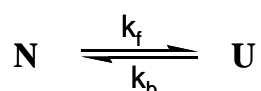
8.4 What is the sign of $\Delta G^\circ(T)$ at temperatures below and above $T_{\frac{1}{2}}$? Select your answer from the following choices.

- Negative both below and above $T_{\frac{1}{2}}$.
- Positive both below and above $T_{\frac{1}{2}}$.
- Positive below $T_{\frac{1}{2}}$, but negative above $T_{\frac{1}{2}}$.
- Negative below $T_{\frac{1}{2}}$, but positive above $T_{\frac{1}{2}}$.

8.5 How does the standard Gibbs free energy change for the process vary when the temperature (i) increases above $T_{\frac{1}{2}}$ and (ii) decreases below $T_{\frac{1}{2}}$? Select your answer from the following choices.

- Decrease in both cases.
- Increase in both cases.
- Increases above $T_{\frac{1}{2}}$, but decreases below $T_{\frac{1}{2}}$.
- Decreases above $T_{\frac{1}{2}}$, but increases below $T_{\frac{1}{2}}$.

The kinetics of unfolding and refolding of a protein has recently become an intense area of study. We could rewrite the chemical equation for the process as follows:



where k_f and k_b denote the forward and backward reaction rate constants, respectively., assuming that both the forward and reverse processes are elementary steps that follow first-order kinetics.

8.6 For the simple chemical equation and elementary kinetic steps used to describe the protein folding-unfolding process outlined above, what is the relationship between equilibrium constant K and the rate constants k_f and k_b ?

8.7 Derive a rate law for the overall process, that is dC_U/dt in terms of only rate constants, C_U and $(C_U)_{\text{eq}}$.

SOLUTION

8.1 Answer: 1

8.2 Answer: 0 kJ mol⁻¹

$$8.3 \quad f_U = \frac{C_U^{\text{eq}}}{C_N^{\text{eq}} + C_U^{\text{eq}}} = \frac{\frac{C_U^{\text{eq}}}{C_N^{\text{eq}}}}{1 + \frac{C_U^{\text{eq}}}{C_N^{\text{eq}}}} = \frac{K}{1 + K}$$

8.4 Correct answer is (c). Positive below $T_{1/2}$, but negative above $T_{1/2}$ 8.5 Correct answer is (d). Decreases above $T_{1/2}$, but increases below $T_{1/2}$.8.6 Answer: $K = k_f / k_b$

$$8.7 \quad \begin{aligned} dC_U/dt &= k_f C_N - k_b C_U \\ &= k_f (C - C_U) - k_b C_U = k_f C - k_f C_U - k_b C_U = k_f C - (k_f + k_b) C_U \end{aligned} \quad (1)$$

$$K = k_f / k_b = (C_U)_{\text{eq}} / (C_N)_{\text{eq}}$$

$$1 / K = k_b / k_f = (C_N)_{\text{eq}} / (C_U)_{\text{eq}}$$

$$\Rightarrow k_b / k_f + 1 = (C_N)_{\text{eq}} / (C_U)_{\text{eq}} + 1$$

$$\Rightarrow (k_b + k_f) / k_f = [(C_N)_{\text{eq}} + (C_U)_{\text{eq}}] / (C_U)_{\text{eq}}$$

$$\Rightarrow (k_b + k_f) / k_f = C / (C_U)_{\text{eq}}$$

$$C = [(k_b + k_f) (C_U)_{\text{eq}}] / k_f \quad (2)$$

Now substitute C obtained from eq (2) to eq (1).

$$\text{We get } k_f \{ [(k_b + k_f) (C_U)_{\text{eq}}] / k_f \} - (k_f + k_b) C_U$$

$$\Rightarrow [(k_b + k_f) (C_U)_{\text{eq}}] - (k_f + k_b) C_U$$

$$\Rightarrow - (k_f + k_b) [C_U - (C_U)_{\text{eq}}]$$

So we get

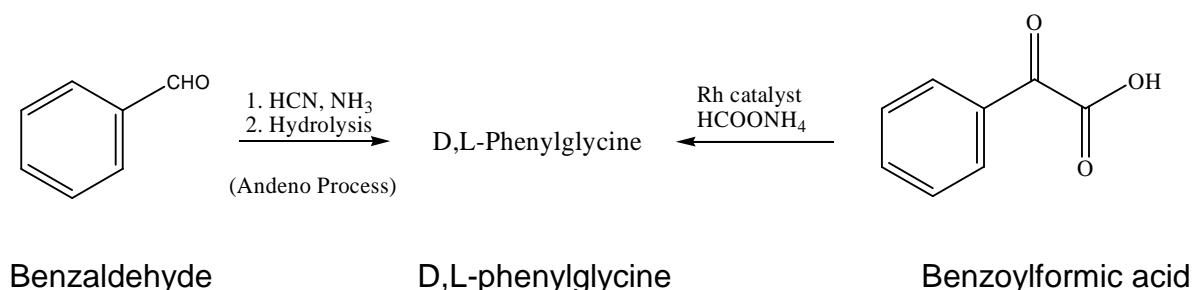
$$dC_U/dt = - (k_f + k_b) [C_U - (C_U)_{\text{eq}}]$$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

The Synthesis of D,L-Phenylglycine and Its Enantiomeric Resolution

One of the enantiomeric forms of phenylglycine is an important raw material for the preparation of β -lactam antibiotics. Industrial production of optically active phenylglycine is prepared by the Andeno process. The starting benzaldehyde was treated with HCN/NH₃ following hydrolysis to give the racemic D,L-phenylglycine. The desired enantiomeric phenylglycine was then resolved by (+)-camphorsulfonic acid [(+)-CSA].



In this experiment, you are going to synthesize racemic D,L-phenylglycine (also referred to as *R*- and *S*-isomers, respectively) from an alternative method called reductive amination. Treatment of benzoylformic acid under Rh metal catalyzed conditions gives D,L-phenylglycine. The racemic D,L-phenylglycine is resolved by the treatment of (+)-CSA in water. The solubility of D-phenylglycine•(+)-CSA salt is 5.75 g/100g H₂O, while that of L-phenylglycine•(+)-CSA salt is >150 g/100g H₂O at 25 °C. The chemical yield and the optical purity of the diastereomeric salt will be measured.

EXPERIMENTAL PROCEDURE

Step 1. Preparation of D,L-phenylglycine

The following pre-weighted chemicals can be used directly without further weighing: Benzoylformic Acid; Ammonium Formate; Rh Catalyst; (+)-camphorsulfonic acid [(+)-CSA].

- To a 50 mL round-bottomed flask is added a magnetic stirring bar, pre-weighed (approximate 1.80 g, exact mass will be on your sample bottle, write down the mass

on your answer sheet and get the lab assistant to confirm the weight.) of benzoylformic acid (NOTE: irritant, do not contact with skin), 7.57 g of ammonium formate (HCO_2NH_4), 37.2 mg of Rh catalyst (NOTE: the catalyst is wrapped in a weighing paper in a plastic bag. Handle with care!) and 22 cm^3 of the pre-mixed solvents at ambient temperature.

- Put a reflux condenser (use the Teflon sleeve; you can trim off 1 cm from the smaller end for a better fit) into the neck of the flask and plug the condenser with a septum. For pressure equilibration, put a needle in the septum before starting the heating. Clamp the apparatus tightly to the stand in your hot plate/stirrer. Put the flask onto a hot water bath [hot water provided by the organizer] and stir the reaction mixture gently. (NOTE: the solvent is air cooled, so there is no tap water running through the condenser.) The temperature of the water bath needs to be maintained in the range of 68 to 72 °C by adjusting the thermostat of the hot plate/stirrer.
- The mixture will become cloudy and the color of the solution will change from clear yellowish to dark-greenish when the product starts to precipitate (generally requiring 25 ~ 35 minutes). The hot water bath should then be removed and the solution allowed to stir in the water bath (ambient temperature) for an additional 10 minutes.
- Add 15 cm^3 of deionized water to the resulting mixture and stir for 10 minutes.
- Pre-weigh the bigger fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Use the stir bar retriever to remove the stir bar. Collect the product by filter suction through a fritted glass funnel under a reduced pressure (rotary aspirator apparatus). Wash the solid four times thoroughly with ethanol (10 cm^3 each). For each washing, **break the aspirator pressure**, use a glass rod to perturb the solid when adding ethanol, and reapply the rotary aspirator.
- For rapid drying, you have to spread the product over the fritted glass funnel. For drying, give the fritted glass funnel to the lab assistant. The product is dried in the oven at 100 °C for 1.5 hour.

During the drying period you can start working on Experiment 2 (analytical experiment) and you will be notified when your product is ready. Step 2 of experiment 1 will need at least 1 hour.

- Weigh the dried product [(D,L)-phenylglycine], record the data and calculate the chemical yield (based on the starting benzoylformic acid). Get the lab assistant to confirm the weight. The purity of the product will be determined by ^1H NMR spectrum

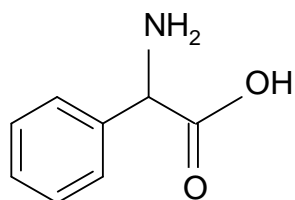
analysis. Turn in the product in a vial (**blue label** with ^1H NMR and your student code) to the lab assistant, and receive a new batch of D,L-phenylglycine for step 2.

Step 2. Enantiomeric Resolution of D,L-phenylglycine by (+)-Camphorsulfonic Acid [(+)-CSA]

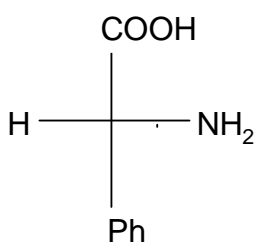
1. To a 25 cm³ round-bottomed flask add the pre-weighed sample of D,L-phenylglycine provided (The exact mass will be on your sample bottle, write down the mass on your answer sheet and get the lab assistant to confirm the weight). To this, add the pre-weighed (+)-camphorsulfonic acid [(+)-CSA] (1.80 g). Clamp the apparatus tightly to a stand in a magnetic stirrer. Add deionized water (4 cm³) and place the flask in a hot water bath and heat it to a temperature in the range of 90 ~ 100 °C. Keep the mixture at this temperature for 10 minutes until it turns clear.
2. Remove the hot water bath and allow the mixture to cool down to ambient temperature for 10~15 minutes. With the flask plugged with a septum, cool the flask in ice bath (Styroform) for 15 minutes. Crystals should appear in about 20 minutes, if not, you may ask for seed crystals to induce the crystallization.
3. Pre-weigh the smaller fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Collect the product by filtering the solution through a fritted glass funnel under a reduced pressure. Wash the solid thoroughly two times with ice cooled distilled water (5 cm³ each).
4. For drying, give the fritted glass funnel to the lab assistant. The product will be dried over in oven at 100 °C for 20 min. You will be notified when your product is ready. Weigh the product, and get the lab assistant to confirm the weight. Record the data and calculate the chemical yield (based on starting D,L-phenylglycine).
5. The optical purity of the diastereomeric salt will be measured using an accurate polarimeter apparatus by the examination committee. Transfer the dried product to a sample vial (pink label labelled with $[\alpha]_D$ and your student code) and give the sample vial to the lab assistant. The organization committee will weigh an appropriate amount of the product (0.055 ~ 0.065g) for measurement of optical purity.

SOLUTION

1.4 Structural formula (A) and stereochemical formula (B) of the isolated phenylglycine:
(Task appeared in the answer sheet only.)



A



B

PROBLEM 2 (Practical)**Identification of Unknown Inorganic Samples**

Note

- (1) This practical exercise is a kind of "spot test". You can do it on the pallet or on a sheet of black film (for white precipitate).
- (2) Please check all items written in the equipment and reagent list.
- (3) Please check carefully the code number of the unknown sample with the Check List accompanied with your unknown samples.
- (4) The volume of each unknown solution is about 1.5 cm^3 (about 30 drops). No more reagents or samples will be provided.
- (5) Be sure to confirm your results before writing your answers in the blanks of the Answer Sheet.
- (6) Make sure the switch on the battery box is closed.
- (7) You will get 8 points for each correct identification.

Introduction

There are 12 unknown samples in your plastic bag: 9 unknown solutions are in droppers and 3 unknown solids are in vials. All unknown samples are numbered with a 3 digit code. Please check the number with the List of Unknown Inorganic Samples carefully, then write your student code, and name on the list. (The list is accompanied with your unknown samples) Each vial contains about 20 mg of crystals or powder of one pure compound. Each dropper contains about 1.5 cm^3 solution of one pure compound dissolved in distilled water. The concentration of unknown solutions is in the range of 0.05 to 0.5 M (mol dm^{-3}).

The unknown samples are as follows:

HCl	H_2O_2	H_2SO_4	ZnCl_2	NH_4SCN
NaOH	Na_2CO_3	Na_2SO_3	BaCl_2	$\text{K}_4\text{Fe}(\text{CN})$

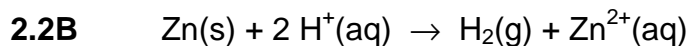
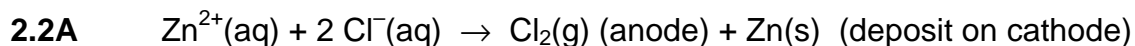
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Note

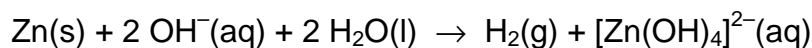
- 1) Two unknown samples are duplicates.

- 2) The crystal water (. H₂O) is omitted in the formulas listed above.
- 2.1** Use the four reagents provided and mutual reactions among the unknown samples, and the simple electrolysis apparatus to identify each unknown sample, and write your answer (3 digit code) in the blanks of your answer sheet.
- 2.2** In this practical work, you have performed a series of tests to identify (or confirm) the unknowns. Show the reactions involved by way of chemical equations.
- A. Write the electrolysis equation that would help you confirm that an unknown sample is ZnCl₂.
- B. Write one equation that shows how to clean the deposit of Zn on the electrode (limited to the items provided in this task).
-

SOLUTION



or



38th



International Chemistry Olympiad

**11 theoretical problems
3 practical problems**

THE THIRTY-EIGHTH INTERNATIONAL CHEMISTRY OLYMPIAD 2-11 JULY 2006, GYEONGSAN, KOREA

THEORETICAL PROBLEMS

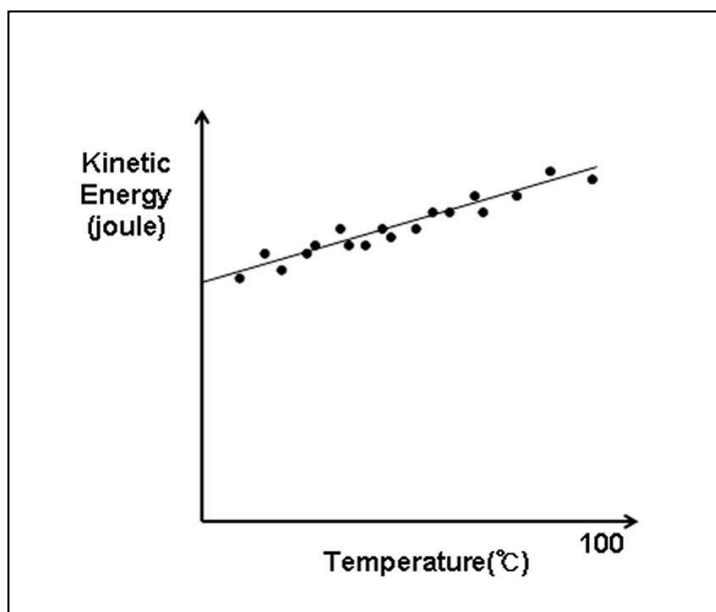
PROBLEM 1

Avogadro's number

Spherical water droplets are dispersed in argon gas. At 27 °C, each droplet is 1.0 micrometer in diameter and undergoes collisions with argon. Assume that inter-droplet collisions do not occur. The root-mean-square speed of these droplets was determined to be 0.50 cm s⁻¹ at 27 °C. The density of a water droplet is 1.0 g cm⁻³.

- 1.1 Calculate the average kinetic energy ($mv^2/2$) of this droplet at 27 °C. The volume of a sphere is given by $(4/3) \pi r^3$ where r is the radius.

If the temperature is changed, then droplet size and speed of the droplet will also change. The average kinetic energy of a droplet between 0 °C and 100 °C as a function of temperature is found to be linear. Assume that it remains linear below 0 °C.



At thermal equilibrium, the average kinetic energy is the same irrespective of particle masses (equipartition theorem).

The specific heat capacity, at constant volume, of argon (atomic weight, 40) gas is $0.31 \text{ J g}^{-1} \text{ K}^{-1}$.

1.2. Calculate Avogadro's number without using the ideal gas law, the gas constant, Boltzmann's constant).

SOLUTION

1.1 The mass of a water droplet:

$$m = V \rho = \left[\frac{4}{3} \pi r^3 \right] \rho = \frac{4}{3} \pi (0.5 \times 10^{-6} \text{ m})^3 (1.0 \text{ g cm}^{-3}) = 5.2 \times 10^{-16} \text{ kg}$$

Average kinetic energy at 27°C :

$$E_k = \frac{m v^2}{2} = \frac{(5.2 \times 10^{-16} \text{ kg}) \times (0.51 \times 10^{-2} \text{ m/s})^2}{2} = 6.9 \times 10^{-21} \text{ kg m}^2/\text{s}^2 = \underline{6.9 \times 10^{-21} \text{ J}}$$

1.2 The average kinetic energy of an argon atom is the same as that of a water droplet.

E_k becomes zero at -273°C .

From the linear relationship in the figure, $E_k = a T$ (absolute temperature) where a is the increase in kinetic energy of an argon atom per degree.

$$a = \frac{E_k}{T} = \frac{6.9 \times 10^{-21} \text{ J}}{(27 + 273) \text{ K}} = 2.3 \times 10^{-23} \text{ J K}^{-1}$$

S: specific heat of argon N : number of atoms in 1g of argon

$$S = 0.31 \text{ J g}^{-1} \text{ K}^{-1} = a \times N$$

$$N = \frac{S}{a} = \frac{0.31 \text{ J g}^{-1} \text{ K}^{-1}}{2.3 \times 10^{-23} \text{ J K}^{-1}} = 1.4 \times 10^{22} \text{ g}^{-1}$$

Avogadro's number (N_A): Number of argon atoms in 40 g of argon

$$N_A = 40 \text{ g mol}^{-1} \times 1.4 \times 10^{22} \text{ g}^{-1} = \underline{5.6 \times 10^{23} \text{ mol}^{-1}}$$

PROBLEM 2

Detection of hydrogen

Hydrogen is prevalent in the universe. Life in the universe is ultimately based on hydrogen.

- 2.1** There are about 1×10^{23} stars in the universe. Assume that they are like our sun (radius, 700,000 km; density, 1.4 g cm^{-3} ; 3/4 hydrogen and 1/4 helium by mass). Estimate the number of stellar protons in the universe to one significant figure.

In the 1920s Cecilia Payne discovered by spectral analysis of starlight that hydrogen is the most abundant element in most stars.

- 2.2** The electronic transition of a hydrogen atom is governed by $\Delta E(n_i \rightarrow n_f) = -C(1/n_f^2 - 1/n_i^2)$, where n is principle quantum number, and C is a constant. For detection of the $\Delta E(3 \rightarrow 2)$ transition (656.3 nm in the Balmer series), the electron in the ground state of the hydrogen atom needs to be excited first to the $n = 2$ state. Calculate the wavelength (in nm) of the absorption line in the starlight corresponding to the $\Delta E(1 \rightarrow 2)$ transition.
- 2.3** According to Wien's law, the wavelength (λ) corresponding to the maximum light intensity emitted from a blackbody at temperature T is given by $\lambda T = 2.9 \times 10^{-3} \text{ m K}$. Calculate the surface temperature of a star whose blackbody radiation has a peak intensity corresponding to the $n = 1 \rightarrow n = 2$ excitation of hydrogen.

The ground state of hydrogen is split into two hyperfine levels due to the interaction between the magnetic moment of the proton and that of the electron. In 1951, Purcell discovered a spectral line at 1420 MHz due to the hyperfine transition of hydrogen in interstellar space.

- 2.4** Hydrogen in interstellar space cannot be excited electronically by starlight. However, the cosmic background radiation, equivalent to 2.7 K, can cause the hyperfine transition. Calculate the temperature of a blackbody whose peak intensity corresponds to the 1420 MHz transition.
- 2.5** Wien generated hydrogen ions by discharge of hydrogen gas at a very low pressure and determined the e/m value, which turned out to be the highest among different

gases tested. In 1919, Rutherford bombarded nitrogen with alpha-particles and observed emission of a positively charged particle which turned out to be the hydrogen ion observed by Wien. Rutherford named this particle the "proton". Fill in the blank.

SOLUTION

$$2.1 \quad \text{Mass of a typical star} = (4/3) \times (3.1) \times (7 \times 10^8 \text{ m})^3 \times (1.4 \times 10^6 \text{ g m}^{-3}) = 2 \times 10^{33} \text{ g}$$

$$\text{Mass of protons of a typical star} = (2 \times 10^{33} \text{ g}) \times (3/4 + 1/8) = 1.8 \times 10^{33} \text{ g}$$

$$\text{Number of protons of a typical star} = (1.8 \times 10^{33} \text{ g}) \times (6 \times 10^{23} \text{ g}^{-1}) = 1 \times 10^{57}$$

$$\text{Number of stellar protons in the universe} = (1 \times 10^{57}) \times (10^{23}) = \underline{1 \times 10^{80}}$$

$$2.2 \quad \Delta E(2 \rightarrow 3) = C(1/4 - 1/9) = 0.1389 C \quad \lambda(2 \rightarrow 3) = 656.3 \text{ nm}$$

$$\Delta E(1 \rightarrow 2) = C(1/1 - 1/4) = 0.75 C$$

$$\lambda(1 \rightarrow 2) = (656.3) \times (0.1389 / 0.75) = 121.5 \text{ nm}$$

$$2.3 \quad T = 2.9 \times 10^{-3} \text{ m K} / 1.215 \times 10^{-7} \text{ m} = 2.4 \times 10^4 \text{ K}$$

$$2.4 \quad \lambda = 3 \times 10^8 \text{ m} / 1.42 \times 10^9 = 0.21 \text{ m}$$

$$T = 2.9 \times 10^{-3} \text{ m K} / 0.21 \text{ m} = 0.014 \text{ K}$$



PROBLEM 3**Interstellar chemistry**

Early interstellar chemistry is thought to have been a prelude to life on Earth. Molecules can be formed in space via heterogeneous reactions at the surface of dust particles, often called the interstellar ice grains (IIGs). Imagine the reaction between H and C atoms on the IIG surface that forms CH. The CH product can either be desorbed from the surface or further react through surface migration with adsorbed H atoms to form CH₂, CH₃, etc.

Depending on how energetically a molecule “jumps” from its anchored site, it either leaves the surface permanently (desorption) or returns to a new position at the surface (migration). The rates of desorption and migratory jump follow the Arrhenius formula, $k = A \exp(-E/RT)$, where k is the rate constant for desorption or migratory jump, A the jumping frequency, and E the activation energy for the respective event.

- 3.1** Desorption of CH from the IIG surface follows first-order kinetics. Calculate the average residence time of CH on the surface at 20 K. Assume that $A = 1 \times 10^{12} \text{ s}^{-1}$ and $E_{\text{des}} = 12 \text{ kJ mol}^{-1}$.
- 3.2** Consider the shortest time it would take for one CH unit to move from its initial position to the opposite side of an IIG by successive migratory jumps. Assume that the activation energy for migration (E_{mig}) is 6 kJ mol^{-1} , and the IIG is a sphere with a $0.1 \text{ }\mu\text{m}$ radius. Each migratory jump laterally advances the molecule by 0.3 nm . Show work and choose your answer from (a) – (e) below.
- (a) $t \leq 1 \text{ day}$ (b) $10 \text{ days} \leq t \leq 10^2 \text{ yr}$ (c) $10^3 \text{ yr} \leq t \leq 10^6 \text{ yr}$
 (d) $10^7 \text{ yr} \leq t \leq 10^{10} \text{ yr}$ (e) $t \geq 10^{11} \text{ yr}$
- 3.3** Consider the reaction of CO with H₂ to form H₂CO. The activation energy on a metal catalyst is 20 kJ mol^{-1} that is produced by formaldehyde at a rate of 1 molecule/s per site at 300 K. Estimate the rate of formaldehyde formation per site if the reaction takes place at 20 K.
- 3.4** Which is a set of all true statements? Circle one.

- (a) Most CH species are desorbed from the IIG surface before encountering other reactants by surface migration.

- (b) IIGs can assist transformation of simple molecules to more complex ones in interstellar space.
- (c) For a reaction on the IIG to occur at an appreciable speed during the age of the Universe (1×10^{10} yr), the reaction energy barrier must be absent or negligible.

(a) (b) (c) (a, b) (a, c) (b, c) (a, b, c)

SOLUTION

3.1 $k_{\text{des}} = A \exp(-E_{\text{des}}/RT) = (1 \times 10^{12} \text{ s}^{-1}) \times (5 \times 10^{-32}) = 5 \times 10^{-20} \text{ s}^{-1}$ at $T = 20 \text{ K}$
 surface residence time, $T_{\text{residence}} = 1 / k_{\text{des}} = 2 \times 10^{19} \text{ s} = \underline{6 \times 10^{11} \text{ yr}}$
 (full credit for $T_{\text{half-life}} = \ln 2 / k_{\text{des}} = 1 \times 10^{19} \text{ s} = 4 \times 10^{11} \text{ yr}$)
 residence time = $2 \times 10^{19} \text{ s}$

3.2 The distance to be traveled by a molecule: $x = \pi r = 300 \text{ nm}$.

$$k_{\text{mig}} = A \exp(-E_{\text{mig}}/RT) = (1 \times 10^{12} \text{ s}^{-1}) \times (2 \times 10^{-16}) = 2 \times 10^{-4} \text{ s}^{-1} \text{ at } T = 20 \text{ K}$$

Average time between migratory jumps, $T = 1 / k_{\text{mig}} = 5 \times 10^3 \text{ s}$

Time needed to move 300 nm = $(300 \text{ nm} / 0.3 \text{ nm}) \text{ jumps} \times (5 \times 10^3 \text{ s/jump}) =$
 $= 5 \times 10^6 \text{ s} = \underline{50 \text{ days}}$

The correct answer is (b).

(Full credit for the calculation using a random-walk model. In this case:

$$t = T(x/d)^2 = 5 \times 10^9 \text{ s} = 160 \text{ yr. The answer is still (b).)$$

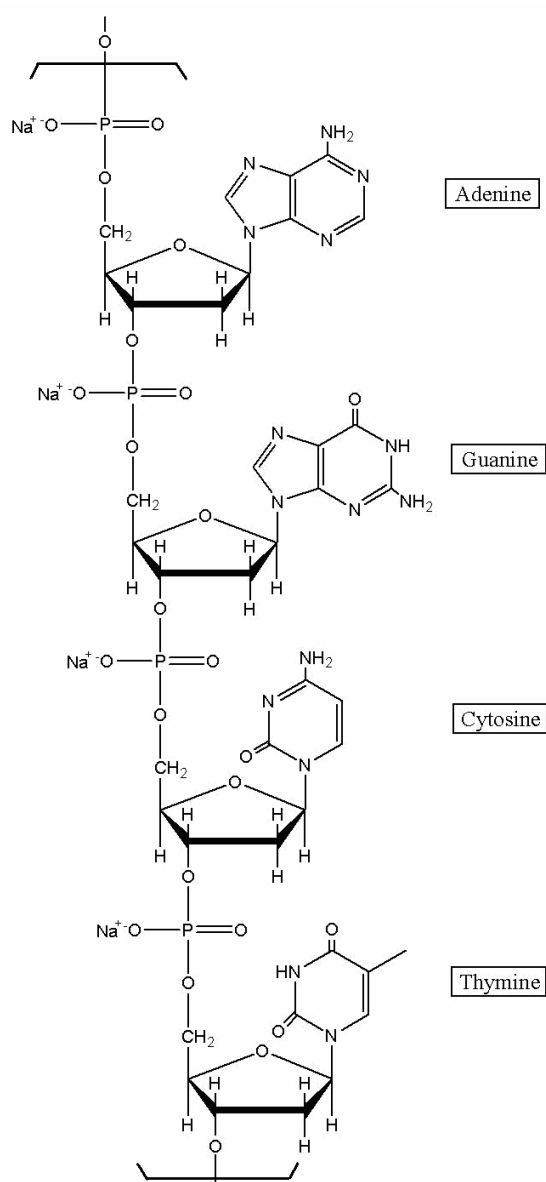
3.3 $k(20 \text{ K}) / k(300 \text{ K}) = \exp[(E/R)(1/T_1 - 1/T_2)] = e^{-112} = \sim 1 \times 10^{-49}$ for the given reaction
 The rate of formaldehyde production at 20 K = $\sim 1 \times 10^{-49}$ molecule/site/s =
 $= \sim 1 \times 10^{-42}$ molecule/site/yr

(The reaction will not occur at all during the age of the universe (1×10^{10} yr).)

3.4 The correct answer is (b, c).

PROBLEM 4**The Chemistry of DNA**

4.1 In 1944 Oswald Avery isolated a genetic material and showed by elemental analysis that it was a sodium salt of deoxyribonucleic acid. A segment of DNA with formula mass of 1323.72 is shown.



Assuming that equimolar amounts of the four bases are present in DNA, write the number of H atoms per P atom. Calculate (to 3 significant figures) the theoretical weight percentage of H expected upon elemental analysis of DNA.

4.2 Chargaff extracted the separated bases and determined their concentrations by measuring UV absorbance. The Beer-Lambert law was used to obtain the molar concentration. Chargaff discovered the following molar ratio for bases in DNA:

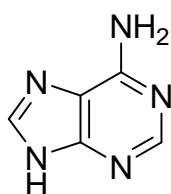
$$\begin{array}{ll} \text{adenine to guanine} = 1.43 & \text{thymine to cytosine} = 1.43 \\ \text{adenine to thymine} = 1.02 & \text{guanine to cytosine} = 1.02 \end{array}$$

Chargaff's discovery suggested that the bases might exist as pairs in DNA. Watson and Crick mentioned in their celebrated 1953 paper in *Nature*: "It has not escaped our notice that the specific pairing we have postulated immediately suggests a possible copying mechanism for the genetic material."

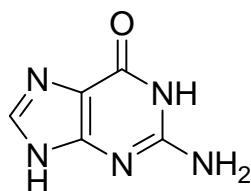
Draw structures of the specific pairing found in DNA. Indicate hydrogen bonds. Omit the sugar-phosphate backbone.

4.3 Mutation can occur through base pairings different from the above. Draw structures of any three alternative base pairs.

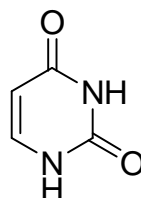
4.4 The plausibility of the formation of purine and pyrimidine bases in the prebiotic atmosphere of the Earth from HCN, NH₃, and H₂O has been demonstrated in the laboratory. Write the minimum number of HCN and H₂O molecules required for formation of the following compounds.



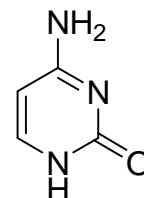
adenine



guanine



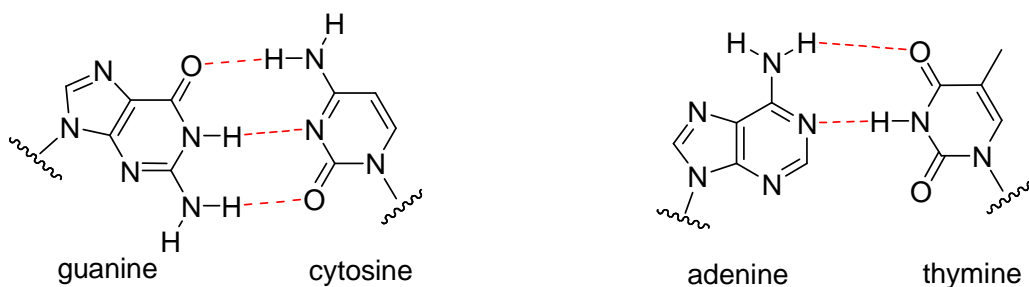
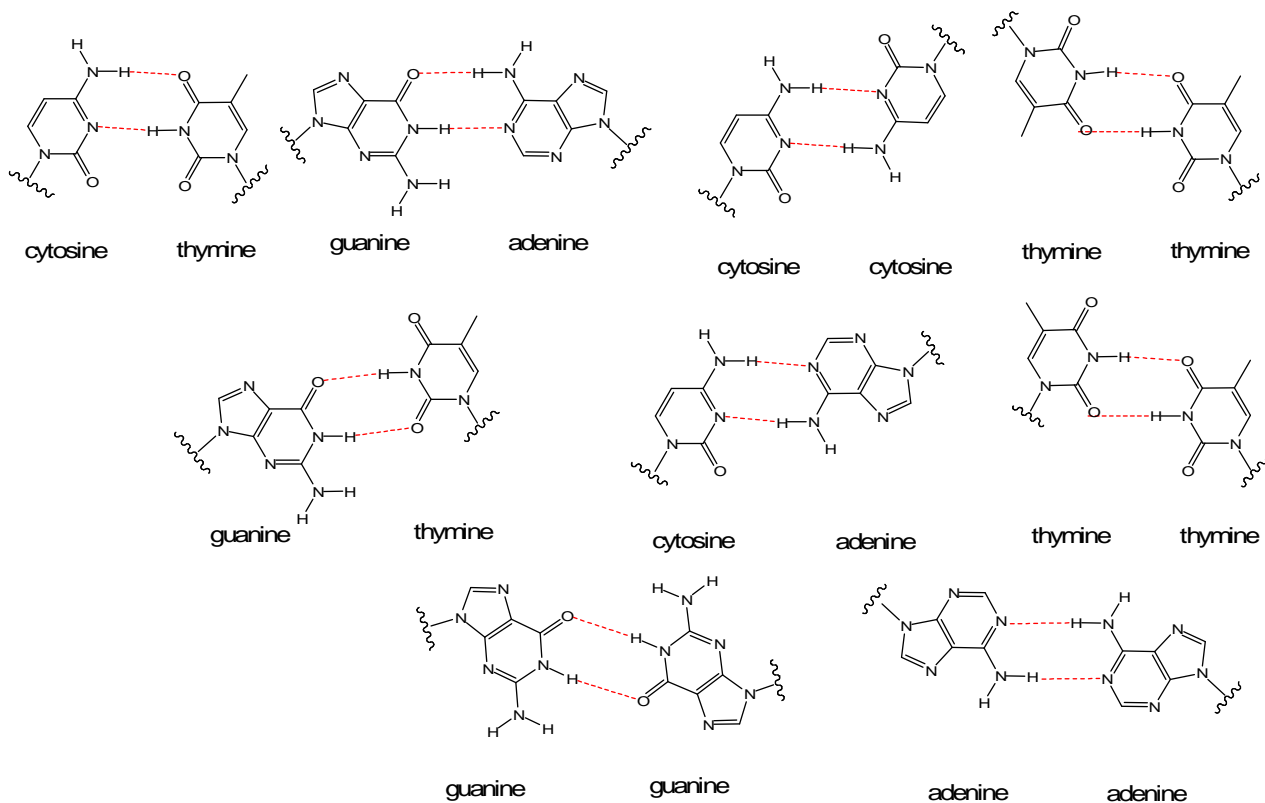
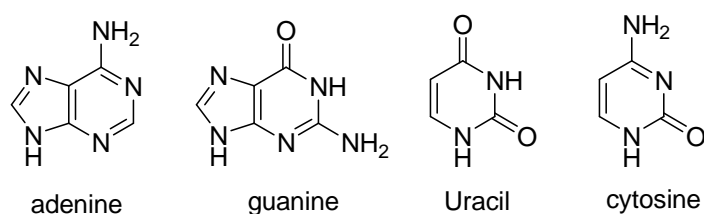
Uracil



cytosine

SOLUTION

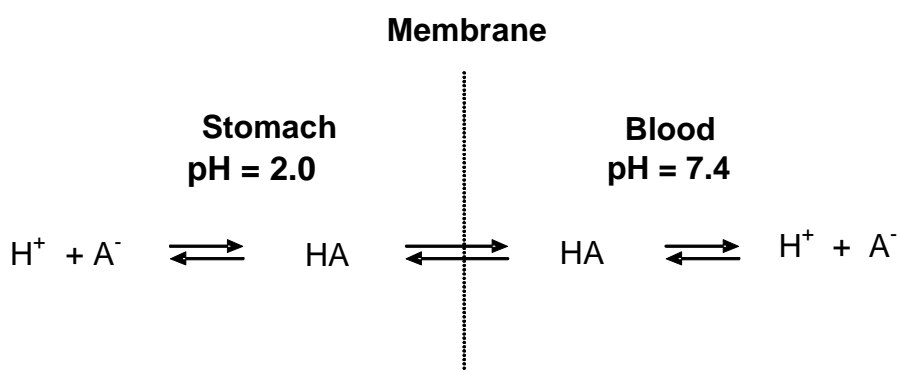
4.1	H	P
Number of atoms:	11.3	1
theoretical wt %:	3.43	

4.2

4.3

4.4


HCN	(5)	(5)	(4)	(4)
H ₂ O	(0)	(1)	(2)	(1)

PROBLEM 5**Acid-Base Chemistry**

- 5.1 Calculate $[H^+]$, $[OH^-]$, $[HSO_4^-]$, and $[SO_4^{2-}]$ in a 1.0×10^{-7} M solution of sulfuric acid ($K_w = 1.0 \times 10^{-14}$, $K_2 = 1.2 \times 10^{-2}$ at 25 °C). In your work you may use mass- and charge-balance equations. Answer with two significant figures.
- 5.2 Calculate the volume of 0.80 M NaOH solution that should be added to a 250 cm³ aqueous solution containing 3.48 cm³ of concentrated phosphoric acid in order to prepare a pH 7.4 buffer. Answer with three significant figures. (H_3PO_4 (aq), purity = 85 mass %, density = 1.69 g/cm³, $M_r = 98.00$) ($pK_1 = 2.15$, $pK_2 = 7.20$, $pK_3 = 12.44$).
- 5.3 The efficacy of a drug is greatly dependent on its ability to be absorbed into the blood stream. Acid-base chemistry plays an important role in drug absorption.



Assume that the ionic form (A^-) of a weakly acidic drug does not penetrate the membrane, whereas the neutral form (HA) freely crosses the membrane. Also assume that equilibrium is established so that the concentration of HA is the same on both sides. Calculate the ratio of the total concentration ($[HA] + [A^-]$) of aspirin (acetylsalicylic acid, $pK = 3.52$) in the blood to that in the stomach.

SOLUTION

- 5.1 1st ionization is complete: $H_2SO_4 \rightarrow H^+ + HSO_4^-$

$$[H_2SO_4] = 0$$

$$\text{2nd ionization: } [\text{H}^+][\text{SO}_4^{2-}] / [\text{HSO}_4^-] = K_2 = 1.2 \times 10^{-2} \quad (1)$$

$$\text{Mass balance: } [\text{H}_2\text{SO}_4] + [\text{HSO}_4^-] + [\text{SO}_4^{2-}] = 1.0 \times 10^{-7} \quad (2)$$

$$\text{Charge balance: } [\text{H}^+] = [\text{HSO}_4^-] + 2[\text{SO}_4^{2-}] + [\text{OH}^-] \quad (3)$$

Degree of ionization is increased upon dilution.

$$[\text{H}_2\text{SO}_4] = 0$$

$$\text{Assume } [\text{H}^+]_{\text{H}_2\text{SO}_4} = 2 \times 10^{-7}$$

$$\text{From (1): } [\text{SO}_4^{2-}] / [\text{HSO}_4^-] = 6 \times 10^4 \quad (\text{2nd ionization is almost complete})$$

$$[\text{HSO}_4^-] = 0$$

$$\text{From (2): } [\text{SO}_4^{2-}] = 1.0 \times 10^{-7}$$

$$\text{From (3): } [\text{H}^+] = (2 \times 10^{-7}) + 10^{-14} / [\text{H}^+]$$

$$[\text{H}^+] = 2.4 \times 10^{-7} \quad (\text{pH} = 6.6)$$

$$[\text{OH}^-] = 1 \times 10^{-14} / (2.4 \times 10^{-7}) = 4.1 \times 10^{-8}$$

From (1):

$$[\text{HSO}_4^-] = [\text{H}^+] [\text{SO}_4^{2-}] / K_2 = (2.4 \times 10^{-7}) \times (1.0 \times 10^{-7}) / (1.2 \times 10^{-2}) = 2.0 \times 10^{-12}$$

Check charge balance:

$$2.4 \times 10^{-7} \approx (2.0 \times 10^{-12}) + 2(1.0 \times 10^{-7}) + (4.1 \times 10^{-8})$$

Check mass balance:

$$0 + 2.0 \times 10^{-12} + 1.0 \times 10^{-7} \approx 1.0 \times 10^{-7}$$

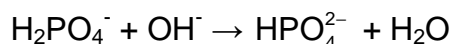
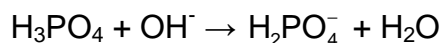
$$\mathbf{5.2} \quad n(\text{H}_3\text{PO}_4) = 0.85 \times 3.48 \text{ cm}^3 \times 1.69 \text{ g cm}^{-3} \times 1 \text{ mol} / 98.00 \text{ g} \times 1000 = 51.0 \text{ mmol}$$

The desired pH is above $\text{p}K_2$.

A 1:1 mixture of H_2PO_4^- and HPO_4^{2-} would have $\text{pH} = \text{p}K_2 = 7.20$.

If the pH is to be 7.40, there must be more HPO_4^{2-} than H_2PO_4^- .

We need to add NaOH to convert H_3PO_4 to H_2PO_4^- and to convert to the right amount of H_2PO_4^- to HPO_4^{2-} .



The volume of 0.80 NaOH needed to react with to convert H_3PO_4 to H_2PO_4^- is:
 $51.0 \text{ mmol} / 0.80 \text{ mol dm}^{-3} = 63.75 \text{ cm}^3$

To get pH of 7.40 we need:



Initial mmol	51.0	x	0
Final mmol	$51.0 - x$	0	x

$$pH = pK_2 + \log [\text{HPO}_4^{2-}] / [\text{H}_2\text{PO}_4^-]$$

$$7.40 = 7.20 + \log \{x / (51.0 - x)\}; \quad x = 31.27 \text{ mmol}$$

The volume of NaOH needed to convert 31.27 mmol is:

$$31.27 \text{ mmol} / 0.80 \text{ mol dm}^{-3} = 39.09 \text{ cm}^3$$

$$\text{The total volume of NaOH} = 63.75 + 39.09 = 102.84 \text{ cm}^3 \approx 103 \text{ cm}^3$$

5.3 $pK = 3.52$

$$pH = pK_a + \log ([A^-] / [HA])$$

$$[A^-] / [HA] = 10^{(pH - pK_a)}$$

$$\text{In blood, } pH = 7.40, \quad [A^-] / [HA] = 10^{(7.40 - 3.52)} = 7586$$

$$\text{Total ASA} = 7586 + 1 = 7587$$

$$\text{In stomach, } pH = 2.00, \quad [A^-] / [HA] = 10^{(2.00 - 3.52)} = 3.02 \times 10^{-2}$$

$$\text{Total ASA} = 1 + 3.02 \times 10^{-2} = 1.03$$

$$\text{Ratio of total aspirin in blood to that in stomach} = 7587 / 1.03 = 7400$$

PROBLEM 6**Electrochemistry**

Water is a very stable molecule, abundant on earth and essential for life. As such, water was long thought to be a chemical element. However, soon after the invention of a voltaic cell in 1800, Nicholson and Carlyle decomposed water into hydrogen and oxygen by electrolysis.

- 6.1** Water can be thought of as hydrogen oxidized by oxygen. Thus, hydrogen can be recovered by reduction of water, using an aqueous solution of sodium sulfate, at a platinum electrode connected to the negative terminal of a battery. The solution near the electrode becomes basic. Write a balanced half-reaction for the reduction of water.
- 6.2** Water can also be thought of as oxygen reduced by hydrogen. Thus, oxygen can be recovered by oxidation of water at the Pt electrode connected to the positive terminal. Write a balanced half-reaction for the oxidation of water.
- 6.3** When copper is used at both electrodes, gas is generated only at one electrode during the initial stage of electrolysis. Write the half-reaction at the electrode that does not generate gas.

Another species in solution that can be reduced is sodium ion. The reduction of sodium ion to metallic sodium does not occur in aqueous solution because water is reduced first. However, as Humphrey Davy discovered in 1807, sodium can be made by electrolysis of fused sodium chloride.

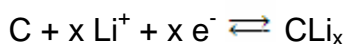
- 6.4** Based on these observations, connect the half-reactions with the standard reduction potential (in volts).

Reduction of copper ion (Cu^{2+})	+ 0.340
Reduction of oxygen	– 2.710
Reduction of water	– 0.830
Reduction of sodium ion (Na^+)	0.000
Reduction of hydrogen ion	+1.230

The electrode potential is affected by other reactions taking place around the electrode. The potential of the Cu^{2+}/Cu electrode in a 0.100 M Cu^{2+} solution changes as $\text{Cu}(\text{OH})_2$ precipitates. Answer with 3 significant figures for the following problems. The temperature is 25 °C. Note that $K_w = 1.00 \times 10^{-14}$ at 25 °C.

- 6.5 Precipitation of $\text{Cu}(\text{OH})_2$ begins at $\text{pH} = 4.84$. Determine the solubility product of $\text{Cu}(\text{OH})_2$.
- 6.6 Calculate the standard reduction potential for $\text{Cu}(\text{OH})_2(\text{s}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s}) + 2 \text{OH}^-$.
- 6.7 Calculate the electrode potential at $\text{pH} = 1.00$.

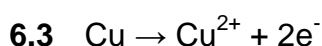
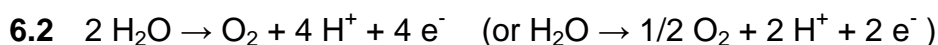
Lithium cobalt oxide and specialty carbon are active ingredients for the positive and negative electrodes, respectively, of a rechargeable lithium battery. During the charge/recharge cycles, the following reversible half-reactions occur.



The total amount of energy a battery can store, is rated in mAh. A battery rated at 1500 mAh can power a device drawing 100 milliamps for 15 hours.

- 6.8 Graphite has lithium intercalation sites between its layers. Assuming a maximum 6 : 1 carbon-to-lithium intercalation stoichiometry, calculate the theoretical charge capacity of 1.00 gram of graphite to intercalate lithium. Answer in mAh/g with 3 significant figures.

SOLUTION



- 6.4 Reduction of sodium ion seldom takes place.

It has a highly negative reduction potential of -2.710 V .

Reduction potential for water to hydrogen is negative (water is very stable).

But, it is not as negative as that for sodium ion. It is -0.830 V.

Reduction of both copper ion and oxygen takes place readily and the reduction potentials for both are positive.

In the present system, the reverse reaction (oxidation) takes place at the positive terminal. Copper is oxidized before water.

Reduction potential for hydrogen ion is defined as 0.000 V.

Reduction of oxygen	_____	-2.710
Reduction of water	_____	-0.830
Reduction of sodium ion (Na^+)	_____	0.000
Reduction of hydrogen ion	_____	+1.230

6.5 $pOH = 14.00 - 4.84 = 9.16$

$$[\text{OH}^-] = 6.92 \times 10^{-10}$$

$$K_{sp} = [\text{Cu}^{2+}] [\text{OH}^-]^2 = 0.100 \times (6.92 \times 10^{-10})^2 = 4.79 \times 10^{-20}$$

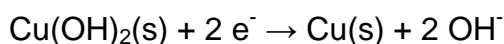
6.6 $E = E^\circ(\text{Cu}^{2+} / \text{Cu}) + (0.0592 / 2) \log [\text{Cu}^{2+}] = +0.340 + (0.0592/2) \log [\text{Cu}^{2+}] =$

$$= +0.340 + (0.0592 / 2) \log (K_{sp} / [\text{OH}^-]^2)$$

$$= +0.340 + (0.0592 / 2) \log K_{sp} - (0.0592 / 2) \log [\text{OH}^-]^2$$

$$= +0.340 + (0.0592 / 2) \log K_{sp} - 0.0592 \log [\text{OH}^-],$$

By definition, the standard potential for



is the potential where $[\text{OH}^-] = 1.00$.

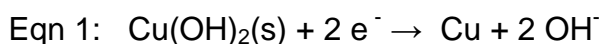
$$E = E^\circ(\text{Cu}(\text{OH})_2 / \text{Cu}) = +0.340 + (0.0592/2) \log K_{sp}$$

$$= +0.340 + (0.0592 / 2) \log (4.79 \times 10^{-20})$$

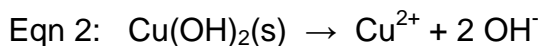
$$= +0.340 - 0.572$$

$$= -0.232 \text{ V}$$

One may solve this problem as follows.



$$E_+^{\circ} = E^{\circ}(\text{Cu(OH)}_2 / \text{Cu}) = ?$$



$$E^{\circ} = (0.05916 / n) \log K_{\text{sp}} = (0.05916 / 2) \log(4.79 \times 10^{-20}) = -0.5715 \text{ V}$$



$$E_-^{\circ} = E_+^{\circ} - E^{\circ} = E^{\circ}(\text{Cu}^{2+} / \text{Cu}) = 0.34 \text{ V}$$

$$\text{Therefore, } E_+^{\circ} = E_-^{\circ} + E^{\circ} = +0.34 + (-0.5715) = -0.232 \text{ V}$$

6.7 Below $pH = 4.84$, there is no effect of Cu(OH)_2 because of no precipitation.

Therefore,

$$\begin{aligned} E &= E(\text{Cu}^{2+} / \text{Cu}) = +0.340 + (0.0592 / 2) \log [\text{Cu}^{2+}] = \\ &= +0.340 + (0.0592 / 2) \log 0.100 = +0.340 - 0.0296 = +0.310 \text{ V} \end{aligned}$$

6.8 1.00 g graphite = 0.0833 mol carbon

6 mol carbon to 1 mol lithium; 1 g graphite can hold 0.0139 mol lithium

To insert 1 mol lithium, 96487 coulombs are needed.

Therefore, 1 g graphite can charge $96487 \times 0.0139 = 1340$ coulombs.

$$1340 \text{ coulombs} / \text{g} = 1340 \text{ A sec} / \text{g} = 1340 \times 1000 \text{ mA} \times (1 / 3600) \text{ h} =$$

$$= 372 \text{ mAh} / \text{g}$$

PROBLEM 7**Hydrogen Economy**

Hydrogen is more energy-dense than carbon, by mass. Thus, historically there has been a move toward fuel with higher hydrogen content: coal → oil → natural gas → hydrogen. Cost-effective production and safe storage of hydrogen are two major hurdles to the successful inauguration of a hydrogen economy.

7.1 Consider hydrogen in a cylinder of 80 MPa at 25 °C. Using the ideal gas law, estimate the density of hydrogen in the cylinder in kg m⁻³.

7.2 Calculate the ratio between heat generated when hydrogen is burned and heat generated when the same weight of carbon is burned. The difference comes to a large extent from the fact that the most abundant isotope of hydrogen has no neutron and hydrogen has no inner electron shell. $\Delta H_f^\circ [\text{H}_2\text{O}(\text{l})] = -286 \text{ kJ/mol}$, $\Delta H_f^\circ [\text{CO}_2(\text{g})] = -394 \text{ kJ/mol}$.

7.3 Calculate the theoretical maximum work produced by the combustion of 1 kg hydrogen (a) from the electric motor using hydrogen fuel cell and (b) from the heat engine working between 25 °C and 300 °C. The efficiency (work done/heat absorbed) of an ideal heat engine working between T_{cold} and T_{hot} is given by $[1 - T_{\text{cold}}/T_{\text{hot}}]$.

$$S_{298}^\circ[\text{H}_2(\text{g})] = 131 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S_{298}^\circ[\text{O}_2(\text{g})] = 205 \text{ J mol}^{-1} \text{ K}^{-1}$$

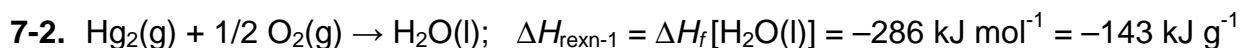
$$S_{298}^\circ[\text{H}_2\text{O}(\text{l})] = 70 \text{ J mol}^{-1} \text{ K}^{-1}$$

If the fuel cell is working at 1 W and the standard potential difference, how long will the electric motor run at what current?

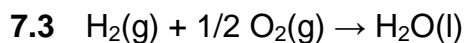
SOLUTION

$$7.1 \quad \frac{n}{V} = \frac{p}{RT} = \frac{80 \times 10^6 \text{ Pa}}{8,314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}} = 32 \text{ kmol m}^{-3}$$

$$\rho = \frac{m}{V} = 32 \text{ kmol m}^{-3} \times 2 \text{ kg kmol}^{-1} = 64 \text{ kg m}^{-3}$$



$$\frac{(-\Delta H_{\text{rexn-1}})}{(-\Delta H_{\text{rexn-2}})} = 4.3 \quad \text{or} \quad \frac{(-\Delta H_{\text{rexn-2}})}{(-\Delta H_{\text{rexn-1}})} = 0.23$$



$$\Delta H_c = -286 \text{ kJ mol}^{-1} = -143 \text{ kJ g}^{-1} = -143 \times 10^3 \text{ kJ kg}^{-1}$$

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

$$\Delta S_c = 70 - 131 - 205/2 = -163.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G_c = -286 \text{ kJ mol}^{-1} + 298 \text{ K} \times 163.5 \text{ J mol}^{-1} \text{ K}^{-1} = -237 \text{ kJ mol}^{-1} = -1.2 \times 10^5 \text{ kJ kg}^{-1}$$

(a) electric motor: $W_{\text{max}} = \Delta G_c \times 1 \text{ kg} = -1.2 \times 10^5 \text{ kJ}$

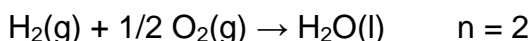
(b) heat engine: $W_{\text{max}} = \text{efficiency} \times \Delta H_c$
 $= (1 - 298 / 573) \times (-143 \times 10^3 \text{ kJ}) = -6.9 \times 10^4 \text{ kJ}$

$$119 \times 10^3 \text{ kJ} = 1 \text{ W} \times t(\text{sec})$$

$$t = 1.2 \times 10^8 \text{ s} = 3.3 \times 10^4 \text{ h} = 1.4 \times 10^3 \text{ days} = 46 \text{ month} = 3.8 \text{ yr}$$

$$\Delta G = -n F E \quad n = \text{number of electrons involved in the reaction}$$

$$F = 96.5 \text{ kC mol}^{-1}$$



$$E = \frac{-\Delta G}{nF} = \frac{237 \text{ kJ mol}^{-1}}{2 \times 96.5 \text{ kC mol}^{-1}} = 1.23 \text{ V}$$

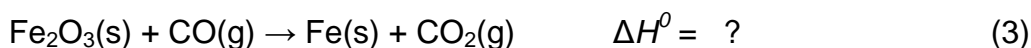
$$I = \frac{W}{E} = 0.81 \text{ A}$$

PROBLEM 8

Chemistry of Iron Oxides

The nucleus of iron is the most stable among all elements and, therefore, iron accumulates at the core of massive red giant stars where nucleosynthesis of many elements essential for life (such as C, N, O, P, S, etc.) takes place. As a result, among heavy elements iron is quite abundant in the universe. Iron is also abundant on Earth.

Development of a technology for reducing iron oxide to iron was a key step in human civilization. Key reactions taking place in the blast furnace are summarized below.

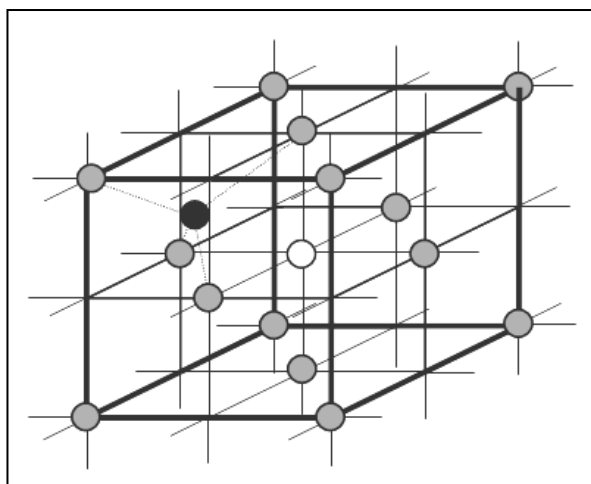


8.1 Indicate the reducing agent in each reaction.

8.2 Balance reaction (3) and calculate the equilibrium constant of reaction (3) at 1200 °C. $\Delta H_f^\circ(\text{Fe}_2\text{O}_3\text{(s)}) = -824.2 \text{ kJ mol}^{-1}$,
 $S^\circ(\text{J mol}^{-1} \text{ K}^{-1})$: Fe(s) = 27.28, Fe₂O₃(s) = 87.40, C(s) = 5.74, CO(g) = 197.674, CO₂(g) = 213.74

In the manufacture of celadon pottery, Fe₂O₃ is partially reduced in a charcoal kiln to mixed oxides of Fe₃O₄ and FeO. The amount of the different oxides seems to be related to the “mystic” color of celadon ceramics. Fe₃O₄ (magnetite) itself is a mixed oxide containing Fe²⁺ and Fe³⁺ ions and belongs to a group of compounds with a general formula of AB₂O₄. The oxide ions form a face-centered cubic array. The figure shows the array of oxygens (gray circles) and representative sites for divalent A and trivalent B cations. The dark circle represents a tetrahedral site and the white circle an octahedral site.





- 8.3** How many available octahedral sites for iron ions are there in one AB_2O_4 unit? Certain sites are shared by neighbouring units.

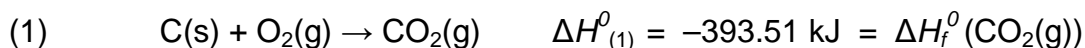
AB_2O_4 can adopt a normal- or an inverse-spinel structure. In normal-spinel structure, two B ions occupy two of the octahedral sites and one A occupies one of the tetrahedral sites. In an inverse-spinel structure, one of the two B ions occupies a tetrahedral site. The other B ion and the one A ion occupy octahedral sites.

- 8.4** What percentage of available tetrahedral sites is occupied by either Fe^{2+} or Fe^{3+} ion in Fe_3O_4 ?
- 8.5** Fe_3O_4 has an inverse-spinel structure. Draw the crystal field splitting pattern of Fe^{2+} and fill out the electrons. The electron pairing energy is greater than the octahedral field splitting.

SOLUTION

- 8.1** (1): C (2): C (3): CO

- 8.2** Balanced equation (3): $Fe_2O_3(s) + 3 CO(g) \rightarrow 2 Fe(s) + 3 CO_2(g)$



From (1) and (2):

$$\Delta H_f^{\circ}(CO(g)) = (1/2) \{172.46 + (-393.51)\} = -110.525 \text{ kJ}$$

$$\Delta H_f^0(\text{Fe}_2\text{O}_3) = -824.2 \text{ kJ}$$

$$\begin{aligned} \Delta H_{(3)}^0 &= 3 \times \Delta H_f^0(\text{CO}_2(\text{g})) - \Delta H_f^0(\text{Fe}_2\text{O}_3) - 3 \times \Delta H_f^0(\text{CO}(\text{g})) \\ &= [3 \times (-393.51)] - (-824.2) - [3 \times (-110.525)] = -24.8 \text{ kJ} \end{aligned}$$

$$\Delta S_{(3)}^0 = (2 \times 27.28) + (3 \times 213.74) - 87.4 - (3 \times 197.674) = 15.36 \text{ J K}^{-1}$$

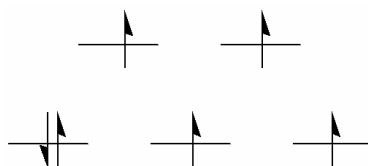
$$\begin{aligned} \Delta G_{(3)}^0 &= \Delta H^0 - T\Delta S^0 = -24.8 \text{ kJ} - (15.36 \text{ J K}^{-1} \times 1 \text{ kJ} / 1000 \text{ J} \times 1473.15 \text{ K}) = \\ &= -47.43 \text{ kJ} \end{aligned}$$

$$K = e^{(-\Delta G^0/RT)} = e^{(47430 \text{ J} / (8.314 \text{ J K}^{-1} \times 1473.15 \text{ K}))} = 48$$

8.3 One AB_2O_4 unit has available 4 ($= 1 + (1/4 \times 12)$) octahedral sites.

8.4 Since one face-centered cube in AB_2O_4 represents one Fe_3O_4 unit in this case, it has 8 available tetrahedral sites. In one Fe_3O_4 unit, 1 tetrahedral site should be occupied by either one Fe^{2+} (normal-spinel) or one Fe^{3+} (inverse-spinel). Therefore, in both cases, the calculation gives $(1/8) \times 100 \% = 12.5 \%$ occupancy in available tetrahedral sites.

8.5

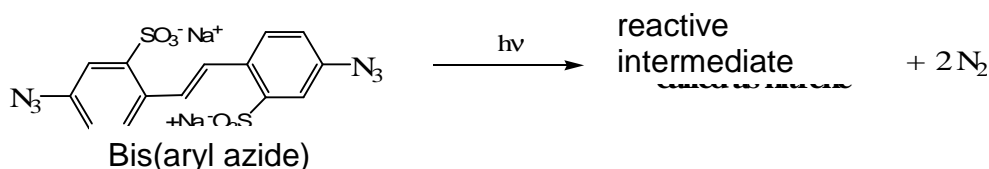


PROBLEM 9

Photolithographic process

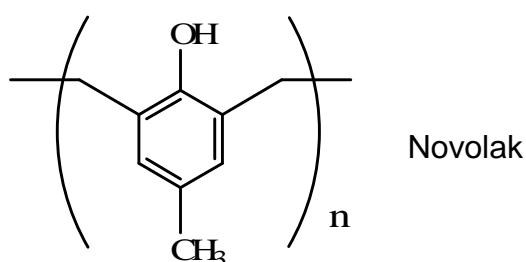
Photolithography is a process used in semiconductor device fabrication to transfer a pattern from a photomask to the surface of a substrate. In a typical photolithography process, light is projected, through a mask that defines a particular circuitry, onto a silicon wafer coated with a thin layer of photoresist.

The earliest photoresists were based on the photochemistry that generates a reactive intermediates from bis(aryl azide). Patterning becomes possible through the cross-linking reaction of the nitrenes generated from the azides.

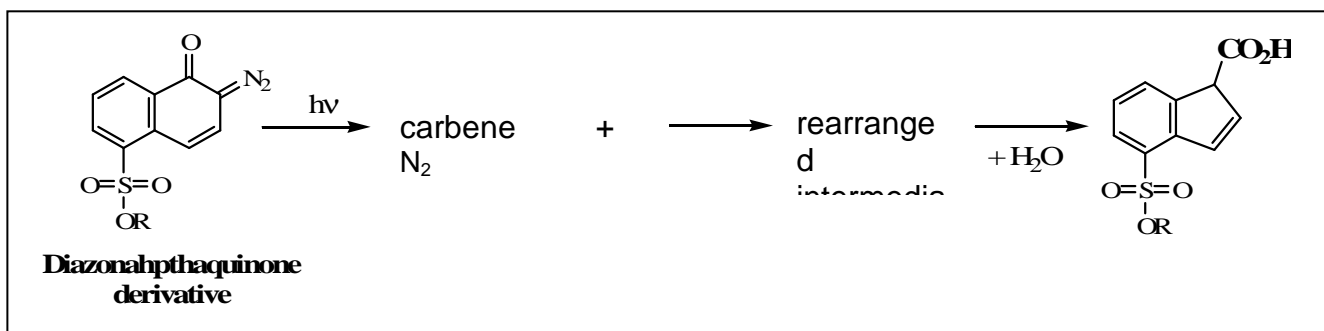


- 9.1** Draw two possible Lewis structures of $\text{CH}_3\text{-N}_3$, the simplest compound having the same active functional group of bis(aryl azide). Assign formal charges.
- 9.2** Draw the Lewis structure of nitrene expected from $\text{CH}_3\text{-N}_3$.
- 9.3** Draw the structures for two possible products, when this nitrene from $\text{CH}_3\text{-N}_3$ reacts with ethylene gas (CH_2CH_2).

Photoresists consisting of Novolak polymers, utilizes acid to change their solubility. The acid component can be produced photochemically from diazonaphthaquinone. In fact, “Novolaks” have been the representative “positive” photoresists of the modern microelectronic revolution.

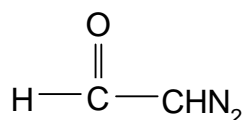


When irradiated, diazonaphthaquinone undergoes photochemical decomposition followed by rearrangement eventually producing a carboxylic acid.



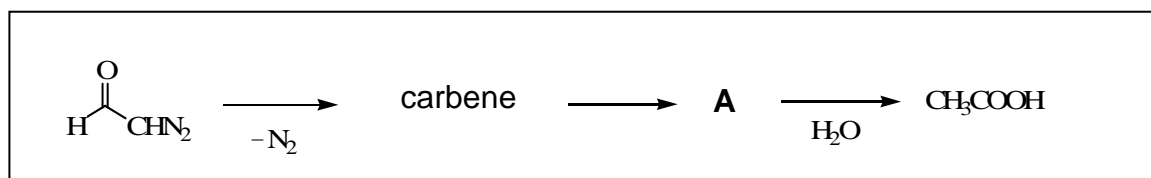
9.4 Draw three Lewis structures of diazoacetaldehyde (see below), the simplest compound having the same active functional group of diazonaphthaquinone. Indicate formal charges.

Diazonaphthaquinone derivative

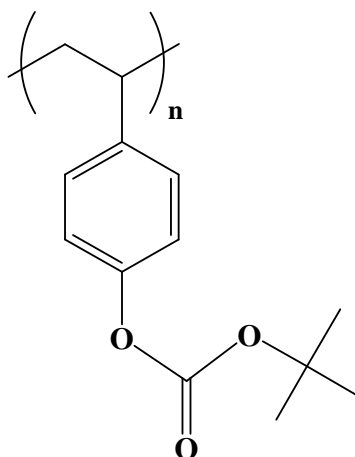


diazoacetaldehyde

9.5 Draw a Lewis structure of the rearranged intermediate, A (see below), generated from diazoacetaldehyde after losing N_2 . A satisfies Lewis' octet rule and reacts with water to form acetic acid, CH_3COOH .

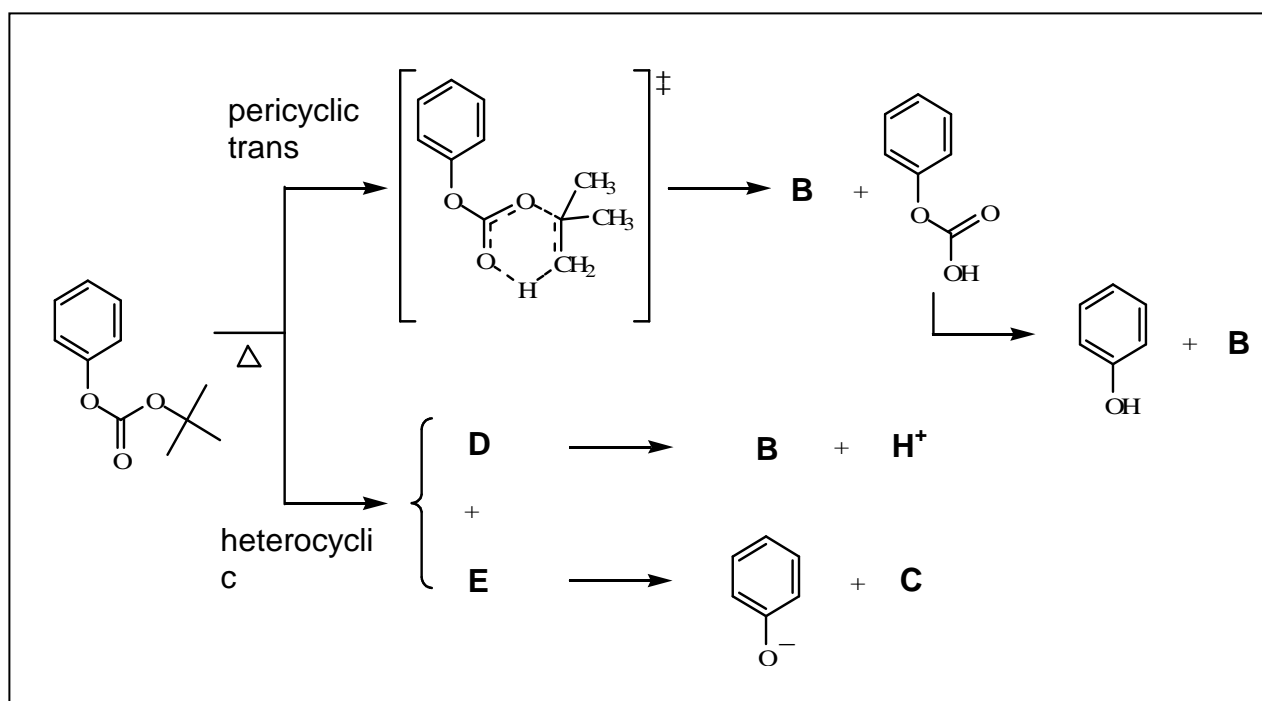


Advanced photoresists were invented in 1982 based on chemical amplification. The most popular chemical amplification for positive-tone involves the acid catalyzed deprotection of poly(*p*-hydroxystyrene) resin protected by various acid-sensitive protecting groups such as *t*-butyloxycarbonyl (*t*-BOC).

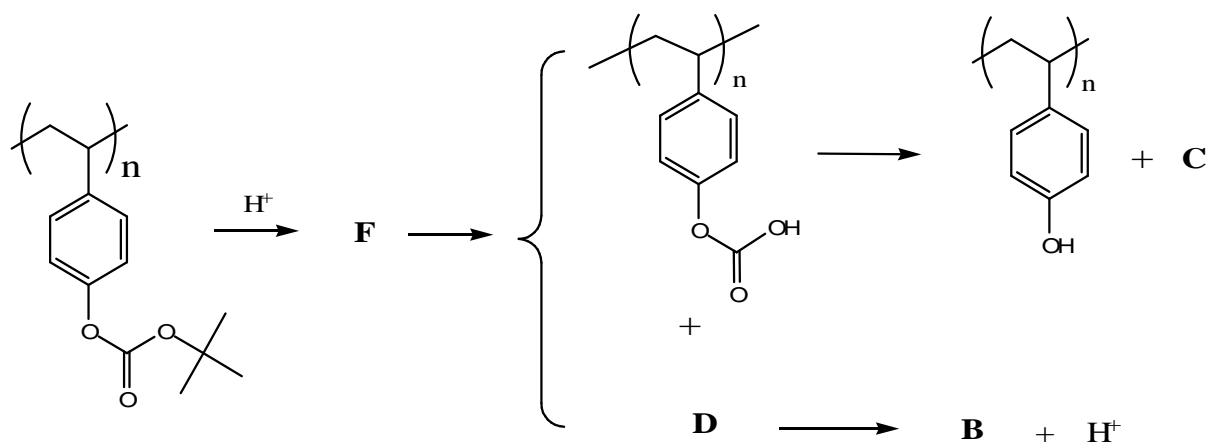


The thermal decomposition of carbonate ester itself normally occurs well above 150 °C.

9.6 Two plausible mechanisms have been suggested for this decomposition reaction having relatively high activation energy. Draw expected intermediates and products from this reaction.

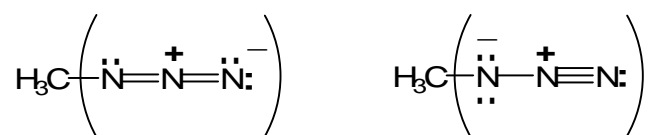


9.7 In the presence of a trace amount of acid, the reaction temperature can be reduced to below 100 °C. Draw expected intermediate **F** from the following chemical amplification process based on using *t*-BOC.

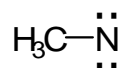


SOLUTION

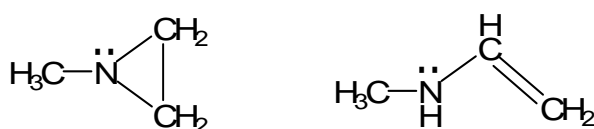
9.1



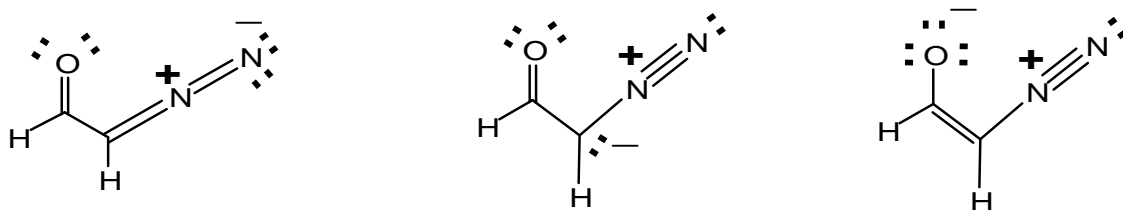
9.2



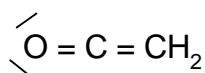
9.3



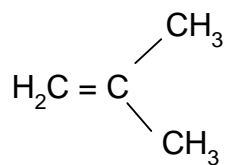
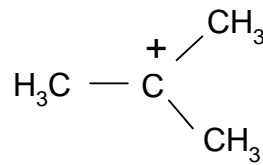
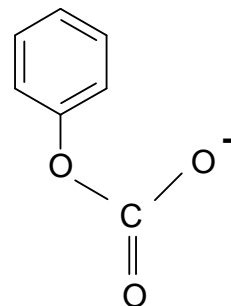
9.4



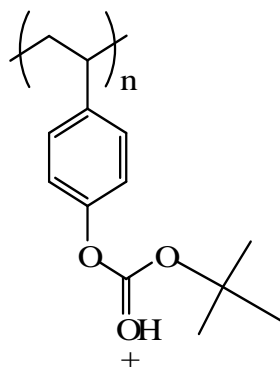
9.5

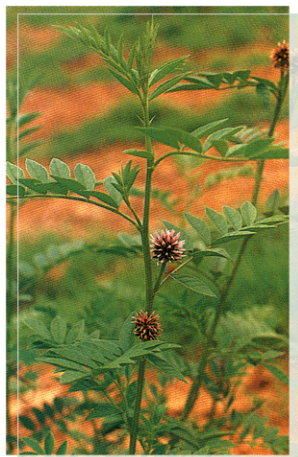


9.6

**B****C****D****E**

9.7

**F**

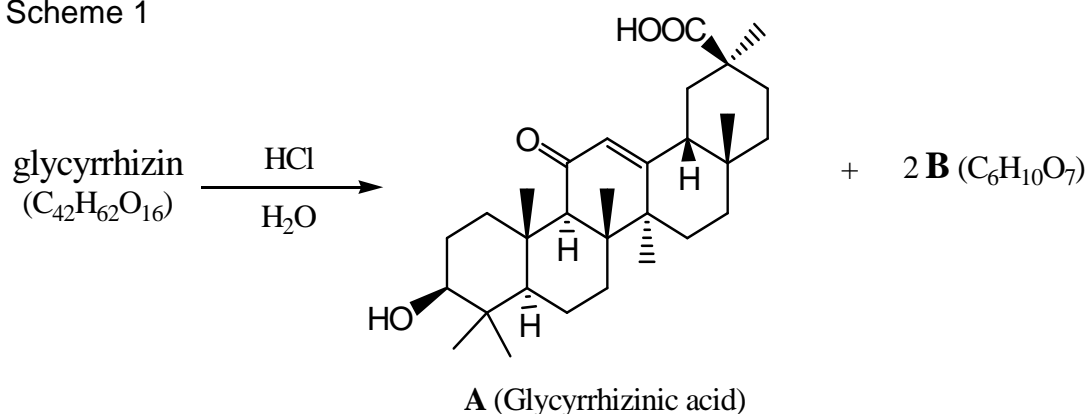
PROBLEM 10**Natural Products – Structural Analysis**Licorice (*Glycyrrhiza. Uralensis*)

Licorice Root

The flavour extracted from the licorice root is 50 – 150 times sweeter than table sugar. The most important and abundant compound responsible for the sweetness and medicinal effects of licorice is *glycyrrhizin* ($C_{42}H_{62}O_{16}$).

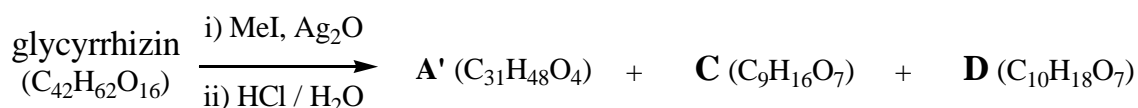
Glycyrrhizin requires three equivalents of NaOH to effect neutralization. When *glycyrrhizin* was subjected to acid hydrolysis, *Glycyrrhizinic acid* (**A** ($C_{30}H_{46}O_4$)) and **B** ($C_6H_{10}O_7$) were obtained in a 1:2 molar ratio (Scheme 1).

Scheme 1



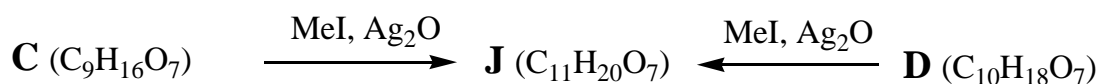
When *glycyrrhizin* was methylated with methyl iodide (MeI) at every possible site before hydrolysis, hydrolysis produced **A'** (methyl glycyrrhizinate), **C** and **D** (Scheme 2). **B**, **C** and **D** exist as mixtures of anomers.

Scheme 2



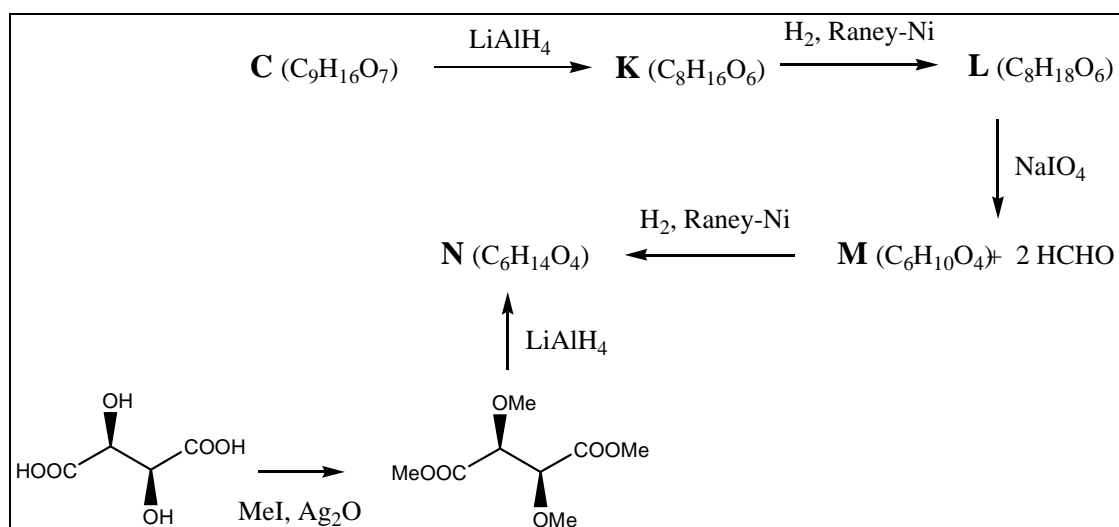
Methylation of **C** and **D** with MeI produced the same isomeric mixture of compounds, **J** (Scheme 3).

Scheme 3



C was reduced with LiAlH₄ to give **K**, and **L** was produced by the reduction of **K**. Oxidative cleavage of vicinal diol of **L** with NaIO₄ produced **M** and two equivalents of formaldehyde. Reduction of **M** produced **N**. The structure and stereochemistry of **N** was confirmed by the synthesis of **N** from D-(-)-tartaric acid through methylation followed by reduction (Scheme 4). A ¹H-NMR spectrum of **L** showed two distinct peaks for methyl groups. (There is no symmetry in **L**)

Scheme 4

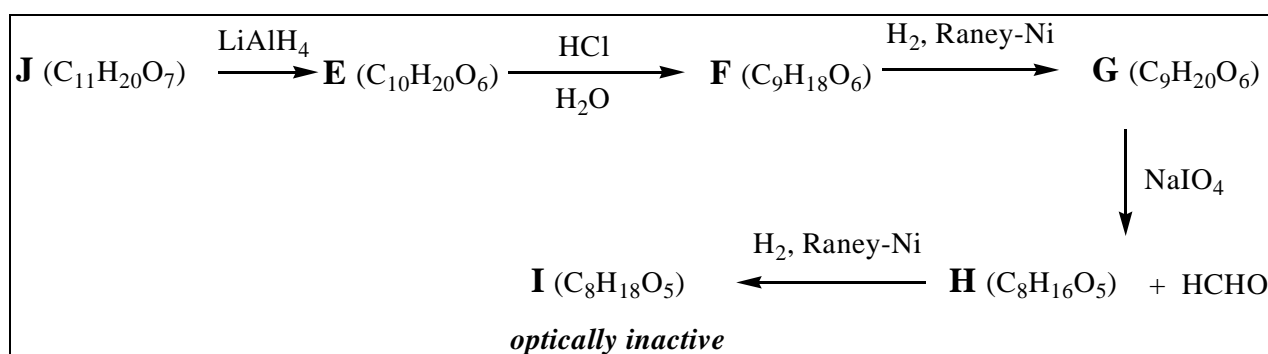


10.1 Complete structures for **L**, **M**, and **N** in the answer sheet.

10.2 How many structures for **C** are possible? Complete possible structures for **C**.

To determine the correct structure of **C**, following set of reactions were performed. **J** was reduced to **E**, and acid hydrolysis of **E** produced **F**. Reduction of **F** generated **G**, and **G** was oxidized with NaIO_4 to **H** with formation of one equivalent of formaldehyde. **I** was obtained from **H** through reduction. Among all compounds from **A** to **I**, only **I** was optically inactive (Scheme 5).

Scheme 5



10.3 Complete structures for **G** and **I**.

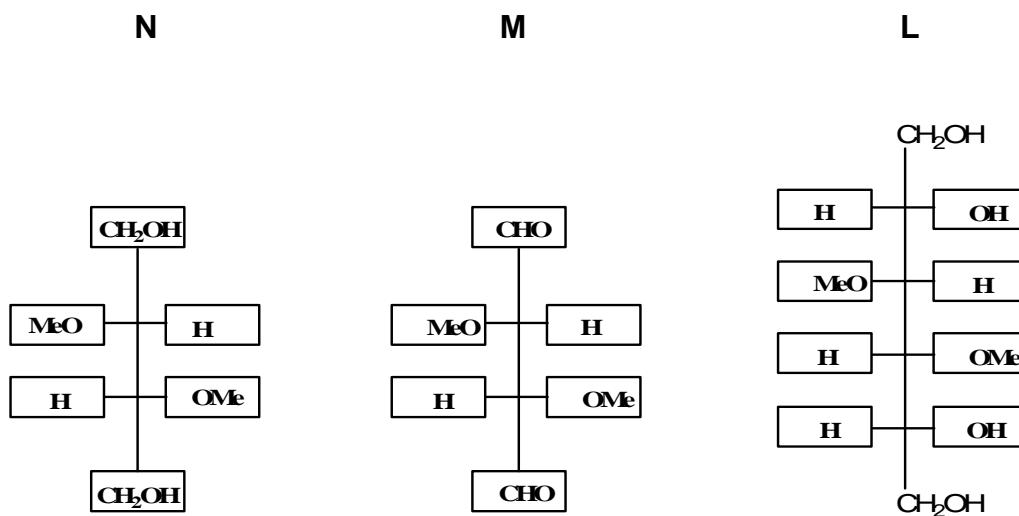
10.4 Which one is the correct structure for **C** among ones you have drawn in 10-2?

10.5 Complete structures for **B**, **D**, and **J**.

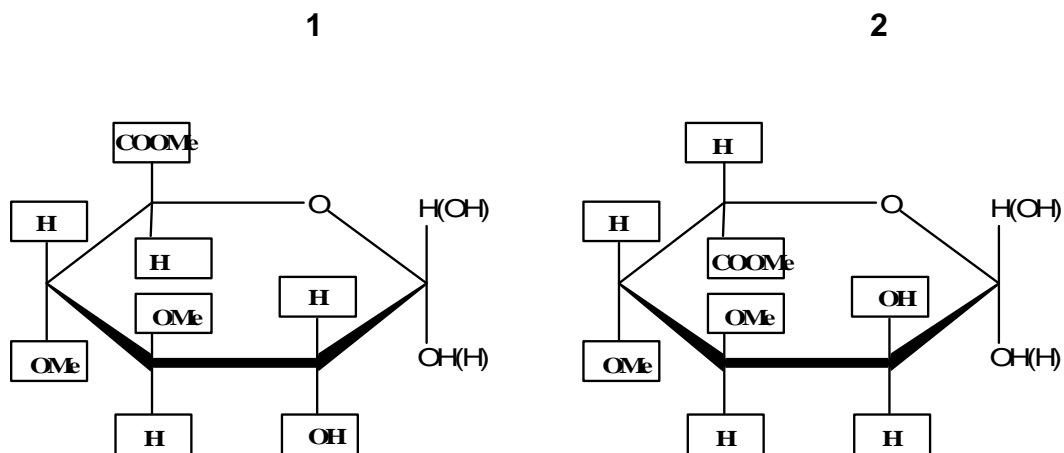
10.6 Complete the structure for Glycyrrhizin.

SOLUTION

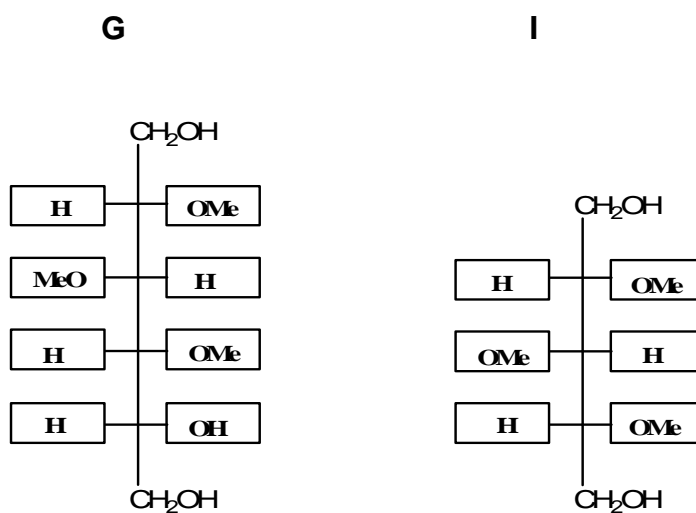
10.1



10.2 Number of possible structures **2**



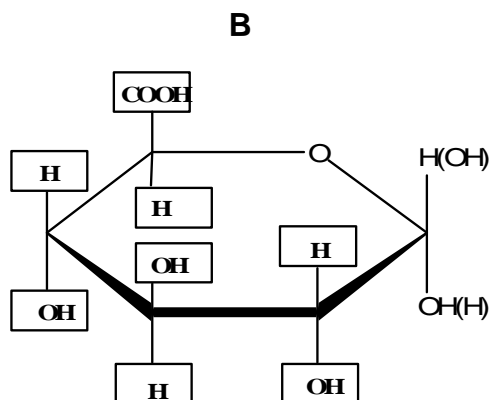
10.3



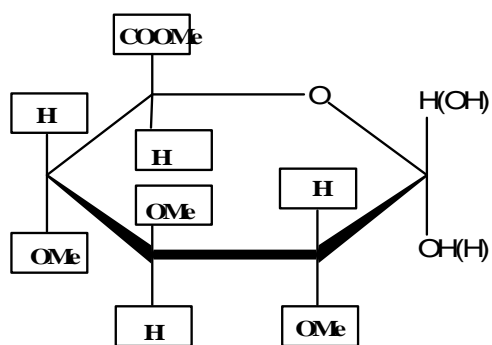
10.4

The correct structure for **C** from 10-2 is No. 1

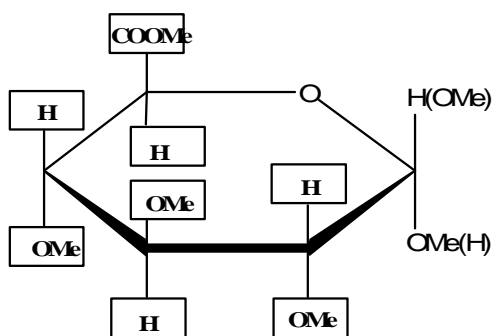
10.5



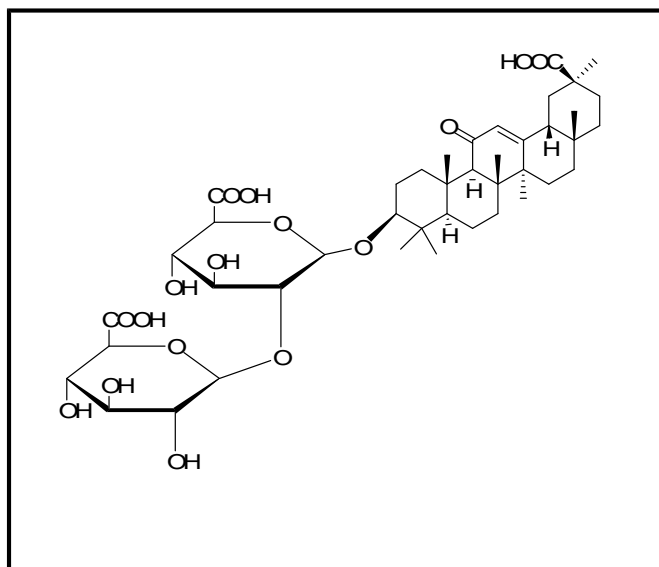
D



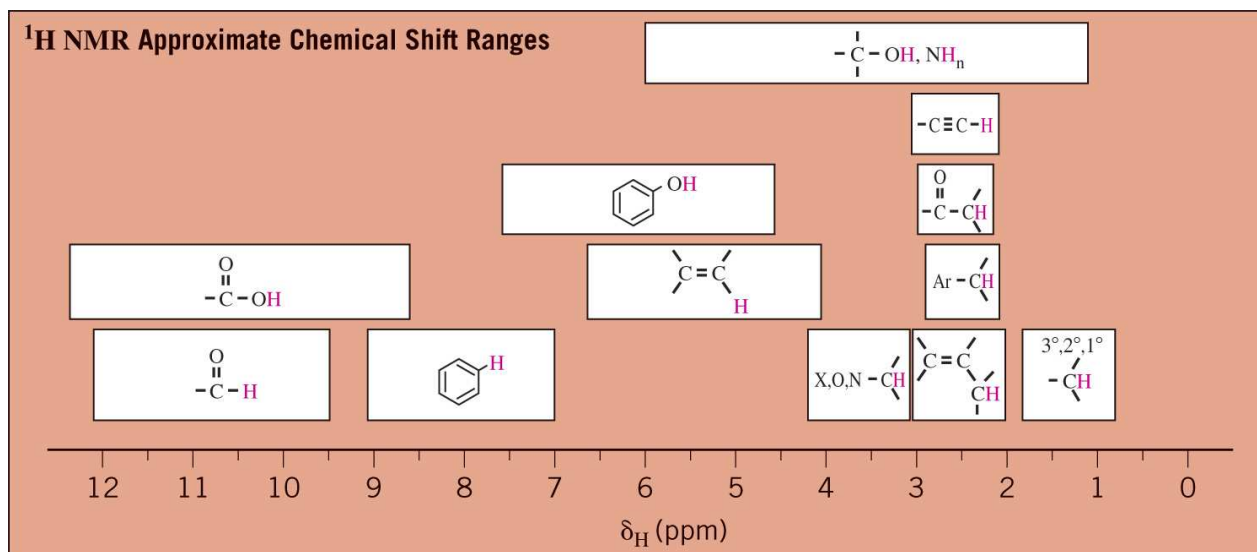
J



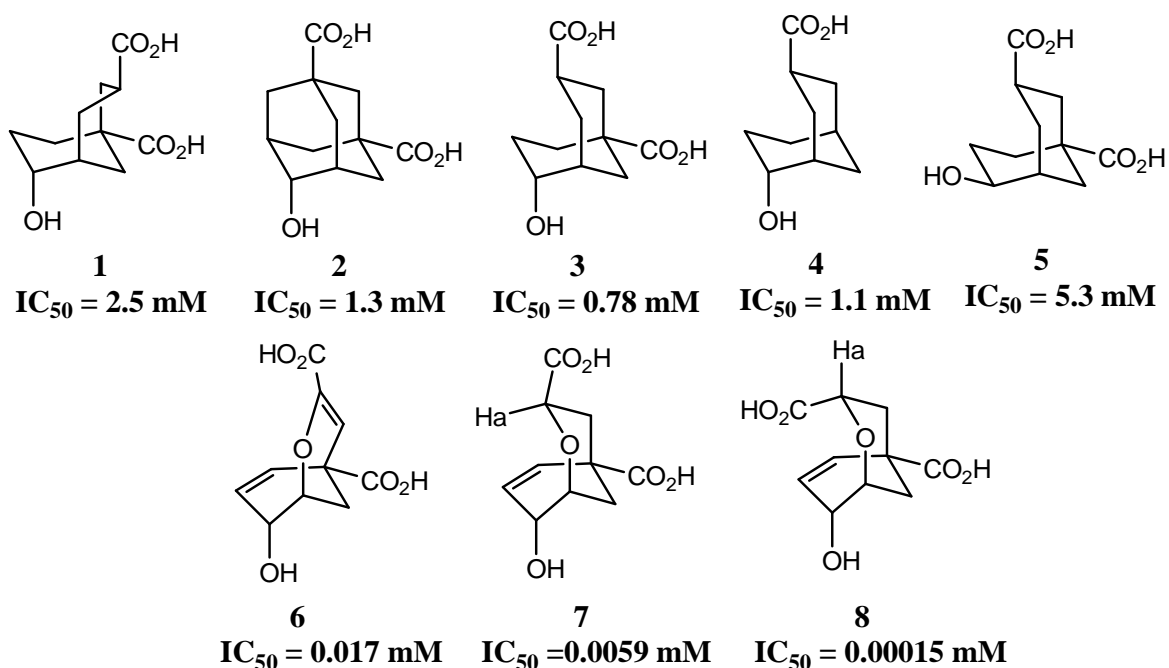
10.6



δ , chemical shift; H, integrals; d, doublet; dd, doublet of doublet; J, coupling constant; t, triplet; s, singlet



Chorismate mutase is believed to stabilize the transition state of Claisen rearrangement. Thus it is an interesting target for inhibitor design. Inhibitors, called transition state analog (TSA)s that resemble the transition state (TS, e.g., the species in brackets “[]” above) of the reaction are designed to occupy the active site. Several inhibitors were designed and synthesized, and among them eight turned out to be potent inhibitors of the enzyme. The lower is the IC_{50} (inhibitor concentration of 50 % of the enzymatic activity) value, the better is the inhibitor.



11.3 Choose all correct statements based on the structures and IC_{50} values of above inhibitors. Increase of factor 5 is considered to be important.

- (a) Configuration of the hydroxyl group plays an important role in the TS and inhibitor design.
- (b) The presence of both carboxylic groups is important in the TS and inhibitor design.
- (c) Transition state of the reaction contains two six-membered rings with one chair and one twist-boat conformation.
- (d) **7** and **8** can be distinguished on the basis of the $^1\text{H-NMR}$ of H_a .

11.4 Draw the transition state of the transformation of chorismic acid to prephenic acid based on the TSA structures and their IC_{50} values.

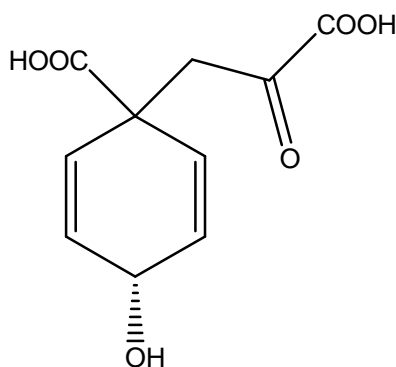
11.5 Compared with the uncatalyzed thermal conversion, chorismate mutase accelerates conversion of chorismic acid to prephenic acid 1.0×10^6 fold at $25\text{ }^\circ\text{C}$ by lowering the activation energy of the reaction. Calculate the decrease in activation energy of chorismate mutase at $25\text{ }^\circ\text{C}$.

$\Delta H^\ddagger_{\text{uncat}}$ is $86,900\text{ J mol}^{-1}$ for the thermal conversion of chorismic acid to prephenic acid. At what temperature will the rate of the *uncatalyzed* thermal conversion be the same as that of the *enzyme-catalyzed* conversion at $25\text{ }^\circ\text{C}$, assuming that $E_a = \Delta H^\ddagger$.

SOLUTION

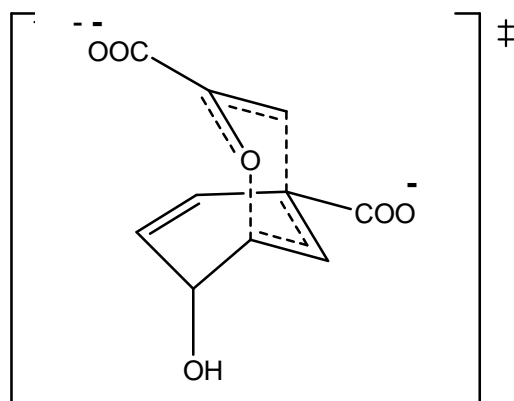
11.1 Hydroxyl group No. 3

11.2



11.3 Correct statements: (a), (c), (d).

11.4



Transition state

11.5 For the enzyme-catalyzed reaction, Arrhenius equation could be applied.

$$\frac{k_{\text{cat}}}{k_{\text{uncat}}} = \frac{A \exp(-E_{a, \text{cat}} / RT)}{A \exp(-E_{a, \text{uncat}} / RT)} = \exp[-\Delta E_{a, \text{cat-uncat}} / RT] =$$

$$= \frac{\exp(-\Delta E_{a, \text{cat-uncat}} (\text{J mol}^{-1}))}{2,480 \text{ J mol}^{-1}} = 1 \times 10^6$$

Therefore, $-\Delta E_{a, \text{cat-uncat}} = 34,300 \text{ J mol}^{-1}$

$$\frac{k_{\text{uncat}, T}}{k_{\text{uncat}, 298}} = \frac{A \exp(-\Delta H^{\ddagger}_{\text{uncat}} / RT)}{A \exp(-\Delta H^{\ddagger}_{\text{uncat}} / 298 R)} = \exp\left[\left(\frac{-\Delta H^{\ddagger}_{\text{uncat}}}{R}\right) \left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

$$\frac{k_{\text{uncat}, T}}{k_{\text{uncat}, 298}} = 13.8 = \exp\left[\left(\frac{-86900}{8.32}\right) \left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

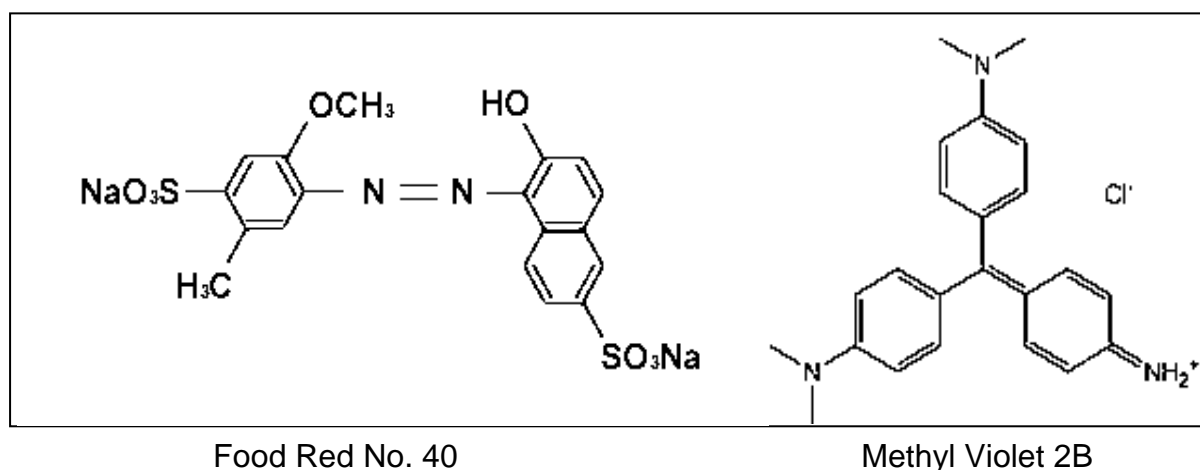
Therefore, $T = 491 \text{ K}$, or $218 \text{ }^{\circ}\text{C}$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Reverse-phase Chromatography: Spectrophotometric Analysis

Chromatographic separation followed by spectrophotometric analysis is one of the most widely practiced analytical techniques in chemical laboratories around the world. For example, organic compounds in a complex mixture are often analyzed by reverse-phase liquid chromatography with spectrophotometric detection. In reverse-phase chromatography, hydrophobic interactions between the stationary phase material (usually octadecyl group) and the non-polar moiety of the analyte is utilized. The chromatogram can be simplified and the compound of interest selectively determined by proper choice of the detector wavelength. In this part of the Practical Test, spectrophotometric analysis of dyes, with and without separation, will be performed.



1.1 Spectrophotometric Analysis of R and B in a Mixed Solution

- a) Measure absorbance of both Solutions R (3.02×10^{-5} M) and B (1.25×10^{-5} M) (Fig. A & B). Fill in the Table in the Answer Sheet with your measurements. Draw absorption spectra for the red dye in red ink and for the blue dye in blue ink (Fig. 1.1).
- b) Repeat absorbance measurements for Solution MD. Solution MD is a mixture of Solution R and B in a certain ratio. Add the spectrum in black ink to Fig. 1.1.

- c) Based on the Beer-Lambert law, determine the molar concentration of both dyes in Solution MD using the data in the Table. Do not determine the fraction of one dye by subtracting the fraction of another dye from 1.

1.2 Chromatographic Separation Followed by Spectrophotometric Analysis

- a) Elute the cartridge with about 10 cm³ of Solution E using 10 cm³ syringe (Fig. C).
- b) Load 1.00 cm³ of solution MD onto the cartridge (Fig. D).
- c) Using 1 cm³ syringe, elute with Solution E (Fig. E). Collect the solution eluting through the outlet in a 10 cm³ volumetric flask. Repeat until the red compound is completely eluted and collected.
- d) Fill the flask to the 10 cm³ mark with Solution E and mix. Call this Solution F.
- e) Obtain the absorption spectrum of solution F as in Experiment 1.1. Dilution takes place during elution. Therefore, multiply the measured absorbance by 10 when drawing the spectrum for Solution F. Draw spectrum with broken line in Fig. 1.1 in red ink.
- f) Dilute Solution R as necessary and construct a calibration curve, at a wavelength of your choice, for analysis of the red dye (R) in Solution F. Draw a calibration curve in the answer sheet (X-axis, concentration; Y-axis, absorbance, Fig. 1.2). Indicate the wavelength used. The calibration curve must have three points in addition to the origin. Mark the position of Solution F on the calibration curve.
- g) Report the concentration of R in the original Solution MD.
- h) Compare this concentration with the value you obtained in Experiment 1-1 and report the recovery (amount eluted/amount loaded) associated with chromatography.
-
-

PROBLEM 2 (Practical)**Reverse-phase Chromatography:****Acid-Base Titration of Acetic Acid and Salicylic Acid**

Acetic acid (AA) and salicylic acid (SA) are slightly different in polarity and thus can be separated on a reverse-phase cartridge using distilled water as eluent. AA is eluted first. The total amount of AA and SA in a mixed solution will be determined by titration. Then, AA and SA will be separately determined following chromatographic separation.

2-1. Determination of the Total Amount of AA and SA in a Mixed Acid (MA) Solution

- Titrate 10 cm³ of distilled water with the NaOH (< 5 mM) solution provided. Report blank acidity in 1 cm³ of distilled water in terms of the volume of the NaOH solution. Take this blank acidity into account for all solutions in subsequent data analyses. Show corrections in the calculation part in the answer sheet.
- Standardize NaOH solution with 2.00 cm³ of the standard KHP (potassium hydrogen phthalate) solution (1.00 x 10⁻² M) provided. Repeat and report the concentration of the NaOH solution. Show how you accounted for the blank acidity.
- Withdraw 1.00 cm³ of Solution MA and determine the total acidity. Repeat and report the total number of moles of AA and SA combined in 1.00 cm³ of Solution MA.

2-2. Reverse-phase Separation and Titration

- Elute a new C-18 cartridge with about 10 cm³ of distilled water using 10 cm³ syringe.
- Load 1.00 cm³ of Solution MA onto the cartridge. Collect the liquid eluting at the outlet in tube 1 (Fraction 1).
- Elute with 1 cm³ of distilled water. Collect the eluent in a test tube (Fraction 2). Repeat until Fraction 20 is collected. You will have 20 test tubes with about 1 cm³ liquid in each tube.

- d) Titrate acidity in each test tube. Report volume of the NaOH solution consumed and the amount of acid(s) in each test tube. Make a graph in the answer sheet (Fig. 2-2) showing the amount of acid(s) in each test tube.
- e) Blank acidity and the background (due to leaching out of residual materials from the column) must be subtracted. In determining the amount of eluted AA, disregard tubes containing only trace amounts of acids. Tube 2 and 3 contain most AA. Calculate the total amount of AA eluted by adding the amount of AA in tubes. Similarly calculate the total amount of SA eluted. Indicate, in Fig. 2-2, which fractions you used to get the amount of each acid.
- f) Calculate the mole percent of AA in solution MA.
-
-

PROBLEM 3 (Practical)

Qualitative Analysis of Organic Compounds

In this experiment your task is to identify seven solid unknowns from the list of compounds on page 7 that are common drugs in everyday life and valuable agents in organic chemistry. To achieve this, perform chemical tests on unknowns according to the following procedures and analyze your results.

Procedure

Helpful Comments

- The weight of a spatula tip-full of a solid is about 15~20 mg.
- Wipe spatula cleanly with Kimwipe between uses.
- After adding any reagent described below to a solution of an unknown sample, mix the contents thoroughly and observe the resulting mixture carefully.
- To get full marks, you should perform all the tests and fill out the table.

Test 1: Solubility test

To a test tube, add a spatula tip-full (15~20 mg) of an unknown sample and 1 cm³ of CH₃CN. Shake the test tube and report the solubility. Repeat the test with 1M HCl, water, and 1M NaOH.

Test 2: 2,4-DNPH test

Place about 15~20 mg of an unknown sample in a test tube and dissolve with 2 cm³ of 95 % EtOH. (For the water soluble unknowns, dissolve about 15~20 mg of an unknown in 1 cm³ of water.) Add five drops of the 2,4-dinitrophenylhydrazine solution in concentrated sulphuric acid and 95% ethanol (labelled as 2,4-DNPH).

Test 3: CAN test

Mix 3 cm³ of the cerium(IV) ammonium nitrate solution in dilute HNO₃ (labelled as CAN) with 3 cm³ of CH₃CN in a test tube. In another test tube add about 15~20 mg of an unknown sample in 1 cm³ of the mixed solution. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown sample in 1 cm³ of water first, and then add 1 cm³ of CAN.) If there is a colour change in the solution, the solution may contain alcohol, phenol or aldehyde.

Test 4: Bayer test

In a test tube, dissolve about 15~20 mg of an unknown sample in 2 cm³ of CH₃CN. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown in 1 cm³ of water.) To the solution, slowly add five drops of the 0.5 % KMnO₄ solution, drop by drop while shaking.

Test 5: pH test

In a test tube, dissolve about 15~20 mg of an unknown sample in 2 cm³ of 95 % EtOH. (For the water soluble unknown samples, dissolve about 15~20 mg of an unknown sample in 1 cm³ of water). Measure the pH of the solution with pH paper.

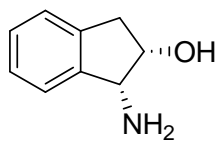
Test 6: Iron(III) chloride test

Take the solution from Test 5 and add five drops of a 2.5 % FeCl₃ solution.

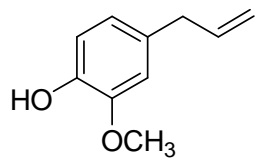
Results

1. Record your test results in the answer sheet. Write *O* if soluble and *X* if insoluble for the solubility tests. Write (+) for the positive reactions and (–) for the negative reactions for tests 2 ~ 4 and 6. Write *a*, *b* and *n* for acidic, basic or neutral, respectively, for pH test 5.
2. Based on your test results, identify the most plausible structures for the unknown compounds from the provided list of compounds. Write the compound initial in appropriate box.

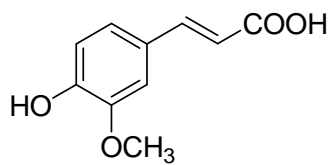
Possible Unknown Compounds (next page):



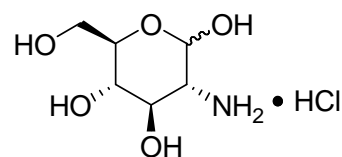
(A)



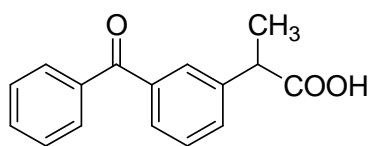
(E)



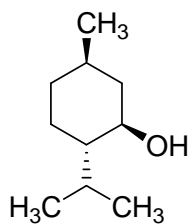
(F)



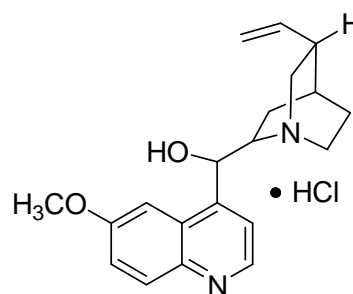
(G)



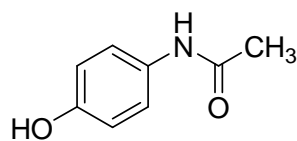
(K)



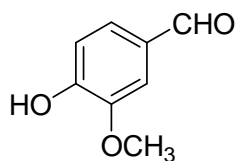
(M)



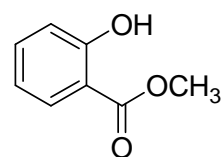
(Q)



(T)



(V)



(W)

39th



International Chemistry Olympiad

**8 theoretical problems
2 practical problems**

THE THIRTY-NINTH INTERNATIONAL CHEMISTRY OLYMPIAD 15–24 JULY 2007, MOSCOW, RUSSIAN FEDERATION

THEORETICAL PROBLEMS

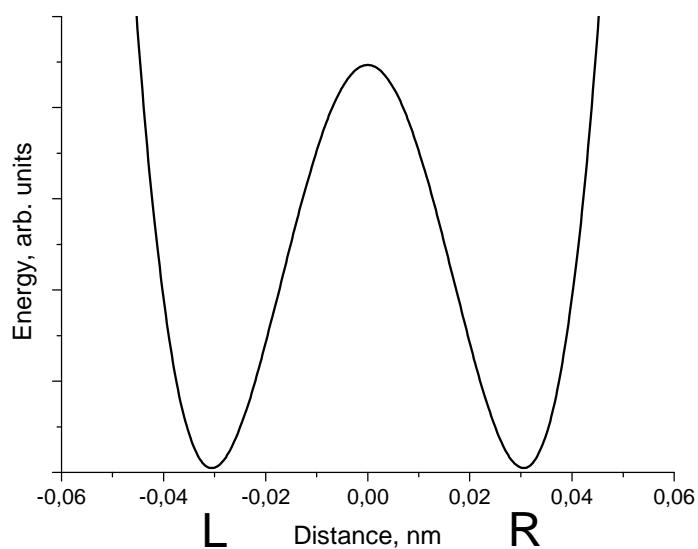
PROBLEM 1

Proton tunneling

Proton tunneling through energy barriers is an important effect, which can be observed in many complex species containing hydrogen bonds (DNA, proteins, etc.). Propanedial (malonaldehyde) is one of the simplest molecules for which intramolecular proton transfer can occur.

- 1.1 Draw the condensed formula of propanedial and the structures of two of its isomers, which can exist in equilibrium with propanedial.
- 1.2 In a water solution propanedial is a weak acid, its strength being comparable with that of acetic acid. Specify the acidic hydrogen atom. Explain its acidity (choose one version in the Answer Sheet).

On the plot below an energy profile of the intramolecular proton transfer is given (the dependence of energy on the distance of proton motion (in nm)). Energy curve has a symmetric double-well form.

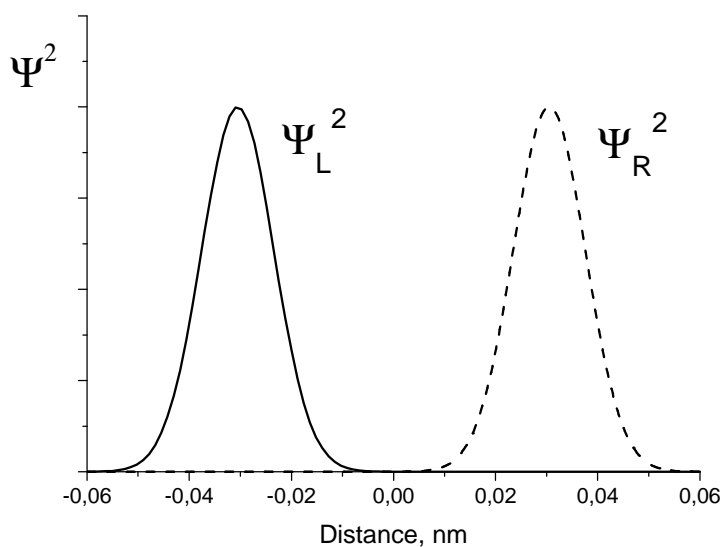


1.3 Draw the structures corresponding to two minima on this curve.

A proton is delocalized between two atoms and oscillates between two minima L and R with an angular frequency $\omega = 6.48 \times 10^{11} \text{ s}^{-1}$. Probability density for a proton depends on time as follows:

$$\Psi^2(x,t) = \frac{1}{2} \left[\Psi_L^2(x) + \Psi_R^2(x) + (\Psi_L^2(x) - \Psi_R^2(x)) \cos(\omega t) \right],$$

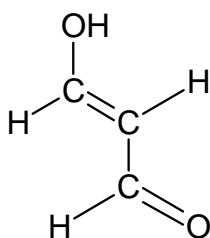
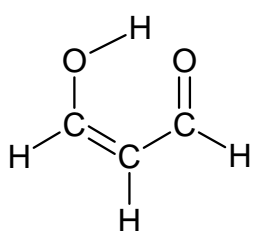
wavefunctions $\Psi_L(x)$ and $\Psi_R(x)$ describe a proton localized in the left and right wells, respectively:



- 1.4 Write down the expressions for the probability density at three moments: (a) $t = 0$, (b) $t = \pi/(2\omega)$, (c) $t = \pi/\omega$. Sketch the graphs of these three functions.
- 1.5 Without calculations, determine the probability of finding the proton in the left well at $t = \pi/(2\omega)$
- 1.6 How much time is required for a proton to move from one well to another? What is the proton mean speed during the transfer?
- 1.7 From the energy curve, estimate the uncertainty of the position of proton forming hydrogen bonds. Estimate the minimal uncertainty of the proton speed. Compare this value with that obtained in 1.6 and draw a conclusion about the proton tunneling (choose one of the versions in the Answer Sheet).

SOLUTION

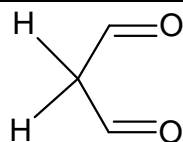
- 1.1 The structures of propanedial and two of its isomers:



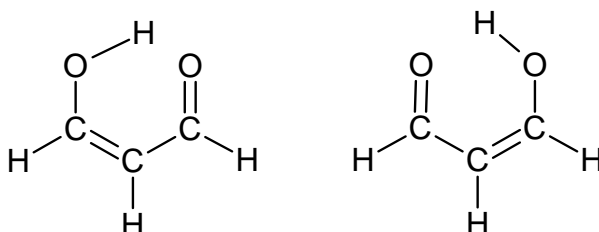
- 1.2 Acidic hydrogen atom is in CH_2 (in enol forms acidic hydrogen is in OH).
The stability of propanedial is caused by (one of the following answers had to be chosen):
- the stability of carbanion due to conjugation with two carbonyl groups,
 - weakness of $\text{C}-\text{H}$ bond in a carbonyl group,
 - hydrogen bonds between two propanedial molecules.

The first answer is correct.

- 1.3 The distance between two minima on the energy curve is 0.06 nm. In a purely aldehyde form



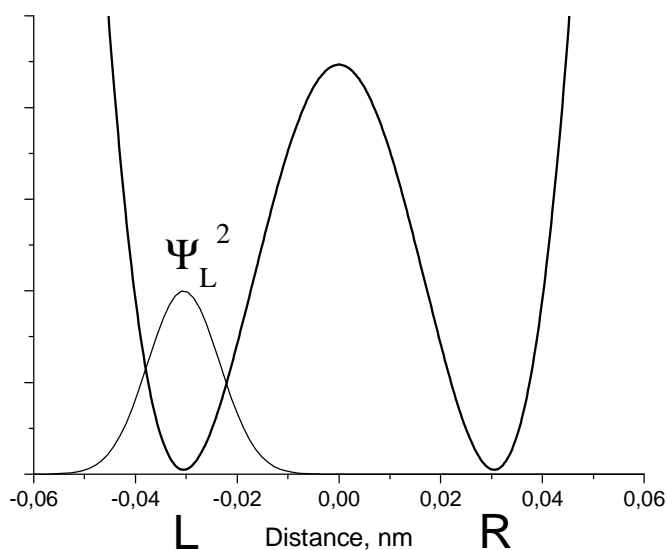
such distance between two possible positions of proton is impossible. Tunneling takes place only in enol Z-form:



1.4 Expressions and plots of probability density

$$(a) \quad \Psi^2(x,0) = \frac{1}{2} [\Psi_L^2(x) + \Psi_R^2(x) + \Psi_L^2(x) - \Psi_R^2(x)] = \Psi_L^2(x)$$

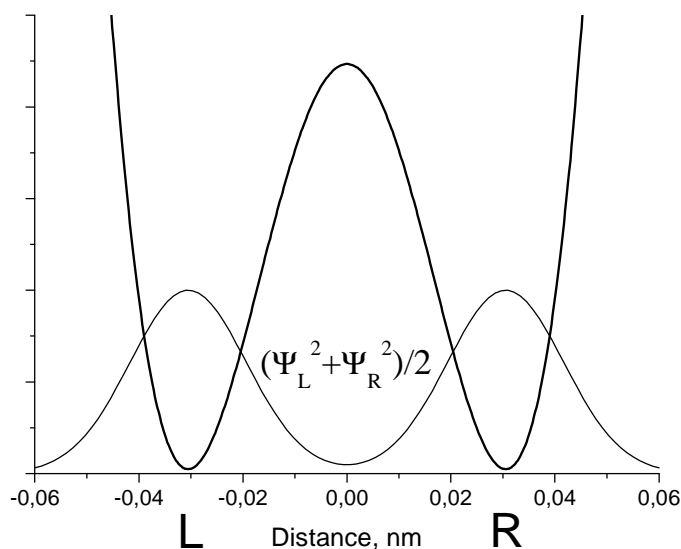
The probability density is concentrated in the left well:



(b) In the middle of the time interval

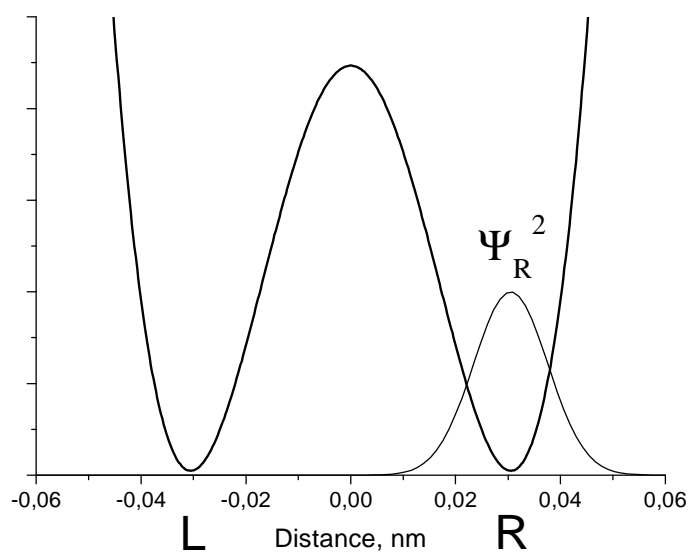
$$\Psi^2\left(x, \frac{\pi}{2\omega}\right) = \frac{1}{2} [\Psi_L^2(x) + \Psi_R^2(x)]$$

The probability density has a symmetric form, a proton is delocalized between two wells:



$$(c) \quad \Psi^2\left(x, \frac{\pi}{\omega}\right) = \frac{1}{2}[\Psi_L^2(x) + \Psi_R^2(x) - \Psi_L^2(x) + \Psi_R^2(x)] = \Psi_R^2(x)$$

The probability density is concentrated in the right well:



1.5 The probability of finding the proton in the left well is 1/2, because probability function is symmetric, and both wells are identical.

1.6 The time of transfer from one well to another is $t = \pi / \omega$.

$$t = \frac{3.14}{6.48 \times 10^{11}} = 4.85 \times 10^{-12} \text{ s.}$$

The proton velocity:

$$v = \frac{0.06 \times 10^{-9}}{4.85 \times 10^{-12}} = 12 \text{ m s}^{-1}.$$

- 1.7** The uncertainty of proton position is approximately equal to half of the distance between minima, that is 0.03 nm (0.06 nm will be also accepted).

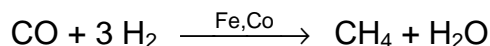
The minimal uncertainty of velocity can be obtained from the uncertainty relation:

$$\Delta v = \frac{h}{2 m \Delta x} = \frac{1.055 \times 10^{-34}}{2 \times \frac{0.001}{6.02 \times 10^{23}} \times 0.03 \times 10^{-9}} \approx 1000 \text{ m s}^{-1}.$$

Comparing this uncertainty with the velocity 12 m s^{-1} we see that the notion of proton velocity during transfer from one well to another is senseless. Therefore, proton tunneling is a purely quantum phenomenon and cannot be described in classical terms. The second conclusion is correct.

PROBLEM 2**Nanochemistry**

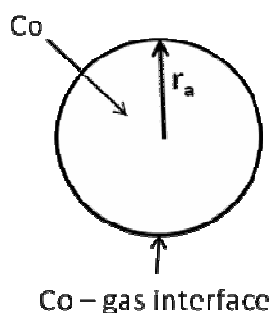
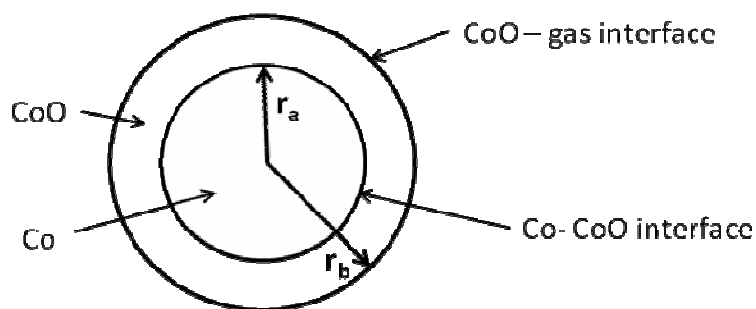
Metals of the iron subgroup are effective catalysts of hydrogenation of CO (Fischer-Tropsch reaction)



Catalyst (e.g. cobalt) is often used in the form of solid nanoparticles that have a spherical structure (fig.1). The reduction in size of the catalyst increases catalytic activity significantly. The unwanted side-reaction however involves the oxidation of the catalyst:



Solid cobalt oxide (bulk) is formed in the reaction vessel. This causes an irreversible loss of the catalyst's mass. Solid cobalt oxide can also be deposited on the surface of Co(s). In this case the new spherical layer is formed around the surface of the catalyst (see figure 2) and the catalytic activity drops.

**Fig. 1****Fig. 2**

Let us see how formation of nanoparticles affects the equilibrium of reaction (1).

$$G^{\circ}(r) = G^{\circ}(\text{bulk}) + \frac{2\sigma}{r} V$$

- 2.1** Calculate the standard Gibbs energy $\Delta_r G^{\circ}(1)$ and the equilibrium constant for the reaction (1) at $T = 500 \text{ K}$.
- 2.2** Calculate the equilibrium constant for reaction (1) when the cobalt catalyst is dispersed in the form of spherical particles (Fig. 1) of radius:

(a) 10^{-8} m ,

(b) 10^{-9} m .

The surface tension at the Co-gas interface is 0.16 J m^{-2} . CoO forms a bulk phase.

The mixture of gases involved in the Fischer-Tropsch (CO , CH_4 , H_2 , H_2O) reaction was put into a reaction vessel containing the cobalt catalyst. The total pressure is $p = 1$ bar, temperature is $T = 500$ K. The mole fraction of hydrogen (%) in the mixture is 0.15 %.

- 2.3** At what minimum mole fraction of water (%) in the gas mixture the unwanted spontaneous oxidation of the catalyst becomes possible so that solid bulk CoO may appear in the system? Assume that cobalt catalyst is in the form of
- a bulk phase
 - spherical nanoparticles with $r_a = 1$ nm (Fig. 1).
- 2.4** What would you suggest to protect Co nanoparticles from the spontaneous oxidation with the formation of bulk CoO at a constant ratio $p(\text{H}_2\text{O})/p(\text{H}_2)$ and a constant temperature:
- to increase r_a ;
 - to decrease r_a ;
 - change of r_a has no effect.

Assume now that solid cobalt oxide forms a spherical layer around a nanoparticle of cobalt. In this case the nanoparticle contains both a reactant (Co) and a product (CoO) (Fig. 2).

In the following problems denote surface tensions as $\sigma_{\text{CoO-gas}}$, $\sigma_{\text{CoO-Co}}$, radii as r_a , r_b , molar volumes as $V(\text{Co})$; $V(\text{CoO})$.

- 2.5** Write down the expression for the standard molar Gibbs function of CoO .
- 2.6** Write down the expression for the standard molar Gibbs function of Co .

Hint. If two spherical interfaces surround a nanoparticle, the excess pressure at its centre is given by the expression

$$P_{in} - P_{ex} = \Delta P = \Delta P_1 + \Delta P_2 = 2 \frac{\sigma_1}{r_1} + 2 \frac{\sigma_2}{r_2}$$

r_i , σ_i are radius and surface tension at the spherical interface i , respectively.

- 2.7** Express the standard Gibbs energy of the reaction (1) $\Delta_r G^0(1, r_a, r_b)$ in terms of $\sigma_{\text{CoO-gas}}$, $\sigma_{\text{CoO-Co}}$, r_a , r_b , $V(\text{Co})$; $V(\text{CoO})$ and $\Delta_r G^0(1)$.
- 2.8** When spontaneous oxidation of Co begins the radii of two layers in the nanoparticle (Fig. 2) are almost equal, $r_a = r_b = r_0$, and $\Delta_r G^0(1, r_a, r_b) = \Delta_r G^0(1, r_0)$. Assume that

$\sigma_{\text{CoO-gas}} = 2\sigma_{\text{CoO-Co}}$. Which plot in the Answer Sheet describes correctly the dependence of $\Delta_r G^0(1, r_0)$ on r_0 ?

- 2.9 What would you choose to protect Co nanoparticles from the spontaneous formation of the external layer of CoO at a constant ratio $p(\text{H}_2\text{O})/p(\text{H}_2)$ and a constant temperature:
- increase r_0
 - decrease r_0
 - change of r_0 has no effect.

Reference data:

Substance	ρ , g cm ⁻³	$\Delta_f G_{500}^0$, kJ mol ⁻¹
Co (s)	8.90	
CoO (s)	5.68	-198.4
H ₂ O (gas)		-219.1

SOLUTION

- 2.1 The Gibbs energy and the equilibrium constant of reaction (1)

$$\Delta_r G_{500}^0(1) = \Delta G_{f,500}^0(\text{CoO}, \text{s}) - \Delta G_{f,500}^0(\text{H}_2\text{O}, \text{g}) = -198.4 + 219.1 = 20.7 \text{ kJ mol}^{-1}$$

$$K = e^{-\frac{\Delta_r G_{500}^0(1)}{RT}} = e^{-\frac{20700}{8.314 \times 500}} = 6.88 \times 10^{-3}$$

- 2.2 The standard Gibbs energy of the reaction (1) with the spherical cobalt nanoparticles of radius r_a is

$$\begin{aligned} \Delta_r G_{500}^0(1, r_a) &= G_{\text{bulk},500}^0(\text{CoO}, \text{s}) + G_{500}^0(\text{H}_2, \text{g}) - G_{500}^0(\text{H}_2\text{O}, \text{g}) - G_{\text{sph}}^0(\text{Co}) = \\ &= G_{500}^0(\text{CoO}, \text{s}) + G_{500}^0(\text{H}_2, \text{g}) - G_{500}^0(\text{H}_2\text{O}, \text{gas}) - \left(G_{500}^0(\text{Co}, \text{s}) + \frac{2\sigma_{\text{Co-gas}} V(\text{Co})}{r_a} \right) = \\ &= \Delta_r G_{500}^0(1) - \frac{2\sigma_{\text{Co-gas}} V(\text{Co})}{r_a}; \end{aligned}$$

$$V(\text{Co}) = \frac{M_{\text{Co}}}{\rho(\text{Co})} = \frac{1 \times 10^{-6} \times 59.0}{8.90} = 6.6 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

for spherical particles with $r_a = 10^{-8}$, 10^{-9} m one gets, respectively

$$\frac{2\sigma_{\text{Co-gas}} V(\text{Co})}{r_a} = 210 \text{ and } 2100 \text{ J mol}^{-1}$$

$\Delta_r G_{500}^0(1, r_a)$ is equal to 20.5 (a), and 18.6 (b) kJ mol^{-1} , respectively.

The equilibrium constant is calculated from the equation

$$K(1, r_a) = \exp\left(-\frac{\Delta_r G_{500}^0(1, r_a)}{RT}\right)$$

$$K(1, r_a) = 7.22 \times 10^{-3}; \quad r_a = 10^{-8} \text{ m} \quad K(1, r_a) = 11.4 \times 10^{-3}; \quad r_a = 10^{-9} \text{ m}$$

2.3 The standard Gibbs energy for reaction (1) involving nanoparticles of cobalt is

$$\Delta_r G_{500}^0(1, r_a) = \Delta_r G_{500}^0(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co})$$

$\Delta_r G_{500}^0(1)$ is 20.7 kJ mol^{-1} . For spherical cobalt particles with $r_a = 1 \text{ nm}$ $\Delta_r G_{500}^0(1, r_a)$ is 18.6 kJ mol^{-1} .

Solid cobalt oxide can be formed spontaneously when Gibbs energy of reaction (1) is negative. The inequality for bulk cobalt is:

$$\Delta_r G(1) = \Delta_r G_{500}^0(1) + RT \ln\left(\frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}\right) = \Delta_r G_{500}^0(1) - RT \ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \leq 0$$

and for spherical cobalt nanoparticles with $r_a = 1 \text{ nm}$:

$$\begin{aligned} \Delta_r G(1, r_a) &= \Delta_r G_{500}^0(1, r_a) + RT \ln\left(\frac{p(\text{H}_2)}{p(\text{H}_2\text{O})}\right) = \\ &= \Delta_r G_{500}^0(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) - RT \ln\left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)}\right) \leq 0 \end{aligned}$$

$\Delta_r G_{500}^0(1)$ is equal to 20.7 kJ mol^{-1} . For spherical cobalt particles with $r_a = 1 \text{ nm}$ equals to 18.6 kJ mol^{-1}

2.4 For the spontaneous oxidation

$$\Delta_r G(1, r_a) = \Delta_r G_{500}^0(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) - RT \ln \left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)} \right) \leq 0$$

and

$$\Delta_r G_{500}^0(1) - \frac{2\sigma_{\text{Co-gas}}}{r_a} V(\text{Co}) \leq RT \ln \left(\frac{p(\text{H}_2\text{O})}{p(\text{H}_2)} \right)$$

The left hand side of the last inequality becomes more positive with the increase of r_a . At certain point the inequality will be disturbed and the spontaneous oxidation will not take place. So, to protect cobalt nanoparticles from the spontaneous oxidation in this case one has to lengthen the radius r_a . The answer (a) is correct.

2.5 The equation for the standard molar Gibbs function of CoO (external layer) reads:

$$G_{\text{sph}}^0(\text{CoO}, r_b) = G_{\text{bulk}}(\text{CoO}) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO}) = G^0(\text{CoO}, \text{s}) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO})$$

2.6 The equation for the standard molar Gibbs function of Co (internal layer) reads:

$$\begin{aligned} G_{\text{sph}}^0(\text{Co}, r_a, r_b) &= G_{\text{bulk}}(\text{Co}) + V(\text{Co}) \left(\frac{2\sigma_{\text{CoO-gas}}}{r_b} + \frac{2\sigma_{\text{CoO-Co}}}{r_a} \right) = \\ &= G^0(\text{Co}, \text{s}) + V(\text{Co}) \left(\frac{2\sigma_{\text{CoO-gas}}}{r_b} + \frac{2\sigma_{\text{CoO-Co}}}{r_a} \right) \end{aligned}$$

The expression in brackets gives the additional pressure in the internal layer (see the Hint).

2.7 The standard Gibbs energy for reaction (1) with the double-layered nanoparticles is

$$\begin{aligned} \Delta_r G^0(1, r_a, r_b) &= G_{\text{sph}}^0(\text{CoO}, r_b) + G^0(\text{H}_2, \text{gas}) - G^0(\text{H}_2\text{O}, \text{gas}) - G_{\text{sph}}^0(\text{Co}, r_a, r_b) = \\ &= G^0(\text{CoO}, \text{s}) + G^0(\text{H}_2, \text{gas}) - G^0(\text{H}_2\text{O}, \text{gas}) - G^0(\text{Co}, \text{s}) + \\ &\quad + \frac{2\sigma_{\text{CoO-gas}}}{r_b} V(\text{CoO}) - 2V(\text{Co}) \left(\frac{\sigma_{\text{CoO-gas}}}{r_b} + \frac{\sigma_{\text{CoO-Co}}}{r_a} \right) = \\ &= \Delta_r G^0(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} (V(\text{CoO}) - V(\text{Co})) - \frac{2\sigma_{\text{CoO-Co}}}{r_a} V(\text{Co}) \end{aligned}$$

2.8 Under the assumptions made

$$\begin{aligned}\Delta_r G^0(1, r_a, r_b) &= \Delta_r G^0(1, r_0) = \\ &= \Delta_r G^0(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_b} (V(\text{CoO}) - V(\text{Co})) - \frac{2\sigma_{\text{CoO-Co}}}{r_a} V(\text{Co}) = \\ &= \Delta_r G^0(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_0} \left(V(\text{CoO}) - \frac{3}{2} V(\text{Co}) \right)\end{aligned}$$

The term in brackets in the right-hand side is positive

$$\left(V(\text{CoO}) - \frac{3}{2} V(\text{Co}) \right) = 6.56 \times 10^{-6} \text{ m}^3$$

$\Delta_r G^0(1, r_0)$ is directly proportional to $\left(\frac{1}{r_0} \right)$. The plot (a) is correct.

2.9 The spontaneous forward reaction (1) is possible, when $\Delta_r G(1, r_0) \leq 0$, and

$$\Delta_r G^0(1) + \frac{2\sigma_{\text{CoO-gas}}}{r_0} \left(V(\text{CoO}) - \frac{3}{2} V(\text{Co}) \right) \leq RT \ln \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}}$$

The term in brackets in the left-hand side is positive. The left hand side of the inequality becomes more positive with the decrease of r_0 . At certain point the inequality will be violated and the spontaneous oxidation will not take place.

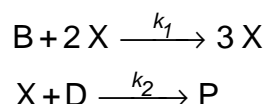
In order to protect nanoparticles from oxidation in this case one has to shorten the radius r_0 .

The answer (b) is correct.

PROBLEM 3**Unstable chemical reactions**

Many chemical reactions display unstable kinetic behavior. At different conditions (concentrations and temperature) such reactions can proceed in various modes: stable, oscillatory or chaotic. Most of these reactions include autocatalytic elementary steps.

Consider a simple reaction mechanism involving autocatalytic step:



(B and D are reagents, X is an intermediate and P is a product).

- 3.1** Write down the overall reaction equation for this two-step mechanism. Write the rate equation for X.
- 3.2** Deduce a rate equation using steady-state approximation. Find the orders:
- a partial reaction order with respect to B;
 - a partial reaction order with respect to D;
 - the overall order of a reaction.

Let the reaction occur in an open system where reagents B and D are being continuously added to the mixture so that their concentrations are maintained constant and equal: $[\text{B}] = [\text{D}] = \text{const}$.

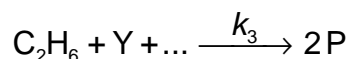
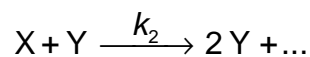
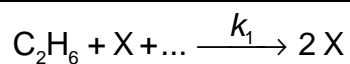
- 3.3** Without solving the kinetic equation draw the kinetic curve $[\text{X}](t)$ for the cases:

$$1) [\text{X}]_0 > \frac{k_2}{k_1}; \quad 2) [\text{X}]_0 < \frac{k_2}{k_1}.$$

- 3.4** Without solving the kinetic equation draw the kinetic curve $[\text{X}](t)$ for the case when the reaction proceeds in a closed vessel with the initial concentrations: $[\text{B}]_0 = [\text{D}]_0$,

$$[\text{X}]_0 > \frac{k_2}{k_1}.$$

Much more complex kinetic behavior is possible for the reactions with several intermediates. Consider a simplified reaction mechanism for cold burning of ethane in oxygen:



Under specific conditions this reaction displays oscillatory behavior:

Intermediates are peroxide $\text{C}_2\text{H}_6\text{O}_2$ and aldehyde $\text{C}_2\text{H}_4\text{O}$, P is a stable product.

3.5 Identify X, Y, and P. Fill the blanks in the reaction mechanism.

Behavior of unstable reactions is often controlled by temperature which affects the rate constants. In the above oxidation mechanism oscillations of concentrations are possible only if $k_1 \geq k_2$. Parameters of the Arrhenius equations were determined experimentally:

Step	A, $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$	E_A , kJ mol^{-1}
1	1.0×10^{11}	90
2	3.0×10^{12}	100

3.6 What is the highest temperature at which oscillatory regime is possible? Show your calculations.

SOLUTION

3.1 The overall reaction equation



The kinetic equation for X

$$\frac{d[\text{X}]}{dt} = k_1[\text{B}][\text{X}]^2 - k_2[\text{D}][\text{X}]$$

3.2 Under the steady-state conditions

$$\frac{d[\text{P}]}{dt} = k_2[\text{D}][\text{X}] = k_1[\text{B}][\text{X}]^2,$$

whence

$$[X] = \frac{k_2[D]}{k_1[B]}$$

$$\frac{d[P]}{dt} = \frac{k_2^2[D]^2}{k_1[B]}$$

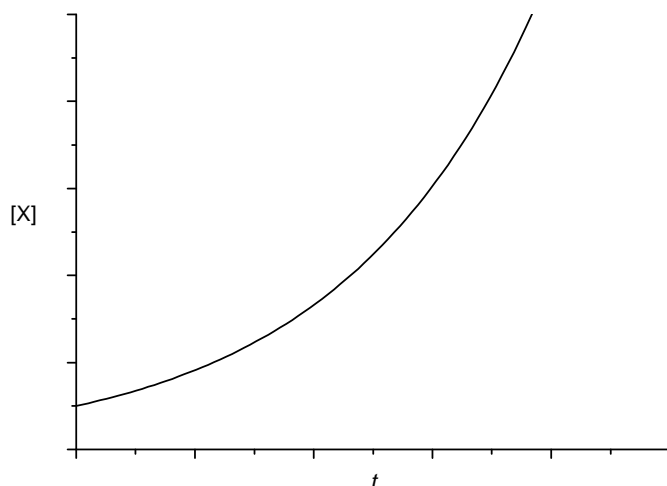
The reaction order is 2 with respect to D, and -1 with respect to B.

The overall order is 1.

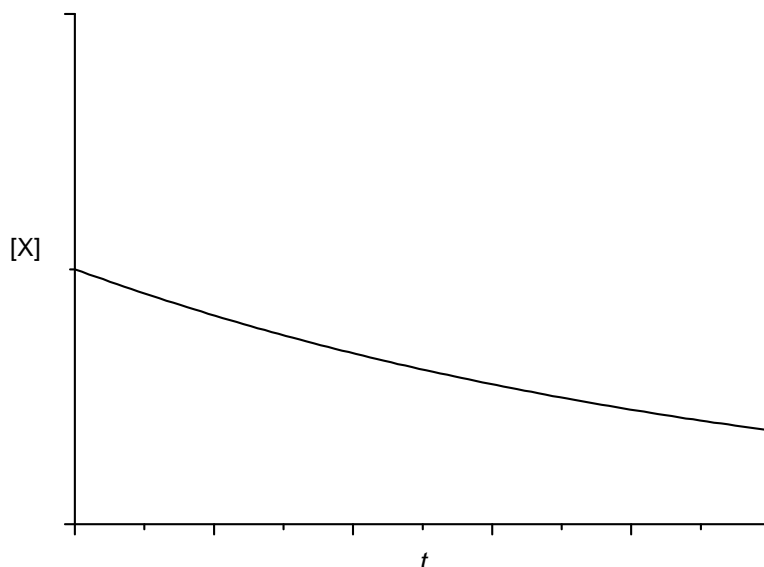
3.3 In an open system the initial reaction rate is:

$$\frac{d[X]}{dt} = [B][X](k_1[X] - k_2)$$

1) If $[X]_0 > k_2/k_1$, then $d[X]/dt > 0$ at any time, and the concentration of X monotonically increases:



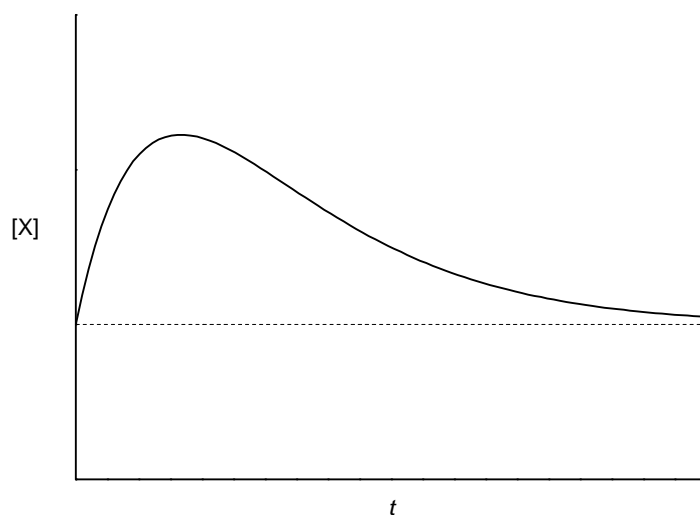
2) If $[X]_0 < \frac{k_2}{k_1}$, then $\frac{d[X]}{dt} < 0$ at any time, and the concentration of X monotonically decreases:



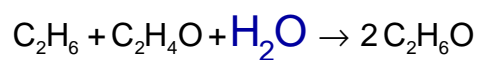
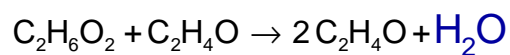
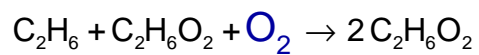
3.4 In a closed system the initial reaction rate is:

$$\left. \frac{d[X]}{dt} \right|_{t=0} = k_1[B]_0[X]_0^2 - k_2[D]_0[X]_0 = [B]_0[X]_0 (k_1[X]_0 - k_2) > 0$$

Hence, at the beginning of the reaction $[X]$ increases but it cannot increase infinitely and finally goes to its initial value, because the second reaction is irreversible:



3.5 X – C₂H₆O₂, Y – C₂H₄O, P – C₂H₆O. Dots denote O₂ and H₂O.



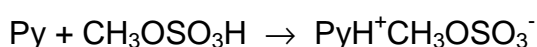
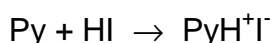
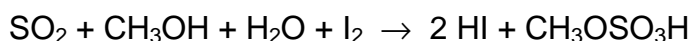
3.6 At the highest possible temperature the rate constants are equal:

$$A_1 \exp\left(-\frac{E_{A,1}}{RT}\right) = A_2 \exp\left(-\frac{E_{A,2}}{RT}\right)$$

$$T = \frac{E_{A,2} - E_{A,1}}{R \ln \frac{A_2}{A_1}} = 354 \text{ K}$$

PROBLEM 4**Determination of water by Fischer titration**

Determination of water by the classical Fischer method involves titration of a sample solution (or suspension) in methanol by a methanolic iodine solution, containing also an excess of SO₂ and pyridine (C₅H₅N, Py) – Fischer reagent. The following reactions occur during the titration:



Iodine content is usually expressed in mg of water reacting with 1 cm³ of the titrant solution (hereunder T, mg cm⁻³), which equals the mass of water (mg) reacting with 1.00 cm³ of the iodine solution. T is determined experimentally by titration of a sample with a known water content. The sample may be, for example, a hydrated compound or a standard solution of water in methanol. In the latter case it should be taken into account that methanol itself can contain certain amount of water.

In all calculations please use the atomic masses accurate to 2 decimal points.

4.1 Sometimes titration of water is performed in pyridine medium without methanol. How would the reaction of I₂ with SO₂ and H₂O occur in this case? Write down balanced reaction equation.

Calculate the T values of iodine solution in each of the following cases:

4.2 12.20 cm³ of Fischer reagent solution were used for titration of 1.352 g of sodium tartrate dihydrate Na₂C₄H₄O₆ · 2 H₂O.

4.3 A known amount of water (21.537 g) was placed into a 1.000 dm³ volumetric flask which was filled by methanol up to the mark. For titration of 10.00 cm³ of the obtained solution, 22.70 cm³ of Fischer reagent solution were needed, whereas 2.20 cm³ of iodine were used for titration of 25.00 cm³ of methanol.

4.4 5.624 g of water were diluted by methanol up to a total volume of 1.000 dm³ (solution **A**); 22.45 cm³ of this solution were used for titration of 15.00 cm³ of a Fischer reagent (solution **B**).

Then 25.00 cm³ of methanol (of the same batch as used for the preparation of solution **A**) and 10.00 cm³ of solution **B** were mixed, and the mixture was titrated by the solution **A**. 10.79 cm³ of the latter solution were spent.

4.5 An inexperienced analyst tried to determine water content in a sample of CaO using Fischer reagent. Write down the equation(s) of reaction(s) demonstrating possible sources of errors.

For the titration of 0.6387 g of a hydrated compound Fe₂(SO₄)₃ · x H₂O, 10.59 cm³ of iodine solution (T = 15.46 mg/cm³) were consumed.

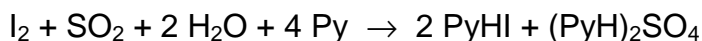
4.6 What other reaction(s), beside those given in the problem, can occur during the titration? Write down the equations of two such processes.

4.7 Write down an equation of the overall reaction of Fe₂(SO₄)₃ · x H₂O with the Fischer reagent.

4.8 Calculate the composition of the hydrate Fe₂(SO₄)₃ · x H₂O (x = integer).

SOLUTION

4.1 Equation:



4.2 T is equal to:

$$M(\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2 \text{H}_2\text{O}) = 230.05 \text{ g mol}^{-1} \quad 2 \times M(\text{H}_2\text{O}) = 36.04 \text{ g mol}^{-1}$$

$$m(\text{H}_2\text{O}) = \frac{1.3520 \times 36.04}{230.05} = 0.2118 \text{ g} = 211.8 \text{ mg}$$

$$T = \frac{211.8}{12.20} = 17.36 \text{ mg cm}^{-3}$$

$$T = 17.36 \text{ mg cm}^{-3}$$

4.3 T is equal to:

$$\text{Volume of iodine consumed for } 10 \text{ cm}^3 \text{ of pure CH}_3\text{OH} = \frac{2.20 \times 10.00}{25.00} = 0.88 \text{ cm}^3$$

$$T = \frac{21.537 \times 0.01 \times 10^3}{22.70 - 0.88} = 9.87 \text{ mg cm}^{-3}$$

More exactly

10.00 cm³ of the solution contains $\frac{(1000 - 21.5) \times 10.00}{1000} = 9.785$ cm³ of methanol.

Volume of iodine consumed for 9,785 cm³ of pure CH₃OH = $\frac{2.20 \times 9,785}{25.00} =$
 $= 0.86$ cm³

$T = \frac{21.537 \times 0.01 \times 10^3}{22.70 - 0.86} = 9.86$ mg cm⁻³

$T = 9.87$ mg cm⁻³

4.4 T is equal to:

Approach 1

Let 1 cm³ of CH₃OH contains x mg H₂O, then 1 cm³ of **A** contains
 [(1.000 - 0.006) x + 5.624] mg H₂O.

15.00 T = 22.45 (0.994 x + 5.624) - 1st titration,

10.00 T = 25.00 x + 10.79 (0.994 x + 5.624) - 2nd titration.

Hence, x = 1.13 mg cm⁻³, T = 10.09 mg cm⁻³ (10.10 without taking into account 0.994 factor)

Approach 2

Let y cm³ of **B** be consumed for the titration of water, contained in 1 cm³ of CH₃OH.

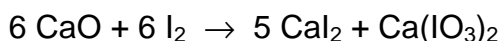
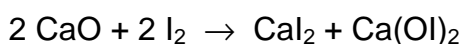
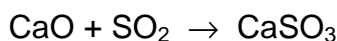
Then $T = \frac{22.45 \times 5.624}{15.00 - 22.45 \times 0.994 \times y}$ (1st titration) = $\frac{10.79 \times 5.624}{10.00 - 25.00 y - 10.79 y}$

(2nd titration).

Hence, y = 0.1116 and T = 10.10 mg cm⁻³

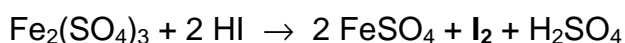
T = 10.09 mg cm⁻³ (10.10 without taking into account 0.994 factor)

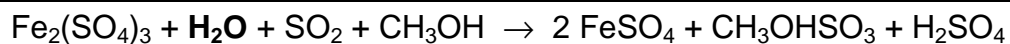
4.5 Equation(s):



(Instead of CaO, Ca(OH)₂ may be written.)

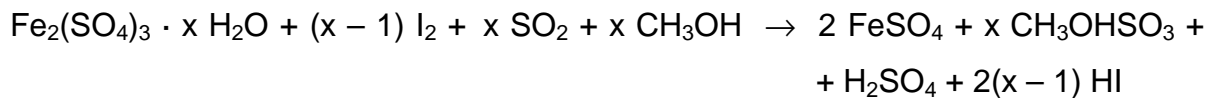
4.6 Equation(s):





(or in ionic form)

4.7 Equation:



4.8 The composition of the crystalhydrate is:

$$M(\text{Fe}_2(\text{SO}_4)_3 \cdot x \text{H}_2\text{O}) = 399.9 + 18.02 x$$

$$m(\text{H}_2\text{O}) = \frac{0.6387 \times 18.02 x}{(399.9 + 18.02 x)}$$

$$m(\text{H}_2\text{O}) = 10.59 \text{ cm}^3 \times 15.46 \text{ mg cm}^{-3} \times 0.001 \text{ g mg}^{-1} \times \frac{x}{x-1}$$

$$0.1637 \times (399.9 + 18.02 x) = 11.51 x - 11.51$$

$$x = 8.994 \approx 9$$

$$\text{Formula: Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$$

PROBLEM 5

A mysterious mixture (organic hide-and-seek game)

An equimolar mixture **X** of three colourless organic liquids **A**, **B**, **C** was treated by water containing a drop of hydrochloric acid at heating to give (after separation from water) a 1 : 2 (molar ratio) mixture of acetic acid and ethanol without any other components. A catalytic amount (one-two drops) of concentrated sulfuric acid was added to the mixture after hydrolysis and after a long reflux (boiling with reflux condenser) a compound **D**, a volatile liquid with pleasant smell, was formed in 85% yield. Compound **D** is not identical with any of **A**, **B**, **C**.

5.1 Draw the structure of compound **D**?

5.2 Which class of organic compounds does **D** belong to? Choose the proper variant from those given in the Answer Sheet.

5.3 Even if the reflux is continued twice as long, the yield of **D** would not exceed 85%. Calculate the expected yield of **D** if 1 : 1 (molar ratio) mixture of ethanol and acetic acid is taken. Assume that: a) volumes do not change during the reactions; b) all concomitant factors, such as solvent effects, non-additivity of volumes, variation of temperature, etc. are negligible. If you cannot make a quantitative estimate, please indicate whether the yield will be: a) the same (85 %); b) higher than 85 %; c) lower than 85 %.

¹H NMR spectra of compounds **A**, **B**, **C** look very similar and each shows singlet, triplet and quartet with the ratio of integral intensities equal to 1 : 3 : 2.

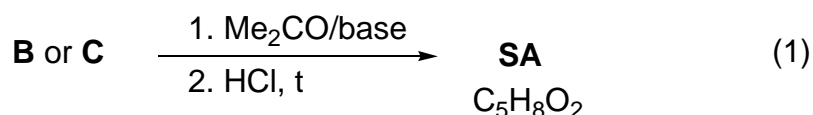
The same mixture **X** was subjected to alkaline hydrolysis. **A** remained unchanged, and was separated. After acidification and short boiling the remaining solution gave 2 : 3 (molar ratio) mixture of acetic acid and ethanol with evolution of gas.

The mixture **X** (3.92 g) was dissolved in diethyl ether and underwent hydrogenation in the presence of Pd on charcoal catalyst. 0.448 dm³ (standard conditions) of hydrogen were absorbed, but after the reaction **A** and **C** were isolated unchanged (3.22 g of mixture were recovered) while neither **B**, nor any other organic compounds, except diethyl ether, could be identified after hydrogenation.

5.4 Determine and draw the structures of **A**, **B**, and **C**.

5.5 Which intermediate compounds are formed during the acidic hydrolysis of **C** and the basic hydrolysis of **B**.

The reaction of either **B** or **C** with acetone (in the presence of a base) with subsequent acidification by dilute HCl at gentle heating gives the same product, senecioic acid (**SA**), a compound widely occurring in Nature. Alternatively, senecioic acid can be obtained from acetone by treating it with concentrated HCl and subsequent oxidation of the intermediate product by iodine in alkaline solution. The latter reaction gives, besides sodium salt of senecioic acid, a heavy yellow precipitate **E** (see the scheme 2).

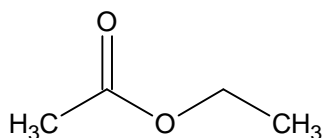


5.6 Determine the structure of senecioic acid and draw the reaction scheme leading to senecioic acid from acetone.

5.7 Give structure of **E**

SOLUTION

5.1 Structure of product **D**



Ethyl acetate, ethyl ethanoate

5.2 Which class of organic compounds does **D** belong to? Check the appropriate box.

ketones	ethers	acetals	esters	alcohols	aldehydes	glycols
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

5.3 The expected yield of **D**

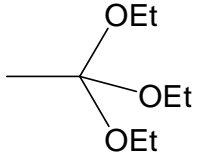
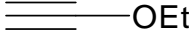
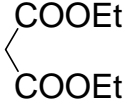
The reaction is an equilibrium without any further actions. Qualitative estimation:
The yield is lower than 85 %.

Assuming that the reaction is at equilibrium and that the equilibrium constant is supposed not to vary with temperature and composition of the reaction mixture, we can calculate:

$$K = \frac{[\text{AcOEt}][\text{H}_2\text{O}]}{[\text{AcOH}][\text{EtOH}]} = \frac{(0.85)^2}{0.15 \times 1.15} = 4.2$$

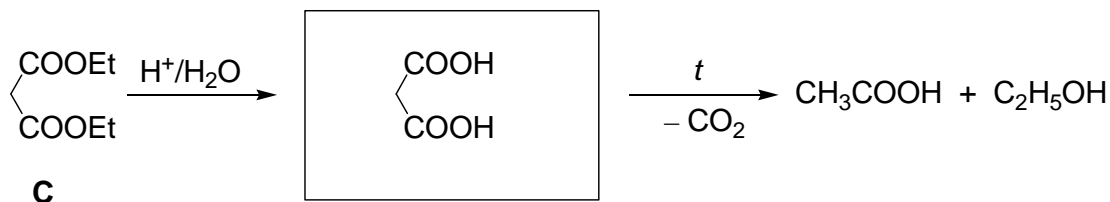
Using this constant calculation of yield in 1 : 1 mixture gives 67 %.

5.4 The structures of **A**, **B**, and **C**.

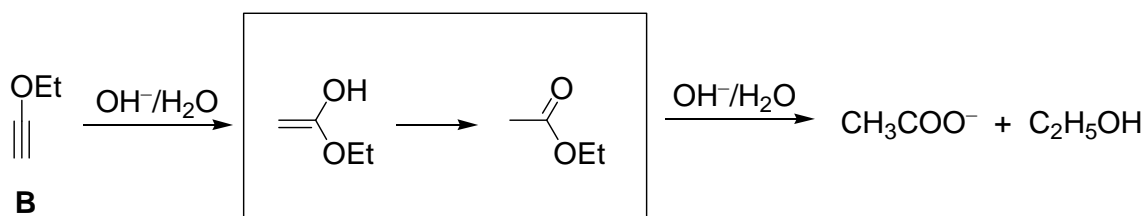
 <p>$\text{CH}_3\text{C}(\text{OEt})_3$</p> <p>triethyl orthoacetate, 1,1,1-triethoxyethane</p>	 <p>$\text{HC}\equiv\text{COEt}$</p> <p>ethoxyacetylene, ethynylethyl ether</p>	 <p>$\text{CH}_2(\text{COOEt})_2$</p> <p>diethyl malonate</p>
A	B	C

5.5 Draw in the boxes intermediate compounds formed during the acidic hydrolysis of **C**, and basic hydrolysis of **B**.

a) Malonic acid is formed as intermediate in the hydrolysis of diethyl malonate:

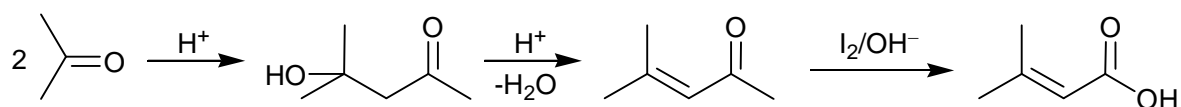


b) Hydrolysis of ethoxyacetylene starts from the addition of hydroxide to the triple bond to give unstable enolic form of ethylacetate, into which it immediately is transformed



5.6 The structure of senecioic acid:

From acetone alone the synthesis includes aldol condensation and dehydration with subsequent iodoform reaction:



5.7 The structure of **E**.

Iodoform, triiodomethane, CHI_3

PROBLEM 6**Silicates as the base of the Earth crust**

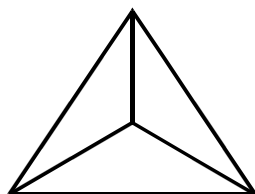
Silica and compounds derived from it, silicates, constitute ca. 90 % of the Earth crust substances. Silica gives rise to a beautiful material – glass. Nobody knows exactly how glass was discovered. There is a well-favored story related to Phoenician sailors who fused occasionally sea sand and soda ash. It is likely that they discovered the secret of “liquid glass” (LGL) – sodium metasilicate (Na_2SiO_3) soluble in water.

6.1 The solution of LGL was used earlier as office glue. Write down the net ionic equation accounting for the ability of LGL to set in air.

Hydrolysis of LGL in water allows obtaining a colloidal solution of silicic acid.

6.2 Complete the Table in the Answer Sheet. Write down the net ionic equations matching the processes enumerated in the Table. For each process check the “Yes” box if it leads to changes of pH. Otherwise check the “No” box.

The structure of species occurring in aqueous solutions of silicates is rather complex. However, it is possible to distinguish the main building block of all species – orthosilicate tetrahedron (SiO_4^{4-} , **1**):

**(1)**

For $[\text{Si}_3\text{O}_9]^{n-}$ ion found in aqueous solutions of silicates:

6.3 Determine the charge (n).

6.4 Determine the number of oxygen atoms bridging adjacent tetrahedra.

6.5 Depict its structure joining together several tetrahedra (**1**). Take into account that any adjacent tetrahedron shares one vertex.

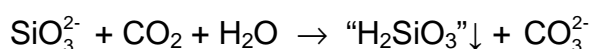
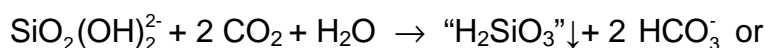
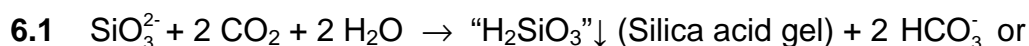
Charged monolayers with the composition $[\text{Si}_4\text{O}_{10}]^{m-}$ are found in kaolinite (clay).

6.6 Using the same strategy as in **6.3 - 6.5**, depict a fragment of the layered structure joining 16 tetrahedra (**1**). Note that 10 tetrahedra have shared vertices with 2 neighbours each, and the rest 6 have shared vertices with 3 neighbours each.

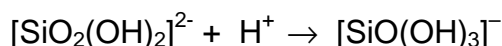
Being placed into the LGL solution, salts of transition metals give rise to fancy “trees” tinted relevant to the colour of the salt of the corresponding transition metal. Crystals of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ produce “trees” of blue colour, whereas those of $\text{NiSO}_4 \cdot 7 \text{H}_2\text{O}$ form green “trees”.

- 6.7** Determine the pH of 0.1 M aqueous solution of copper sulphate at 25 °C assuming that its hydrolysis occurs in small degree only. Use the value of the first acidity constant of $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ $K_a^1 = 1 \times 10^{-7}$.
- 6.8** Write down equation of a reaction between aqueous solutions of CuSO_4 and sodium metasilicate (LGL). Take into account the pH values of aqueous solutions of the salts.

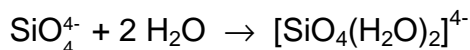
SOLUTION



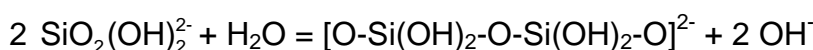
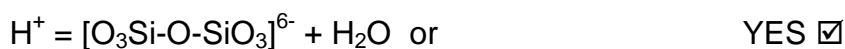
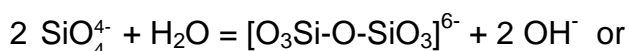
- 6.2** a) protonation of ortho-silicate ions leading to the formation of Si-OH groups:



- b) formation of hydrated $[\text{SiO}_4(\text{H}_2\text{O})_2]^{4-}$ anions NO



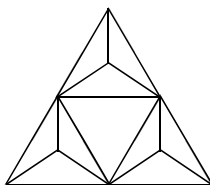
- c) polycondensation of ortho-silicate ions leading to the formation of Si-O-Si bonds



6.3 $n = 6$ (assuming oxidation numbers of silicon (+4) and oxygen (-2), or taking into account its structure and the charge of orthosilicate ion (-4))

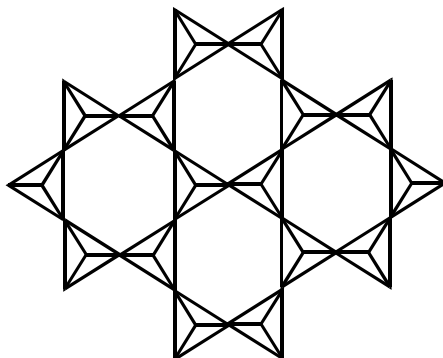
6.4 $\text{Si}_3\text{O}_9 \equiv 3 [\text{SiO}_4] - 3 \text{O}$, i.e. there are 3 oxygen atoms bridging adjacent tetrahedra

6.5



6.6 $m = 4$ (assuming oxidation numbers of silicon (IV) and oxygen (-II), or taking into account its structure and the charge of orthosilicate ion (-4))

$\text{Si}_4\text{O}_{10} \equiv 4[\text{SiO}_4] - 6 \text{O}$, i. e. the formula of the tetrahedron is now $\text{SiO}_{2.5}$, which is possible if 1 O atom belongs to this tetrahedron and the other three are shared between 2 tetrahedra (their contribution = 3/2). This is possible if the tetrahedra are set on a plane and joined together through all apexes of their bases.



6.7 $\text{Cu}(\text{H}_2\text{O})_4^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{OH})(\text{H}_2\text{O})_3^+ + \text{H}_3\text{O}^+$,
 $[\text{H}^+] \approx (c K_a)^{1/2} = 1 \times 10^{-4}$, $\text{pH} = -\log[\text{H}^+] = 4$
 $\text{pH} = 4$

6.8 $\text{CuSO}_4 + \text{Na}_2\text{SiO}_3 + 2 \text{H}_2\text{O} \rightarrow \text{Cu}(\text{OH})_2 \downarrow + \text{“H}_2\text{SiO}_3\text{”} \downarrow + \text{Na}_2\text{SO}_4$

or

$2 \text{CuSO}_4 + \text{Na}_2\text{SiO}_3 + 2 \text{H}_2\text{O} \rightarrow \text{Cu}_2(\text{OH})_2\text{SO}_4 \downarrow + \text{“H}_2\text{SiO}_3\text{”} \downarrow + \text{Na}_2\text{SO}_4$

This (or those) reaction(s) (apart from formation of copper silicate) can be deduced from the fact that the reaction describes mutual (self-amplifying) hydrolysis. It comes

from the previous parts of the task: pH of LGL is greater than 7 (see questions **6.2**), and pH of copper sulfate solution is less than 7 (see **6.7**).

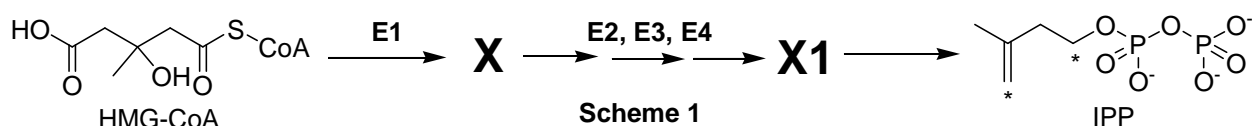
PROBLEM 7

Atherosclerosis and intermediates of cholesterol biosynthesis

Cholesterol is a lipid wide-spread in living nature. Disruption of its metabolism leads to atherosclerosis and related potentially fatal diseases.

Substances **X** and **Y** are two key intermediates of cholesterol biosynthesis in animals.

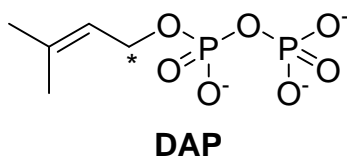
X is an optically active monocarboxylic acid composed of atoms of only three elements. It is formed in organisms from (S)-3-hydroxy-3-methylpentanedioyl-coenzyme A (HMG-CoA). This reaction is catalyzed by enzyme **E1** (which catalyses two types of reactions) and does not involve water as a substrate. **X** is further metabolized into **X1** through a three-stage process requiring enzymes **E2**, **E3**, **E4**, which catalyze reactions of one and the same (and only one) type. Finally, **X1** spontaneously (non-enzymatically) decomposes to give isopentenyl pyrophosphate (3-methylbut-3-enyl diphosphate, IPP) and inorganic products:



7.1 In the Answer Sheet, choose the reaction type(s) for **E1** and **E3**.

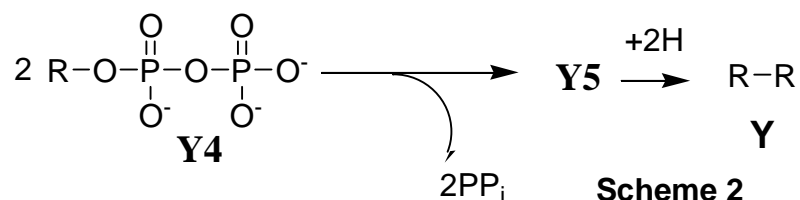
7.2 Draw the structure of **X** with stereochemical details and indicate absolute configuration (R or S) of the stereocenter.

Y is an unsaturated acyclic hydrocarbon. Its reductive ozonolysis leads to a mixture of only three organic substances **Y1**, **Y2** and **Y3** in a molar ratio of 2:4:1. **Y** is formed as a result of a number of successive coupling reactions of two isomeric substances: IPP and dimethyl allyl pyrophosphate (3-methylbut-2-enyl diphosphate, DAP) with subsequent reduction of a double bond in the final coupling product **Y5**. Carbon atoms IPP and DAP involved in the formation of C-C bonds during biosynthesis of **Y** are marked with asterisks.



7.3 Write down the overall reaction equation for reductive ozonolysis of DAP, if dimethyl sulfide is used as the reducing agent.

The product of the final coupling reaction (hydrocarbon **Y5**) is formed when two hydrocarbon residues (R) of intermediate **Y4** are combined:



At each coupling stage but that shown in Scheme 2, pyrophosphate is released in a molar ratio of 1 : 1 to the coupling product.

- 7.4** Determine molecular formula of **Y**, if it is known that **Y2** and **Y3** contain 5 and 4 carbon atoms, respectively.
- 7.5** Calculate the number of IPP and DAP molecules needed to give **Y5**, if it is known that all carbon atoms of isomeric pyrophosphates are incorporated into **Y**.
- 7.6** Draw the product of coupling reaction of one IPP molecule with one DAP molecule (C-C bond can be formed only by carbon atoms marked with asterisks), if it is known that subsequent reductive ozonolysis of the product of the coupling reaction gives **Y1**, **Y2** and one more product, the latter containing phosphorus.

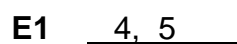
The only double bond reduced in **Y5** during its metabolism into **Y** was formed in the reaction described in Scheme 2. All double bonds in **Y** and **Y4** exist in trans configuration.

7.7 Draw structures of **Y** and **Y4** with stereochemical details.

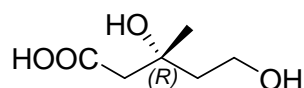
SOLUTION

7.1 **E2 - E4** catalyze one and the same (and only one) reaction type. The only reaction which can be carried out three times in a row is monophosphorylation (all the rest reaction types are not consistent with either initial or final products). This is also supported by presence of pyrophosphate residue in IPP and liberation of inorganic products (including inorganic phosphate) upon spontaneous decomposition of **X1**.

X is a monocarboxylic acid composed of atoms of three elements: carbon, hydrogen and oxygen. It can contain neither sulfur which is found in CoA nor phosphorus which is introduced into intermediates on the pathway from HMG-CoA towards IPP or present in CoA. Thus, **E1** catalyzes non-hydrolytic removal of CoA from HMG-CoA and is not involved in phosphorylation. Since water is not a substrate in this reaction, liberation of CoA must be conjugated with another reaction which affects the carboxylic group esterified in HMG-CoA. The only possible variant is its 4 electron reduction towards hydroxyl group. **E1** can not catalyze dehydration because of optical activity of **X** (removal of water leads to the loss of sole chiral center). Decarboxylation is excluded, since **X**, being an acid, must contain a carboxylic group. Oxidation of tertiary hydroxyl group in HMG-CoA according to β -oxidation mechanism is impossible. Further evidence comes from the fact that the carboxylic group initially involved in thioester bond formation is present as the residue of hydroxyl group in IPP. So:

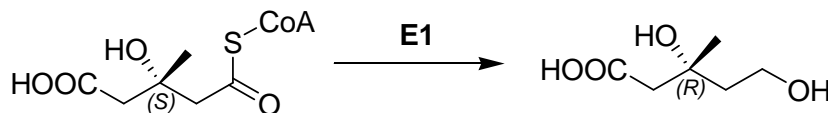


7.2 Based on the reaction types catalyzed by **E1** and configuration of HMG-CoA stereocenter, the structure of **X** is:

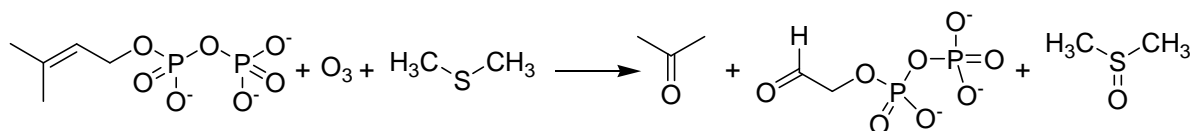


X, mevalonic acid

Note the absolute configuration of the chiral center is changed as a result of HMG-CoA metabolism into mevalonic acid due to alteration of substituents priority.



7.3 Reaction equation for reductive ozonolysis:



7.4 DAP molecule contains only one carbon atom which can be involved in the formation of C–C bond during **Y** biosynthesis. Irrespective of the way this molecule is incorporated in **Y**, ozonolysis of this fragment will lead to dimethyl ketone (acetone). (See DAP ozonolysis reaction in 7.2.1). Thus, acetone can be unambiguously attributed to **Y1**, since it contains 3 carbon atoms (**Y2** and **Y3** contain 5 and 4 carbon atoms, respectively). Taking into account the ratio between ozonolysis products, we have:

$$n_Y(\text{C}) = 2 \cdot n_{Y1}(\text{C}) + 4 \cdot n_{Y2}(\text{C}) + n_{Y3}(\text{C}) = 2 \cdot 3 + 4 \cdot 5 + 4 = 30$$

Y is an acyclic molecule, thus DAP residues can be found only at its ends. **Y** has only two ends, since IPP contains only two elongation sites (at least three such sites are needed to get a branched molecule). Since reductive ozonolysis of one **Y** molecule produces two acetone molecules, **Y** contains 30 carbon atoms.

To determine the number of hydrogen atoms double bonds in **Y** should be counted. Formation of each double bond reduces by 2 the number of hydrogen atoms in the coupling product as compared to the sum of atoms of starting substances. The ratio of **Y** to the sum of its ozonolysis products is 1:7 (2+4+1), which corresponds to 6 double bonds in **Y**. Then, by using the general formula for alkanes we have:

$$n(\text{H}) = 2 \cdot n_Y(\text{C}) + 2 - 2 \cdot n_{\text{C}=\text{C}} = 30 \cdot 2 + 2 - 6 \cdot 2 = 50$$

Y (squalene) formula – $\text{C}_{30}\text{H}_{50}$.

Number of carbon atoms: <u>30</u>	Work: $n_Y(\text{C}) = 2 \cdot n_{Y1}(\text{C}) + 4 \cdot n_{Y2}(\text{C}) + n_{Y3}(\text{C}) = 2 \cdot 3 + 4 \cdot 5 + 4 = 30$
Number of hydrogen atoms: <u>50</u>	Work: $n(\text{H}) = 2 \cdot n_Y(\text{C}) + 2 - 2 \cdot n_{\text{C}=\text{C}} = 30 \cdot 2 + 2 - 6 \cdot 2 = 50$

Gross formula of **Y** $\text{C}_{30}\text{H}_{50}$

7.5 IPP and DAP are structural isomers containing 5 carbon atoms each. Since all carbon atoms of these substances are found in **Y**, one can calculate the total quantity of IPP and DAP molecules needed to synthesize **Y**:

$$n(\text{IPP\&DAP}) = n_Y(\text{C})/5 = 30/5 = 6$$

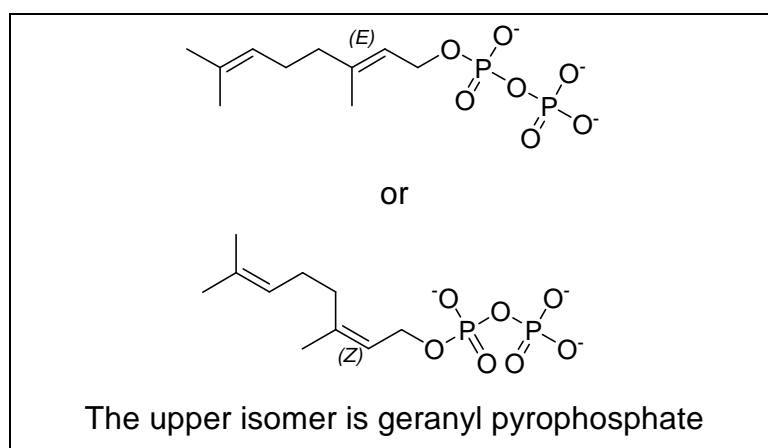
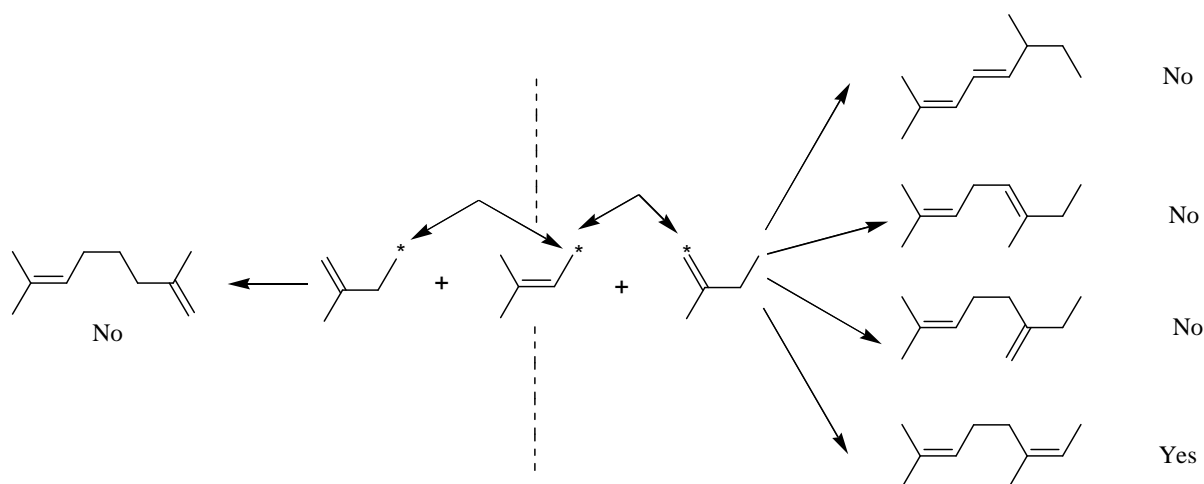
The number of DAP molecules was determined earlier and is equal to 2. Then, 4 molecules of IPP are needed.

$$n(\text{IPP\&DAP}) = n_{\text{Y}}(\text{C})/5 = 30/5 = 6$$

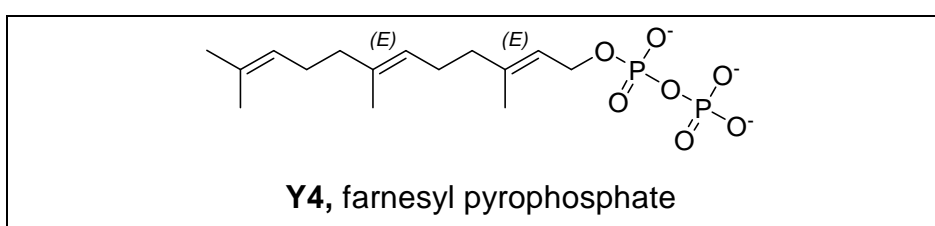
Number of DAP molecules: 2

Number of IPP molecules: 4

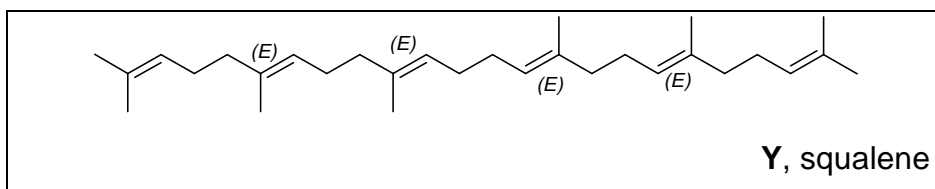
7.6 All possible combinations that do not alter hydrocarbon skeleton are given below (pyrophosphate fragments not shown). Two groups of products differing in carbon atoms involved in coupling reaction are separated by the dashed line. IPP fragments should be attached to DAP so that ozonolysis of the product leads to **Y2** containing 5 carbon atoms. Only one variant is possible if stereochemistry is not taken into consideration and two variants with stereochemical details



7.7 It is seen from the coupling reaction (Scheme 2) that **Y4** contains 15 carbon atoms or 1 DAP and 2 IPP fragments, the latter being attached to the former consecutively. It is important to note that **Y3** can not be found in two hydrocarbon residues originating for **Y4**, since **Y3** is formed as a result of ozonolysis in a molar ratio of 1 : 1 to **Y**. Thus, geranyl phosphate is the intermediate on the way to **Y** (all double bonds in trans configuration). Attachment of the next IPP fragment to geranyl phosphate leads to the product giving 1 molecule of **Y1** and 2 molecules of **Y2** upon its ozonolysis. Thus, **Y4** structure with stereochemical details:



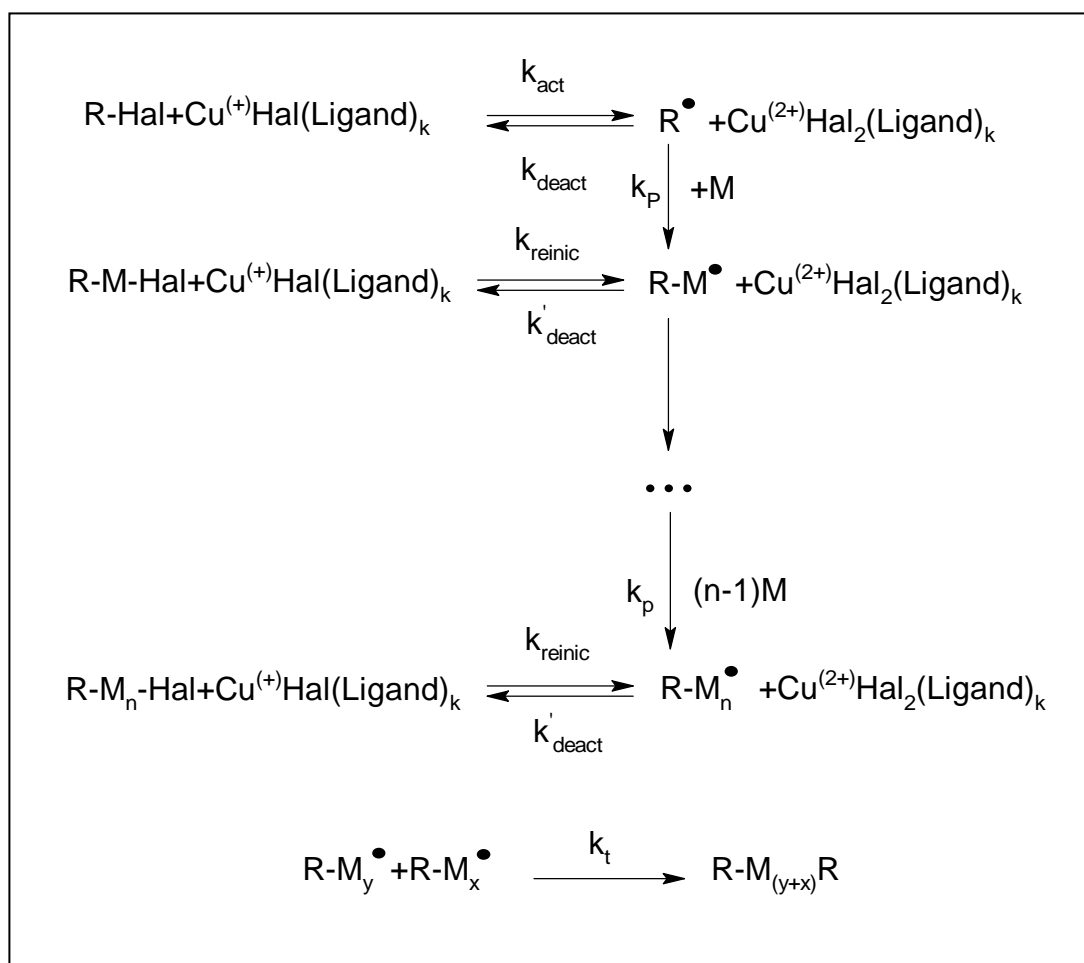
Combining two hydrocarbon fragments of **Y4** and taking into account that the double bond between them is being reduced we get the following structure of **Y**:



PROBLEM 8

ATRP allows new polymers

ATRP (Atom Transfer Radical Polymerization) is one of the most promising novel approaches towards polymer synthesis. This modification of radical polymerization is based on a redox reaction of organic halides with complexes of transition metals, Cu (I) in particular. The process can be described by the following scheme (M – monomer, Hal – halogen):



The reaction rate constants are:

k_{act} - all activation reactions, k_{deact} – all reversible deactivation reactions, k_p - chain propagation, and k_t - irreversible termination.

8.1 Write down expressions for the rates of ATRP elementary stages: activation (v_{act}), deactivation (v_{deact}), propagation (v_p) and termination (v_t). Write down generalized equation assuming just one reacting species R'X.

Consider that the total number of polymeric chains is equal to that of initiator molecules. Assume that at each moment throughout polymerization all chains are of the same length.

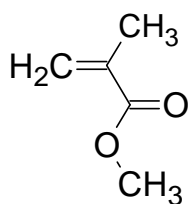
8.2 Compare the rate of deactivation to the rates of ATRP elementary stages.

Dependence of monomer concentration ($[M]$) on reaction time (t) for ATRP is:

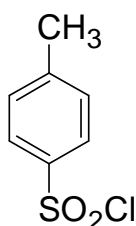
$$\ln\left(\frac{[M]}{[M]_0}\right) = -k_p [R\cdot] t,$$

$[M]_0$ - initial monomer concentration, k_p - rate constant of propagation, $[R\cdot]$ - concentration of active radicals.

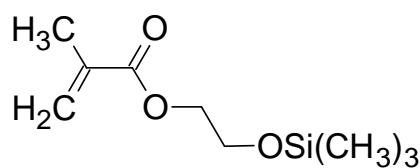
To prepare a polymer sample by using ATRP, catalytic amounts of CuCl, organic ligand (L) and 31.0 mmol of monomer (methylmethacrylate, or MMA) were mixed. The reaction was initiated by adding 0.12 mmol of tosyl chloride (TsCl). Polymerization was conducted for 1400 s. k_p is $1616 \text{ L mol}^{-1}\text{s}^{-1}$, and the steady state concentration of radicals is $1.76 \times 10^{-7} \text{ mol dm}^{-3}$.



MMA



TsCl



HEMA-TMS

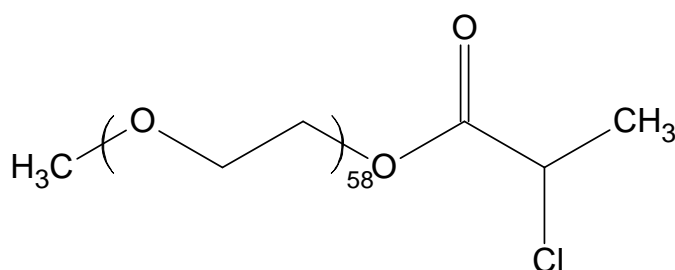
8.3 Calculate mass (m) of the polymer obtained.

In another experiment the time of MMA polymerization was changed, all the rest reaction conditions being the same. The mass of the obtained polymer was 0.73 g. Then 2-(trimethylsilyloxy)ethyl methacrylate, HEMA-TMS (23.7 mmol) was added to the mixture and polymerization was continued for another 1295 s. MMA and HEMA-TMS reactivities are the same under reaction conditions.

8.4 Calculate degree of polymerization (DP) of the obtained polymer.

8.5 Depict the structure of the obtained polymer (including end groups), showing MMA and HEMA-TMS units as A and B, respectively. If necessary, use the symbols in the copolymer structure representation: block (block), stat (statistical), alt (alternating), grad (gradient), graft (grafted). For example, (A₆₅-graft-C₁₀₀)-stat-B₃₄ means that chains of polymer C are grafted on units A in the statistical copolymer of A and B.

ATRP was applied to synthesize two block copolymers, P₁ and P₂. One block in both block-copolymers was the same and was synthesized from mono-(2-chloropropionyl)-polyethylene oxide used as a macroinitiator:



The other block in P₁ consisted of styrene (C), and in P₂ of p-chloromethylstyrene (D) units.

¹H NMR spectra of the macroinitiator, P₁ and P₂ are given below. Integral intensities of characteristic signals can be found in the table.

- 8.6** Assign ¹H NMR signals to substructures given in the Answer Sheet.
- 8.7** Determine molar fractions of units C and D and molecular weights of P₁ and P₂.
- 8.8** Write down all possible reactions of activation occurring during the synthesis of P₁ and P₂. You may use R symbol to depict any unchanged part of the macromolecule, but you should specify what substructure you use it for.
- 8.9** Draw the structure of P₁ and one of possible structures of P₂ representing poly(ethylene oxide) chain by a wavy line and showing units of co-monomers as C and D, respectively.

Thus:

$$V_{\text{deact}} \gg V_{\text{act}}$$

The portion of active radicals must be small, so the equilibrium is shifted towards dormant species.

$$V_{\text{deact}} \gg V_p$$

Propagation rate should be much slower than that of deactivation to make chains propagate with equal rate.

$$V_{\text{deact}} \gg V_t$$

Termination does not occur since the total number of polymer chains is equal to a certain constant number – number of initiator molecules.

$$V_{\text{deact}} \gg V_{\text{act}}$$

$$V_{\text{deact}} \gg V_p$$

$$V_{\text{deact}} \gg V_t$$

8.3 Calculation of mass (m) of the obtained polymer.

1st variant

$$[M] = [M]_0 \exp(-k_p [R\cdot] t) \text{ or } n(\text{MMA}) = n_0(\text{MMA}) \exp(-k_p [R\cdot] t)$$

Quantity of MMA monomer remaining after polymerization during 1400 s is

$$31.0 \times \exp(-1616 \times 1.76 \times 10^{-7} \times 1400) = 20.8 \text{ mmol.}$$

Quantity of monomer consumed during polymerization: $31 - 20.8 = 10.2 \text{ mmol}$

Mass of the obtained polymer is

$$m = \Delta n(\text{MMA}) \times M(\text{MMA}) = \frac{10.2}{1000} \times 100.1 = 1.03 \text{ g}$$

2nd variant

$$[M] = [M]_0 \exp(-k_p [R\cdot] t) \text{ or } n(\text{MMA}) = n_0(\text{MMA}) \exp(-k_p [R\cdot] t)$$

Quantity of MMA monomer consumed during 1400 seconds of polymerization is

$$\begin{aligned} \Delta n(\text{MMA}) &= n_0(\text{MMA}) (1 - \exp(-k_p \times [R\cdot] \times t)) = 31.0 \times (1 - 1616 \times 1.76 \times 10^{-7} \times 1400) = \\ &= 10.2 \text{ mmol} \end{aligned}$$

Mass of the obtained polymer is:

$$m = \Delta n(\text{MMA}) \times M(\text{MMA}) = (10.2 / 1000) \times 100.1 = 1.03 \text{ g}$$

3rd variant

$$\ln\left(\frac{[M]}{[M]_0}\right) = -k_p[R\cdot]t = -1616 \times 1.76 \times 10^{-7} \times 1400 = -0.398$$

$$\frac{[M]}{[M]_0} = e^{-0.398} = 0.672$$

$$\frac{[M]}{[M]_0} = \frac{n(\text{MMA})}{n_0(\text{MMA})}$$

$$n(\text{MMA}) = 0.672 \times n_0(\text{MMA}) = 20.8 \text{ mmol}$$

Quantity of monomer consumed during polymerization is $31 - 20.8 = 10.2$ mmol.

Mass of the obtained polymer is

$$m = \Delta n(\text{MMA}) \times M(\text{MMA}) = (10.2/1000) \times 100.1 = 1.03 \text{ g}$$

8.4 Calculation of degree of polymerization (DP) of the obtained polymer.

The number of growing chains is equal to the number of TsCl molecules (0.12 mmol)

At the first stage, 7.3 mmol of MMA was consumed (0.73 / 100.1).

The total quantity of monomers at the beginning of the 2nd stage is $23.7 + 23.7 = 47.4$ mmol.

Since the monomers have the same reactivity, they will be involved in polymerization with the same rate.

Quantity of monomers consumed during the second stage is

$$\Delta n = n_0(1 - \exp(-k_p[R\cdot]t)) = 47.4(1 - \exp(-1616 \times 1.76 \times 10^{-7} \times 1295)) = 14.6 \text{ mmol.}$$

Totally $7.3 + 14.6 = 21.9$ mmol of monomers was polymerized during two stages.

$$\text{DP} = 21.9 / 0.12 = 182.5$$

DP = 182 – 183 (all answers within this range are credited)

8.5 Structure of the obtained polymer.

The product of polymerization is a block copolymer because it was obtained by sequential polymerization on living chains.

The first block is built of MMA units solely. The DP is $7.3 / 0.12 = 60.8 \approx 61$ monomer units.

The second block is obtained by copolymerization of two competing monomers with the same reactivity. So, it is a statistical copolymer. Fractions of A and B in the 2nd block are equal because their concentrations in the reaction mixture at the beginning

of the 2nd stage were equal. The DP of the 2nd block is $183 - 61 = 122$ monomer units (121 is also correct if the total DP in **8.2.2** is 182).

Ts-A₆₁-block-(A-stat-B)₆₁-Cl or Ts-A₆₁-block-(A₆₁-stat-B₆₁)-Cl

8.6 Assignment of NMR signals to substructures given in the Answer Sheet.

	a, b, g
	c
	d
	e
	f

8.7 Determination of molar fractions of units C and D and molecular weights of P₁ and P₂.

Intensity of multiplets b and g is 40.2, so intensity per 1 proton is $40.2 / 4 / 58 = 0.173$ for both copolymer spectra

Intensity of multiplet c is 13.0, which is equivalent to $13.0 / 0.173 = 75$ protons. Taking into account that each styrene ring has 5 aromatic protons, DP of styrene block is $75 / 5 = 15$.

Molar fraction of styrene units in P₁ is $15 / (15 + 58) = 20.5 \%$

Intensity of multiplet d is 10.4, which is equivalent to $10.4 / 0.173 = 60$ protons. Since each monomer unit of p-chloromethylstyrene has 4 protons, DP of PCS is $60 / 4 = 15$.

Molar fraction of D is $15 / (15 + 58) = 20.5\%$

$$M(P_1) = 15.03 + 58 \times 44.05 + 72.06 + 15 \times 104.15 + 35.45 = \mathbf{4240}$$

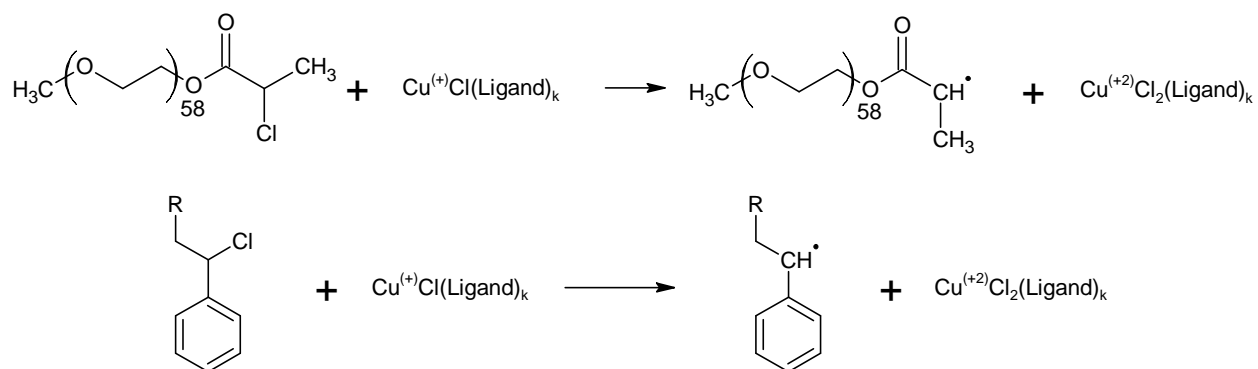
$$M(P_2) = 15.03 + 58 \times 44.05 + 72.06 + 15 \times 152.62 + 35.45 = \mathbf{4967}$$

$$M(P_1) = 4240 \quad ; \quad M(P_2) = 4967$$

$$n(C) = 20.5\% ; \quad n(D) = 20.5\%$$

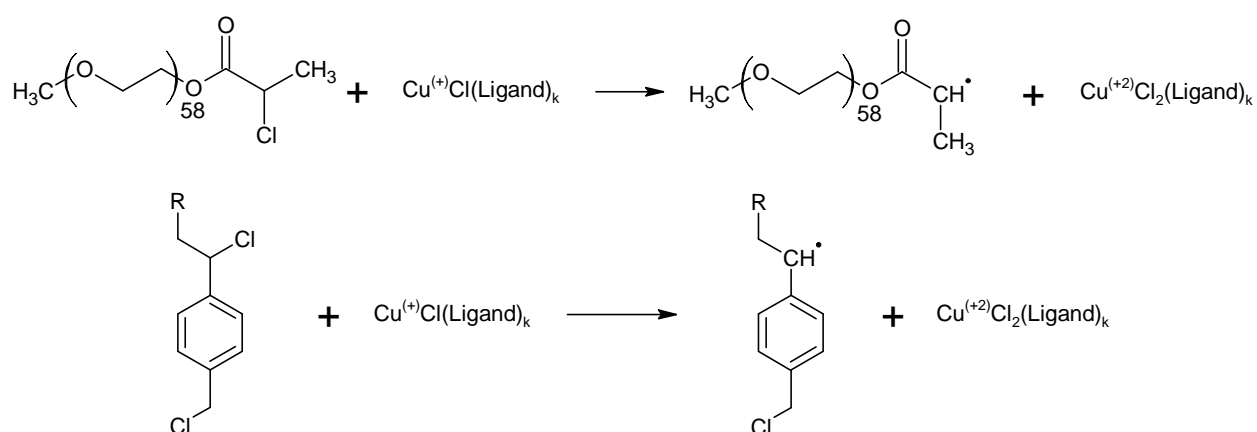
8.8 All possible reactions of activation occurring during the synthesis of P₁ and P₂.

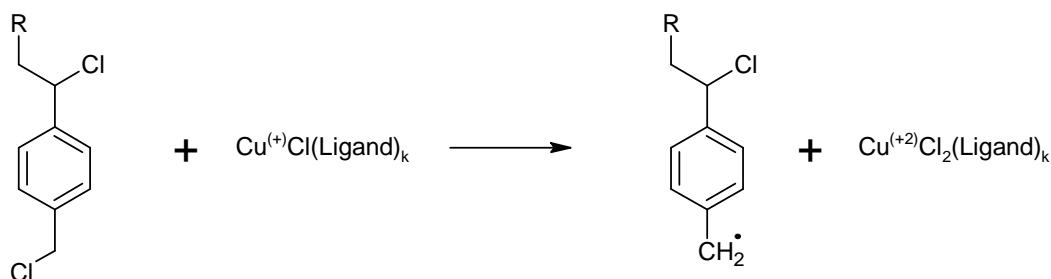
P₁:



Here R is used for the macroinitiator fragment with one or several styrene units attached.

P₂:





Here R is used for the macroinitiator fragment with one or several p-chloromethylstyrene units attached.

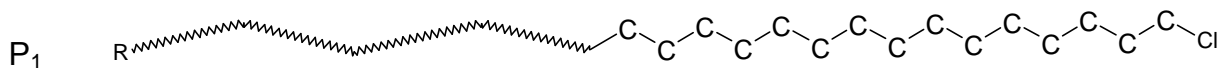
8.9 The structure of P₁ and one of possible structures of P₂

P₁ is a block copolymer of PEO and PS. The PS block contains 15 units.

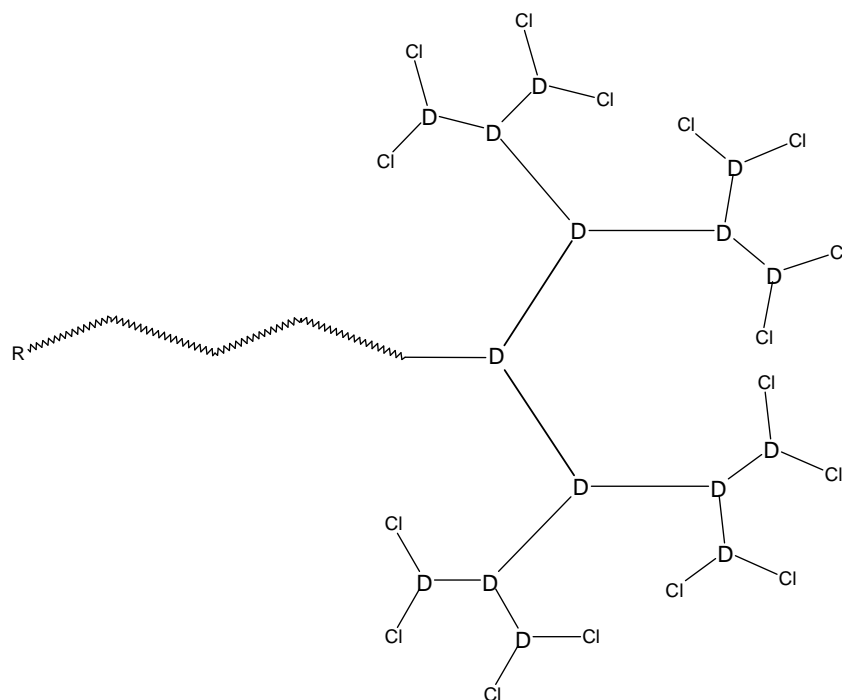
P₂ is a block copolymer composed of PEO block and branched styrene block.

The integral intensity of multiplet f is 2.75, so $2.75/0.173=15.9$, that is about 16 protons or 8 chloromethyl groups.

d) If there is no branching in molecule P₂, it would contain 15 chloromethyl groups. Each branching reduces the number of such groups by 1. Thus P₂ has $15 - 8 = 7$ branchings. Every structure with 7 branchings is correct if each monomer unit is linked with not more than 3 other monomer units



P₂

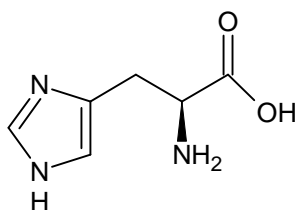


PRACTICAL PROBLEMS

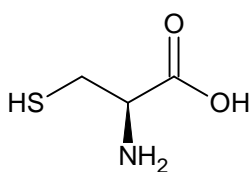
PROBLEM 1 (Practical)

Ion-exchange chromatography of amino acids

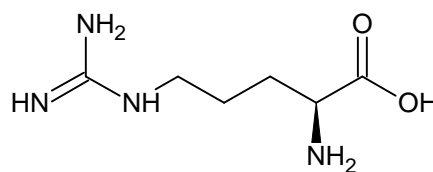
Ion-exchange chromatography is an important analytical and preparative method, which allows fractioning of charged substances. Interaction of ionic groups of the substances with counterions attached to the resin is behind the method. In this task you will have to carry out separation of a given mixture of three amino acids followed by quantitative assay of individual amino acids eluted from the column by using specific chromogenic reactions. Since queues of students are possible at spectrophotometers, we strongly suggest you starting the exam with Problem 1.



His



Cys



Arg

Three amino acids (see the structures above) are present in the mixture. These are histidine, cysteine, and arginine. Cross-linked sulfonated polystyrene is used as a cation-exchange resin (see the picture of the system below). At the beginning of the experiment the column is equilibrated with Eluent 1 (*pH* 4.9).

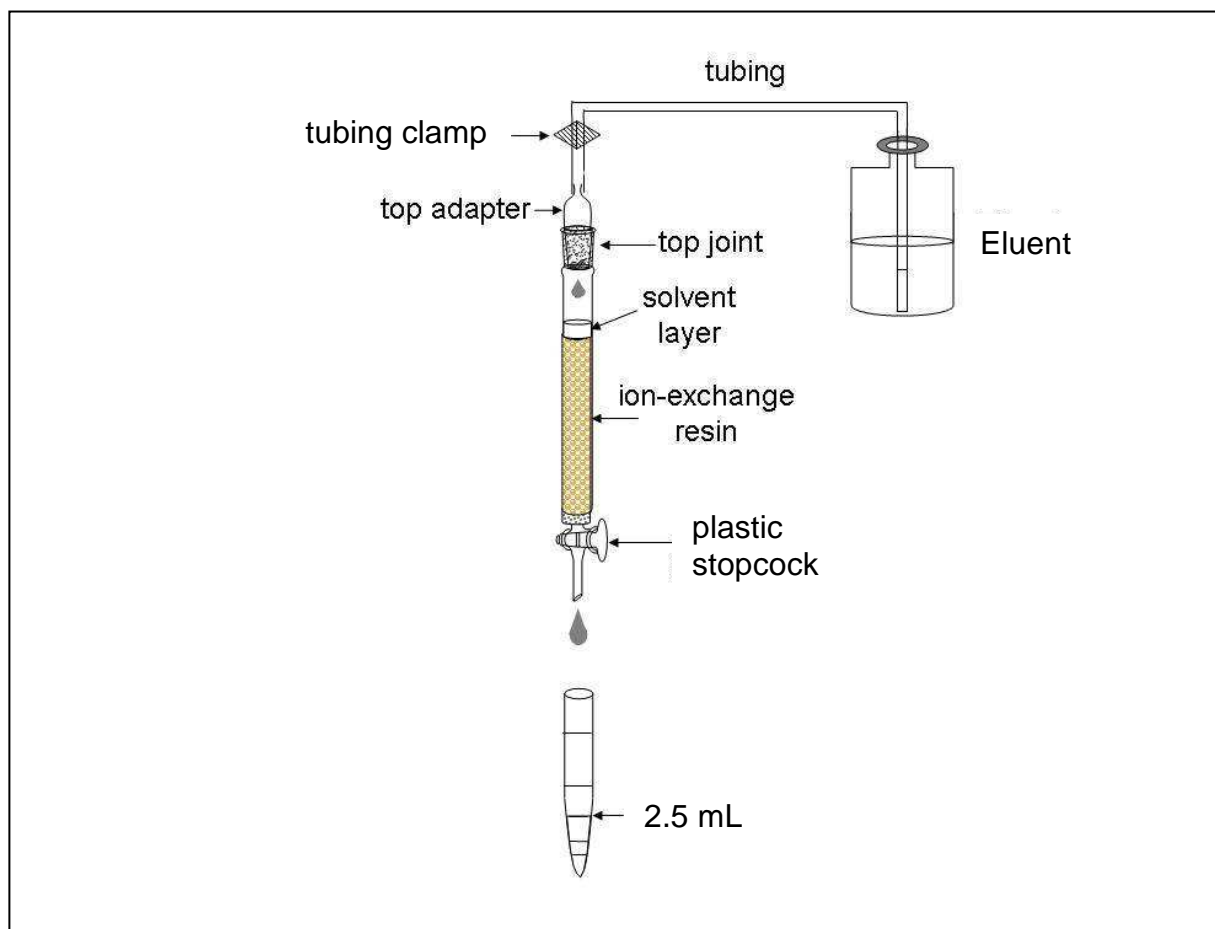
Procedure

Chromatography. Step 1

Apply the given solution of a mixture of amino acids to the column. First, open the stopcock to allow the solvent in the column draining into the Erlenmeyer flask labelled "Waste" so that the solvent is level with the top of packing material, still preventing the resin surface from drying off. Close the stopcock and carefully add the analyzed solution to the top of the column by using a syringe. Open the stopcock and let the sample soak inside the gel (drain the solvent into the "Waste" flask). Close the stopcock and add about 1 cm³ of Eluent 1 (corresponds to ~ 1 cm of liquid in the column) by carefully releasing the

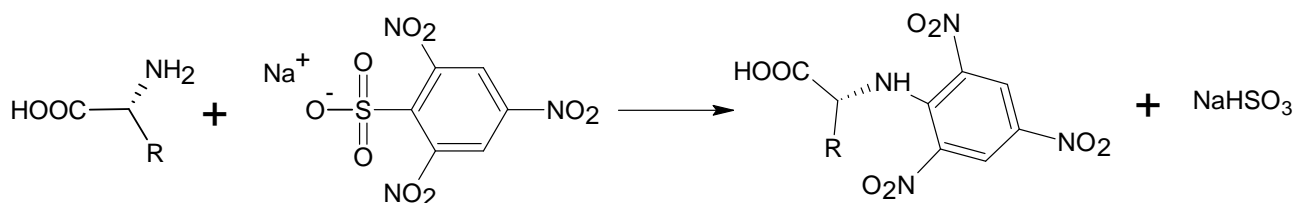
tubing clamp. Attach the top joint tightly, fixing the column with one hand and the adaptor with the other (be sure that the joint is fitted closely to the column). Replace the "Waste" flask at the stand with the test tubes in the rack. Release the tubing clamp and open the stopcock to let the eluent flow down through the column. Proceed with elution. (Always pen the stopcock to start elution and close the stopcock to stop it).

Collect the fractions in the test tubes up to the volume of 2.5 cm³ (as shown in the Picture). If needed, label them with marker. After collecting each 4 to 8 fractions stop elution and carry out qualitative analysis of the collected samples.



Qualitative analysis of samples

Qualitative assay of amino acids is based on the reaction of their α -amino groups with sodium 2,4,6-trinitrobenzene sulfonate (TNBS):



The assay is carried out in the wells of a polystyrene plate, each well corresponding to a definite test tube. Before starting the assay, mix 1 cm³ of TNBS solution with 10 cm³ of carbonate buffer solution and place 0.1 cm³ of the resulting mixture into half of the plate wells (from A1 to H5). Then add 0.1 cm³ of the analyzed fraction into a well. Start with A1 well and continue with B1, C1, etc (move top to bottom and left to right). If an amino acid is present in the analyzed fraction, intense yellow coloration will develop in the corresponding well within 3 min. Use the coloration in the first well as the reference. To reliably estimate the coloration, place the plate on the white sheet of paper.

Note: all aliquots of 0.1 cm³ should be added by using the pipettor. We expect you to use one tip for all fractions of a single peak.

1.1 a Draw the profile of coloration intensity (qualitatively) on the plate sketch in the Answer Sheet. Use the following symbols: (-) – no coloration, 1 – weak coloration, 2 – moderate coloration and 3 – intense coloration. Keep drawing the profile during the whole chromatography process.

Continue collecting fractions and analyzing them until you get at least two wells with coloration as in A1 well, which will indicate that the first amino acid has left the column completely (end of the first peak).

Chromatography. Step 2

As soon as you are finished with collecting the first peak, change to Eluent 2. To do so, close the stopcock, fix the tubing clamp (Important!), disconnect the tubing leading to the bottle with Eluent 1 and connect the tubing leading to the bottle with Eluent 2. Attach the top joint tightly.

1.1 b Indicate when the eluents have been changed by drawing lines between the corresponding wells on the plate sketch.

Continue elution, collecting fractions and carrying out qualitative analysis of samples as described above.

Chromatography. Step 3

As soon as you are finished with collecting the second peak, change to Eluent 3 as described in Step 2. Continue chromatography until the third amino acid leaves the column completely.

Stop chromatography by closing the stopcock and fixing the clamp.

Based on the results of qualitative analysis, choose the fractions which contain the amino acids.

1.1 Write down in the Answer Sheet the labels of wells corresponding to the chosen fractions.

1.2 Combine the fractions from each peak and measure the volumes of combined fractions using a measuring cylinder. Report the volumes of combined fractions excluding amounts used for the qualitative analysis. Write down the obtained results in the Answer Sheet.

Pour combined fractions in the amber glass vials labelled "Peak 1", "Peak 2", "Peak 3". Prepare samples for quantitative spectrophotometric analysis as described below.

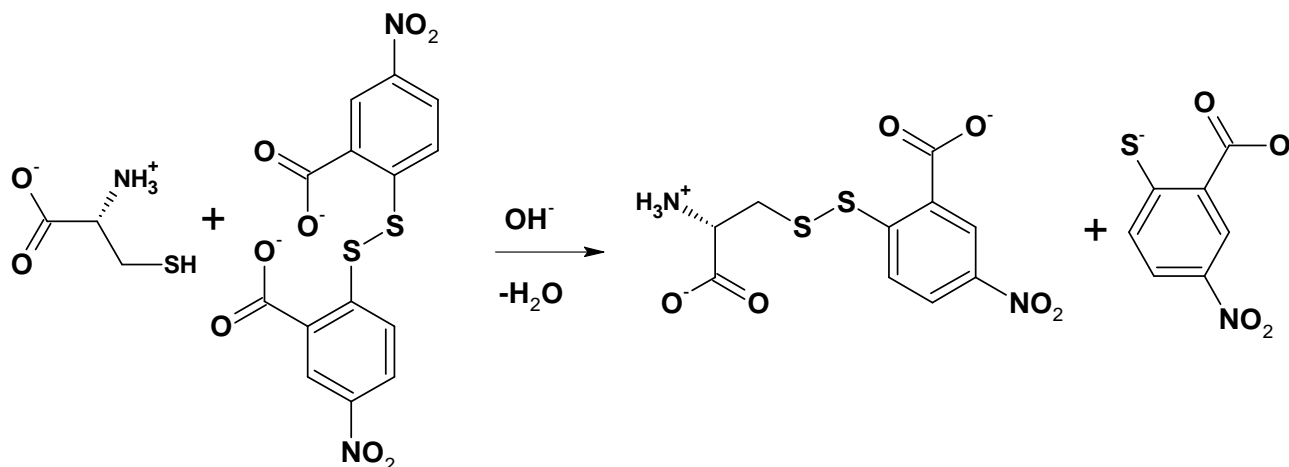
When finished with Practical exam, close the vials and leave them on the table. The combined fractions will be subsequently analyzed by lab staff.

Spectrophotometric analysis

For each probe, you should submit two cells to the operator. Prepare the probes as follows.

Important! When storing, always put cell in the cell holder! All cells have 2 ribbed and 2 working vertical surfaces. While operating with cells, do not touch working surfaces, otherwise you may get incorrect values of absorbance.

Assay 1 (peak 1). Cysteine concentration is determined by the Ellmann reaction:



Test tube A₁ (Reference).

Place 0.1 cm³ of Eluent 1 from plastic microtube into a test tube and add 2.9 cm³ of Ellmann reagent (DTNB).

Test tube B₁ (Sample).

Place 0.1 cm³ of the analyzed solution into a test tube and add 2.9 cm³ of Ellmann reagent (DTNB).

Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cells labelled A₁ (for reference) and B₁ (for sample).

Assay 2 (peak 2). Determination of histidine concentration is based on the ability of imidazole moiety to react with diazonium compounds (Pauli reaction).

Test tube A₂ (Reference).

Place 2.8 cm³ of Tris-HCl buffer solution into a test tube, add 0.1 cm³ of Eluent 2 from plastic microtube and 0.1 cm³ of Pauli reagent.

Test tube B₂ (Sample).

Place 2.8 cm³ of Tris-HCl buffer solution into a test tube, add 0.1 cm³ of the analyzed solution and 0.1 cm³ of Pauli reagent.

Mix the contents of the test tubes thoroughly and transfer each mixture to the corresponding cells labelled A₂ (for reference) and B₂ (for sample).

Assay 3 (peak 3).

Determination of arginine concentration is based on the ability of guanidinium moiety to react with some phenols under alkaline and oxidative conditions (Sakaguchi reaction).

Test tube A₃ (Reference).

Place 0.1 cm³ of Eluent 3 into a test tube and add 1.5 cm³ of 10 % NaOH solution, 1 cm³ of 8-hydroxyquinoline solution and 0.5 cm³ of sodium hypobromite solution.

Test tube B₃ (Sample).

Place 0.1 cm³ of the analyzed solution into a test tube and add 1.5 cm³ of 10 % NaOH solution, 1 cm³ 8-hydroxyquinoline solution and 0.5 cm³ of sodium hypobromite solution.

Shake the test tubes vigorously for 2 min (**Important!**) and observe formation of orange colour. Add 0.2 cm³ of 8 M urea solution to each test tube, mix the contents and transfer about 3 cm³ of each mixture to the corresponding cells labelled A₃ (for reference) and B₃ (for sample).

All mixtures should be analyzed by spectrophotometry not earlier than 10 min and not later than 2 h after preparation. Submit the set of 6 cells to the spectrophotometer operator. In case of a queue at the spectrophotometer, ask the operator to put your student code on the list at the signboard. You will be invited by the operator in due time. Meanwhile, you can answer the theoretical question and start fulfilling Problem No 2.

In case your sample(s) have not been subjected to studies within the proper time interval (which is quite improbable), prepare the sample(s) afresh.

Get the print-offs with the spectra of your samples and check it. Sign the print-offs and get the operator's signature.

1.3 Determine absorbance at the corresponding wavelengths and calculate the content (in mg) of each amino acid in the mixture you were given. The optical length is 1.0 cm. Complete the Answer Sheets taking into account that one mole of each amino acid gives one mole of the corresponding product.

Reference data:

The values of extinction coefficients: Product of Ellmann reaction: 13600 M ⁻¹ cm ⁻¹ at 410 nm Product of Pauli reaction: 6400 M ⁻¹ cm ⁻¹ at 470 nm Product of Sakaguchi reaction: 7700 M ⁻¹ cm ⁻¹ at 500 nm	Molar masses of the amino acids. Cysteine: 121 g mol ⁻¹ Histidine: 155 g mol ⁻¹ Arginine: 174 g mol ⁻¹
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1.4 Draw three resonance structures of the species responsible for mixture coloration as a result of Ellmann reaction.

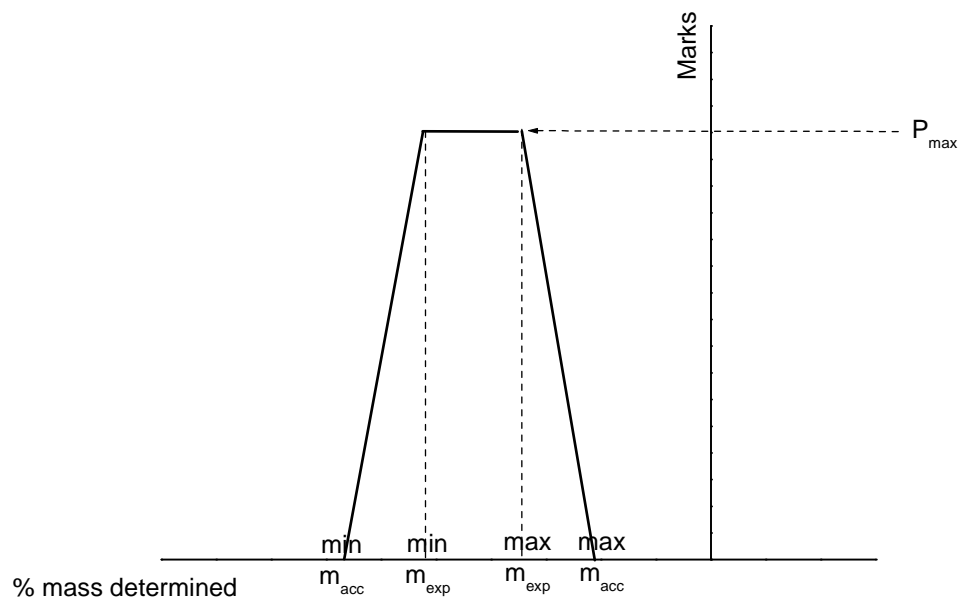
SOLUTION

1.2 – 1.3

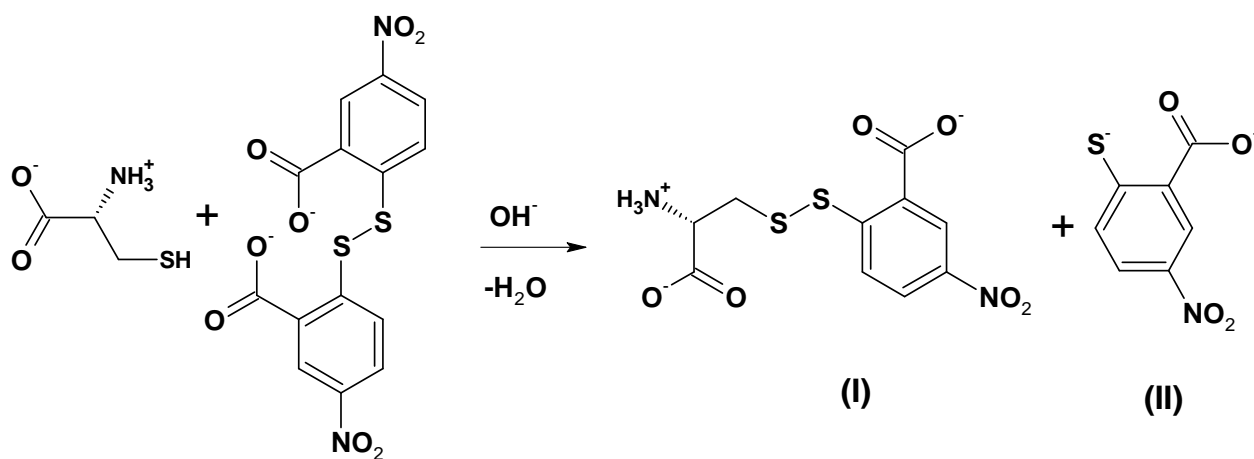
$$\text{Content of an amino acid} = \frac{A_{\lambda} n V M}{\epsilon l},$$

A_{λ} is the absorbance of the sample calculated from the spectra, l is the optical length (1.0 cm), n is the dilution factor determined as a ratio of the aliquot of analyzing solution (0.1 cm³) and the final volume of the sample in the cells, V is the volume of the combined fraction from the corresponding peak, and M is the molar mass of the amino acid.

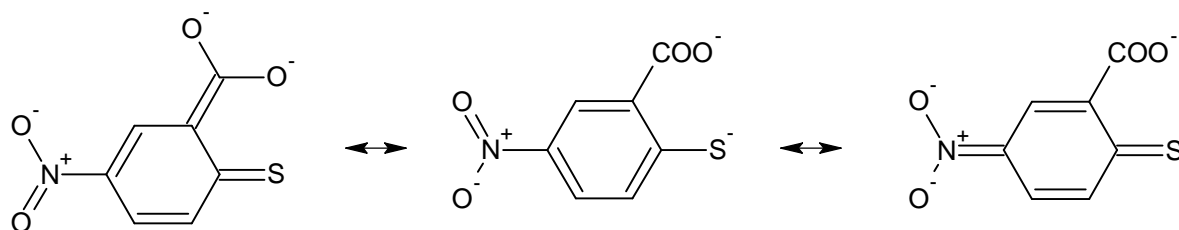
Content of each amino acid is determined by using the following plot (values recalculated from volumes reported by students and absorbance values recorded by spectrophotometer).



1.4 As it is given in the task text, mixed disulfide and 2-thio-5-nitrobenzoic acid are formed in the reaction.



Under slightly alkaline conditions, thiol group of (II) dissociates, and thiophenolate-anion is formed. Resonance structures can be realized for this compound:



The electronic structure of asymmetrical disulfide (I) does not differ considerably from that of the original Ellmann reagent. Therefore, it can be concluded that the compound responsible for coloration is thiophenolate-anion (a form containing $\text{C}=\text{S}$ bond).

PROBLEM 2 (Practical)

Determination of Carbonate and Hydrogen Phosphate in an Abrasive Sample

Na_2CO_3 , CaCO_3 and Na_2HPO_4 are the main constituents of abrasive powders. In this task you will have to determine carbonate and hydrogen phosphate ions in an abrasive sample by two acid-base titrations.

First, the exactly known amount of hydrochloric acid (taken in an excess) is added to the sample. As a result, hydrogen phosphates are transformed into H_3PO_4 , whereas carbonates into CO_2 which is further removed by boiling. Calcium ions initially present in the sample pass into the solution. Because of possible interference in subsequent analysis, they are precipitated as CaC_2O_4 and filtered off prior to the titration.

Next, the phosphoric acid formed is subjected to two titrations with pre-standardized NaOH solution and two different indicators: Bromocresol Green (BCG) and Thymolphthalein (TP). First, H_3PO_4 (and excess of HCl) is titrated to H_2PO_4^- ion, the endpoint lying in slightly acidic medium (pH of ~ 4.5). It corresponds to the colour change of BCG from yellow to blue. The second titration proceeds till HPO_4^{2-} is formed. The endpoint of the second titration corresponds to the color change of TP from colourless to blue (moderately alkaline medium, pH of ~ 10).

The content of CO_3^{2-} ions in the sample is calculated by finding the difference between:

- the amount of the titrant equivalent to the initial amount of HCl (taken for the sample dissolution) and
- the amount of the titrant corresponding to the second endpoint (TP).

The content of HPO_4^{2-} is calculated by finding the difference between the amounts of the titrant consumed to achieve two endpoints (TP and BCG).

Procedure

Step 1. Dissolution of the sample and removal of CO_2

To the sample of the abrasive powder in a beaker covered with watch glass add 10.00 cm^3 (exactly, with a pipette! Carefully, not removing the glass and avoiding losses because of splashing!) of ca. 1 mol dm^{-3} HCl (see the exact concentration of the acid on the label). After the most intensive stage of gas evolution is completed, heat

carefully the solution in the beaker (covered with watch glass) on a heating plate until the gas evolution stops. Then bring the solution to boiling and boil it carefully for 2 – 3 min.

Step 2. Precipitation of calcium

Remove the beaker from the plate; wash the steam condensate from the watch glass down to the beaker with distilled water. Add 1 – 2 cm³ of 15 % K₂C₂O₄ solution with measuring cylinder. Put the beaker aside until the most part of the precipitate is formed (usually takes 10 to 20 min). Spend this time for standardization of the titrant solution of NaOH (see the procedure hereunder).

Step 3. Standardization of NaOH solution

Place with a pipette 10.00 cm³ of HCl solution into a 100 cm³ volumetric flask, make up to the mark with distilled water and mix. Fill the burette with NaOH solution. Transfer with a pipette 10.00 cm³ of the diluted HCl solution from the volumetric flask to an Erlenmeyer flask. Add 1 – 2 drops of Thymolphthalein solution and titrate with NaOH solution until blue coloration stable on swirling for 5 – 10 s appears.

Here and after. Repeat the titrations as necessary. It is desirable that the highest and the lowest titrant volume values differ not more than by 0.10 cm³. Report all the final volume values with 0.01 cm³ accuracy.

2.1 a Complete the table in the Answer Sheet.

2.1 b Calculate the concentration of NaOH solution (in mol dm⁻³).

Step 4. Filtering off calcium oxalate

After the most part of CaC₂O₄ precipitates filter the precipitate off collecting the filtrate into a 100 cm³ volumetric flask. Slight turbidity in the filtrate is admissible, since small amounts of calcium oxalate do not interfere in the titration. Wash the filter with distilled water; make up the solution in the flask to the mark with distilled water and mix. Put the used filter into the waste basket.

Step 5. Sample titration against Bromocresol Green

Transfer with a pipette a 10.00 cm³ aliquot of the sample solution coming from the

step 4 from the volumetric flask to an Erlenmeyer one, and add 3 drops of BCG solution. Prepare in another Erlenmeyer flask a reference solution by adding 3 drops of 15 % NaH_2PO_4 solution and 3 drops of BCG solution to 15 – 20 cm^3 of distilled water. Titrate the sample solution with NaOH solution until the colour coincides with that of the reference solution.

2.2 Complete the table in the Answer Sheet.

Step 6. Sample titration against thymolphthalein

Transfer with a pipette a 10.00 cm^3 aliquot of the sample solution coming from the step 4 from the volumetric flask to an Erlenmeyer one. Add 2 drops of TP solution and titrate with NaOH solution until blue coloration stable on mixing for 5 – 10 s appears.

2.3 Complete the table in the Answer Sheet.

Step 7. Calculations

2.4 Calculate the mass of CO_3^{2-} in the sample.

2.5 Calculate the mass of HPO_4^{2-} in the sample.

Step 8. Additional questions to the problem

Answer the additional questions in the Answer Sheets.

2.6a Indicate one reaction (write down the equation) for a process interfering in the sample analysis you have carried out in the presence of Ca^{2+} .

2.6b A list of mistakes possible at different steps is given in the table in the answer sheet.

Indicate which of the mistakes can lead to errors in CO_3^{2-} and/or HPO_4^{2-} content determination. Use the following symbols: “0” if no error is expected, “+” or “–” if the result is higher (positive error) or lower (negative error) than the true one.

SOLUTION

2.1 a, 2.2, 2.3

The values of the final volumes $V_{1,f}$, $V_{2,f}$, and $V_{3,f}$, (as reported in the Answer Sheet) were graded according to a scheme approved by the International Jury.

The values of $\Delta V_{\text{expected}}$ and $\Delta V_{\text{acceptable}}$ (in cm^3) are listed in the table below.

	$\Delta V, \text{cm}^3$	
	expected	acceptable
$V_{1,f}$	0.10	0.25
$V_{2,f}$	0.15	0.40
$V_{3,f}$	0.15	0.40

2.1 b Calculation of NaOH concentration

$$c(\text{NaOH}) = \frac{c(\text{HCl}) \times V(\text{HCl}) \times V(\text{aliquot})}{V(\text{flask}) \times V(\text{NaOH})} = \frac{1.214 \text{ mol dm}^{-3} \times 10.00 \text{ cm}^3 \times 10.00 \text{ cm}^3}{100.0 \text{ cm}^3 \times V_{1,f} \text{ cm}^3}$$

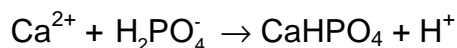
2.4 Calculation of the mass of CO_3^{2-}

$$\begin{aligned} m(\text{CO}_3^{2-}) &= M(\text{CO}_3^{2-}) \times 1/2 \times \frac{c(\text{NaOH}) \times (V_{1,f} - V_{3,f}) \times V(\text{flask})}{V(\text{aliquot})} = \\ &= 60.01 \text{ g mol}^{-1} \times 1/2 \times \frac{c(\text{NaOH}) \text{ mol dm}^{-3} \times (V_{1,f} - V_{3,f}) \text{ cm}^3 \times 100.0 \text{ cm}^3}{10.00 \text{ cm}^3} \times 0.001 \text{ dm}^3/\text{cm}^3 = \end{aligned}$$

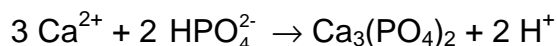
2.5 Calculation of the mass of HPO_4^{2-}

$$\begin{aligned} m(\text{HPO}_4^{2-}) &= M(\text{HPO}_4^{2-}) \times \frac{c(\text{NaOH}) \times (V_{3,f} - V_{2,f}) \times V(\text{flask})}{V(\text{aliquot})} = \\ &= 95.98 \text{ g mol}^{-1} \times \frac{c(\text{NaOH}) \text{ mol dm}^{-3} \times (V_{3,f} - V_{2,f}) \text{ cm}^3 \times 100.0 \text{ cm}^3}{10.00 \text{ cm}^3} \times 0.001 \text{ dm}^3/\text{cm}^3 = \end{aligned}$$

2.6 a



or



40th



International Chemistry Olympiad

**9 theoretical problems
3 practical problems**

THE FORTIETH INTERNATIONAL CHEMISTRY OLYMPIAD 12–21 JULY 2008, BUDAPEST, HUNGARY

THEORETICAL PROBLEMS

PROBLEM 1

The label on a bottle containing a dilute aqueous solution of an acid became damaged. Only its concentration was readable. A *pH* meter was nearby, and a quick measurement showed that the hydrogen ion concentration is equal to the value on the label.

1.1 Give the formulae of four acids that could have been in the solution if the *pH* changed one unit after a tenfold dilution.

1.2 Could it be possible that the dilute solution contained sulfuric acid?

Sulfuric acid: $pK_{a2} = 1.99$

Yes No

If yes, calculate the *pH* (or at least try to estimate it) and show your work.

1.3 Could it be possible that the solution contained acetic acid?

Acetic acid: $pK_a = 4.76$

Yes No

If yes, calculate the *pH* (or at least try to estimate it) and show your work.

1.4 Could it be possible that the solution contained EDTA (ethylene diamino tetraacetic acid)? You may use reasonable approximations.

EDTA: $pK_{a1} = 1.70$, $pK_{a2} = 2.60$, $pK_{a3} = 6.30$, $pK_{a4} = 10.60$

Yes No

If yes, calculate the concentration.

SOLUTION

1.1 Any univalent, strong acid (HCl, HBr, HI, HNO₃, HClO₄) is acceptable. HF is not!

1.2 Yes No

No, the first dissociation step can be regarded as complete in aqueous solutions, thus $[H^+] > c_{\text{acid}}$.

No text or calculations are needed.

1.3 Yes No

Yes, but it can happen only in quite dilute solutions.

$$c = [HA] + [A^-] = [H^+]$$

$$[H^+] = [A^-] + [OH^-]$$

This means that $[HA] = [OH^-]$

$$K = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]([H^+] - [OH^-])}{[OH^-]} = \frac{[H^+]^3}{K_w} - [H^+]$$

The *pH* of the solution must be acidic, but close to 7.

6.5 is a good guess.

A good approximation is: $[H^+] = \sqrt[3]{(KK_w)}$

The full equation can be solved through iteration: $[H^+] = \sqrt[3]{(K + [H^+])K_w}$

Starting with a neutral solution two cycles of iteration give identical results:

$5.64 \times 10^{-7} \text{ mol dm}^{-3}$ as the required concentration. Exact *pH* is 6.25.

1.4 Yes No

We can suppose that this solution would be quite acidic, so the 3rd and 4th dissociation steps can be disregarded. The following equations are thus true:

$$c = [H_4A] + [H_3A^-] + [H_2A^{2-}] = [H^+]$$

$$[H^+] = [H_3A^-] + 2 [H_2A^{2-}]$$

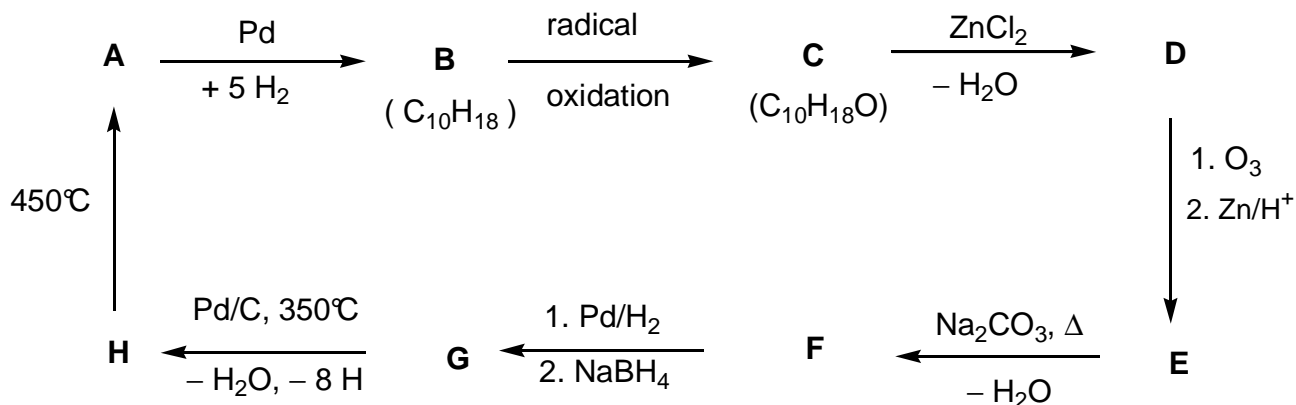
This means that $[H_4A] = [H_2A^{2-}]$

$$K_1 K_2 = \frac{[H^+]^2 [H_2A^{2-}]}{[H_4A]} = [H^+]^2 \quad (\text{or } pH = (pK_1 + pK_2) / 2 = 2.15)$$

$$c = 0.0071 \text{ mol dm}^{-3}$$

PROBLEM 2

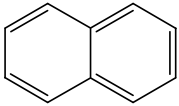
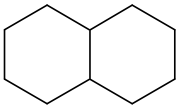
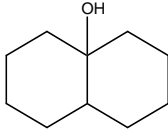
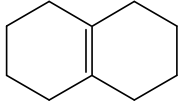
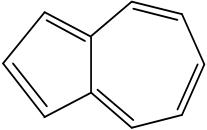
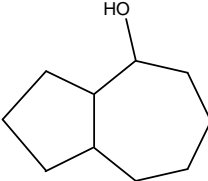
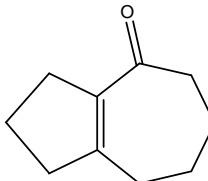
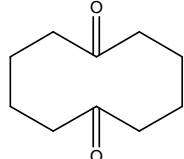
Determine the structure of the compounds **A - H** (stereochemistry is not expected), based on the information given in the following reaction scheme:



Hints:

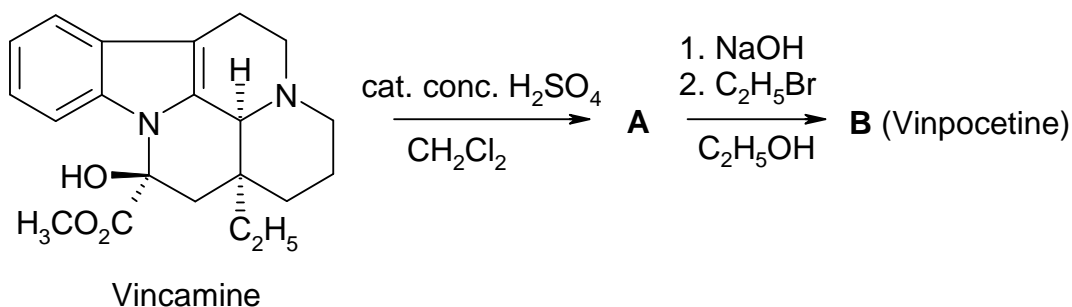
- **A** is a well-known aromatic hydrocarbon.
- A hexane solution of **C** reacts with sodium (gas evolution can be observed), but **C** does not react with chromic acid.
- ¹³C NMR spectroscopy shows that **D** and **E** contain only two kinds of CH₂ groups.
- When a solution of **E** is heated with sodium carbonate an unstable intermediate forms at first, which gives **F** on dehydration.

SOLUTION

A 	B 	C 	D 
H 	G 	F 	E 

PROBLEM 3

Vincopetine (Cavinton®, Calan®) is one of the best selling original drugs developed in Hungary. Its preparation relies on a natural precursor, (+)-vincamine (C₂₁H₂₆ N₂O₃), which is isolated from the vine plant, *vinca minor*. The transformation of (+)-vincamine to vincopetine is achieved in two steps depicted below.



All compounds (**A** to **F**) are enantiomerically pure compounds.

- The elementary composition of **A** is: C 74.97%, H 7.19%, N 8.33%, O 9.55%.
- **B** has 3 other stereoisomers.

3.1 Propose structures for the intermediate **A** and vincopetine (**B**).

A study of the metabolism of any drug forms a substantial part of its documentation. There are four major metabolites each formed from vincopetine (**B**): **C** and **D** are formed in hydrolysis or hydration reactions, while **E** and **F** are oxidation products.

Hints:

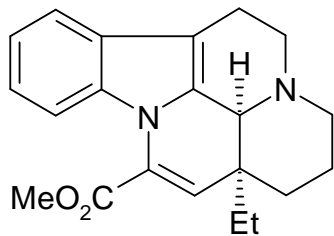
- The acidity of the metabolites decreases in the order **C** >> **E** >> **D**. **F** does not contain an acidic hydrogen.
- **C** and **E** each have 3 other stereoisomers, while **D** and **F** each have 7 other stereoisomers.
- **F** is a pentacyclic zwitterion and it has the same elementary analysis as **E**: C 72.11 %, H 7.15 %, N 7.64 %, O 13.10 %.
- The formation of **E** from **B** follows an electrophilic pattern.
- The formation of **D** from **B** is both regio- and stereoselective.

3.2 Propose one possible structure for each of the metabolites **C**, **D**, **E** and **F**!

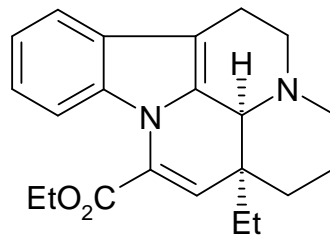
3.3 Draw a resonance structure for **B** that explains the regioselective formation of **D** and the absence of the alternate regioisomer in particular.

SOLUTION

3.1



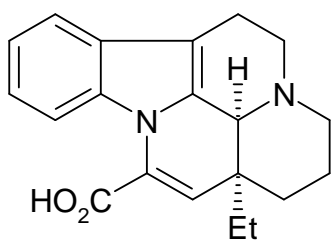
A



B

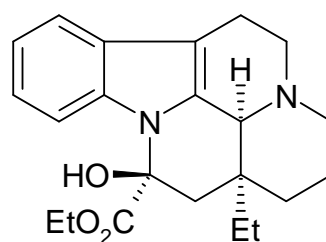
3.2

C



apovincaminic acid

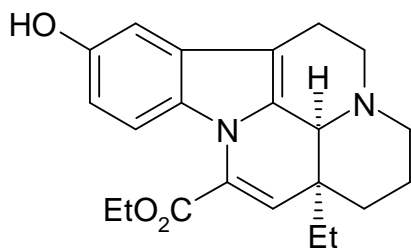
D



ethyl vincamate

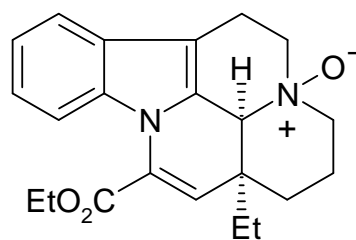
Both stereoisomers around the new chiral center are acceptable.

E



10-hydroxyvinpocetine

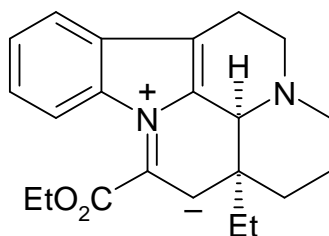
F



vinpocetine N-oxide

All aromatic positions for the OH are acceptable in **E**.

3.3



All aromatic positions for the OH are acceptable in **E**.

PROBLEM 4

A major transformation route for oxiranes (epoxides) is ring opening. This may be accomplished in various ways.

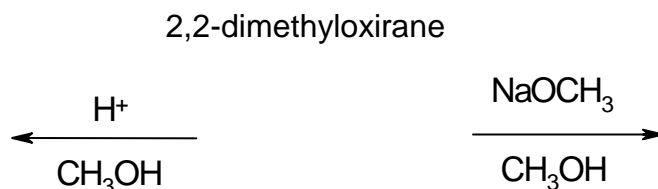
On acid catalysis the reactions proceed through cation-like (carbenium ion-like) species. For substituted oxiranes the direction of ring opening (which C–O bond is cleaved) depends on the stability of the intermediate carbenium ion. The more stable the intermediate carbenium ion the more probable its formation. However, an open carbenium ion (with a planar structure) only forms if it is tertiary, benzylic or allylic.

On base catalysis the sterically less hindered C–O bond is cleaved predominantly. Keep stereochemistry in mind throughout the whole problem. To depict stereochemistry use only the \blacktriangleleft \cdots — bond symbols and nothing else where necessary.

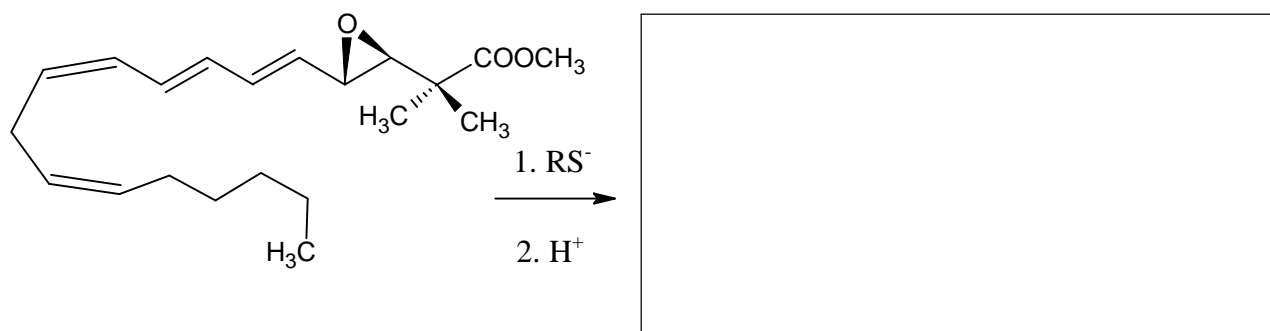
4.1 Draw the structure of the reactant and the predominant products when 2,2-dimethyloxirane (1,2-epoxy-2-methylpropane) reacts with methanol at low temperatures, catalysed by

(i) sulphuric acid

(ii) NaOCH₃.



4.2 Draw the structure of the predominant product when the epoxide ring of the following leukotriene derivative is opened with a thiolate (RS[−]).



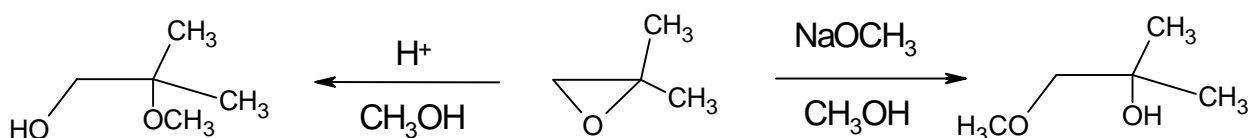
Different porous acidic aluminosilicates can also be used to catalyse the transformation of alkyl oxiranes. In addition to ring opening, cyclic dimerisation is found to be the main reaction pathway producing mainly 1,4-dioxane derivatives (six-membered saturated rings with two oxygen atoms in positions 1,4).

- 4.3 Draw the structure(s) of the most probable 1,4-dioxane derivative(s) when the starting compound is (*S*)-2-methyloxirane ((*S*)-1,2-epoxypropane). Give the structure of the reactant as well.
- 4.4 Draw the structure(s) of the substituted 1,4-dioxane(s) when the epoxide reacting is (*R*)-1,2-epoxy-2-methylbutane ((*R*)-2-ethyl-2-methyloxirane). Give the structure of the reactant as well.
- 4.5 Give the structure(s) of the substituted 1,4-dioxane(s) when this reaction is carried out with racemic 1,2-epoxy-2-methylbutane (2-ethyl-2-methyloxirane).

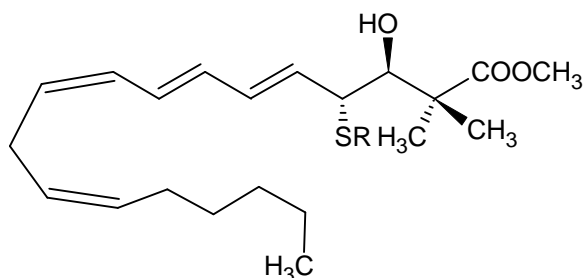
SOLUTION

4.1

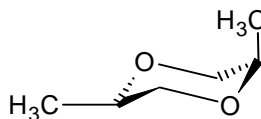
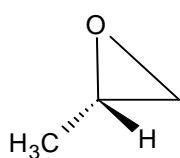
2,2-dimethyloxirane



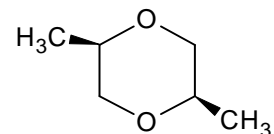
4.2



4.3



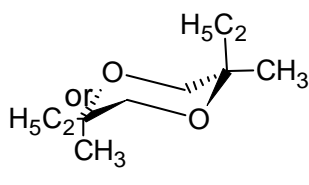
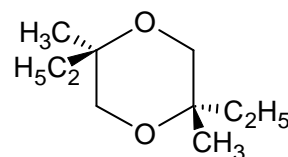
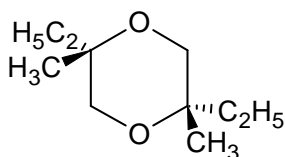
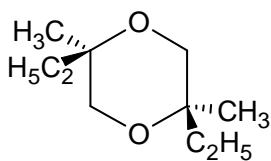
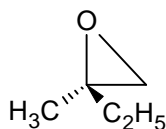
or



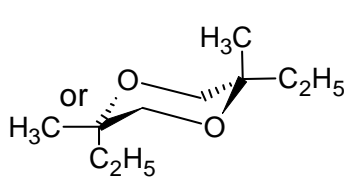
(S)-2-methyloxirane

product

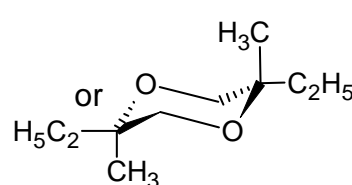
4.4 (R)-1,2-epoxy-2-methylbutane:



R,R

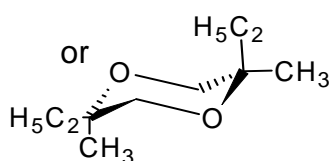
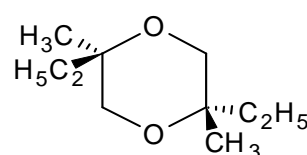
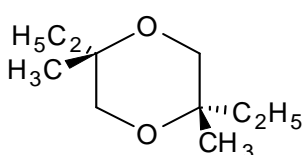
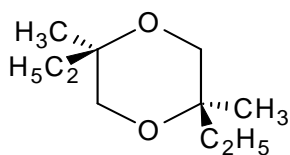


S,S

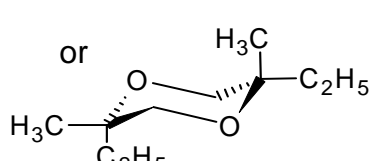


R,S

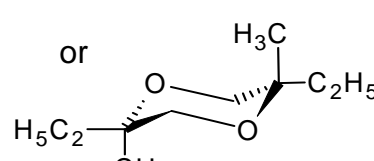
4.5



R,R



S,S



R,S

PROBLEM 5

A and **B** are white crystalline substances. Both are highly soluble in water and can be moderately heated (up to 200 °C) without change but both decompose at higher temperatures. If an aqueous solution of 20.00 g **A** (which is slightly basic, $pH \approx 8.5-9$) is added to an aqueous solution of 11.52 g **B** (which is slightly acidic, $pH \approx 4.5-5$) a white precipitate **C** forms that weighs 20.35 g after filtering, washing and drying. The filtrate is essentially neutral and gives a brown colour reaction with an acidified KI solution. When boiled, the filtrate evaporates without the appearance of any residue.

The white solid **D** can be prepared by the heating of **A** in the absence of air. The exothermic reaction of **D** with water gives a colourless solution. This solution, if kept in an open container, slowly precipitates a white solid **E** and leaves water. Upon prolonged exposure to air at room temperature, solid **D** is transformed into **E** as well. However, heating **D** in air at 500 °C produces a different white substance **F**, which is barely soluble in water and has a mass of only 85.8% of the **E** formed from the same amount of **D**. **F** gives a brown colour reaction with an acidified solution of KI.

E can be converted back into **D** but ignition above 1400 °C is required for this purpose. The reaction of **B** and **D** in water forms the precipitate **C** and is accompanied by a characteristic odour.

5.1 Give the formulae of the substances A - F

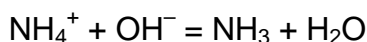
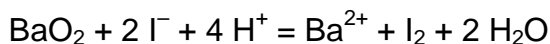
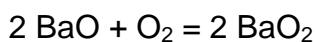
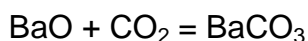
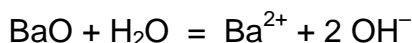
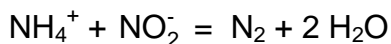
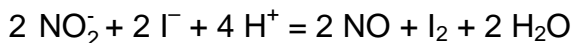
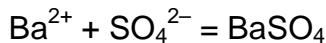
5.2 Write balanced equations for all the reactions mentioned. (The equation for the thermal decomposition of **B** is not required.)

SOLUTION

5.1 The formulae of the substances A – F:

A Ba(NO ₂) ₂	B (NH ₄) ₂ SO ₄	C BaSO ₄
D BaO	E BaCO ₃	F BaO ₂

5.2 Equations:



Detailed solution:

The problem contains quite a number of clues to the identification of the compounds. It is clear that **A**, **D**, **E**, and **F** all contain the same element; with a water-soluble solid compound stable at 1400 °C, probably a metal. The aqueous solution of a metal compound giving a precipitate and pure water upon standing in the air strongly hints at the formation of a carbonate, possibly from a soluble hydroxide. A likely conclusion is that **D** is an oxide, limiting the choice of the metal to Sr or Ba. (One might also consider Li, Ca, or Tl which are less satisfactory because $\text{Ca}(\text{OH})_2$ is poorly soluble while the solubilities of Li_2CO_3 and Tl_2CO_3 are quite significant.) If **E** is an alkaline earth metal carbonate, then the molar mass of **F** could be either $M_{\text{Ca}} + 45.8$, or $M_{\text{Sr}} + 39.05$, or $M_{\text{Ba}} + 32$. Since **F** is formed by heating the oxide in air, the former two do not make any sense while the latter is consistent with BaO_2 . This is confirmed by the oxidative capability of **F**.

The odour appearing in the reaction of **B** with $\text{Ba}(\text{OH})_2$ indicates that the former might be an ammonium salt. Assuming that the reaction of **A** and **B** is a simple precipitation between a barium salt and an ammonium salt, we get an equivalent mass of 48 for the anion of the precipitate. This might be either SO_4^{2-} or HPO_4^{2-} but the acidity of **B** is consistent with the former and, in addition, $(\text{NH}_4)_2\text{HPO}_4$ would not

give the same BaHPO_4 precipitate with Ba(OH)_2 as with $\text{Ba(NO}_2)_2$. If we accept that **B** is $(\text{NH}_4)_2\text{SO}_4$, we obtain an equivalent mass of 46 for the anion of **A**. This and the surrounding chemistry are consistent with the nitrite ion.

PROBLEM 6

A feathery, greenish solid precipitate can be observed if chlorine gas is bubbled into water close to its freezing point. Similar precipitates form with other gases such as methane and noble gases. These materials are interesting because vast quantities of the so-called methane-hydrates are supposed to exist in nature (comparable in quantity with other natural gas deposits).

These precipitates all have related structures. The molecules of water just above its freezing point form a hydrogen-bonded structure. The gas molecules stabilize this framework by filling in the rather large cavities in the water structure forming clathrates. The crystals of chlorine and methane clathrates have the same structure. Their main characteristics are dodecahedra formed from 20 water molecules. The unit cell of the crystal can be thought as a body-centered cubic arrangement built from these dodecahedra which are almost spherical objects. The dodecahedra are connected via additional water molecules located on the faces of the unit cell. Two water molecules can be found on each face of the unit cell. The unit cell has an edge dimension of 1.182 nm. There are two types of cavities in this structure. One is the internal space in the dodecahedra (**A**). These are somewhat smaller than the other type of voids (**B**), of which there are 6 for each unit cell.

- 6.1 How many type **A** cavities can be found in a unit cell?
- 6.2 How many water molecules are there in a unit cell?
- 6.3 If all cavities contain a guest molecule, what is the ratio of the number of water to the number of guest molecules?
- 6.4 Methane hydrate is formed with the structure in **c**) at temperatures between 0-10 °C. What is the density of the clathrate?
- 6.5 The density of chlorine hydrate is 1.26 g/cm³. What is the ratio of the number of water and guest molecules in the crystal?
Which cavities are likely to be filled in a perfect chlorine hydrate crystal? Mark one or more.

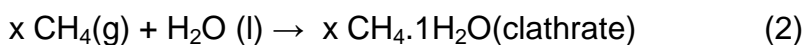
Some **A** Some **B** All **A** All **B**

Covalent radii reflect atomic distances when the atoms are covalently bonded. Non-bonded or van der Waals radii give a measure of the atomic size when they are not bonded covalently (modelled as hard spheres).

Atom	Covalent radius (pm)	Nonbonded radius (pm)
H	37	120
C	77	185
O	73	140
Cl	99	180

6.6 Based on the covalent and non-bonded radii of these atoms estimate lower and upper bounds for the average radii of the cavities where possible. Show your reasoning.

Let us consider the following processes



6.7 What are the signs of the following molar quantities referring to these reactions in the given direction at 4 °C? Mark with a –, 0 or +.

	sign
$\Delta G_m(1)$	
$\Delta G_m(2)$	
$\Delta H_m(1)$	
$\Delta H_m(2)$	
$\Delta S_m(1)$	
$\Delta S_m(2)$	
$\Delta S_m(2) - \Delta S_m(1)$	
$\Delta H_m(2) - \Delta H_m(1)$	

SOLUTION

6.1 The number of A cavities in a unit cell: 2

6.2 The number of water molecules in a unit cell?

$$46 = 20 \times 2 \text{ (dodecahedra)} + 6 \times 2 / 2 \text{ (faces)}$$

6.3 The number of water to the number of guest molecules?

$$46 : 8 = 5.75$$

6.4 A unit cell has a volume of $1.182^3 \text{ nm}^3 = 1.651 \text{ nm}^3$.

It contains 8 methane and 46 water molecules with a mass of $957 \text{ g mol}^{-1} / N_A = 1.589 \times 10^{-21} \text{ g}$.

The density is $1.589 / 1.651 = 0.962 \text{ g/cm}^3$.

6.5 The mass of a unit cell with this density is: $1.651 \text{ nm}^3 \times 1.26 \text{ g cm}^{-3} = 2.081 \times 10^{-21} \text{ g}$, meaning 1253 g/mol for the contents.

Subtracting the waters, this means 424.3 g mol^{-1} for the chlorine atoms, giving 11.97 chlorine atoms in a unit cell.

The ratio is then 6 (5.98) chlorine molecules for the 46 waters, or a ratio of 7.68.

It is expected that only the 6 larger B type cavities contain chlorine. Thus:

Some A Some B All A All B

6.6 Methane fits in both cavities, its radius is approximately $37 + 77 + 120 \text{ pm} = 234 \text{ pm}$.

The chlorine molecule, with a radius of $180 + 99 \text{ pm} = 279 \text{ pm}$, fits only in B.

Thus $234 \text{ pm} < r(\text{A}) < 279 \text{ pm}$ and $279 \text{ pm} < r(\text{B})$

6.7

	sign
$\Delta G_m(1)$	+
$\Delta G_m(2)$	-
$\Delta H_m(1)$	-
$\Delta H_m(2)$	-
$\Delta S_m(1)$	-
$\Delta S_m(2)$	-
$\Delta S_m(2) - \Delta S_m(1)$	-
$\Delta H_m(2) - \Delta H_m(1)$	-

Under these conditions, methane clathrate forms, while ice melts to water, so the Gibbs energy changes are of opposite signs.

Freezing is an exothermic process with an entropy decrease in both cases.

The entropy decrease of the clathrate formation is larger in magnitude, as it involves a gas-solid transition.

The relation of the reaction enthalpies can be inferred from these facts:

$$\Delta G_m(1) > \Delta G_m(2)$$

$$\Delta H_m(1) - T \Delta S_m(1) > \Delta H_m(2) - T \Delta S_m(2)$$

$$T (\Delta S_m(2) - \Delta S_m(1)) > \Delta H_m(2) - \Delta H_m(1)$$

$$\text{a negative quantity} > \Delta H_m(2) - \Delta H_m(1)$$

PROBLEM 7

The dithionate ion ($\text{S}_2\text{O}_6^{2-}$) is a rather inert inorganic ion. It can be prepared by bubbling sulphur-dioxide continuously into ice-cooled water to which manganese dioxide is added in small increments. Dithionate and sulphate ions are formed under these circumstances.

7.1 Write the balanced chemical equations for the two reactions.

After the reaction is complete, $\text{Ba}(\text{OH})_2$ is added to the mixture until the sulphate ions are fully precipitated. This is followed by the addition of Na_2CO_3 .

7.2 Write the balanced equation for the reaction that takes place upon addition of Na_2CO_3 .

Sodium dithionate is then crystallized by evaporating some of the solvent. The prepared crystals dissolve readily in water and do not give a precipitate with BaCl_2 solution. When the solid is heated and maintained at 130 °C, 14.88 % weight loss is observed. The resulting white powder dissolves in water and does not give a precipitate with BaCl_2 solution. When another sample of the original crystals is kept at 300 °C for a few hours, 41.34 % weight loss occurs. The resulting white powder dissolves in water and gives a white precipitate with BaCl_2 solution.

7.3 Give the composition of the prepared crystals and write balanced equations for the two processes that occur during heating.

Although dithionate ion is a fairly good reducing agent thermodynamically, it does not react with oxidants in solution at room temperature. At 75 °C, however, it can be oxidized in acidic solutions. A series of kinetic experiments were carried out with bromine as an oxidant.

7.4 Write the balanced chemical equation for the reaction between bromine and dithionate ion.

The initial rates (v_0) of the reaction were determined in a number of experiments at 75 °C.

$[\text{Br}_2]_0$ (mmol dm^{-3})	$[\text{Na}_2\text{S}_2\text{O}_6]_0$ (mol dm^{-3})	$[\text{H}^+]_0$ (mol dm^{-3})	v_0 ($\text{nmol dm}^{-3}\text{s}^{-1}$)
0.500	0.0500	0.500	640
0.500	0.0400	0.500	511
0.500	0.0300	0.500	387
0.500	0.0200	0.500	252
0.500	0.0100	0.500	129
0.400	0.0500	0.500	642
0.300	0.0500	0.500	635
0.200	0.0500	0.500	639
0.100	0.0500	0.500	641
0.500	0.0500	0.400	511
0.500	0.0500	0.300	383
0.500	0.0500	0.200	257
0.500	0.0500	0.100	128

7.5 Determine the order of the reaction with respect to Br_2 , H^+ and $\text{S}_2\text{O}_6^{2-}$, the experimental rate equation, and the value and unit of the rate constant.

In similar experiments, chlorine, bromate ion, hydrogen peroxide and chromate ion have all been used as oxidizing agents at 75 °C. The rate equations for these processes are analogous to the one observed with bromine, the units of all rate constants are the same, the values are 2.53×10^{-5} (Cl_2), 2.60×10^{-5} (BrO_3^-), 2.56×10^{-5} (H_2O_2), and 2.54×10^{-5} ($\text{Cr}_2\text{O}_7^{2-}$).

Experiments were also carried out in acidic sodium dithionate solution without any oxidizing agent. When following the processes by UV spectrophotometry, the slow appearance of a new absorption band around 275 nm was observed. Although hydrogen sulphate ion is a detectable product of the reaction, it does not absorb any light above 200 nm.

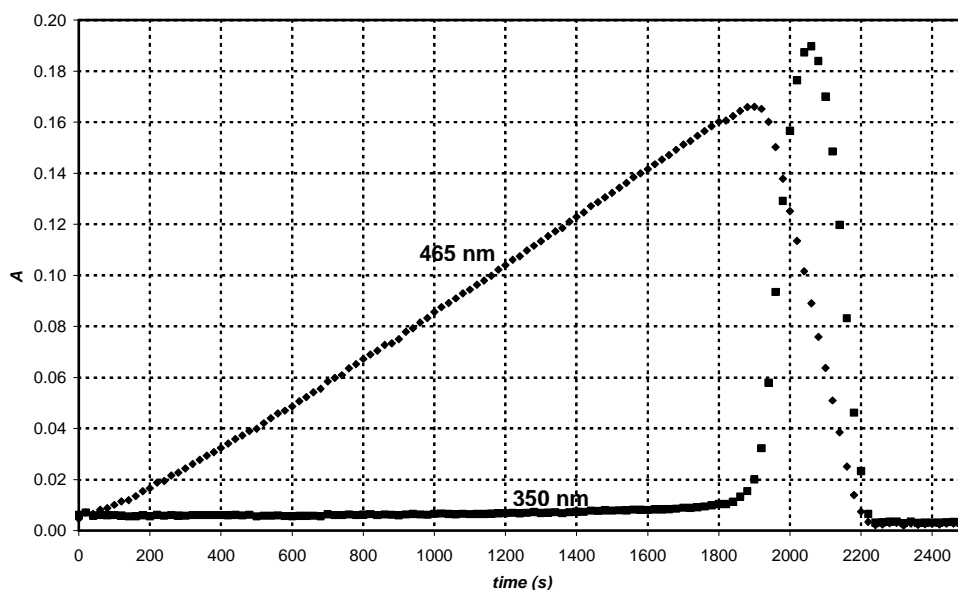
7.6 Give the formula of the major species causing the new absorption band and write the balanced equation of the chemical reaction occurring in the absence of oxidants.

An experiment was carried out to follow the absorbance at 275 nm with initial concentrations: $[\text{Na}_2\text{S}_2\text{O}_6] = 0.0022 \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 0.70 \text{ mol dm}^{-3}$, and the temperature was 75 °C. A pseudo first-order kinetic curve was found with a half-life of 10 hours and 45 minutes.

7.7 Calculate the rate constant of the reaction.

Suggest a balanced chemical equation for the rate determining step of the reactions that used an oxidizing agent.

When periodate ion (which is present as H_4IO_6^- in aqueous solution) was used as an oxidant for dithionate ion, the two kinetic curves depicted in the graph were detected at 75 °C in the same experiment at two different wavel engths. The initial concentrations were $[\text{H}_4\text{IO}_6^-] = 5.3 \cdot 10^{-4} \text{ mol dm}^{-3}$, $[\text{Na}_2\text{S}_2\text{O}_6] = 0.0519 \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 0.728 \text{ mol dm}^{-3}$. At 465 nm, only I_2 absorbs and its molar absorption coefficient is $715 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. At 350 nm, only I_3^- absorbs and its molar absorption coefficient is $11000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The optical path length was 0.874 cm.

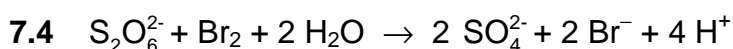
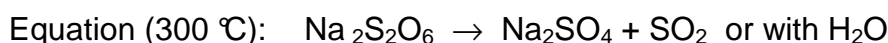
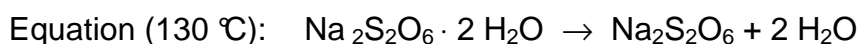
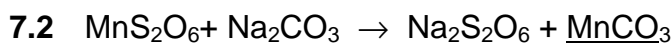
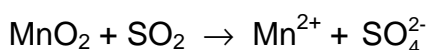
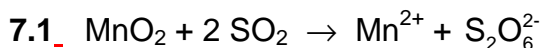


7.8 Write balanced chemical equations for the reactions that occur in the region where the absorbance increases at 465 nm, and in the region where the absorbance decreases at 465 nm.

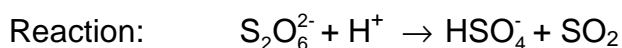
Calculate the expected time for the maximum absorbance of the kinetic curve measured at 465 nm.

Estimate the expected ratio of the slopes of the increasing and decreasing regions in the kinetic curve measured at 465 nm.

SOLUTION



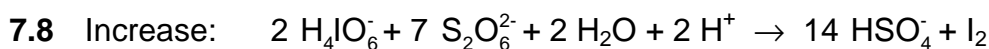
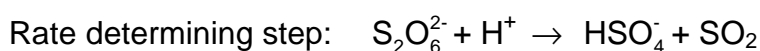
$$k = 2.56 \cdot 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

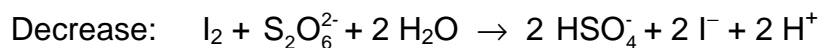


7.7 $t_{1/2} = 10 \text{ h } 45 \text{ min} = 3.87 \cdot 10^4 \text{ s}$

$$k_{\text{obs}} = \ln 2 / t_{1/2} = 1.79 \times 10^{-5} \text{ s}^{-1}$$

$$k = k_{\text{obs}} / [\text{H}^+] = 2.56 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$





The expected time for the maximum absorbance of the kinetic curve measured at 465 nm:

$$t_{\max} = \frac{7}{2} \frac{[\text{H}_4\text{IO}_6^-]_0}{k[\text{S}_2\text{O}_6^{2-}]_0[\text{H}^+]_0} = \frac{7 \times 5.3 \times 10^{-4} \text{ M}}{2 \times 2.56 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1} \times 0.0519 \text{ M} \times 0.728 \text{ M}} = 1900 \text{ s}$$

The expected ratio of the slopes of the increasing and decreasing regions in the kinetic curve measured at 465 nm: 1; -7 (it reflects the stoichiometry).

PROBLEM 8

Ms. Z was a bright student, whose research project was to measure the complexation of all lanthanide(III) ions with newly designed complexing ligands. One day she monitored the UV-VIS absorption with Ce(III) and a particularly poor complexing ligand in a spectrophotometer. She noticed that some small bubbles had formed in the closed cell by the end of the 12-hour experiment. Soon she realized that the presence of the ligand is not necessary to see the bubble formation, and continued her experiments with an acidified CeCl₃ solution. Bubble formation never occurred when she just kept the solution in the spectrophotometer without turning on the instrument. Next, Ms. Z used a small quartz flask, in which she dipped a chloride ion selective electrode and could also withdraw samples regularly for spectrophotometric measurements. She calibrated the chloride ion selective electrode using two different NaCl solutions and obtained the following results:

c_{NaCl} (mol/dm ³)	E (mV)
0.1000	26.9
1.000	-32.2

8.1 Give a formula to calculate the chloride ion concentration of an unknown sample based on the electrode voltage reading (E).

Ms. Z also determined the molar absorption coefficient for Ce³⁺ ($\epsilon = 35.2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) at 295 nm, and, as a precaution, also for Ce⁴⁺ ($\epsilon = 3967 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

8.2 Give a formula to calculate the Ce³⁺ concentration from an absorbance reading at 295 nm (A) measured in a solution containing CeCl₃ (cuvette path length: 1.000 cm).

Ms. Z prepared a solution which contained 0.0100 mol/dm³ CeCl₃ and 0.1050 mol/dm³ HCl, and began her experiment by turning on a quartz lamp. HCl does not absorb at 295 nm.

8.3 What were the expected initial absorbance ($A_{295\text{nm}}$) and voltage (E) readings?

Before the quantitative experiment Ms. Z collected the gas formed into a carefully neutralized solution of methyl orange (acid-base and redox indicator). Although she saw bubbles going through the solution, the colour did not change or fade even after a day.

8.4 Give the formula of two gases, comprised of elements in the illuminated sample, which could not be present given the results of this experiment.

During her quantitative experiment she recorded the absorbance and voltage values regularly. The uncertainty of the spectrophotometric measurements is ± 0.002 and the accuracy of the voltage measurements is ± 0.3 mV.

time (min)	0	120	240	360	480
$A_{295\text{ nm}}$	0.349	0.348	0.350	0.348	0.349
	6	8	4	9	9
E (mV)	19.0	18.8	18.8	19.1	19.2

8.5 Estimate the average rate of change in the concentrations of Ce^{3+} , Cl^- , and H^+ .
 $d[\text{Ce}^{3+}]/dt = d[\text{Cl}^-]/dt = d[\text{H}^+]/dt = ?$

The following day, Ms. Z used an intense monochromatic light beam (254 nm) with an intensity of 0.0500 W. She passed this light through a 5-cm long quartz photoreactor filled with the same acidic CeCl_3 solution she had used before. She measured the molar absorption coefficient for Ce^{3+} ($\epsilon = 2400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) at 254 nm.

8.6 What percentage of the light is absorbed in this experimental setup?

The equipment allowed her to lead the gas first through a drying tube that removed traces of water vapour and then into a closed chamber, whose volume was 68 cm^3 . The chamber was equipped with a high-precision manometer and an igniter. She first filled the chamber with dry argon to a pressure of 102165 Pa and then she turned on the lamp. In 18.00 hours, the pressure reached 114075 Pa. The temperature of the equipment was $22.0 \text{ }^\circ\text{C}$.

8.7 Estimate the amount of substance of the gas collected in the chamber.

At this point, Ms. Z turned off the light and pressed the ignition button. When the chamber cooled down to the initial temperature, the final pressure was 104740 Pa.

- 8.8 Suggest the formula(s) of the gas(es) formed and collected, and give the balanced equation for the original chemical reaction taking place under illumination.
- 8.9 What would be the final pressure after the ignition if the chamber was being filled for 24 hours before ignition?
- 8.10 Estimate the quantum yield of product formation in the Ce(III) solution.

SOLUTION

$$8.1 \quad [\text{Cl}^-] = 10^{-(E+32.2\text{mV})/59.1\text{mV}}$$

$$8.2 \quad [\text{Ce}^{3+}] = \frac{A_{295\text{nm}}}{35.2\text{dm}^3\text{mol}^{-1}}$$

$$8.3 \quad [\text{Ce}^{3+}] = 0.0100\text{ mol/dm}^3 \Rightarrow A_{295\text{nm}} = 0.352$$

$$[\text{Cl}^-] = 3 \cdot 0.0100\text{ mol/dm}^3 + 0.1050\text{ mol/dm}^3 = 0.1350\text{ mol/dm}^3 \Rightarrow E = 19.2\text{ mV}$$

8.4 HCl, Cl₂, (O₃, ClO₂) (no oxidation of indicator)

$$8.5 \quad d[\text{Ce}^{3+}]/dt = ? \quad d[\text{Cl}^-]/dt = ? \quad d[\text{H}^+]/dt = ?$$

No significant change in either Cl⁻ or Ce³⁺ concentrations.

$$[\text{H}^+] = [\text{Cl}^-] - 3[\text{Ce}^{3+}], \text{ no significant change.}$$

All three values are zero.

8.6 What percentage of the light is absorbed in this experimental setup?

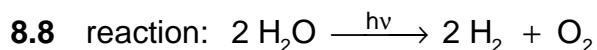
$$A = 2400\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1} \times 5\text{ cm} \times 0.0100\text{ M} = 120 \Rightarrow (100 - 10^{-118})\% \approx 100\%$$

$$8.7 \quad p_{\text{partial}} = p_{\text{final}} - p_{\text{initial}} = 114075\text{ Pa} - 102165\text{ Pa} = 11910\text{ Pa}$$

$$n = p_{\text{partial}} V / (RT) = 11910\text{ Pa} \cdot 0.000068\text{ m}^3 / (8.314\text{ J mol}^{-1}\text{ K} \times 295.15\text{ K}) =$$

$$= 3.3 \times 10^{-4}\text{ mol}$$

identity of gases: H₂, O₂



8.9 Final pressure: 104740 Pa (saturated water vapour)

8.10 Quantum yield:

3.3×10^{-4} mol gas formed altogether: 2.2×10^{-4} mol H_2 and 1.1×10^{-4} mol O_2 .

$$\text{Light beam intensity } 0.0500 \text{ J s}^{-1} \Rightarrow \frac{0.0500 \text{ J s}^{-1} \lambda}{h c N_A} = 1.06 \times 10^{-7} \text{ mol s}^{-1} \text{ photon}$$

Total time 18.00 h = 64800 s

Total number of absorbed photons: $64800 \text{ s} \times 1.06 \times 10^{-7} \text{ mol s}^{-1} = 6.87 \times 10^{-3} \text{ mol}$

Quantum yield for H_2 production: $\Phi = 2.2 \times 10^{-4} \text{ mol} / 6.87 \times 10^{-3} \text{ mol} = 0.032$

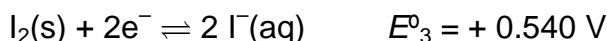
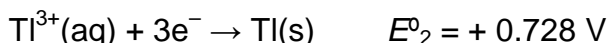
Quantum yield for O_2 production: $\Phi = 1.1 \times 10^{-4} \text{ mol} / 6.87 \times 10^{-3} \text{ mol} = 0.016$

Either value or the quantum yield of the gas production (0.048) is acceptable when demonstrated in a calculation.

PROBLEM 9

Thallium exists in two different oxidation states: Tl^+ and Tl^{3+} . Iodide ions can combine with iodine to form tri-iodide ions (I_3^-) in aqueous solutions,

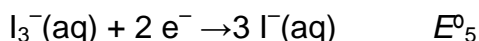
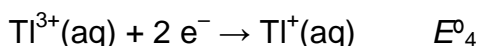
The standard redox potentials for some relevant reactions are:



The equilibrium constant for the reaction $\text{I}_2(\text{s}) + \text{I}^-(\text{aq}) \rightarrow \text{I}_3^-(\text{aq})$: $K_1 = 0.459$.

Use $T=25 \text{ }^\circ\text{C}$ throughout this problem.

9.1 Calculate the redox potentials E°_4 and E°_5 for the following reactions:



9.2 Write empirical formulae for all theoretically possible neutral compounds that contain one thallium ion and any number of iodide and/or tri-iodide ion(s) as anion(s).

There is an empirical formula that could belong to two different compounds. Which one? Based on the standard redox potentials, which of the two isomers mentioned above is the stable one at standard conditions? Write the chemical reaction for the isomerisation of the other isomer of thallium iodide.

Complex formation can shift this equilibrium. The cumulative complex formation constant for the reaction $\text{Tl}^{3+} + 4\text{I}^- \rightarrow \text{TlI}_4^-$ is $\beta_4 = 10^{35.7}$

9.3 Write the reaction that takes place when a solution of the more stable isomer of thallium iodide is treated with an excess of KI. Calculate the equilibrium constant K_2 for this reaction.

If the solution of the more stable isomer is treated with a strong basic reagent precipitation of a black substance can be observed. After the water content of the precipitate is removed, the remaining material contains 89.5% thallium (by mass).

9.4 What is the empirical formula of this compound? Show your calculations. Write a balanced equation for its formation.

SOLUTION

$$9.1 \quad E_4^0 = \frac{3E_2^0 - E_1^0}{2} = 1.26 \text{ V}$$

$$E_5^0 = E_3^0 + 0.059 / 2 \log(1 / K_1) = 0.550 \text{ V}$$

9.2 Tl I, Tl I₃, Tl I₅, Tl I₇, Tl I₉

Tl I₃ can be either Tl³⁺(I⁻)₃ or Tl⁺(I₃⁻)

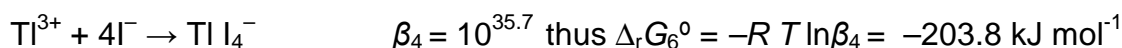
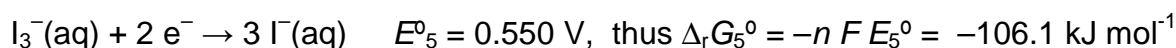
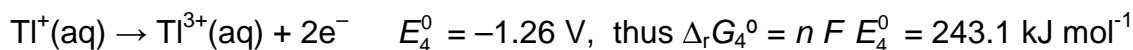
More stable: Tl⁺(I₃⁻)

as $E_4^0 > E_5^0$ or E_3^0 ,

Isomerisation: Tl³⁺ + 3 I⁻ = Tl⁺ + I₃⁻

9.3 Reaction: Tl⁺ + I₃⁻ + I⁻ → Tl I₄⁻

This reaction could be regarded as sum of three reactions:



The net free enthalpy change is $\Delta_r G_7^0 = \Delta_r G_4^0 + \Delta_r G_5^0 + \Delta_r G_6^0 = -66.8 \text{ kJ mol}^{-1}$

$$\text{Thus } K_2 = \exp\left(-\frac{\Delta_r G_7^0}{RT}\right) = 4.96 \cdot 10^{11}$$

9.4 Supposing that the substance contains Tl and an anion, the formula of the compound is Tl_aX_b and the following equation holds:

$$\frac{a \cdot 204.4}{a \cdot 204.4 + bM_X} = 0.895$$

From the values $b = 1, 3$ and $a = 1, 2, 3$ only $b = 3, a = 2$ gives a realistic:

$$M_X = 16.0 \text{ g mol}^{-1}.$$

X is oxygen.

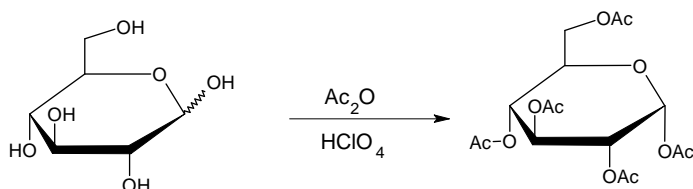
Formula: Tl₂O₃.

Equation: 2 Tl I₃ + 6 OH⁻ → Tl₂O₃ + 6 I⁻ + 3 H₂O

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis of α -D-glucopyranose pentaacetate

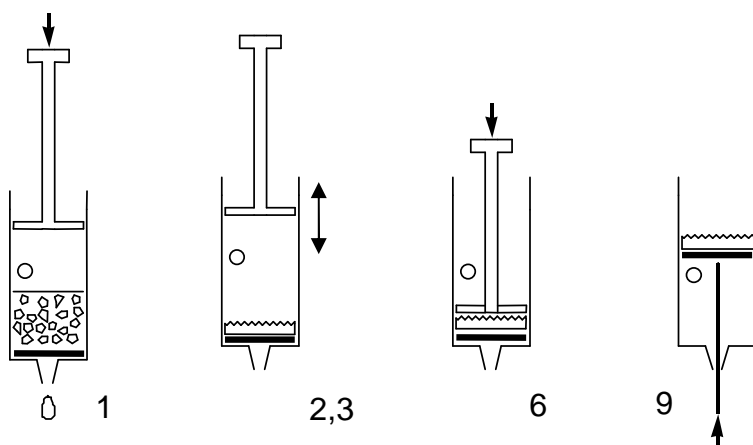


Caution: Use gloves while manipulating acetic acid and acetic anhydride. Let the lab supervisors know if any is spilled.

Add and mix 12 cm³ of pure acetic acid to 12 cm³ of acetic anhydride (provided in an Erlenmeyer flask) and add 3.00 g glucose (acetic anhydride is in excess). Add with a Pasteur-pipette 5 drops of 30% HClO₄ dissolved in acetic acid. After the addition of the catalyst the solution might warm up considerably.

Let the mixture rest covered for 10 minutes and swirl it from time to time. Pour the reaction mixture into 100 cm³ of water in a beaker. Scratch the wall of the beaker with a glass rod to initiate crystallization, and let it crystallize for 10 minutes. Filter and wash the product two times with 10 cm³ of water using the syringe and the porous polypropylene filter disc.

Filtration using a plastic syringe



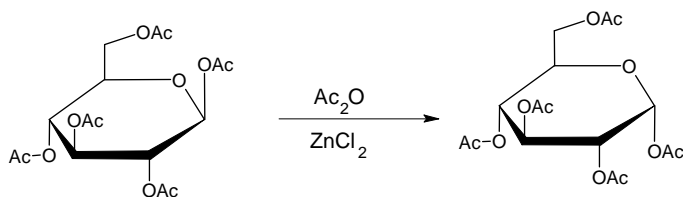
1. Pull out the piston. Fill the syringe from above with the suspension to be filtered. The syringe can be filled to the level of the hole. Replace piston.
2. Cover the hole with your finger and press in the piston as far as the hole.
3. Open the hole and draw the piston back. Do not draw in air through the filter.
4. Repeat steps 2-3 a few times to expel the liquid.
5. Repeat steps 1-4 until all solids are on the filter.
6. Press the piston against the filter cake and squeeze out the liquid.
7. Wash the product twice with 10 cm³ of water repeating steps 1-4.
8. Press the piston against the filter cake and squeeze out the water.
9. Pull the piston out with the hole closed to lift out the filter cake. (Pushing with the end of the spatula can help.)

1.1 Place your product in the open Petri dish marked with your code. Leave it on your table. The organizers will dry it, weigh it and check it for purity.

1.2 Calculate the theoretical yield (mass) of your product in g. ($M(C) = 12 \text{ g mol}^{-1}$, $M(O) = 16 \text{ g mol}^{-1}$, $M(H) = 1.0 \text{ g mol}^{-1}$)

Synthesis of α -D-glucopyranose pentaacetate from β -D-glucopyranose pentaacetate

An alternative synthesis of α -D-glucopyranose pentaacetate starts from readily available β -D-glucopyranose pentaacetate. In this experiment we will study the kinetics of this reaction with thin layer chromatography.



Add 1.5 cm³ acetic anhydride to 50 mg of anhydrous ZnCl₂ (preweighed in a test tube). Add 100 mg of pure β -D-glucopyranose pentaacetate (BPAG) and swirl until dissolved. Take three drops from this mixture into an Eppendorf tube, add 0.5 cm³ methanol and save it.

Place the test tube in the heating apparatus under the hood closest to your desk. Place the test tube in the heating block preadjusted to 70°C. Mix the contents of the test tube from time to time. During the reaction take three drops of sample from the mixture

with a Pasteur pipet after 2, 5, 10, and 30 minutes. Mix immediately each sample with 0.5 cm³ of methanol to stop the reaction in an Eppendorf tube.

Prepare a silica TLC plate with the collected samples to study the reaction kinetics. Apply the necessary reference compounds as well to help identification of the spots on the plate. Mark the spots with a pencil, and develop the plate in isobutyl acetate/ isoamyl acetate (1:1) eluent. Heat the plates with a heat-gun (under the hood!) to visualise the spots (the colour is stable). You can ask for a second plate without penalty points if needed for proper evaluation.

1.3 Copy your plate on the answer sheet and place your plate in the labelled zip lock bag.

1.4 Interpret your experiment and choose the correct answer.

The acetylation reaction of glucose is exothermic.

- a) Yes
- b) No
- c) Cannot be decided based on these experiments

The isomerisation reaction of β -D-glucopyranose pentaacetate can be used for the preparation of pure α -D-glucopyranose pentaacetate.

- a) Yes
- b) No
- c) Cannot be decided based on these experiments

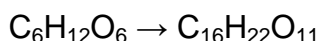
SOLUTION

1.1 Yield of the product in g, measured by the organizer.

The samples are dried by the organisers. The typical yield is 70 %.

Purity is checked by solubility (acetone) and TLC. If there is no insoluble material and no impurity is detectable by TLC, the full points for the yield are received.

1.1 Calculation of the theoretical yield of the product in g:



$$m = \frac{3.00 \text{ g} \times 390 \text{ g mol}^{-1}}{180 \text{ g mol}^{-1}} = 6.50 \text{ g}$$

1.3 The developed TLC plate was expected to be sketched on the answer sheet.

Full points were given if both standards and all samples are present.

1.4 Solutions: a), a).

PROBLEM 2 (Practical)

When potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$ is added to a solution containing zinc ions, an insoluble precipitate forms immediately. Your task is to find out the composition of the stoichiometric precipitate that contains no water of crystallization.

The precipitation reaction is quantitative and so quick that it can be used in a titration. The end point can be detected using redox indication, but first the concentration of the potassium hexacyanoferrate(II) solution has to be determined.

Preparation of $K_4[Fe(CN)_6]$ solution and determination of its exact concentration

Dissolve the solid $K_4[Fe(CN)_6] \cdot 3H_2O$ ($M = 422.41$ g/mol) sample in the small Erlenmeyer flask and quantitatively transfer it into the 100.00 cm³ volumetric flask. Take 10.00 cm³ portions of the hexacyanoferrate(II) solution. Add 20 cm³ 1 mol/dm³ sulfuric acid and two drops of the ferroin indicator solution to each sample before titration. Titrate with the 0.05136 mol/dm³ Ce^{4+} solution. Repeat titration as necessary. Cerium(IV) is a strong oxidant under acidic conditions forming Ce(III).

2.1 Report the Ce^{4+} solution volumes consumed.

2.2 Give the equation for the titration reaction. What was the mass of your $K_4[Fe(CN)_6] \cdot 3H_2O$ sample?

The reaction between zinc ions and potassium hexacyanoferrate(II)

Take 10.00 cm³ of the hexacyanoferrate(II) solution and add 20 cm³ 1 mol/dm³ sulfuric acid. Add three drops of indicator solution (diphenyl amine) and two drops of $K_3[Fe(CN)_6]$ solution. The indicator only works if the sample contains some hexacyanoferrate(III), $[Fe(CN)_6]^{3-}$. Titrate slowly with the zinc solution. Continue until a bluish violet colour appears. Repeat titration as necessary.

2.3 Report the zinc solution volumes consumed.

2.4 Interpret the titration answering the questions on the answer sheet.

Mark the correct answer:

The diphenyl amine indicator changes in colour at the end point

- a) because the concentration of the Zn^{2+} ions increases.
- b) because the concentration of the $[Fe(CN)_6]^{4-}$ ions decreases.
- c) because the concentration of the $[Fe(CN)_6]^{3-}$ ions increases.
- d) because the indicator is liberated from its complex.

Which form of the indicator is present before the end point?

- a) Oxidized
 b) Reduced
 c) Complexed to a metal ion

At the beginning of the titration the redox potential for the hexacyanoferrate(II) - hexacyanoferrate(III) system is lower than the redox potential of the diphenyl amine indicator.

- a) True
 b) False

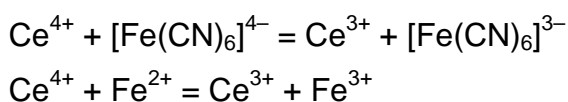
2.5 Determine the formula of the precipitate.

SOLUTION

2.1 Ce^{4+} consumptions:

Full marks if V_1 is within 0.15 cm^3 of the expected value recalculated from the $\text{K}_4[\text{Fe}(\text{CN})_6]$ mass. Zero marks if deviation is more than 0.50 cm^3 . Linear scale is applied in between.

2.2 The titration reaction:



2.3 Zinc consumptions:

Full marks (25 pts.) if V_2 is within 0.15 cm^3 of the expected value recalculated from $\text{K}_4[\text{Fe}(\text{CN})_6]$ mass, zinc concentrations and empirical ratio. Zero marks if the deviation is more than 0.50 cm^3 . Linear scale is applied in between.

2.4 Solutions: b), b), a)

2.5 Determine the formula of the precipitate. Show your work.

The mole ratio of the zinc : hexacyanoferrate(II) in the precipitate can be evaluated as:

$$\frac{n(\text{Zn})}{n(\text{Fe}(\text{CN})_6)} = \frac{10 c(\text{Zn}) V_2 M}{m}$$

Values for $c(\text{Zn})$ are distributed according to a certain plan.

The empirical ratio obtained from the experiments is 1.489.

Calculating the zinc/hexacyanoferrate(II) ratio:

Cations are needed to make the precipitate neutral and only potassium is present.

The precipitate is $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$.

Any other reasonable calculation giving the same result is accepted.

Hydrogen instead of potassium ($\text{H}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ or $\text{KHZn}_3[\text{Fe}(\text{CN})_6]_2$) is also acceptable.

PROBLEM 3 (Practical)

Caution:

Handle all unknown solutions as if they were toxic and corrosive. Discard them only in the appropriate waste container.

The heat gun heats the expelled air up to 500 °C. Do not direct the stream towards combustible materials or body parts. Be careful with the hot nozzle.

Always place a single piece of pumice into liquids before heating to avoid bumping. Never point the mouth of a heated test tube towards a person.

You have eight unknown aqueous solutions. Each solution contains only one compound. The same ion may appear in more than one solution. Every compound formally consists of one type of cation and one type of anion from the following list:

Cations: H^+ , NH_4^+ , Li^+ , Na^+ , Mg^{2+} , Al^{3+} , K^+ , Ca^{2+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Sr^{2+} , Ag^+ , Sn^{2+} , Sn^{4+} , Sb^{3+} , Ba^{2+} , Pb^{2+} , Bi^{3+}

Anions: OH^- , CO_3^{2-} , HCO_3^- , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$, NO_2^- , NO_3^- , F^- , HPO_4^{2-} , H_2PO_4^- , SO_4^{2-} , HSO_4^- , S^{2-} , HS^- , Cl^- , ClO_4^- , MnO_4^- , Br^- , I^-

You have test tubes and heating at your disposal but no additional reagents apart from distilled water and *pH* paper.

Identify the compounds in the solutions **1-8**. You can use the solubility table for some of the anions on the next page. If you are unable to identify an ion exactly, give the narrowest selection possible.

Remarks: The unknown solutions may contain minor impurities arising from their exposure to air. The concentration of all solutions is around 5 % by mass so you can expect clearly observable precipitates from the main components. In some cases, precipitation does not occur instantaneously; some substances may remain in an oversaturated solution for a while. Don't draw negative conclusions too hastily, wait 1-2 minutes where necessary. Always look carefully for all signs of a reaction.

Keep in mind that heating accelerates all processes, increases the solubility of most substances, and may start reactions that do not take place at room temperature.

SOLUTION

The solutions received by the students contain the following compounds in eight test-tubes: AgNO_3 , BaI_2 , KHCO_3 , MgSO_4 , NaHS , NaOH , NH_4ClO_4 , $\text{Pb}(\text{CH}_3\text{COO})_2$ ($\text{Pb}(\text{OAc})_2$). There were eight sets of samples differing in order of the compounds in particular test tubes.

The problem can be approached in many ways. A systematic solution is given here for one of the sets of test tubes with the following order of the compounds:

Test tube No	1	2	3	4	5	6	7	8
Compound	AgNO_3	KHCO_3	NH_4ClO_4	NaOH	NaHS	$\text{Pb}(\text{OAc})_2$	BaI_2	MgSO_4

All solutions are colourless (NaHS may be slightly yellowish because of polysulfide impurity). Solutions **1**, **3**, **6**, **7**, and **8** are practically neutral (pH paper reading about 5-6). Solution **2** is basic ($\text{pH} = 9$) while solutions **4** and **5** are very strongly basic ($\text{pH} > 11$).

We can exclude all ions that only form coloured compounds in aqueous solutions: Cr^{3+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and MnO_4^- . (In principle we should also exclude Mn^{2+} but its solutions have a very light pink colour that might be mistaken for colourless. The yellowish solution is strongly basic hence its colour cannot be attributed to iron.) The compounds of H^+ , Sn^{2+} , Sn^{4+} , Sb^{3+} , Bi^{3+} , and HSO_4^- with the possible counter-ions could only exist in markedly acidic solutions; therefore they can also be safely excluded.

Thus the list of possible ions is:

Cations: NH_4^+ , Li^+ , Na^+ , Mg^{2+} , Al^{3+} , K^+ , Ca^{2+} , Mn^{2+} , Zn^{2+} , Sr^{2+} , Ag^+ , Ba^{2+} , Pb^{2+} .

Anions: OH^- , CO_3^{2-} , HCO_3^- , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$, NO_2^- , NO_3^- , F^- , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , SO_4^{2-} , S^{2-} , HS^- , Cl^- , ClO_4^- , Br^- , I^- .

The unknown solutions react with each other as follows (\downarrow = precipitate; \uparrow = volatile product; "no change" means even when boiled, unless indicated otherwise):

	1 AgNO ₃	2 KHCO ₃	3 NH ₄ ClO ₄	4 NaOH	5 NaHS	6 Pb(OAc) ₂	7 BaI ₂	8 MgSO ₄
1 AgNO ₃	—	—	—	—	—	—	—	—
2 KHCO ₃	↓ light yellow ↑ neutral, odourless	—	—	—	—	—	—	—
3 NH ₄ ClO ₄	no change	↓ white crystals (*)	—	—	—	—	—	—
4 NaOH	↓ brown-black	no change	boiling: ↑ basic, odour of ammonia	—	—	—	—	—
5 NaHS	↓ black solution turns acidic	no change	boiling: ↑ basic, odour of NH ₃ , H ₂ S	no change	—	—	—	—
6 Pb(OAc) ₂	↓ white crystals	↓ white ↑ neutral, odourless	no change	↓ white	↓ black	—	—	—
7 BaI ₂	↓ yellow	↓ white ↑ (**)	no change	no change	no change	↓ yellow	—	—
8 MgSO ₄	↓ white crystals	no change (***)	no change	↓ white	no change (****)	↓ white	↓ white	—

(*): upon boiling, the formation of NH₃ is detectable by its odour and by *pH* paper.

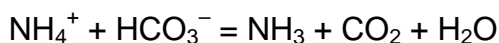
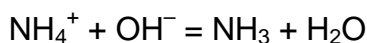
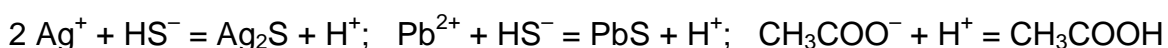
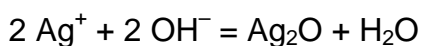
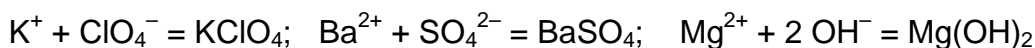
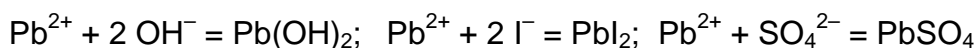
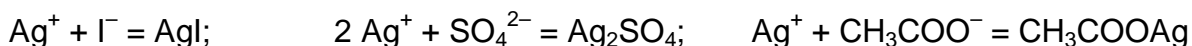
(**): gas bubbles are usually not observed when **2** is in excess.

(***): upon boiling, an odourless gas evolves and a white precipitate forms.

(****): upon boiling, a white precipitate forms and the odour of H₂S appears.



$\text{Mg}^{2+} + 2 \text{HCO}_3^- = \text{MgCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ (more accurately, basic carbonates of variable composition are formed)



Two groups of the observed phenomena give instant clues to the identification of some of the ions.

First, the reactions of **2** are often accompanied with the formation of a colourless and odourless gas that can only be CO_2 . Thus **2** contains CO_3^{2-} or HCO_3^- .

Second, there are only 3 dark precipitates that can be formed from the given ions: Ag_2O , Ag_2S , and PbS . This fact, together with the *pH* of the solutions, instantly identifies the cation of **1** as Ag^+ , the cation of **6** as Pb^{2+} , the anion of **4** as OH^- , and the anion of **5** as sulfide or hydrosulfide (confirmed by the distinct smell of the solution).

The choice between the latter two can be made by measuring the *pH* of the solution formed in the reaction of **5** with an excess of **1** or **6**. In the case of **1**, the reaction mixture is strongly acidic. Thus the anion of **5** is HS^- .

The evolution of CO_2 in the reaction with Ag^+ and Pb^{2+} also identifies the anion of **2** as HCO_3^- . (in accord with the moderately basic *pH*)

The reaction of **3** and **4** yields ammonia. **4** is obviously not a solution of NH_3 itself. Thus the cation of **3** is NH_4^+ .

2+4 form either a precipitate or ammonia. The cations of **2** and **4** are Na^+ or K^+ .

2+5 do not form either a precipitate or ammonia. The cation of **5** is an alkali metal.

3 is the only solution that does not give a precipitate with Ag^+ . Accordingly, it can be ammonium nitrate, fluoride, or perchlorate. But it does give a precipitate with **2**, a hydrocarbonate of Na^+ or K^+ . Thus the anion of **3** is ClO_4^- and the cation of **2** is K^+ . **4** does not give a precipitate with NH_4ClO_4 . The cation of **4** is Na^+ .

5 does not give a precipitate either with NH_4ClO_4 (K^+) or with a mixture of KHCO_3 and NaOH (Li^+). The cation of **5** is **Na⁺**.

7 forms no precipitate or ammonia with NaOH but gives a precipitate with KHCO_3 . **7** cannot be an alkali metal perchlorate because it forms yellow precipitates with **1** and **6**. Thus the cation of **7** is **Ba²⁺** and the anion of **7** is **I⁻**.

At room temperature **8** gives a precipitate with OH^- but not with HS^- which means it can only be a salt of a Group 2A metal. Thus the reaction of **8** with BaI_2 is obviously one between Ba^{2+} and the anion of **8**. The latter is very likely SO_4^{2-} but HCO_3^- and H_2PO_4^- are also theoretically possible. The solution of **8** is unchanged upon boiling and gives a white precipitate with Ag^+ . This excludes both HCO_3^- and H_2PO_4^- . Thus the anion of **8** is **SO₄²⁻**. This instantly identifies the cation of **8** as **Mg²⁺**.

6 is a soluble compound of lead. The anion could be CH_3COO^- , NO_2^- , NO_3^- , or ClO_4^- . The slight odour of acetic acid might give a clue. Unlike **1**, the reaction of an excess of **6** with HS^- does not yield a markedly acidic solution which shows that **6** is a salt of a weak acid. If **6** were a nitrite, it would give a yellowish precipitate with Ag^+ . It would also react with NH_4ClO_4 upon heating with the evolution of N_2 (and nitrogen oxides from the reaction with HS^- would also be noticeable). The absence of these reactions indicates that the anion of **6** is **CH₃COO⁻**.

Soluble salts of silver are even less numerous, the only choices are NO_3^- , F^- , and ClO_4^- . The anion can be examined if one removes the silver ions from the solution of **1** with an excess of NaOH . The Ag_2O precipitate quickly separates from the solution which can be easily poured off. This solution, containing the anion of **1**, does not give a precipitate with BaI_2 which rules out F^- . The solubility of KClO_4 is quite significant; therefore the absence of a precipitate with KHCO_3 is inconclusive. The anion of **1** is therefore either **NO₃⁻** or **ClO₄⁻**.

QUANTITIES AND THEIR UNITS USED IN THIS PUBLICATION**SI Basic Units**

Length	<i>l</i>	metre	m
Mass	<i>m</i>	kilogram	kg
Time	<i>t</i>	second	s
Electric current	<i>I</i>	ampere	A
Temperature	<i>T</i>	kelvin	K
Amount of substance	<i>n</i>	mole	mol

Special names and symbols for certain derived SI Units

Force	<i>F</i>	Newton	N
Pressure	<i>p</i>	pascal	Pa
Energy	<i>E</i>	joule	J
Power	<i>P</i>	watt	W
Electric charge	<i>Q</i>	coulomb	C
Electric potential difference	<i>U</i>	volt	V
Electric resistance	<i>R</i>	ohm	Ω

Other derived SI Units used in chemistry

Area	<i>S</i>	square metre	m^2
Volume	<i>V</i>	cubic metre	m^3
Density	<i>ρ</i>	kilogram per cubic metre	$kg\ m^{-3}$
Concentration	<i>c</i>	mole per cubic metre	$mol\ m^{-3}$ ($mol\ dm^{-3}$)
Molar mass	<i>M</i>	kilogram per mole	$kg\ mol^{-1}$ ($g\ mol^{-1}$)

Some other quantities and constants

Relative atomic mass of an element	A_r
Relative molecular mass of a compound	M_r
Molar fraction	x
Mass fraction	w
Volume fraction	φ
Enthalpy	H
Entropy	S
Gibbs energy	G
Temperature in Celsius scale	$^{\circ}\text{C}$

Elementary charge, e	$1.6021892 \times 10^{-19} \text{ C}$
Planck constant, h	$6.626176 \times 10^{-34} \text{ J s}$
Avogadro constant, A	$6.022045 \times 10^{23} \text{ mol}^{-1}$
Faraday constant, F	$9.648456 \times 10^4 \text{ C mol}^{-1}$
Gas constant, R	$8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$
Zero of Celsius scale, T_0	$273.15 \text{ K (exactly)}$
Normal pressure, p_0	$1.01325 \times 10^5 \text{ (exactly)}$
Standard molar volume of ideal gas, V_0	$2.241383 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}$

Abbreviations and Mathematical symbols

ICHO	International Chemistry Olympiad
STP	Standard temperature and pressure (T_0, p_0)
M	molar, mol dm ⁻³
N	normal
$\hat{=}$	corresponds to
\approx	approximately equal to
\sim	proportional to
\Rightarrow	implies