THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS

Volume 4

46th – 50th IChO
2014 – 2018

Edited by Anton Sirota

IChO International Information Centre,

Bratislava, Slovakia, 2019

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS,
Volume 4
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ISBN 978-80-8072-173-2

Issued by IUVENTA – Slovak Youth Institute, in 2019
with the financial support of the Ministry of Education of the Slovak Republic

Number of copies: 200
Not for sale.

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Preface

This publication contains 44 theoretical and 15 practical competition problems from the 46st – 50th International Chemistry Olympiads (IChO) organized in the years 2014 – 2018. It has been published by the IChO International Information Centre in Bratislava (Slovakia) as a continuation of the preceding Volumes 1, 2 and 3 with the titles:

- The competition problems from the International Chemistry Olympiads, Volume 1,
  1st – 20th IChO, 1968 – 1988 (IUVENTA, Bratislava, 2008), pp. 1 – 405.
- The competition problems from the International Chemistry Olympiads, Volume 2,
  21st – 40th IChO, 1989 – 2008 (IUVENTA, Bratislava, 2009), pp. 406 – 1139.
- The competition problems from the International Chemistry Olympiads, Volume 3,
  41st – 45th IChO, 2009 – 2013 (IUVENTA, Bratislava, 2013), pp. 1140 – 1424.

Not less than 362 theoretical and 125 practical problems were set in the IChO during the fifty years of its existence. In the elaboration of this collection the editor had to face certain difficulties because the aim was not only to make use of the past recordings but also to give them such a form that they may be used in practice and further chemical education. Consequently, it was necessary to make some corrections in order to unify the form of the problems (numbering of the tasks in the particular problems, solution inserted immediately after the text of the problem, solutions without grading points and special graphs used for grading of practical problems). Nevertheless, the mentioned corrections and changes do not concern the contents and language of the competition problems.

The practical problems set in the IChO competitions, contain as a rule some instructions, list of apparatuses available, chemicals on each desk and those available in the laboratory, and the risk and safety phrases with regard to the chemicals used. All of these items are important for the competitors during the competition but less important for those who are going to read the competition tasks of this collection and thus, they are omitted. Some parts of the solutions of practical problems are also left out since they require the experimental data which could be obtained by experiments during the practical part of the IChO competition.

In this publication SI quantities and units are preferred. Only some exceptions have been made when, in an effort to preserve the original text, the quantities and units have been used that are not SI.

Although the numbers of significant figures in the results of some solutions do not obey the criteria generally accepted, they were left without change.

Unfortunately, the authors of the particular competition problems are not known and due to the procedure of creation of the IChO competition problems, it is impossible to assign any author's name to a particular problem. Nevertheless, responsibility for the scientific content and language of the problems lies exclusively with the organizers of the particular International Chemistry Olympiads.

This review of the competition problems from the 46th – 50th IChO should serve to both competitors and their teachers as a source of further ideas in their preparation for this difficult competition. For those who have taken part in some of these International Chemistry Olympiads the collection of the problems could be of help as archival and documentary material.

In the previous fifty years many known and unknown people – teachers, authors, pupils, and organizers proved their abilities and knowledge and contributed to the success of this already well known and world-wide competition. We wish to all who will organize and attend the future International Chemistry Olympiads, success and happiness.

Bratislava, July 2019

Anton Sirota, editor

46th

9 theoretical problems
3 practical problems

THE FORTY-SIXTH
INTERNATIONAL CHEMISTRY OLYMPIAD
21–29 JULY 2014, HANOI, VIETNAM

THEORETICAL PROBLEMS

PROBLEM 1

Particles in a box: polyenes

In quantum mechanics, the movement of π electrons along a neutral chain of conjugated carbon atoms may be modeled using the 'particle in a box' method. The energy of the π electrons is given by the following equation:

$$E_n = \frac{n^2 h^2}{8\,m\,L^2}$$

where n is the quantum number (n = 1, 2, 3, …), h is Planck's constant, m is the mass of electron, and L is the length of the box which may be approximated by $L = (k + 2)\times 1.40$ Å (k being the number of conjugated double bonds along the carbon chain in the molecule). A photon with the appropriate wavelength λ may promote a π electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). An approximate semi-empirical formula based on this model which relates the wavelength λ, to the number of double bonds k and constant B is as follows:

$$\lambda(\text{nm}) = B \times \frac{(k+2)^2}{(2k+1)} \qquad \text{Equation 1}$$

1.1 Using this semi-empirical formula with $B = 65.01$ nm calculate the value of the wavelength λ (nm) for octatetraene (CH_2=CH–CH=CH–CH=CH–CH=CH_2).

1.2 Derive equation 1 (an expression for the wavelength λ (nm) corresponding to the transfer of an electron from the HOMO to the LUMO) in terms of k and the fundamental constants, and hence calculate theoretical value of the constant $B_{\text{calc.}}$.

1.3 We wish to synthesize a linear polyene for which the excitation of a π electron from the HOMO to the LUMO requires an absorption wavelength of close to 600 nm. Using your expression from part 2, determine the number of conjugated double bonds (k) in this polyene and give its structure. [*If you did not solve Part 2, use the semi-empirical Equation 1 with B = 65.01 nm to complete Part 3.*]

1.4 For the polyene molecule found in Part 3, calculate the difference in energy between the HOMO and the LUMO, ΔE, (kJ mol^{-1}).

In case that Part 3 was not solved, take k = 5 to solve this problem.

The model for a particle in a one-dimensional box can be extended to a three dimensional rectangular box of dimensions L_x, L_y and L_z, yielding the following expression for the allowed energy levels:

$$E_{n_x,n_y,n_z} = \frac{h^2}{8\,m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

The three quantum numbers n_x, n_y, and n_z must be integer values and are independent of each other.

1.5 Give the expressions for the three different lowest energies, assuming that the box is cubic with a length of L.

1.6 Levels with the same energy are said to be degenerate. Draw a sketch showing all the energy levels, including any degenerate levels, that correspond to quantum numbers having values of 1 or 2 for a cubic box.

SOLUTION

1.1 From the given semi-empirical formula, the wavelength λ (nm) is calculated as follows:

$$\lambda(\text{nm}) = 65.01 \times \frac{(k + 2)^2}{(2k + 1)}$$

For octatetraene molecule, with $k = 4$; $\lambda = 260.0$ nm

1.2 The formula

$$E_\text{n} = \frac{n^2 h^2}{8\, m\, L^2} \qquad (1)$$

ΔE is calculated as:
$$\Delta E = E_\text{LUMO} - E_\text{HOMO} = h\nu = \frac{hc}{\lambda} \qquad (2)$$

In which, λ and ν are wavelength and frequency for the corresponding photon respectively, k is the quantum number for the HOMO, which is equal to the number of double bonds. So, we have:

$$\Delta E = \frac{h^2}{8mL^2}[(k+1)^2 - k^2] = \frac{hc}{\lambda} = \frac{h^2}{8mL^2}[2k+1] \qquad (3)$$

Replace $L = (k + 2) \times 1.40$ Å into (3):

$$\frac{hc}{\lambda} = \frac{h^2\,(2k + 1)}{8m\,[(k + 2) \times 1.40 \times 10^{-10}]^2} \Rightarrow \lambda = \frac{8mc\,[(k + 2) \times 1.40 \times 10^{-10}]^2}{h\,(2k+1)}$$

$$\Rightarrow \lambda = \frac{8 \times 9.1094 \times 10^{-31} \times 2.9979 \times 10^{8} \times (1.40 \times 10^{-10})^2}{6.6261 \times 10^{-34}} \times \frac{(k + 2)^2}{(2k+1)}$$

$$\Rightarrow \lambda(\text{m}) = 6.462 \times 10^{-8} \times \frac{(k + 2)^2}{(2k + 1)} \Rightarrow \lambda(\text{nm}) = 64.62 \times \frac{(k + 2)^2}{(2k + 1)} \qquad (4)$$

$B_\text{calc.} = 64.6$ nm

1.3. With $\lambda = 600$ nm, we have

$$\frac{600}{64.62} = \frac{(k + 2)^2}{(2k+1)} = 9\,285 \Rightarrow k^2 - 14.57 - 5285 = 0$$

Solve the equation to obtain: $k_1 = 14.92$, $k_2 = - 0.355$ (Eliminated).

Thus, $k = 15$.

So, the formula of polyene is:

$CH_2{=}CH{-}(CH{=}CH)_{13}{-}CH{=}CH_2$

1.4

$$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} = \frac{h^2}{8mL^2}\left[(k+1)^2 - k^2\right]$$

$$\Delta E = \frac{(6.6261\times10^{-34})^2\times10^{-3} \times 6.022\times10^{23}}{8 \times 9.1094\times10^{-31} \times (1.40\times10^{-10})^2} \times\left[\frac{2k+1}{(k+2)^2}\right] \text{ (kJ mol}^{-1}\text{)}$$

$$\Delta E = 1851 \times\left[\frac{2k+1}{(k+2)^2}\right] \text{ (kJ mol}^{-1}\text{)}$$

For polyene with $k = 15$; $\Delta E = 199\ \text{kJ}\cdot\text{mol}^{-1}$.

Taking the value of $k = 5$; $\Delta E = 415\ \text{kJ}\cdot\text{mol}^{-1}$

1.5

$$L_x = L_y = L_z\ ; \quad E_{xyz} = \frac{h^2(n_x^2 + n_y^2 + n_z^2)}{8mL^2}$$

$$E_{111} = \frac{h^2\,(1^2 + 1^2 + 1^2)}{8mL^2} = \frac{3h^2}{8mL^2}$$

$$E_{112} = \frac{h^2\,(1^2 + 1^2 + 2^2)}{8mL^2} = \frac{6h^2}{8mL^2} = E_{121} = E_{211}$$

$$E_{122} = \frac{h^2\,(1^2 + 2^2 + 2^2)}{8mL^2} = \frac{9h^2}{8mL^2} = E_{212} = E_{221}$$

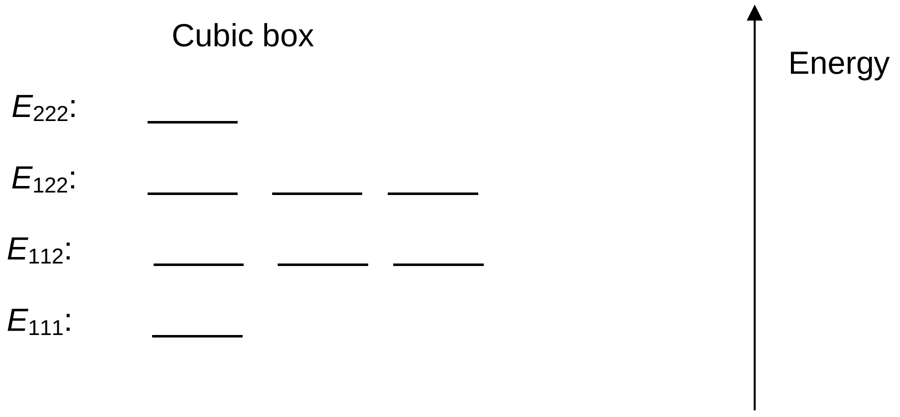
1.6 E_{111}: only a single state.

E_{112}: triple degenerate, either n_x, n_y or n_z can equal to 2.

E_{122}: triple degenerate, either n_x, n_y or n_z can equal to 1.

E_{222}: single state.

Energy diagram:



PROBLEM 2

Dissociating gas cycle

Dinitrogen tetroxide forms an equilibrium mixture with nitrogen dioxide:

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$

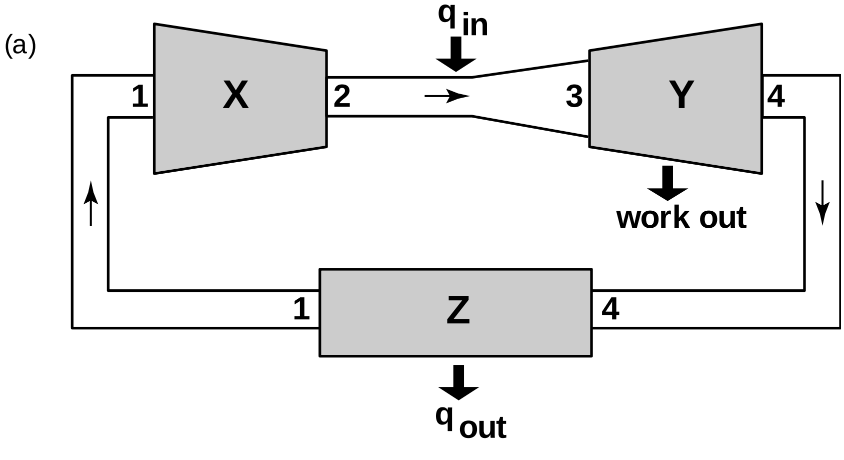
1.00 mol of N_2O_4 was put into an empty vessel with a fixed volume of 24.44 dm^3. The equilibrium gas pressure at 298 K was found to be 1.190 bar. When heated to 348 K, the gas pressure increased to its equilibrium value of 1.886 bar.

2.1 Calculate ΔG^0 of the reaction at 298K, assuming the gases are ideal.

2.2 Calculate ΔH^0 and ΔS^0 of the reaction, assuming that they do not change significantly with temperature.

Note: If you cannot calculate ΔH^0, use ΔH^0 = 30.0 kJ mol^{-1} *for further calculations.*

The tendency of N_2O_4 to dissociate reversibly into NO_2 enables its potential use in advanced power generation systems. A simplified scheme for one such system is shown below in Figure (a). Initially, "cool" N_2O_4 is compressed (1→2) in a compressor (**X**), and heated (2→3). Some N_2O_4 dissociates into NO_2. The hot mixture is expanded (3→4) through a turbine (**Y**), resulting in a decrease in both temperature and pressure. The mixture is then cooled further (4→1) in a heat sink (**Z**), to promote the reformation of N_2O_4. This recombination reduces the pressure, thus facilitates the compression of N_2O_4 to start a new cycle. All these processes are assumed to take place reversibly.



To understand the benefits of using reversible dissociating gases such as N_2O_4, we will focus on step 3 → 4 and consider an ideal gas turbine working with 1 mole of air (which we assume to be an inert, non-dissociating gas). During the reversible adiabatic expansion in the turbine, no heat is exchanged.

2.3 Give the equation to calculate the work done by the system w(air) during the reversible adiabatic expansion for 1 mol of air during stage 3 → 4. Assume that $C_{v,m}$(air) (the isochoric molar heat capacity of air) is constant, and the temperature changes from T_3 to T_4.

2.4 Estimate the ratio $w_{N2O4)}$ /$w_{(air)}$, in which $w_{(N2O4)}$ is the work done by the gas during the reversible adiabatic expansion process 3 → 4 with the cycle working with 1 mol of $N_2O_{4,}$ T_3 and T_4 are the same as in part 2. Take the conditions at stage 3 to be T_3 = 440 K and p_3 = 12.156 bar and assume that:

(i) the gas is at its equilibrium composition at stage 3;

(ii) $C_{v,m}$ for the gas is the same as for air;

(iii) the adiabatic expansion in the turbine takes place in a way that the composition of the gas mixture (N_2O_4 + NO_2) is unchanged until the expansion is completed.

SOLUTION

2.1

	N_2O_4	$\rightleftharpoons$	$2\ NO_2$
Initial molar number	1		0
At equilibrium	$1 - x$		$2x$

$n_{\text{total,eq.}} = 1 - x + 2x = 1 + x$ (mol)

$p_{\text{total,eq}} = p_{\text{ini}}(1 + x)$

(p_{ini} – initial pressure; $n_{\text{total,eq.}}$ – total molar number of gases at equilibrium;

$p_{\text{total,eq}}$ – total pressure of gases at equilibrium; x – number of moles N_2O_4 dissociated). 1

$$n_{\text{total,equi}} = \frac{pV}{\text{RT}} = \frac{1.190\ \text{bar}\left(\frac{10^5\ \text{Pa}}{1\ \text{bar}}\right) \times 24.44\ \text{dm}^3\left(\frac{1\ \text{m}^3}{1000\ \text{dm}^3}\right)}{8.3145\ \text{J K}^{-1}\text{mol}^{-1} \times 298\ \text{K}} = 1.174\ \text{mol}$$

$1.174 = 1 + x$

$x = 0.174$ (mol)

<u>ΔG^0 at 298 K</u>

At equilibrium:

$$p_{N_2O_4} = \frac{1 - x}{1 + x}\, p_{total} = \frac{1 - 0.174}{1 + 0.174} \times 1.190 = 0.837\ \text{bar}$$

$$p_{NO_2} = \frac{2x}{1 + x}\, p_{total} = \frac{2 \times 0.174}{1 + 0.174} \times 1.190 = 0.353\ \text{bar}$$

$$K_{298} = \frac{\left(\frac{p_{NO_2}}{p^o}\right)^2}{\left(\frac{p_{N_2O_4}}{p^o}\right)} = \frac{\left(\frac{0.353}{1}\right)^2}{\left(\frac{0.837}{1}\right)} = 0.1485$$

At 298 K,

$\Delta G^0 = -\ \text{RT}\ \ln K_{298} = -\ 8{,}3145 \times 298 \times \ln 0.1489 = 4719\ \text{J mol}^{-1} = 4.72\ \text{kJ mol}^{-1}$

2.2 <u>ΔG^0 at 348 K</u>

$$n_{\text{total,equi}} = \frac{p\,V}{R\,T} = \frac{1.886\text{ bar}\left(\frac{10^5\text{ Pa}}{1\text{ bar}}\right) \times 22.44\text{ dm}^3\left(\frac{1\text{ m}^3}{1000\text{ dm}^3}\right)}{8.314\text{ J K}^{-1}\text{ mol}^{-1} \times 348\text{ K}} = 1.593\text{ mol}$$

1.593 = 1 + x

x = 0.593 mol

At equilibrium:

$$p_{N_2O_4} = \frac{1-x}{1+x}\,p_{\text{total}} = \frac{1-0.593}{1+0.593} \times 1.886\text{ bar} = 0.482\text{ bar}$$

$$p_{NO_2} = \frac{2\,x}{1+x}\,p_{\text{total}} = \frac{2\times 0.593}{1+0.593} \times 1.886\text{ bar} = 1.404\text{ bar}$$

$$\Rightarrow\ K_{348} = \frac{\left(\frac{p_{NO_2}}{p^o}\right)^2}{\left(\frac{p_{N_2O_4}}{p^o}\right)} = \frac{\left(\frac{1.404}{1}\right)^2}{\left(\frac{0.482}{1}\right)} = 4.0897$$

At 348 K,

$\Delta G^o = -RT\ln K_{348} = -8.3145 \times 348 \times \ln 4.0897 = -4075\text{ J mol}^{-1} = -4.08\text{ kJ mol}^{-1}$

For ΔS^0:

$\Delta G^0_{348} = -4.08\text{ kJ} = \Delta H - 348\,\Delta S$ (1)

$\Delta G^0_{298} = 4.72\text{ kJ} = \Delta H - 298\,\Delta S$ (2)

(2) – (1) → $\Delta S = 0.176\text{ kJ mol}^{-1}\text{ K}^{-1}$

For ΔH^0:

$\Delta H^0 = 4.720 + 298 \times 0.176 = 57.2\text{ (kJ mol}^{-1})$

2.3 $\Delta U = q + w$; work done by turbine $w_{\text{air}} = -w$

$q = 0$, thus $w_{\text{air}} = \Delta U = C_{v,m\,\text{(air)}}\,[T_3 - T_4]$

2.4

$$\ln\frac{K_{440}}{K_{348}} = \frac{\Delta H^o}{R}\left(\frac{1}{348} - \frac{1}{440}\right) = \frac{57200}{8.314}\left(\frac{1}{348} - \frac{1}{440}\right)$$

$$\ln K_{440} = \ln K_{348} + \frac{57200}{8.314}\left(\frac{1}{348} - \frac{1}{440}\right) = \ln 4.0897 + \frac{57200}{8.314}\left(\frac{1}{348} - \frac{1}{440}\right) = 5.542$$

→ $K_{440} = 255.2$

	N_2O_4	$\rightleftharpoons$	$2\ NO_2$	(1)
Initial molar number:	1		0	
At equilibrium	1 – x		2x	

n_{total} = 1 – x + 2 x = (1 + x) mol; p_{total} = 12.156 bar

At equilibrium:

$$p_{N_2O_4} = \frac{1-x}{1+x} \times 12.156 \text{ bar} \qquad p_{NO_2} = \frac{2x}{1+x} \times 12.156 \text{ bar}$$

$$\Rightarrow K_{440} = \frac{\left(\dfrac{p_{NO_2}}{p^o}\right)^2}{\left(\dfrac{p_{N_2O_4}}{p^o}\right)} = \frac{\left(\dfrac{\frac{2x}{1+x} \times 12{,}156}{1}\right)^2}{\left(\dfrac{\frac{1-x}{1+x} \times 12{,}156}{1}\right)} = 255.2$$

(p^0 = 1 bar) →

$$\frac{\left(\frac{2x}{1+x}\right)}{\left(\frac{1-x}{1+x}\right)} = 20.99 \Rightarrow \frac{4x^2}{1-x^2} = 20.99 \Rightarrow$$

$4x^2 = 20.99 - 20.99\ x^2$ → $24.99\ x^2 = 20.99$ → x = 0.92;

n_{total} = 1 + x = 1.92

$$\rightarrow w_{N_2O_4} = 1.92 \times C_{v,air} \times (T_3 - T_4); \rightarrow \frac{w_{N_2O_4}}{w_{air}} = 1.92$$

PROBLEM 3

High-valent silver compounds

Silver chemistry is dominated by Ag (I) compounds. Compounds of silver in higher oxidation state (from +2 to +5) are not very abundant due to their instability with respect to reduction. High-valent silver compounds are very reactive and can be synthesized from Ag(I) compounds in electro-chemical oxidations or in chemical oxidations using powerful oxidizing agents.

In some peroxydisulfate ($S_2O_8^{2-}$) oxidations catalyzed by Ag^+, black solid (**A**) with the composition AgO can be isolated.

3.1 Choose the appropriate magnetic behavior of **A** if it exists as $Ag^{II}O$.

Single crystal X - ray studies reveal that the lattice of **A** contains two nonequivalent Ag atom sites (in equal proportions) of which one denoted as Ag1 and the other denoted as Ag2. Ag1 shows a linear O atom coordination (O-Ag-O) and Ag2 shows a square-planar O atom coordination. All O atoms are in equivalent environments in the structure. Thus, **A** should be assigned as $Ag^{I}Ag^{III}O_2$ rather than $Ag^{II}O$.

3.2. Assign the oxidation number of Ag1 and Ag2.

3.3 What is the coordination number of O atoms in the lattice of A?

3.4 How many Ag^{I} and Ag^{III} bond to one O atom in the lattice of A?

3.5 Predict the magnetic behavior of **A.** Check the appropriate box below.

3.6 The compound **A** can also be formed on warming a solution of Ag^+ with peroxydisulfate. Write down the equation for the formation of **A**.

Among the silver oxides which have been crystallographically characterized, the most surprising is probably that compound A is not a $Ag^{II}O$. Thermochemical cycles are useful to understand this fact. Some standard enthalpy changes (at 298 K) are listed:

Atom	Standard enthalpy of formation (kJ·mol^{-1})	1st ionization (kJ·mol^{-1})	2nd ionization (kJ·mol^{-1})	3rd ionization (kJ·mol^{-1})	1st electron affinity (kJ·mol^{-})	2nd electron affinity (kJ·mol^{-1})
Cu(g)	337.4	751.7	1964.1	3560.2		
Ag(g)	284.9	737.2	2080.2	3367.2		

O(g)	249.0				-141.0	844.0

Compounds	ΔH°_f (kJ·mol^{-1})
$Ag^IAg^{III}O_{2\,(s)}$	–24.3
$Cu^{II}O_{\,(s)}$	–157.3

The relationship between the lattice dissociation energy (U_{lat}) and the lattice dissociation enthalpy (ΔH_{lat}) for monoatomic ion lattices is: $\Delta H_{lat} = U_{lat} + nRT$, where n is the number of ions in the formula unit.

3.7 Calculate U_{lat} at 298 K of $Ag^IAg^{III}O_2$ and $Cu^{II}O$. Assume that they are ionic compounds.

The lattice dissociation energies for a range of compounds may be estimated using this simple formula:

$$U_{lat} = C \times \left(\frac{1}{V_m}\right)^{\frac{1}{3}}$$

where: V_m (nm^3) is the volume of the formula unit and C (kJ·nm·mol^{-1}) is an empirical constant which has a particular value for each type of lattice with ions of specified charges.

The formula unit volumes of some oxides are calculated from crystallographic data as the ratio between the unit cell volume and the number of formula units in the unit cell and listed as below:

Oxides	V_m (nm^3)
$Cu^{II}O$	0.02030
$Ag^{III}_2O_3$	0.06182
$Ag^{II}Ag^{III}_2O_4$	0.08985

3.8 Calculate U_{lat} for the hypothetical compound $Ag^{II}O$. Assume that $Ag^{II}O$ and $Cu^{II}O$ have the same type of lattice, and $V_m(Ag^{II}O) = V_m(Ag^{II}Ag^{III}_2O_4) - V_m(Ag^{III}_2O_3)$.

3.9 By constructing an appropriate thermodynamic cycle or otherwise, estimate the enthalpy change for the solid-state transformation from $Ag^{II}O$ to 1 mole of $Ag^IAg^{III}O_2$.

Note: Use $U_{lat}(Ag^{II}O)$ = 3180.0 kJ·mol^{-1} and U_{lat} ($Ag^IAg^{III}O_2$) = 8310.0 kJ·mol^{-1} if you cannot calculate $U_{lat}(Ag^{II}O)$ in Part 3.8).

3.10 Indicate which compound ($Ag^{II}O$ or $Ag^{I}Ag^{III}O_2$) is thermodynamically more stable. (Check the corresponding box.)

3.11 When $Ag^{I}Ag^{III}O_2$ is dissolved in aqueous $HClO_4$ solution, a paramagnetic compound (B) is first formed then slowly decomposes to form a diamagnetic compound (C). Given that B and C are the only compounds containing silver formed in these reactions, write down the equations for the formation of B and C.

Oxidation of Ag^+ with powerful oxidizing agents in the presence of appropriate ligands can result in the formation of high-valent silver complexes. A complex **Z** is synthesized and analyzed by the following procedures:

An aqueous solution containing 0.500 g of $AgNO_3$ and 2 cm^3 of pyridine (d = 0.982 g cm^{-3}) is added to a stirred, ice-cold aqueous solution of 5.000 g of $K_2S_2O_8$. The reaction mixture becomes yellow, then an orange solid (**Z**) is formed which has a mass of 1.719 g when dried.

Elemental analysis of **Z** shows the mass percentages of C, H, N elements are 38.96 %, 3.28 %, 9.09 %, respectively.

A 0.6164 g **Z** is added to aqueous NH_3. The suspension is boiled to form a clear solution during which stage the complex is destroyed completely. The solution is acidified with excess aqueous HCl and the resulting suspension is filtered, washed and dried (in darkness) to obtain 0.1433 g of white solid (**D**). The filtrate is collected and treated with excess $BaCl_2$ solution to obtain 0.4668 g (when dry) of white precipitate (**E**).

3.12 Determine the empirical formula of **Z** and calculate the percentage yield in the preparation.

3.13 Ag (IV) and Ag (V) compounds are extremely unstable and found only in few fluorides. Thus, the formation of their complexes with organic ligands in water can be discounted. To confirm the oxidation number of silver in **Z**, the effective magnetic moment (μ_{eff}) of **Z** was determined and found to be 1.78 BM. Use the spin only formula to determine the number of unpaired electrons in Z and the molecular formula of **Z.** (**Z** contains a mononuclear complex with only one species of Ag and only one type of ligand in the ligand sphere.)

3.14 Write down all chemical equations for the preparation of **Z**, and its analysis.

SOLUTION

3.1

☐ Diamagnetic

☒ Paramagnetic

3.2 Oxidation number of Ag1 : ……….+1

Oxidation number of Ag2 : ……… +3

3.3 The coordination number of O atoms = 3

3.4 Number of Ag^{I} = 1

Number of Ag^{III} = 2

3.5

☒ Diamagnetic

☐ Paramagnetic

The Ag^{I} is d^{10} hence diamagnetic; the Ag^{III} is square planar d^{8} also diamagnetic

3.6 $S_2O_8^{2-}{}_{(aq)} + 2\ Ag^{+}{}_{(aq)} + 2\ H_2O_{(l)} \longrightarrow 2\ SO_4^{2-}{}_{(aq)} + Ag^{I}Ag^{III}O_{2\,(s)} + 4\ H^{+}{}_{(aq)}$

3.7 <u>U_{lat} of $Ag^{I}Ag^{III}O_2$</u>

Calculations:

ΔH_{lat} ($Ag^{I}Ag^{III}O_2$) = 2 ΔH^{o}_{f} (O^{2-}) + ΔH^{o}_{f} (Ag^{+}) + ΔH^{o}_{f} (Ag^{3+}) – ΔH^{o}_{f} ($Ag^{I}Ag^{III}O_2$)

= (2×249 – 2 × 141 + 2 × 844) + (284.9 + 737.2) + (284.9 + 737.2 +

+ 2080.2 + 3367.2) – (–24.3) = +9419.9 (kJ mol$^{–1}$) U_{lat}

($Ag^{I}Ag^{III}O_2$) = ΔH_{lat} ($Ag^{I}Ag^{III}O_2$) – 4 RT

= + 9419.9 – 10.0 = + 9409.9 kJ mol$^{–1}$

<u>U_{lat} of $Cu^{II}O$</u>

Calculations for: U_{lat} of $Cu^{II}O$

ΔH_{lat} ($Cu^{II}O$) = ΔH^{o}_{f} ($O^{2–}$) + ΔH^{o}_{f} (Cu^{2+}) – ΔH^{o}_{f} ($Cu^{II}O$)

= (249 – 141 + 844) + (337.4 + 751.7 + 1964.1) – (–157.3)

= 4162.5 (kJ·mol$^{–1}$)

U_{lat} ($Cu^{II}O$) = ΔH_{lat}($Cu^{II}O$) – 2 RT = 4162.5 – 5.0 = 4157.5 kJ mol$^{–1}$

Note: If you can not calculate the U_{lat} of $Ag^{I}Ag^{III}O_2$ and $Cu^{II}O$, use the following values for further calculations: U_{lat} of $Ag^{I}Ag^{III}O_2$ = 8310.0 kJ mol^{-1}; U_{lat} of $Cu^{II}O$ = 3600.0 kJ mol^{-1}.

3.8 $V_m\,(Ag^{II}O) = V_m\,(Ag^{II}Ag^{III}{}_2O_4) - V_m\,(Ag^{III}{}_2O_3) = 0.08985 - 0.06182 = 0.02803\ m^3$

From the relationship $U_{lat} = C\times(V_m)^{-1/3}$ we have

$$\frac{U_{lat}\text{ (Ag oxide)}}{U_{lat}\text{(Cu oxide)}} = \left[\frac{V_m\text{(Cu oxide)}}{V_m\text{(Ag oxide)}}\right]^{1/3}$$

$$U_{lat}(Ag^{II}O) = 4157.5 \times \sqrt[3]{\frac{0.02030}{0.02803}} = 3733.6\ \text{kJ mol}^{-1}$$

[or 3232.9 kJ mol^{-1} if using U_{lat} $Cu^{II}O$ = 3600 kJ mol^{-1}]

3.9

$$\begin{tikzcd}
2\,Ag^{II}O_{\,(s)} \arrow[r, "\Delta H_{rxn}"] \arrow[d, "2\,U_{lat}(AgO) + 4\,RT"] & Ag^{I}Ag^{III}O_{2\,(s)} \\
2\,Ag^{2+}_{(g)} + 2\,O^{2-}_{(g)} \arrow[r, "IE_3(Ag) - IE_2(Ag)"] & Ag^{+}_{(g)} + Ag^{3+}_{(g)} + 2\,O^{2-}_{(g)} \arrow[u, "- U_{lat}(Ag^{I}Ag^{III}O) - 4\,RT"']
\end{tikzcd}$$

Calculations:

$$\begin{aligned}\Delta H_{rxn} &= 2\,U_{lat}\,(Ag^{II}O) + 4RT + IE_3 - IE_2 - U_{lat}\,(Ag^{I}Ag^{III}O_2) - 4RT \\ &= 2 \times 3733.6 + 3367.2 - 2080.2 - 9409.9 \\ &= -655.7\ \text{(kJ/mol) or - 663.0 kJ/mol using given } U_{lat} \text{ values}\end{aligned}$$

3.10

$Ag^{II}O$	$Ag^{I}Ag^{III}O_2$
☐	☒

3.11 For B: $Ag^{I}Ag^{III}O_{2(s)} + 4\,HClO_{4\,(aq)} \longrightarrow 2\,Ag(ClO_4)_{2\,(aq)} + 2\,H_2O_{\,(l)}$

For C: $4\,Ag(ClO_4)_{2\,(aq)} + 2\,H_2O_{\,(l)} \longrightarrow 4\,AgClO_{4\,(aq)} + 4\,HClO_{4\,(aq)} + O_{2\,(g)}$

3.12 **m**ol Ag in 0.6164 g of **Z** = mol of AgCl = 0.001 mol

mol SO_4^{2-} from 0.6160 g of **Z** = mol $BaSO_4$ = 0.002 mol

Mass percentage of Ag = 0.001×107.87/0.6164 = 17.50 %

Mass percentage of SO_4^{2-} = 0.002×96.06/0.6164 = 31.17 %

From EA:

$$\text{Ratio } Ag^{2+} : SO_4^{2-} : C : H : N = \frac{17.50}{107.87} : \frac{31.17}{192.12} : \frac{38.96}{12.01} : \frac{3.28}{1.01} : \frac{9.09}{14.01} = 1 : 2 : 20 : 20 : 4$$

The empirical formula of **Z** is: $C_{20}H_{20}AgN_4O_8S_2$

$$\text{Yield} = \frac{1.719}{\frac{0.500}{169.87} \times 616.4} \times 100 = 94.7\ \%$$

3.13 $\sqrt{n(n+2)} = 1.78$ (n is number of unpaired electron of Ag)

n = 1, corresponds to Ag^{II} (d^9)

Most rational molecular formula of **Z** is $[Ag^{II}(Py)_4](S_2O_8)$

3.14 Formation of **Z**:

$$2\ Ag^+_{(aq)} + 8\ Py_{(l)} + 3\ S_2O_8^{2-}{}_{(aq)} \longrightarrow 2\ [Ag^{II}(Py)_4](S_2O_8)_{(s)} + 2\ SO_4^{2-}{}_{(aq)}$$

Destruction of **Z** with NH_3:

$$[Ag^{II}(Py)_4](S_2O_8)_{(s)} + 6\ NH_{3(l)} \longrightarrow$$

$$\longrightarrow [Ag(NH_3)_2]^+_{(aq)} + ½\ N_{2(g)} + 2\ SO_4^{2-}{}_{(aq)} + 3\ NH_4^+{}_{(aq)} + 4\ Py_{(l)}$$

Formation of **D**:

$$[Ag(NH_3)_2]^+_{(aq)} + 2\ H^+_{(aq)} + Cl^-_{(aq)} \longrightarrow AgCl_{(s)} + 2\ NH_4^+{}_{(aq)}$$

Formation of **E**:

$$Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \longrightarrow BaSO_{4\ (s)}$$

PROBLEM 4

Zeise's salt

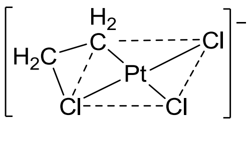
Zeise's salt, $K[PtCl_3C_2H_4]$, was one of the first organometallic compounds to be reported. W. C. Zeise, a professor at the University of Copenhagen, prepared this compound in 1827 by reacting $PtCl_4$ with boiling ethanol and then adding potassium chloride (Method 1). This compound may also be prepared by refluxing a mixture of $K_2[PtCl_6]$ and ethanol (Method 2). The commercially available Zeise's salt is commonly prepared from $K_2[PtCl_4]$ and ethylene (Method 3).

4.1 Write balanced equations for each of the above mentioned preparations of Zeise's salt, given that in methods 1 and 2 the formation of 1 mole of Zeise's salt consumes 2 moles of ethanol.

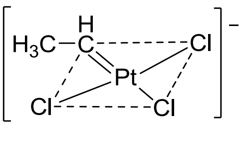
4.2 Mass spectrometry of the anion $[PtCl_3C_2H_4]^-$ shows one set of peaks with mass numbers 325-337 *au* and various intensities. Calculate the mass number of the anion which consists of the largest natural abundance isotopes (using given below data).

Isotope	$^{192}_{78}Pt$	$^{194}_{78}Pt$	$^{195}_{78}Pt$	$^{196}_{78}Pt$	$^{198}_{78}Pt$	$^{35}_{17}Cl$	$^{37}_{17}Cl$	$^{12}_{6}C$	$^{13}_{6}C$	$^{1}_{1}H$
Natural abundance, %	0.8	32.9	33.8	25.3	7.2	75.8	24.2	98.9	1.1	99.99

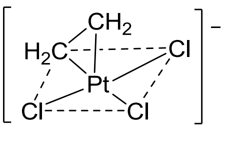
Some early structures proposed for Zeise's salt anion were:



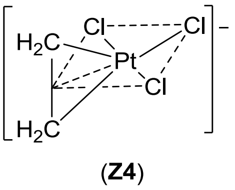
(**Z1**)



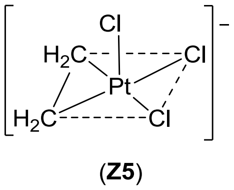
(**Z2**)



(**Z3**)



(**Z4**)



(**Z5**)

In structure **Z1**, **Z2**, and **Z5** both carbons are in the same plane as dashed square. [You should assume that these structures do not undergo any fluxional process by interchanging two or more sites.]

NMR spectroscopy allowed the structure for Zeise's salt to be determined as structure **Z4**.

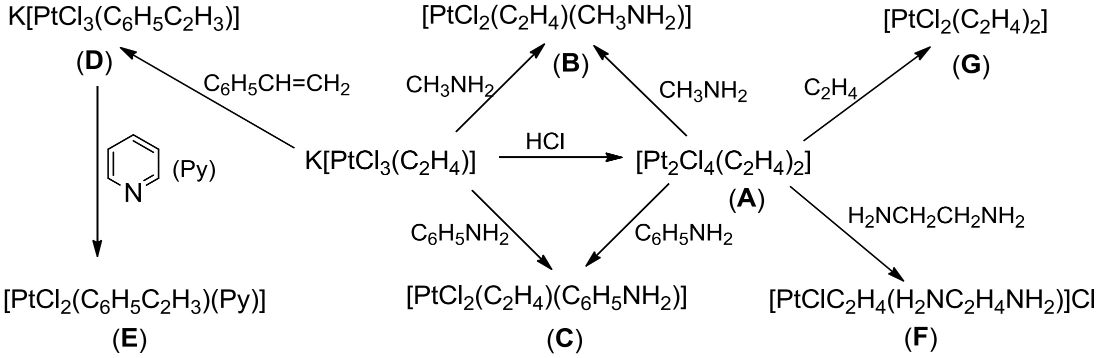
4.3 For each structure **Z1** – **Z5**, indicate in the table below how many hydrogen atoms are in different environments, and how many different environments of hydrogen atoms there are, and how many different environments of carbon atoms there are?

Structure	Number of different environments of hydrogen	Number of different environments of carbon
Z1	2	2
Z2	2	2
Z3	2	2
Z4	1	1
Z5	2	1

For substitution reactions of square platinum(II) complexes, ligands may be arranged in order of their tendency to facilitate substitution in the position *trans* to themselves (*the trans effect*). The ordering of ligands is:

$$CO , CN^- , C_2H_4 > PR_3 , H^- > CH_3^- , C_6H_5^- , I^- , SCN^- > Br^- > Cl^- > Py > NH_3 > OH^- , H_2O$$

In above series a left ligand has a stronger *trans effect* than that of the right ligand. Some reactions of Zeise's salt and the complex $[Pt_2Cl_4(C_2H_4)_2]$ are given below.



4.4 Draw the structure of A, given that the molecule of this complex has a centre of symmetry, no Pt-Pt bond, and no bridging alkene.

4.5 Draw the structures of **B**, **C**, **D**, **E**, **F** and **G**.

4.6 Suggest the driving force(s) for the formation of **D** and **F** by choosing one or more of the following statements (for example, i and ii):

i) formation of gas,
ii) formation of liquid,
iii) trans effect,
iv) chelate effect.

SOLUTION

$H[PtCl_3C_2H_4] + KCl \rightarrow K[PtCl_3C_2H_4] + HCl$

$K_2[PtCl_6] + 2\ C_2H_5OH \rightarrow K[PtCl_3C_2H_4] + CH_3CH{=}O + KCl + 2\ HCl + H_2O$

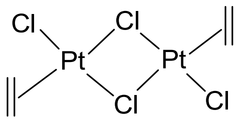
$K_2[PtCl_4] + C_2H_4 \rightarrow K[PtCl_3C_2H_4] + KCl$

4.2 Calculation: $195 + (3\times35) + (2\times12) + (4\times1) = 328$

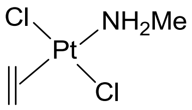
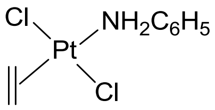
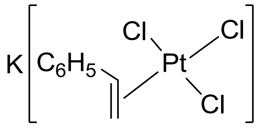
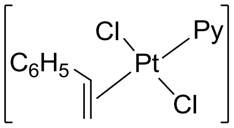
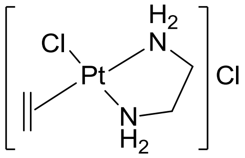
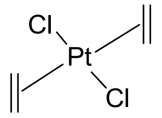
4.3

Structure	Number of different environments of hydrogen	Number of different environments of carbon
Z1	2	2
Z2	2	2
Z3	2	2
Z4	1	1
Z5	2	1

4.4

Structure of **A**	

4.5

B 	**C** 	**D** 
E 	**F** 	**G** 

4.6

Structure	**D**	**F**
Driving force(s)	i	iii and iv

PROBLEM 5

Acid-base equilibria in water

A solution (**X**) contains two weak monoprotic acids (those having *one* acidic proton); HA with the acid dissociation constant of K_{HA} = 1.74×10^{-7}, and HB with the acid dissociation constant of K_{HB} = 1.34×10^{-7}. The solution **X** has a pH of 3.75.

5.1 Titration of 100 cm^3 of solution **X** requires 100 cm^3 of NaOH solution (c = 0.220 mol·dm^{-3}) for completion. Calculate the initial (total) concentration (mol·dm^{-3}) of each acid in the solution **X**.

Use reasonable approximations where appropriate. [K_w = 1.00×10^{-14} at 298 K]

5.2 Calculate the pH of the solution **Y** in which the concentration of NaA initially was 6.00×10^{-2} mol·dm^{-3} and that of NaB 4.00×10^{-2} mol·dm^{-3}.

5.3 Adding large amounts of distilled water to solution **X** gives a very (infinitely) dilute solution where the total concentrations of the acids are close to zero. Calculate the percentage of dissociation of each acid in this dilute solution.

5.4. A buffer solution is added to solution **Y** to maintain a pH of 10.0. Assume no change in volume of the resulting solution **Z**. Calculate the solubility (in mol·dm^{-3}) of the substance $M(OH)_2$ in **Z**, taking into consideration that the anions A^- and B^- can form complexes with M^{2+}:

$M(OH)_2 \rightleftharpoons M^{2+} + 2\,OH^-$ K_{sp} = 3.10×10^{-12}

$M^{2+} + A^- \rightleftharpoons [MA]^+$ K_1 = 2.1×10^3

$[MA]^+ + A^- \rightleftharpoons [MA_2]$ K_2 = 5.0×10^2

$M^{2+} + B^- \rightleftharpoons [MB]^+$ K'_1 = 6.2×10^3

$[MB]^+ + B^- \rightleftharpoons [MB_2]$ K'_2 = 3.3×10^2

SOLUTION

5.1 In solution **X**, H^+ was produced from the reactions :

$HA \rightleftharpoons H^+ + A^-$ and $HB \rightleftharpoons H^+ + B^-$ and $H_2O \rightleftharpoons H^+ + OH^-$

The positive and negative charges in an aqueous solution must balance. Thus the charge balance expression is:

$[OH^-] + [A^-] + [B^-] = [H^+]$ (Eq.1)

In the acidic solution (pH = 3.75) the concentration of $[OH^-]$ can be neglected, and thus:

$[A^-] + [B^-] = [H^+]$ (Eq. 2)

From the equilibrium expression:

$$\frac{[H^+]\,[A^-]}{[HA]} = K_{HA}$$

and $[HA] = [HA]_i - [A^-]$ (where $[HA]_i$ is the initial concentration)

Then $[H+]\,[A^-] = K_{HA}\,[HA] = K_{HA}\,([HA]_i - [A^-])$

Thus, the equilibrium concentration of $[A^-]$ can be presented as:

$$[A^-] = \frac{K_{HA}\,[HA]_i}{K_{HA} + [H^+]}$$

Similarly, the equilibrium concentration of $[B^-]$ can be presented as:

$$[B^-] = \frac{K_{HB}\,[HB]_i}{K_{HB} + [H^+]}$$

Substitute equilibrium concentrations of $[A^-]$ and $[B^-]$ into Eq.2:

$$\frac{K_{HA}\,[HA]_i}{K_{HA} + [H^+]} + \frac{K_{HB}\,[HB]_i}{K_{HB} + [H^+]} = [H^+]$$

Since K_{HA}, K_{HB} are much smaller than $[H^+]$:

$$\frac{K_{HA}\,[HA]_i}{[H^+]} + \frac{K_{HB}\,[HB]_i}{[H^+]} = [H^+]$$

or $1.74 \times 10^{-7} \times [HA]_i + 1.34 \times 10^{-7} \times [HB]_i = [H^+]^2 = (10^{-3.75})^2$

$1.74 \times [HA]_i + 1.34 \times [HB]_i = 0.316$ (Eq. 3)

Neutralization reactions:

$$HA + NaOH \longrightarrow NaA + H_2O$$

$$HB + NaOH \longrightarrow NaB + H_2O$$

$n_{HA} + n_{HB} = n_{NaOH}$

or $([HA]_i + [HB]_i) \times 0.1\ dm^3 = 0.220\ mol\ dm^{-3} \times 0.1\ dm^3$

$[HA]_i + [HB]_i = 0.220\ mol\ dm^{-3}$ (Eq. 4)

Solving Eq.3 and Eq.4 gives: $[HA]_i = 0.053\ mol\ dm^{-3}$ and $[HB]_i = 0.167\ mol\ dm^{-3}$

Concentration of HA = 0.053 mol dm^{-3}

Concentration of HB = 0.167 mol dm^{-3} .

5.2 Solution **Y** contains NaA (0.06 mol dm^{-3}**)** and NaB (0.04 mol dm^{-3}**)**. The solution is basic since $OH^–$ is produced from the reactions:

$NaA + H_2O \rightleftharpoons HA + OH^–$ $K_{b,A} = K_w / K_{HA} = 5.75 \times 10^{-8}$

$NaB + H_2O \rightleftharpoons HB + OH^–$ $K_{b,B} = K_w / K_{HB} = 7.46 \times 10^{-8}$

$H_2O \rightleftharpoons H^+ + OH^–$ $K_w = 1.00\ 10^{-14}$

Then

$[H^+] + [HA] + [HB] = [OH^–]$ (Eq. 5)

In the basic solution $[H^+]$ can be neglected, and thus:

$[HA] + [HB] = [OH^–]$ (Eq. 6)

From equilibrium expression:

$$\frac{[OH^-]\ [HA]}{[A^-]} = K_{b,A}$$

and $[A^–] = 0.06 – [HA]$

Thus, the equilibrium concentration of HA can be presented as:

$$[HA] = \frac{K_{b,A} \times 0.06}{K_{b,A} + [OH^-]}$$

Similarly, the equilibrium concentration of HB can be presented as:

$$[HB] = \frac{K_{b,B} \times 0.04}{K_{b,B} + [OH^-]}$$

Substitution of equilibrium concentrations of HA and HB into Eq. 6:

$$\frac{K_{b,A} \times 0.06}{K_{b,A} + [OH^-]} + \frac{K_{b,B} \times 0.04}{K_{b,B} + [OH^-]} = [OH^-]$$

When assumed that $K_{b,A}$ and $K_{b,B}$ are much smaller than $[OH^–]$ (*), then:

$[OH^–]^2 = 5.75\times10^{–8} \times 0.06 + 7.46\times10^{–8} \times 0.04$

$[OH^–] = 8.02\times10^{–5}$ (the assumption (*) is justified)

and pOH = 4.10 and pH = 9.90

5.3 Solution: HA in the dilute solution:

$[A^–] = \alpha \times [HA]_i$

$[HA] = (1 – \alpha) \times [HA]_i$

$[H^+] = 10^{–7}$

Substitution of the above equilibrium concentrations into K_{HA} expression:

$$\frac{10^{-7}\alpha\,[HA]_i}{(1-\alpha)\,[HA]_i} = K_{HA} \quad \text{or} \quad \frac{10^{-7}\alpha}{(1-\alpha)} = 1.74\times10^{-7}$$

The solving of the equation gives: $\alpha = 0.635$

Similarly, for HB:

$$\frac{10^{-7}\alpha}{(1-\alpha)} = 1.34\times10^{-7}$$

The solving of the equation gives: $\alpha = 0.573$

- The percentage of dissociation of HA = **65.5 %**

- The percentage of dissociation of HB = **57.3 %**

5.4 $M(OH)_2 \rightleftharpoons M^{2+} + 2OH^–$ $K_{sp} = 3.10\times10^{-12}$

$H_2O \rightleftharpoons H^+ + OH^–$ $K_w = 1.00\times10^{-14}$

$M^{2+} + A^– \rightleftharpoons [MA]^+$ $K_1 = 2.10\times10^3$

$[MA]^+ + A^– \rightleftharpoons [MA_2]$ $K_2 = 5.00\times10^2$

$M^{2+} + B^– \rightleftharpoons [MB]^+$ $K'_1 = 6.20 \times 10^3$

$[MB]^+ + B^– \rightleftharpoons [MB_2]$ $K'_2 = 3.30\times10^2$

Solubility of $M(OH)_2 = s = [M^{2+}] + [MA^+] + [MA_2] + [MB^+] + [MB_2]$

pH of **Z** = 10.0

$$[M^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{3.10\times10^{-12}}{(1\times10^{-4})^2} = 3.10\times10^{-4} \qquad \text{Eq. 1}$$

At pH = 10.0

$$[A^-]_{total} = \frac{K_{HA}\times 0.06}{(K_{HA}+1\times10^{-10})} = 0.06$$

$[MA^+] = K_1[M^{2+}][A^-] = 2.1\times10^3 \times 3.10\times10^{-4} \times [A^-] = 0.651 \times [A^-]$ Eq. 3

$[MA_2] = K_1K_2\,[M^{2+}][A^-]^2 = 325.5\times [A^-]^2$ Eq. 4

$[A^-]_{total} = [A^-] + [MA^+] + 2 \times [MA_2] = 0.06$ Eq. 5

Substitution of the equations Eq. 3 and Eq. 4 into Eq. 5:

$[A^-] + 0.651 \times [A^-] + 2 \times 325.5 \times [A^-]^2 = 0.06$

Solution of this equation gives: $[A^-] = 8.42\times 10^{-3}$

After substitution of this value into Eq. 3 and Eq. 4:

$[MA^+] = 0.651 \times [A^-] = 5.48 \times 10^{-3}$

$[MA_2] = 325.5 \times [A^-]^2 = 2.31 \times 10^{-2}$

Similarly,

$[B^-]_{total} = 0.04$

$[MB^+] = K_1'\,[M^{2+}][B^-] = 6.2\times10^{-3}\ x\ 3.10\times10^{-4}\ x\ [B^-] = 1.92 \times [B^-]$ Eq. 6

$[MB_2] = K_1'\,K_2'\,[M^{2+}][B^-]^2 = 634.3\times[B^-]^2$ Eq..7

$[B^-]_{total} = [B^-] + [MB^+] + 2 \times [MB_2] = 0.04$ Eq. 8

After substitution of Eq. 6 and Eq. 7 into Eq. 8:

$[B^-] + 1.92 \times [B^-] + 2 \times 634.3 \times [B^-]^2 = 0.04$

Solution of this equation: $[B^-] = 4.58 \times 10^{-3}$

Substitution of this value into Eq. 6 and Eq. 7:

$[MB^+] = 1.92 \times[B^-] = 8.79 \times 10^{-3}$

$[MB_2] = 634.3 \times[B^-]^2 = 1.33 \times 10^{-2}$

Thus, solubility of $M(OH)_2$ in **Z** is **s'**

s' = $3.10\times10^{-4} + 5.48\times10^{-3} + 2.31\times10^{-2} +$

$+\ 8.79\times10^{-3} + 1.33\times10^{-2} = 5.10\times10^{-2}$

Answer: Solubility of $M(OH)_2$ is $s = 5.10\times10^{-2}$ mol dm^{-3}.

PROBLEM 6

Chemical kinetics

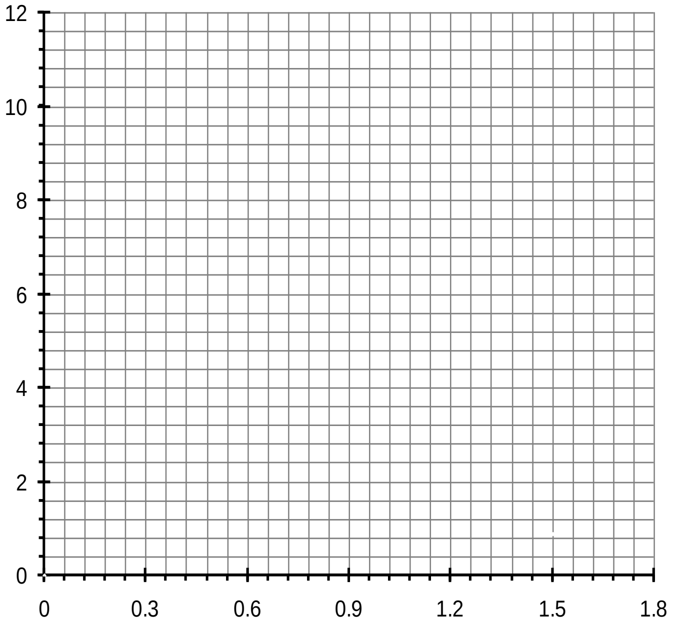
The transition-metal-catalyzed amination of aryl halides has become one of the most powerful methods to synthesize arylamines. The overall reaction for the nickel-catalyzed amination of aryl chloride in basic conditions is:

$$\text{ArCl} + \text{RNH}_2 \xrightarrow[\text{NaO}^t\text{Bu, solvent}]{\text{NiLL'}} \text{Ar}-\text{NHR} + \text{HCl}$$

in which NiLL' is the nickel complex catalyst. The reaction goes through several steps in which the catalyst, reactants, and solvent may be involved in elementary steps.

To determine the reaction order with respect to each reactant, the dependence of the initial rate of the reaction on the concentrations of each reagent was carried out with all other reagents present in large excess. Some kinetic data at 298 K are shown in the tables below. (Use the grids if you like.)

[ArCl] (mol dm^{-3})	0.1	0.2	0.4	0.6
Initial rate (mol dm^{-3} s^{-1})	1.88×10^{-5}	4.13×10^{-5}	9.42×10^{-5}	1.50×10^{-4}



[**NiLL**’] (mol dm^{-3})	6×10^{-3}	9×10^{-3}	1.2×10^{-2}	1.5×10^{-2}
Initial rate (mol dm^{-3} s^{-1})	4.12×10^{-5}	6.01×10^{-5}	7.80×10^{-5}	1.10×10^{-4}

[**L**’] (mol dm^{-3})	0.06	0.09	0.12	0.15
Initial rate (mol dm^{-3} s^{-1})	5.8×10^{-5}	4.3×10^{-5}	3.4×10^{-5}	2.8×10^{-5}

6.1 Determine the order with respect to the reagents assuming they are integers.

To study the mechanism for this reaction, ^{1}H, ^{31}P, ^{19}F, and ^{13}C NMR spectroscopy have been used to identify the major transition metal complexes in solution, and the initial rates were measured using reaction calorimetry. An intermediate, NiL(Ar)Cl, may be isolated at room temperature. The first two steps of the overall reaction involve the dissociation of a ligand from NiLL’ (step 1) at 50 ^{o}C, followed by the oxidation addition (step 2) of aryl chloride to the NiL at room temperature (rt):

$$\text{NiLL'} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{NiL} + \text{L'} \qquad (1)$$

$$\text{NiL} + \text{ArCl} \xrightarrow{k_2} \text{NiL(Ar)Cl} \qquad (2)$$

6.2 Using the steady state approximation, derive an expression for the rate equation for the formation of [NiL(Ar)Cl].

The next steps in the overall reaction involve the amine (RNH_2) and ^{t}BuONa. To determine the order with respect to RNH_2 and ^{t}BuONa, the dependence of the initial rates of the reaction on the concentrations of these two reagents was carried with the other reagents present in large excess. Some results are shown in the tables below.

[NaO^{t}Bu] (mol dm^{-3})	0.2	0.6	0.9	0.12
Initial rate (mol dm^{-3} s^{-1})	4.16×10^{-5}	4.12×10^{-5}	4.24×10^{-5}	4.20×10^{-5}

[RNH_2] (mol dm^{-3})	0.3	0.6	0.9	1.2
Initial rate (mol dm^{-3} s^{-1})	4.12×10^{-5}	4.26×10^{-5}	4.21×10^{-5}	4.23×10^{-5}

6.3 Determine the order with each of these reagents, assuming each is an integer. (Use the grids if you like)

During a catalytic cycle, a number of different structures may be involved which include the catalyst. One step in the cycle will be rate-determining. A proposed cycle for the nickel-catalyzed coupling of aryl halides with amines is as follows:

$$\mathrm{NiLL'} \xrightleftharpoons[k_{-1}]{k_1} \mathrm{NiL} + \mathrm{L'} \qquad (1)$$

$$\mathrm{NiL} + \mathrm{ArCl} \xrightarrow{k_2} \mathrm{Ni\,L(Ar)Cl} \qquad (2)$$

$$\mathrm{Ni\,L(Ar)Cl} + \mathrm{NH_2R} + \mathrm{NaO^tBu} \xrightarrow{k_3} \mathrm{NiL(Ar)NHR} + \mathrm{{}^tBuOH} + \mathrm{NaCl} \qquad (3)$$

$$\mathrm{NiL(Ar)NHR} \xrightarrow{k_4} \mathrm{ArNHR} + \mathrm{NiL} \qquad (4)$$

6.4 Use the steady-state approximation and material balance equation to derive the rate law for d[ArNHR] /dt for the above mechanism in terms of the initial concentration of the catalyst $[\mathrm{NiLL'}]_0$ and concentrations of [ArCl], $[\mathrm{NH_2R}]$, $[\mathrm{NaO^tBu}]$, and [L’].

6.5 Give the simplified form of the rate equation in 6.4 assuming that k_1 is very small**.**

SOLUTION

6.1 Order with respect to [ArCl] = 1

Order with respect to [NiLL’] = 1

Order with respect to [L’] = **– 1**

6.2 The rate law expression for the formation of NiLAr(Cl)

$$\text{rate} = \frac{k_1\, k_2\, [\text{NiLL}']\, [\text{ArCl}]}{k_{-1}[\text{L}'] + k_2[\text{ArCl}]} = \frac{k_1\,(k_2/k_{-1})[\text{NiLL}']\, [\text{ArCl}]}{[\text{L}'] + (k_2/k_{-1})[\text{ArCl}]}$$

6.3 Order with respect to [NaO^{t}Bu] = 0

- Order with respect to [RNH_2] = 0

6.4 Using the mechanism depicted by reaction (1) through (4), the rate equation:

$$\frac{d[\text{NiLL}']}{dt} = -\,k_1\,[\text{NiLL}'] + k_{-1}\,[\text{NiL}]\,[\text{L}']$$

$$\frac{d[\text{NiL}]}{dt} = k_1\,[\text{NiLL}'] - k_{-1}\,[\text{NiL}]\,[\text{L}'] - k_2[\text{NiL}]\,[\text{ArCl}] + k_4[\text{NiL(Ar)NHR}]$$

Apply the steady-state approximation to the concentrations for the intermediates:

$$\frac{d[\text{NiL}]}{dt} = 0$$

k_1[NiLL’] = k_{-1}[NiL][L’] + k_2[NiL][ArCl] – k_4[NiL(Ar)HNR] (Equation 1)

$$\frac{d[\text{NiL(Ar)Cl}]}{dt} = k_2[\text{NiL}]\,[\text{ArCl}] - k_3\,[\text{RNH}_2]\,[\text{NaOBu}]\,[\text{NiL(Ar)Cl}] = 0$$

$$[\text{NiL(Ar)Cl}] = \frac{k_2}{k_3}\,\frac{[\text{ArCl}][\text{NiL}]}{[\text{NH}_2\text{R}]\,[\text{NaOBu}]}$$ (Equation 2)

$$\frac{d[\text{NiL(Ar)NHR}]}{dt} = k_3\,[\text{NiL(Ar)Cl}]\,[\text{NH}_2\text{R}]\,[\text{NaOBu}] - k_4[\text{NiL(Ar)NHR}] = 0$$

$$[\text{NiL(Ar)NHR}] = \frac{k_3}{k_4}\,[\text{NiL(Ar)Cl}]\,[\text{NH}_2\text{R}]\,[\text{NaOBu}]$$ (Equation 3)

Substitute Equation 2 into Equation 3:

$$[\text{NiL(Ar)NHR}] = \frac{k_3}{k_4}\,[\text{NH}_2\text{R}]\,[\text{NaOBu}] \times \frac{k_2}{k_3}\,\frac{[\text{NiL}]\,[\text{ArCl}]}{[\text{NH}_2\text{R}]\,[\text{NaOBu}]} = \frac{k_2}{k_4}\,[\text{ArCl}]\,[\text{NiL}]$$ (Eq. 4)

Substitute Equation 4 into Equation 1:

k_1[NiLL’] = k_{-1} [NiL][L’] + k_2 [NiL][ArCl] - k_4 [NiL(Ar)NHR]

k_1[NiLL’] = k_{-1} [NiL][L’] + k_2 [NiL][ArCl] – k_4 × k_2/k_4 [ArCl][NiL] = k_{-1} NiL[NiL] [L’] (Eq.5)

The material balance equation with respect to the catalyst is$[NiLL']_0$ = [NiLL'] + [NiL] + [NiLAr(Cl)] + [NiLAr(Cl)NHR]

$$[NiLL']_0 = \frac{k_{-1}}{k_1}[NiL][L'] + [NiL] + \frac{k_2}{k_3}\frac{[NiL][ArCl]}{[NH_2R][NaOBu]} + \frac{k_2}{k_4}[NiL][ArCl]$$

$$[NiLL']_0 = [NiL]\left[\frac{k_{-1}}{k_1}[L'] + 1 + \frac{k_2}{k_3}\frac{[ArCl]}{[NH_2R][NaOBu]} + \frac{k_2}{k_4}[ArCl]\right]$$

$$[NiL] = [NiLL']_0 \times \frac{k_1\,k_3\,k_4\,[NH_2R]\,[NaOBu]}{k_{-1}k_3k_4\,[L'][NH_2R][NaOBu] + k_1k_3k_4\,[NH_2R][NaOBu] + k_1k_2k_4\,[ArCl] + k_1k_2k_3\,[ArCl][NH_2R][NaOBu]}$$

(Equation 6)

Substituting Equation 6 into the differential rate for [ArCl]:

$$-\frac{d[ArCl]}{dt} = k_2[NiL]\,[ArCl]$$

results in the following predicted rate law expression for the reaction mechanism:

$d[ArNHR] / dt = – d[ArCl] / dt =$

$= k_2\,[ArCl]\,[NiL] = k_1k_2k_3k_4\,[ArCl]\,[NiLL']_0\,[NaO^tBu]\,[NH_2R]\,/$

$/\,\{k_{-1}\,k_3\,k_4\,[NH_2R]\,[NaOBu]\,[L'] + k_1k_3k_4\,[NaOBu]\,[NH_2R] + k_1k_2k_4\,[ArCl] +$

$+\,k_1k_2k_3\,[ArCl]\,[NH_2R]\,[NaOBu]\}$

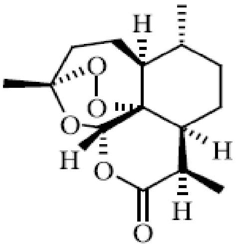
6.5 $d[ArNHR]/dt = – d[ArCl]/dt = k_2[ArCl][NiL] = k_1k_2[ArCl][NiLL']_0\,/\,k_{-1}[L']$

(i.e. consistent with all the orders of reaction as found in the beginning)

PROBLEM 7

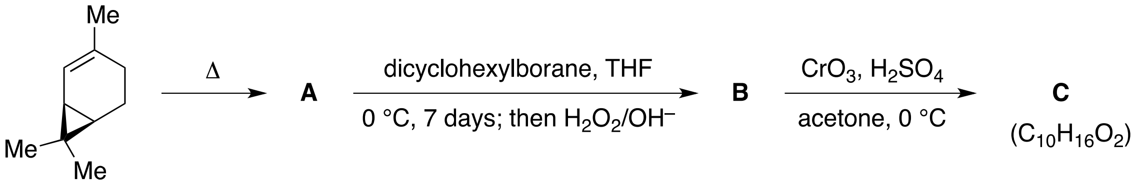
Synthesis of artemisinin

(+)-Artemisinin, isolated from *Artemisia annua* L. (Qinghao, *Compositae*) is a potent antimalarial effective against resistant strains of *Plasmodium*. A simple route for the synthesis of Artemisinin is outlined below.



(+)-Artemisinin

First, pyrolysis of (+)-2-Carene broke the cyclopropane ring forming, among other products, (1*R*)-(+)-*trans*-isolimonene **A** ($C_{10}H_{16}$), which then was subjected to regioselective hydroboration using dicyclohexylborane to give the required alcohol **B** in 82% yield as a mixture of diastereoisomers. In the next step, **B** was converted to the corresponding γ,δ-unsaturated acid **C** in 80% yield by Jones' oxidation.



2-Carene

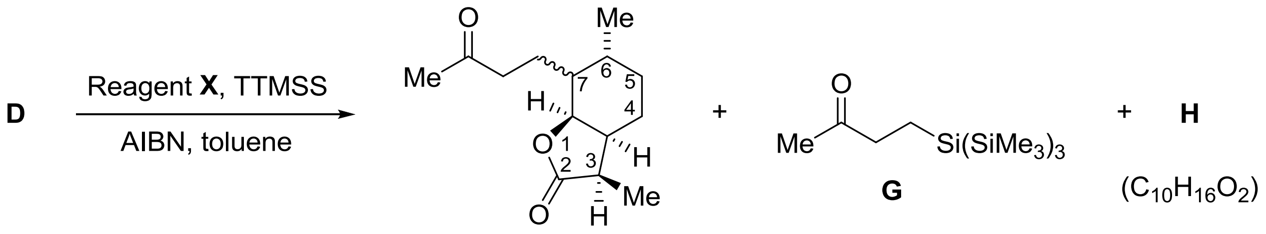
7.1 Draw the structures (with stereochemistry) of the compounds **A - C**.

The acid **C** was subjected to iodolactonization using KI, I_2 in aqueous. $NaHCO_3$ solution to afford diastereomeric iodolactones **D** and **E** (which differ in stereochemistry only at C_3) in 70% yield.

$$\mathbf{C} \xrightarrow[\text{48 h, dark}]{I_2\text{, KI, NaHCO}_3\text{(aq)}} \mathbf{D} + \mathbf{E}$$

7.2 Draw the structures (with stereochemistry) of the compounds **D** and **E**.

The iodolactone **D** was subjected to an intermolecular radical reaction with ketone **X** using tris(trimethylsilyl)silane (TTMSS) and AIBN (azobisisobutyronitrile) in a catalytic amount, refluxing in toluene to yield the corresponding alkylated lactone **F** in 72% yield as a mixture of diastereoisomers which differ only in stereochemistry at C_7 along with compound **G** (~10%) and the reduced product **H**, $C_{10}H_{16}O_2$ (<5%).



F

7.3 Draw the structures (with stereochemistry) of compound **H** and the reagent **X**.

The keto group of **F** reacted with ethanedithiol and $BF_3•Et_2O$ in dichloromethane (DCM) at 0 °C to afford two diastereomers: thioketal lactones **I** and **J** in nearly quantitative yield (98%). The thioketalization facilitated the separation of the major isomer **J** in which the thioketal group is on the opposite face of the ring to the adjacent methyl group.

$$\mathbf{F} \xrightarrow[BF_3 \cdot Et_2O,\ DCM,\ 0\ ^\circ C]{HSCH_2CH_2SH} \mathbf{I} + \mathbf{J}$$

7.4 Draw the structures (with stereochemistry) of the compounds **I** and **J**.

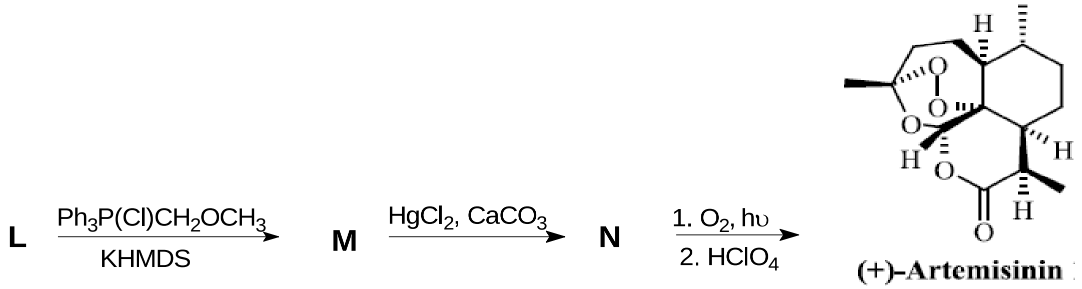
The isomer **J** was further subjected to alkaline hydrolysis followed by esterification with diazomethane providing hydroxy methyl ester **K** in 50% yield. The hydroxy methyl ester **K** was transformed into the keto ester **L** using **PCC** (**P**yridium **C**hloro**C**hromate) as the oxidizing agent in dichloromethane (DCM).

A two-dimensional NMR study of the compound **L** revealed that the two protons adjacent to the newly-formed carbonyl group are *cis* to each other and confirmed the structure of **L**.

$$\mathbf{J} \xrightarrow[3)\ CH_2N_2/Et_2O]{1)\ 10\%\ NaOH \quad 2)\ 1\%\ HCl} \mathbf{K} \xrightarrow{PCC,\ 0\ ^\circ C} \mathbf{L}$$

7.5 Draw the structures (with stereochemistry) of the compounds **K** and **L**.

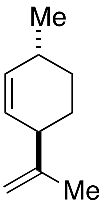
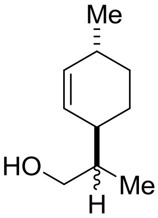
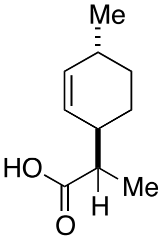
The ketone **L** was subjected to a Wittig reaction with methoxymethyl triphenylphosphonium chloride and KHMDS (**P**otassium **H**exa**M**ethyl**D**i**S**ilazid - a strong, nonnucleophilic base) to furnish the required methyl vinyl ether **M** in 45% yield. Deprotection of thioketal using $HgCl_2$, $CaCO_3$ resulted in the key intermediate **N** (80%). Finally, the compound **N** was transformed into the target molecule Artemisinin by photo-oxidation followed followed by acid hydrolysis with 70 % $HClO_4$.



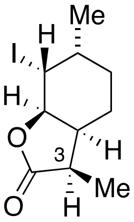
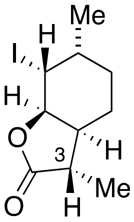
7.6 Draw the structures (with stereochemistry) of the compounds M and N.

SOLUTION

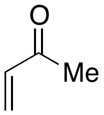
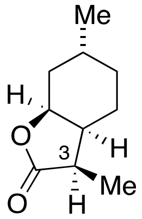
7.1

A	**B**	**C**
		

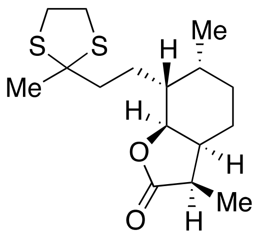
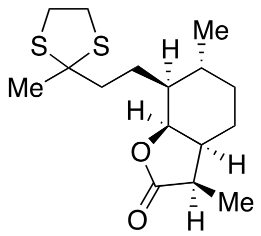
7.2 The acid **C** was converted to diastereomeric iodolactones **D** and **E** (epimeric at the chiral center C_3). Look at the number-indicated in the structure **F** in the next step.

D	**E**
	

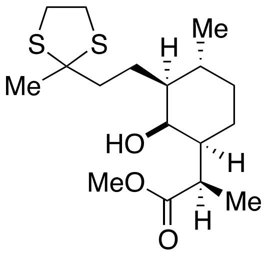
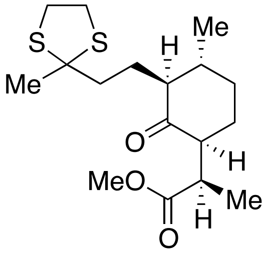
7.3 Because alkylated lactone **F** is known, we can deduce the reagent **X** as methyl vinyl ketone. **H** is the reduced product of **D**.

X	**H**
 methyl vinyl ketone	

7.4 The keto group of lactone **F** reacted with ethanedithiol and $BF_3{\cdot}Et_2O$ in dichloromethane to afford thioketal lactones, **I** and the major isomer **J**.

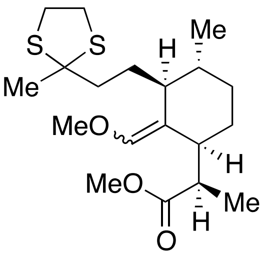
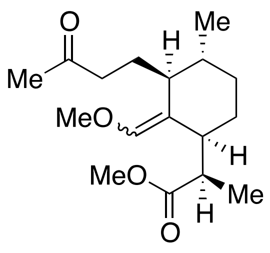
	J
	

7.5 Hydrolysis followed by esterification of **J** provided hydroxy ester **K**. Oxidation of the hydroxy group in **K** by PCC resulted in the keto ester **L** in which two protons adjacent to the carbonyl group are cis-oriented.

K	**L**
	

7.6 The Wittig reaction of the ketone **L** resulted in the formation of methyl vinyl ether **M**.

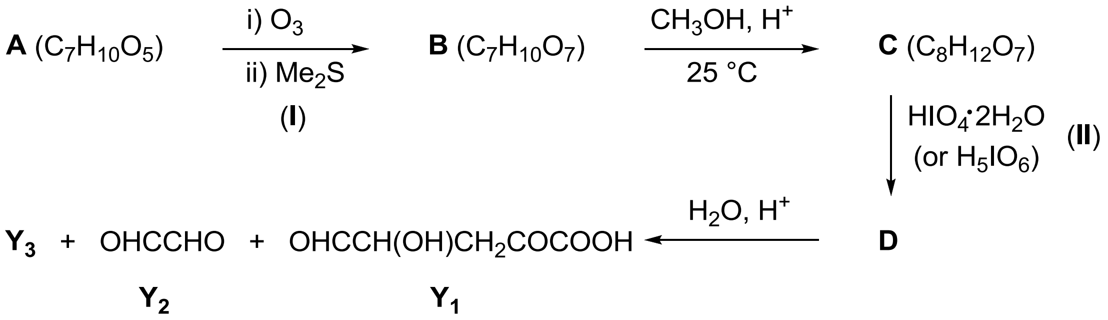
Deprotection of the thioketal group forms the intermediate **N**.

M	**N**
	

PROBLEM 8

Star anise

Illicium verum, commonly called *Star anise*, is a small native evergreen tree grown in northeast Vietnam. *Star anise* fruit is used in traditional Vietnamese medicine. It is also a major ingredient in the making the flavor of *'phở'*, a Vietnamese favorite soup. Acid **A** is isolated from the *star anise* fruit. The constitutional formula of **A** has been deduced from the following sequence of reactions:

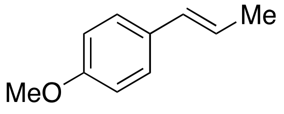


(**I**): this overall process results in alkene cleavage at the C=C bond, with each carbon of this becoming doubly bonded to an oxygen atom.

(**II**): this oxidative cleavage process of 1,2-diols breaks C(OH)–C(OH) bond and produces corresponding carbonyl compounds.

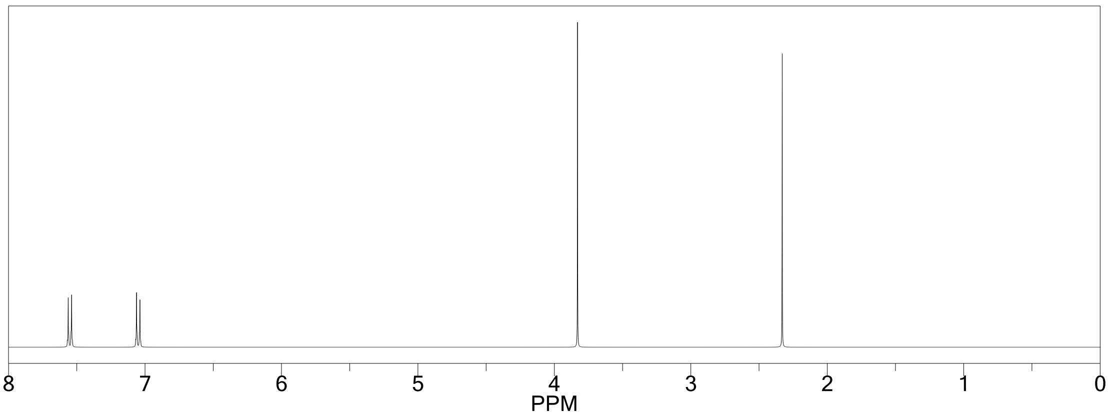
8.1 Draw the structures for the compounds $\mathbf{Y_1}$ and $\mathbf{Y_2}$ and hence deduce the structure of $\mathbf{Y_3}$ and **A**, **B**, **C, D**, given that in **A** there is only one ethylenic hydrogen atom.

Anethole, a main component of star anise oil, is an inexpensive chemical precursor for the production of many pharmaceutical drugs.



Anethole

Treating anethole with sodium nitrite in acetic acid gives a crystalline solid **E** ($C_{10}H_{10}N_2O_3$). The IR spectrum of **E** shows there is no non-aromatic C=C double bond. The ^{1}H NMR spectrum of **E** is given below.



8.2 **What differences** in the structure between **E** and anethole can be obtained from the ^{1}H NMR data? Pick one of the following statements.

i) **E** contains a *cis*-C=C ethylenic bond while that of anethole is *trans*.

ii) **E** cannot contain a non-aromatic C=C bond.

iii) **E** is the adduct of anethole and N_2O_2.

iv) **E** is the adduct of anethole and N_2O_3.

v) **E** does not contain two *trans* ethylenic protons as anethole.

On heating at 150 °C for several hours, **E** is partially isomerized into **F**. Under the same conditions, **F** gives the identical equilibrium mixture to that obtained from **E**. On heating with phosphorus trichloride, both **E** and **F** lose one oxygen atom giving compound **G**. Compounds **E** and **F** have the same functional groups.

$$\mathbf{G} \xleftarrow[-\ POCl_3]{PCl_3} \mathbf{E} \xrightleftharpoons{150\ ^oC} \mathbf{F} \xrightarrow[-\ POCl_3]{PCl_3} \mathbf{G}$$

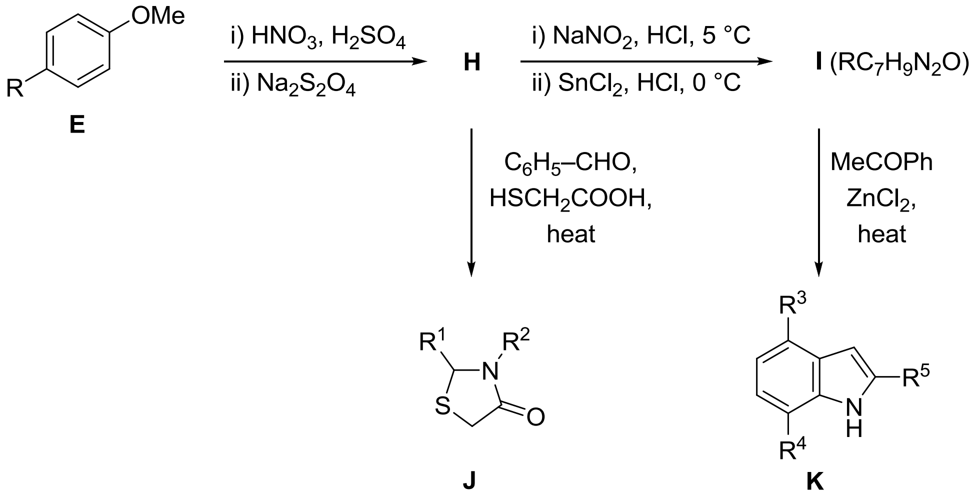
The chemical shifts of methyl protons in **E**, **F** and **G** are given below.

	E	**F**	**G**
CH_3-O	3.8 ppm	3.8 ppm	3.8 ppm
CH_3-C	2.3 ppm	2.6 ppm	2.6 ppm

8.3 Suggest structures for **E**, **F** and **G**, assuming that they do NOT contain three-membered rings.

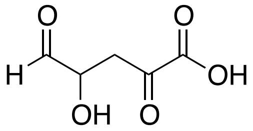
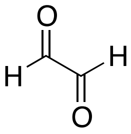
A simplified structure for compound **E** is shown below; the R group does not change throughout the rest of this question. Compound **E** is nitrated and subsequently reduced with sodium dithionite to **H**. Treatment of **H** with sodium nitrite and hydrochloric acid at 0–5 ^oC and subsequently reduced with stannous chloride to provide **I** ($R–C_7H_9N_2O$). One-pot reaction (three component reaction) of **H**, benzaldehyde and thioglycolic acid ($HSCH_2CO_2H$) leads to the formation of **J**. Reaction of **I** and methyl phenyl ketone in the presence of $ZnCl_2$ affords **K**.

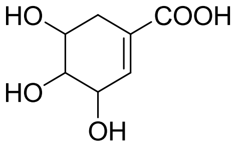
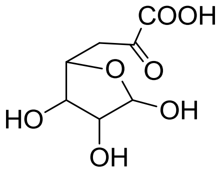
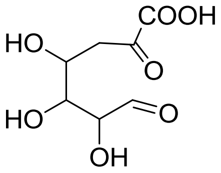
8.4 Give the structures for **H**, **I**, **J** and **K** in the following scheme:

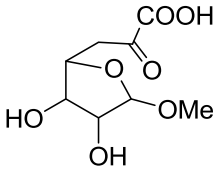
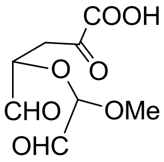


SOLUTION

8.1

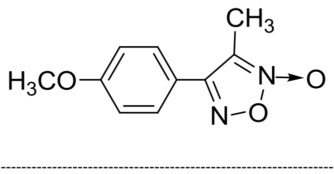
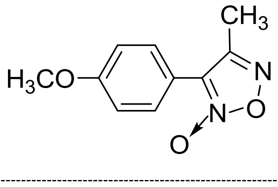
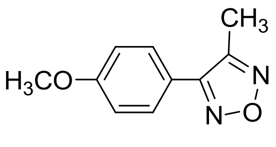
Y_1	Y_2	Y_3
		CH_3OH

A	B
	 or 

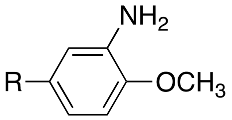
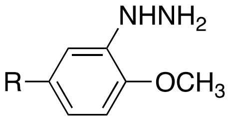
C	D
	

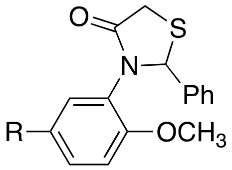
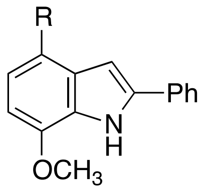
8.2 From ^{1}H NMR data *v*) [only]: **E** does not contain two *trans* ethylenic protons as anethole.

8.3

E	F	G
		

8.4

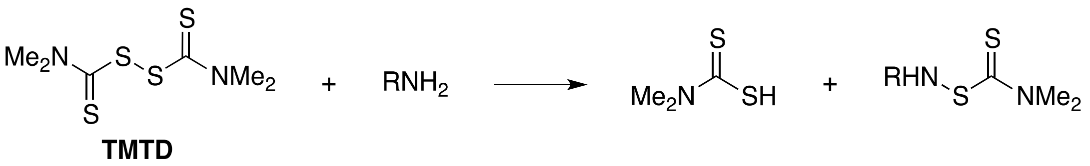
H	**I**
	

J	**K**
	

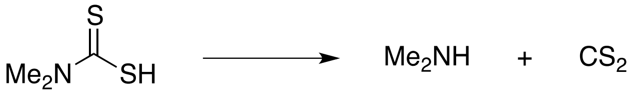
PROBLEM 9

Heterocycle preparation

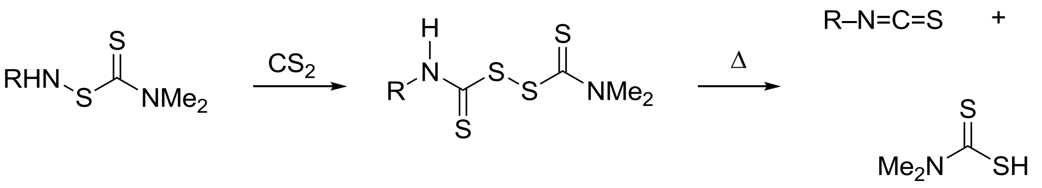
Tetramethylthiurame disulfide (**TMTD**) is emerging as a useful reagent to prepare many sulfur-nitrogen functional groups and heterocycles in organic chemistry. The reactions of **TMTD** with primary amines, as well some corresponding post-transformations of the resulting product(s) are presented in the following schemes:



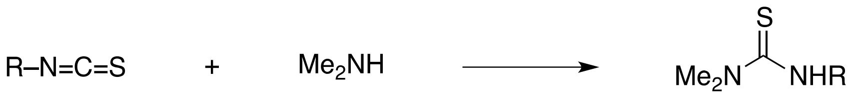
(1)



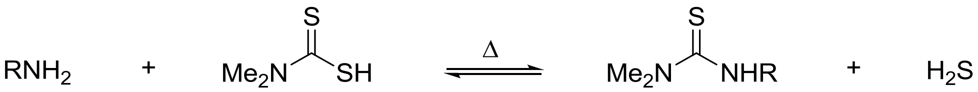
(2)



(3)



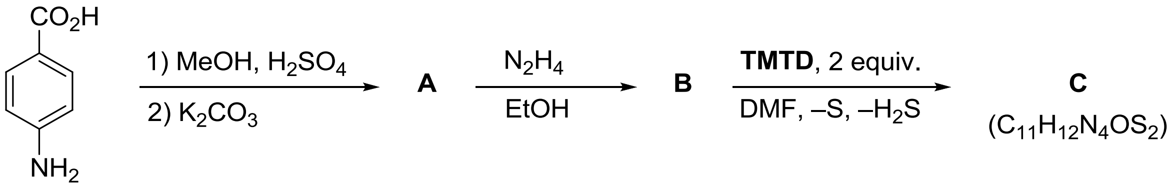
(4)



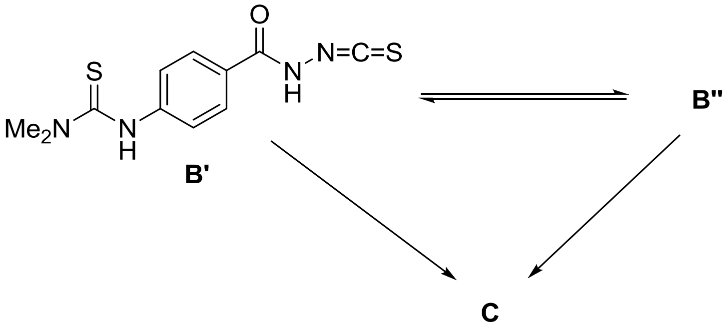
(5)

Similar transformations of benzohydrazides (containing nucleophilic NH_2 group) and **TMTD** have been observed.

In the synthetic scheme below, the thiocarbamoylation reaction of an aroyl hydrazine with **TMTD** produces compound **C** containing a heterocyclic moiety from *p*-aminobenzoic acid.



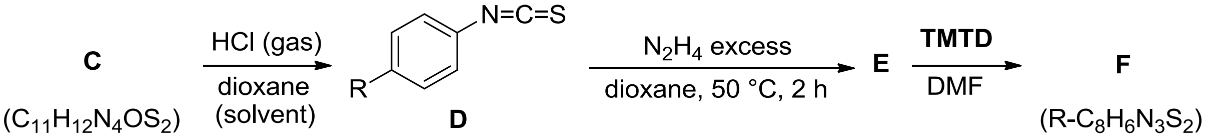
During the formation of **C** from **B**, an intermediate **B'** was observed. This intermediate tautomerizes to **B''**. **C** can be formed from **B'** or **B''**.



9.1 Give the structures of **A**, **B**, and **C**.

9.2 Suggest a structure for the tautomer **B''** and give a curly-arrow mechanism for the formation of **C**.

Compound **C** was then converted to **F** by the following pathway:



[The group R remains exactly the same throughout the rest of the question.]

9.3 Draw the structures of **E**, and **F**. (You do not need to draw the structure for the R group from this point.)

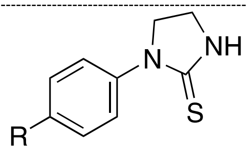
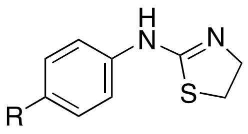
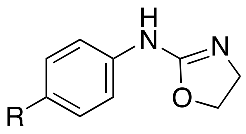
E was only obtained when **D** was slowly added to the solution of excess N_2H_4 in dioxane. If N_2H_4 was added to the solution of **D** in dioxane instead, a major side product **D'** ($R_2C_{14}H_{12}N_4S_2$) was formed.

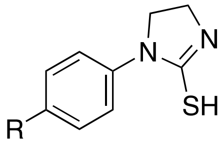
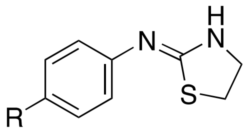
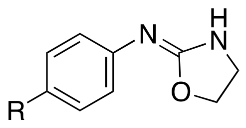
9.4 Give the structure of **D'**.

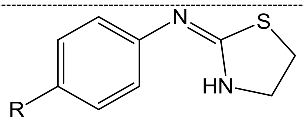
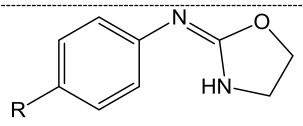
Slightly heating of **D** with ethanolamine ($HOCH_2CH_2NH_2$) in dioxane for 2 hours yielded **G** ($R–C_9H_{11}N_2OS$).

9.5 Draw the structural formula of **G**.

9.6 Heating **G** in the presence of *p*-toluenesulfonic acid as the catalyst could form a number of different five-membered heterocyclic products:

H_1	**H_2**	**H_3**
		

H_4	**H_5**	**H_6**
		

H_7	**H_8**
	

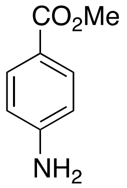
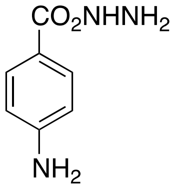
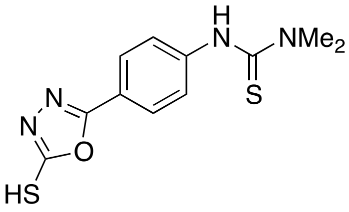
i) Draw 2 structures that have different molecular formulae.

ii) Draw 2 structures that are constitutional isomers.

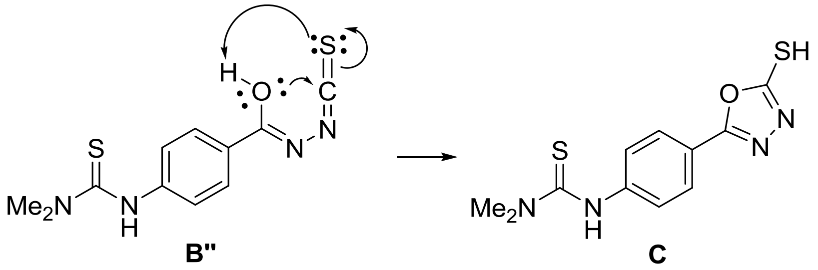
iii) Draw 2 structures that are stereoisomers.

SOLUTION

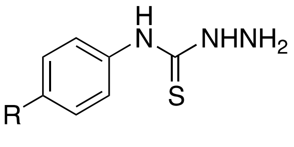
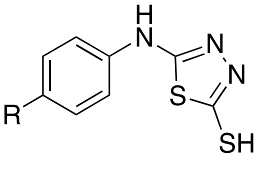
9.1

A	B	C
		 **C**: $C_{11}H_{12}N_4OS_2$

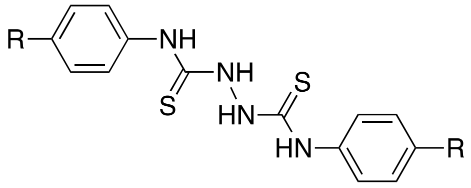
9.2



9.3

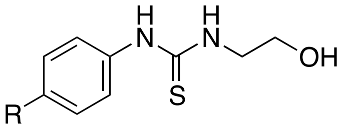
E	F
	

9.4



D': $R_2C_{14}H_{12}N_4S_2$

9.5

G


9.6 **i)** For example: **H1** and **H3**

ii) For example: **H1** and **H5**

iii) For example: **H5** and **H7**

PRACTICAL PROBLEMS

PROBLEM 1P (Practical)

The oxidation of iodide by iron(III) ions – a kinetic study based on the thiosulfate clock reaction

Clock reactions are commonly used as demonstrations by chemical educators owing to their visual appeal. Oxidation of iodide by iron(III) ions in a weakly acidic medium is a reaction that can be transformed into a clock reaction. In the presence of thiosulfate and starch, chemical changes in this clock reaction can be presented by the following equations:

$Fe^{3+}(aq) + S_2O_3^{2-}(aq) \leftrightarrows [Fe(S_2O_3)]^+(aq)$ (1) fast

$2\ Fe^{3+}(aq) + 3\ I^-(aq) \rightarrow 2\ Fe^{2+}(aq) + I_3^-(aq)$ (2) slow

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

$2\ I_3^-(aq) + \text{starch} \rightarrow \text{starch} - I_5^- + I^-(aq)$ (4) fast

Reaction (1) is a fast reversible equilibrium which occurs in the reaction mixture giving a reservoir of iron(III) and thiosulfate ions. After being produced in reaction (2), iodine in the form of triiodide ion (I_3^-), is immediately consumed by thiosulfate in reaction (3). Therefore, no iodine accumulates in the presence of thiosulfate. When thiosulfate is totally depleted, the triiodide ion accumulates and it may be detected by use of starch indicator according to reaction (4).

The kinetics of reaction (2) is easily investigated using the initial rates method. One has to measure the time elapsed between mixing the two solutions and the sudden color change.

For the oxidation of iodide by iron(III) ions (reaction 2), the reaction rate can be defined as:

$$v_0 = -\frac{d[Fe^{3+}]}{dt} \qquad (5)$$

The initial reaction rate can then be approximated by:

$$v_0 = -\frac{\Delta[Fe^{3+}]}{\Delta t} \qquad (6)$$

with $\Delta[Fe^{3+}]$ being the change in the concentration of iron(III) ions in the initial period of the reaction. If Δt is the time measured, then $\Delta[Fe^{3+}]$ is the change in iron(III) ion concentration from the moment of mixing to the moment of complete thiosulfate consumption (assume that the reaction rate does not depend on thiosulfate concentration). Therefore, from the reactions' stoichiometry it follows:

$$-\Delta[Fe^{3+}] = [S_2O_3^{2-}]_0 \qquad (7)$$

and consequently:

$$v_0 = -\frac{[S_2O_3^{2-}]_0}{\Delta t} \qquad (8)$$

The initial thiosulfate concentration is constant and significantly lower than that of iron(III) and iodide ions. The above expression enables us to determine the initial reaction rate by measuring the time required for the sudden color change to take place, Δt.

The rate of reaction is first order with respect to $[Fe^{3+}]$, and you will determine the order with respect to $[I^-]$. This means the initial reaction rate of reaction can be expressed as:

$$v_0 = k\,[Fe^{3+}]_0\,[I^-]_0^y \qquad (9)$$

where k is the rate constant and y is the order with respect to $[I^-]$.

We assume that the reaction rate does not depend on the thiosulfate concentration, and that the reaction between Fe^{3+} and $S_2O_3^{2-}$ is negligible. You have to observe carefully the color changes during the clock reaction and to determine the reaction order with respect to $[I^-]$, and the rate constant of clock reaction.

Experimental part

Equipment

- 1 hotplate stirrer
- 1 magnetic stirring bar
- 1 plastic wash bottle filled with distilled water
- 1 glass beaker for inorganic waste liquid (ca. 1 dm^3)
- 1 conical flask for organic waste liquid, 250 cm^3
- 1 graduated pipette, 1 cm^3
- 1 graduated pipette, 5 cm^3

- 1 graduated pipette, 5 cm^3, labeled ‘MeOH’ (for Problem 2)
- 1 graduated pipette, 10 cm^3
- 1 volumetric pipette, 10 cm^3
- 1 graduated pipette, 25 cm^3
- 2 Pasteur pipettes and bulb
- 2 glass spatula spoon
- 1 cleaning brush
- 1 large glass stirring rod
- 1 glass funnel
- 1 bag of paper towels
- 1 digital thermometer
- 1 three-way pipette bulb with a little rubber adapter for bigger pipettes
- 1 ceramic Büchner funnel with fitted rubber bung
- 1 Büchner flask
- 1 digital stop watch
- 6 glass beakers (100-cm^3)

Chemicals

- KI, aqueous solution, c = 0.100 mol dm^{-3}, 120 cm^3
- solution **A1** in a glass bottle containing KI, $Na_2S_2O_3$, and starch indicator in distilled water, 40 cm^3
- solution **B1** in a glass bottle containing $Fe(NO_3)_3$, HNO_3 in distilled water, 40 cm^3
- solution **A2-1** in a glass bottle containing $Na_2S_2O_3$ (c = 5.883×10^{-4} mol dm^{-3}), KNO_3 and starch indicator in distilled water, 360 cm^3
- solution **B2** in a glass bottle containing $Fe(NO_3)_3$ (c = 0.1020 mol dm^{-3}) and HNO_3 in distilled water, 100 cm^3
- distilled water, 1 dm^3

Procedure

Solution **A** (containing $Na_2S_2O_3$, KI, KNO_3 and starch) is first placed in the beaker and is stirred using the magnetic bar. The rate of stirring is set at level 8 as indicated in

Figure 1. Solution **B** (containing $Fe(NO_3)_3$ and HNO_3) is quickly added into solution **A** and the stopwatch is simultaneously started. The time is recorded at the moment the solution suddenly turns dark blue. The temperature of the solution is recorded using the digital thermometer.

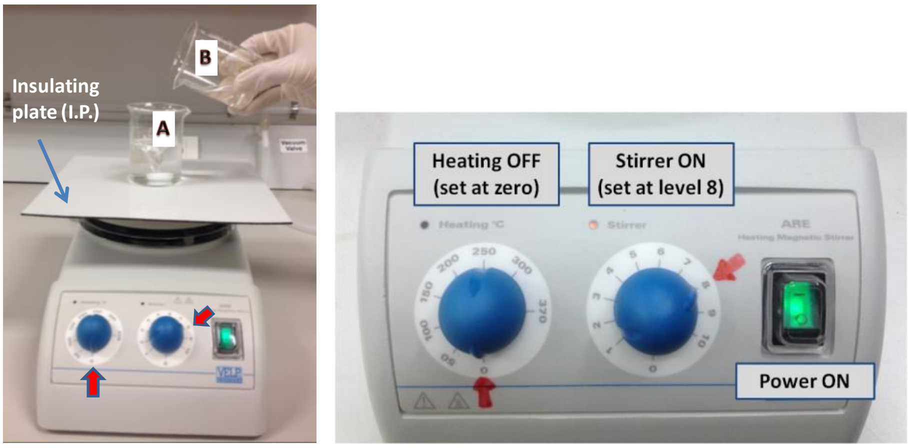


Figure 1. The apparatus employed for kinetic study of the clock reaction.

1. Practice run to observe the color changes

There is no need to measure accurately the volumes used in this part – just use the marks on the beaker as a guide.

- Pour ca. 20 cm^3 of solution **A1** (containing KI, $Na_2S_2O_3$, and starch in water) to a 100 cm^3 graduated beaker containing a magnetic stirrer bar. Place the beaker on top of the insulating plate on the magnetic stirrer.
- Pour ca. 20 cm^3 of solution **B1** (containing $Fe(NO_3)_3$ and HNO_3 in water) in another 100 cm^3 graduated beaker.
- Quickly pour the solution **B1** into solution **A1** and start stopwatch simultaneously. Stop stopwatch when the color of the mixture changes. There is no need to record this time. Answer the following questions.

1.1 Write down the molecular formula of the limiting reactant for the given clock reaction.

1.2 What are the ions or compounds responsible for the colors observed in this experiment? Tick the appropriate box.

Color	Compound
Purple	☐ Fe^{3+} ☐ $[Fe(S_2O_3)]^+$ ☐ Fe^{2+} ☐ starch-I_5^- ☐ I_3^-
Dark blue	☐ Fe^{3+} ☐ $[Fe(S_2O_3)]^+$ ☐ Fe^{2+} ☐ starch-I_5^- ☐ I_3^-

2. Determination of the order with respect to $[I^-]$ (*y*), and the rate constant (*k*)

In this section, Δ*t* is determined for different initial concentrations of KI according to the table below. The experiment is repeated as necessary for each concentration of KI.

Hint: Use 25 cm^3 graduated pipette for solution **A2-1**, 10 cm^3 graduated pipette for KI, 5 cm^3 graduated pipette for solution **B2**, and one of the burettes for water (you will need to refill the burette from the wash bottle for each measurement).

- Prepare 55 cm^3 of solution **A2** in a 100 cm^3 beaker containing a magnetic stirrer bar and place it on top of the insulating plate on the stirrer. Solution **A2** contains solution **A2-1**, KI, and distilled water (see the table below for the volume of each component).
- Add 5 cm^3 of solution **B2** in another 100 cm^3 beaker.

Quickly pour prepared solution **B2** into solution **A2**. Determine the time (Δ*t*) necessary for the color change by a stopwatch. The temperature of the solution is recorded.

1.3 Record the time (Δ*t*) for each run in the table below. (You DO NOT need to fill all three columns for the runs.) For each concentration of KI, record your accepted reaction time ($\Delta t_{\text{accepted}}$) and temperature. You will be only graded on your values of $\Delta t_{\text{accepted}}$ and T_{accepted}.

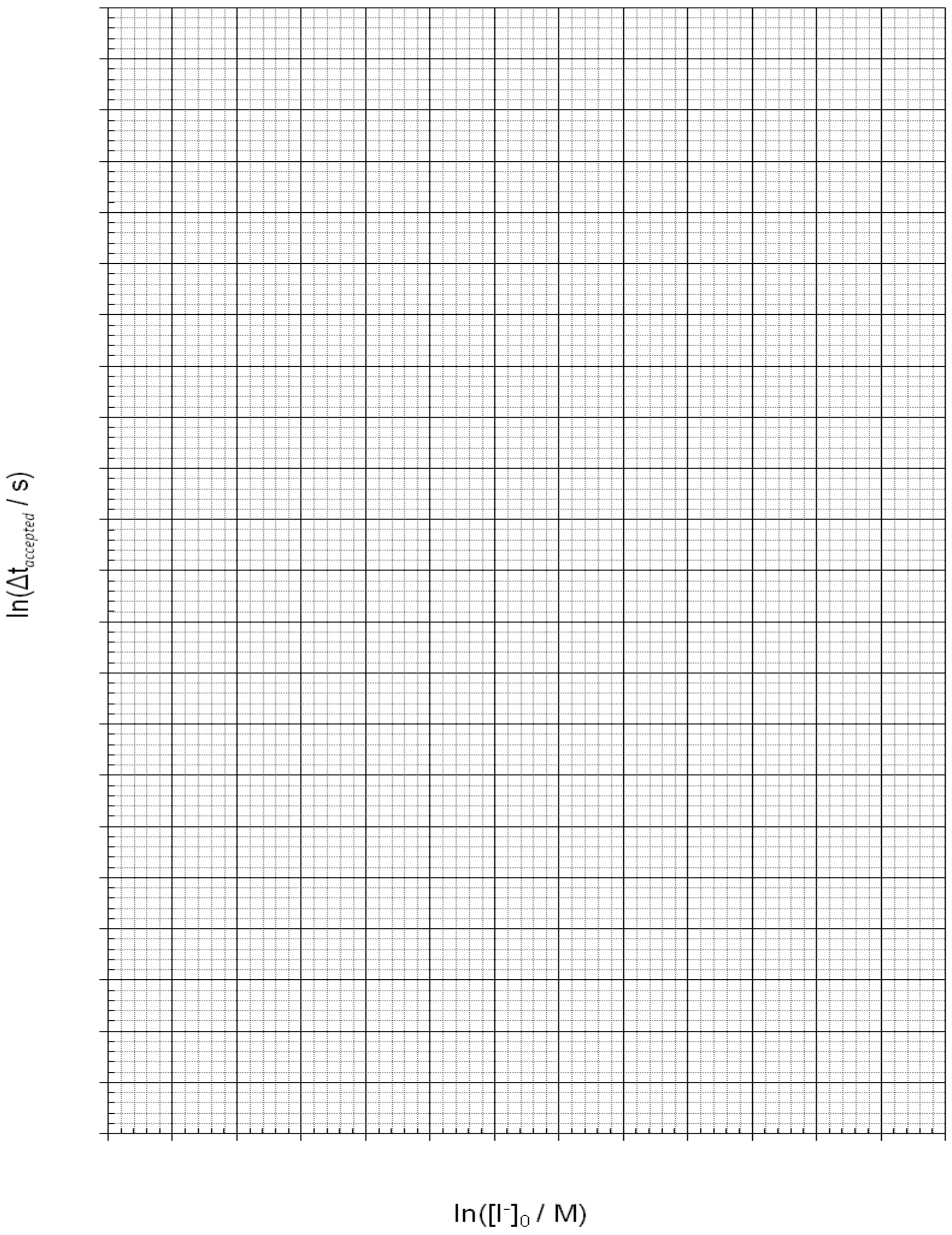
No	**55** cm^3 **of solution A2**									$\Delta t_{accepted}$ (s)	$T_{accepted}$ (ºC)
	A2-1 (cm^3)	H_2O (cm^3)	0.100 mol dm^{-3} KI(cm^3)	Run 1		Run 2		Run 3			
				Δt (s)	T (ºC)	Δt (s)	T (ºC)	Δt (s)	T (ºC)		
1	20.4	31.6	3.0								
2	20.4	30.1	4.5								
3	20.4	28.6	6.0								
4	20.4	27.4	7.2								
5	20.4	25.6	9.0								

When you are satisfied you have all the necessary data for Problem 1. Before continuing with the analysis, it is strongly recommended that you start the practical procedure for Problem 2 since there is a reaction time of one hour in that Problem.

1.4 Fill in the table below and plot the results in the graph.

Hint: Make sure your data is graphed as large as possible in the provided space.

No.	1	2	3	4	5
$\ln([I^-]_0 / M)$	– 5.30	– 4.89	– 4.61	– 4.42	– 4.20
$\Delta t_{accepted}$ (s)					
$\ln(\Delta t_{accepted} / s)$					



1.5 Draw the best fit line on your graph and use it to determine the order with respect to [I$^-$] (y).

y = ………………………………

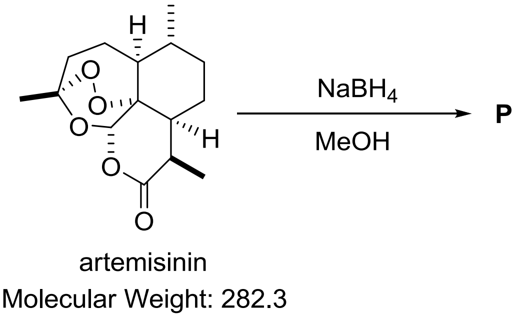
1.6 Complete the table below and calculate *k* for each of the concentrations of iodide. Report your accepted value for the rate constant, giving the appropriate unit. Remember that the order with respect to [Fe^{3+}] is equal to one.

No	$\Delta t_{\text{accepted}}$ (s)	$[Fe^{3+}]_0 \times 10^{-3}$ (mol dm^{-3})	$[I^-]_0 \times 10^{-3}$ (mol dm^{-3})	$[S_2O_3^{2-}]_0 \times 10^{-3}$ (mol dm^{-3})	k
1			5.0		
2			7.5		
3			10.0		
4			12.0		
5			15.0		
k_{accepted} = …………………					

PROBLEM 2P (Practical)

Synthesis of a derivative of artemisinin

Artemisinin (also known as Quinghaosu) is an antimalarial drug isolated from the yellow flower herb *Artemisia annua* L., in Vietnam. This drug is highly efficacious against the chloroquine-resistant *Plasmodium falciparum*. However, artemisinin has a poor solubility in both oil and water so that one needs to prepare its new derivatives to improve the applicability of this drug. The reduction of artemisinin is an attractive method to synthesize new derivatives of artemisinin as shown in Scheme 1.



Scheme 1

In this practical exam you are going to reduce artemisinin to product **P** and check its purity using Thin-Layer Chromatography (TLC).

Experimental part

Glass and equipment

- 1 hotplate stirrer, 1 magnetic stirring bar, 1 plastic wash bottle filled with distilled water, 1 glass beaker for inorganic waste liquid (ca. 1 dm^3), 1 conical flask for organic waste liquid, 250 cm^3, 1 graduated pipette (1 cm^3), 1 graduated pipette (5 cm^3), 1 graduated pipette (5 cm^3, labeled 'MeOH'), 1 graduated pipette (10 cm^3), 1 volumetric pipette (10 cm^3), 1 graduated pipette (25 cm^3), 2 Pasteur pipettes and bulbs, 2 glass spatula spoons, 1 cleaning brush, 1 large glass stirring rod, 1 glass funnel, 1 bag of paper towels, 1 digital thermometer, 1 three-way pipette bulb with a little rubber adapter for bigger pipettes, 1 ceramic Büchner funnel with fitted rubber bung, 1 Büchner flask;
- 1 graduated measuring cylinder, 5 cm^3
- 2 graduated measuring cylinders, 50 cm^3
- two-neck round bottom flask with plastic stopper (in ice bath), 100 cm^3

- conical (Erlenmeyer) flask, 100 cm^3
- hair dryer
- Petri dish with cover containing 1 TLC plate, 2 capillaries in paper holder
- Plastic pot for ice bath
- stand & clamp
- TLC developing chamber with glass lid
- 2 tweezers
- metal spatula
- 2 very small test tubes for TLC in container,
- zipper store bag (containing cotton wool, round filter paper, watch glass
- Petri dish with cover

Chemicals

- Artemisinin, 1.000 g,
- Sodium borohydride, $NaBH_4$, 0.53 g
- CH_3OH, 20 cm^3
- *n*-Hexane, 30 cm^3
- cerium staining reagent for TLC, 3-5 cm^3
- Ceri reagent
- CH_3COOH, 1 cm^3, in vial
- Ethyl acetate, 5 cm^3
- Bag of NaCl for salt (ice) bath
- $CaCl_2$ in drying tube, 5-10 g

Experimental Set-up

- The experimental set-up is shown in Figure 2.1.
- By moving the finger clamp, you can adjust the position of the two-neck round-bottom flask

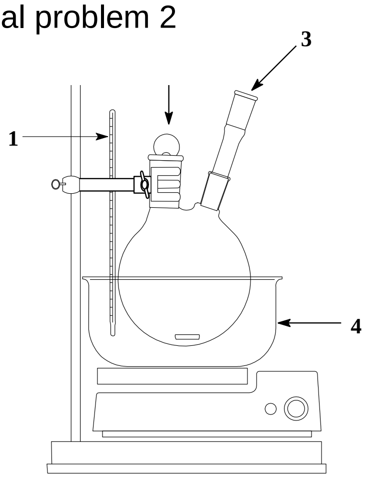
Procedure

Step 1. Synthesis of a Derivative of Artemisinin

1. Prepare an ice bath with a temperature between –20 and –15 °C by mixing ice and sodium chloride in the plastic pot (approximate ratio of NaCl : crushed ice = 1 scoop :

3 scoops). Use the digital thermometer to monitor the temperature. Place the bath on the magnetic stirrer. Put a layer of three tissues between the bath and the stirrer.

Fig. 2.1
Apparatus for practical problem 2



1: digital thermometer;
2: plastic stopper;
3: $CaCl_2$ drying tube;
4: ice bath

2. Place a magnetic stirring bar into the dry round-bottom flask and set up the reaction system onto the clamp-stand so that the system is immersed in the ice bath. Monitor the temperature using the digital thermometer.
3. *Setting aside a tiny amount* (ca. 2 mg) of artemisinin for TLC analysis, open the stopper and add the 1 gram of artemisinin through the bigger neck.
4. Use the glass funnel to add 15 cm^3 of methanol (measured using the 50-cm^3 graduated cylinder). Close the stopper and turn on the magnetic stirrer. (Set the magnetic stirrer to level 4). Start the stopwatch to keep track of the time.
5. After *ca.* 5 min stirring, open the stopper and add carefully 0.53 g of $NaBH_4$ in small portions over 15 min using a spatula. Close the stopper in between addition. *(Caution: Adding $NaBH_4$ rapidly causes side-reactions and overflowing).* Keep stirring for 50 min. Maintain the temperature of the ice bath below –5 ^{o}C; remove some of the liquid and add more NaCl-crushed ice mixture if necessary. Cool the vial containing 1 cm^3 of acetic acid in the ice bath.
7. Prepare 50 cm^3 of ice-cold distilled water *(cooled in the ice bath)* in the 100 cm^3-conical flask. Measure *ca.* 20 – 22 cm^3 *n*-hexane in the 50 cm^3 measuring cylinder and cool it in the ice bath. After the reaction is complete, keep the reaction flask in the ice bath below 0 ^{o}C. Remove the $CaCl_2$ tube, open the stopper, and add gradually *ca* 0.5

cm^3 of the cold acetic acid from the vial into the reaction flask until the pH is between 6 and 7. (Use the glass rod to spot the reaction mixture on to the pH paper.) With stirring, slowly add the 50 cm^3 of ice cold water over 2 min. A white solid precipitates in the reaction flask.

8. Assemble the vacuum filtration apparatus. Put a filter paper onto the Büchner funnel, wet the filter paper with distilled water and open the vacuum valve. Transfer the reaction mixture on to the filter and remove the stirring bar from the reaction flask using the spatula. Wash the product three times with portions of 10 cm^3 ice-cold water *(cooled in the ice bath).* Wash the product two times with portions of 10 cm^3 ice-cold *n*-hexane *(cooled in the ice bath).* Continue to use the pump to dry the solid on the filter. After *ca.* 5 min, carefully transfer the dried powder on to the watch glass labeled with your code and put into the labeled Petri dish. Turn off the vacuum valve when you do not use it!

   Note: Your sample will be collected, dried and weighed later by the lab assistant.

Task 2.1 The recording of your yield – will be performed after the exam by the lab assistant.

Step 2. TLC Analysis of the product

1. Check your TLC plate before use. Unused damaged plates will be replaced upon request without penalty. Use the pencil to draw the start front line, and the line where the solvent front will be run to **exactly as shown in Figure 2.2**. Write your student code on the top of the TLC plate in pencil.

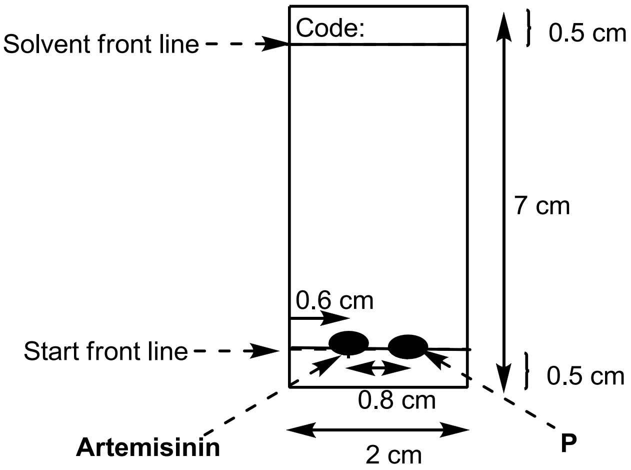


Figure 2.2. Instruction of TLC plate preparation

2. Dissolve *ca.* 1 mg of artemisinin *(a spatula tip)* in *ca.* 0.5 cm^3 of methanol in the labeled very small test tube (use the labeled 5 cm^3 graduated pipette). Dissolve *ca.* 1 mg of the product in *ca.* 1 cm^3 of methanol in the labeled test tube.
3. Spot the artemisinin solution and the product solution on the TLC plate using two different glass capillary spotters so the finished plate is as shown in Figure 2.2.
4. Prepare the TLC developing chamber. Use the 5 cm^3 graduated cylinder to make 5 cm^3 of a mixture of *n*-hexane/ethyl acetate (7/3, v/v) as the solvent system. Pour tme mixture of *n*-hexane/ethyl acetate into the chamber *(Note: The solvent level should not reach the spots on the plate if prepared as shown).* Cover and swirl the chamber and allow it to stand for 2 min.

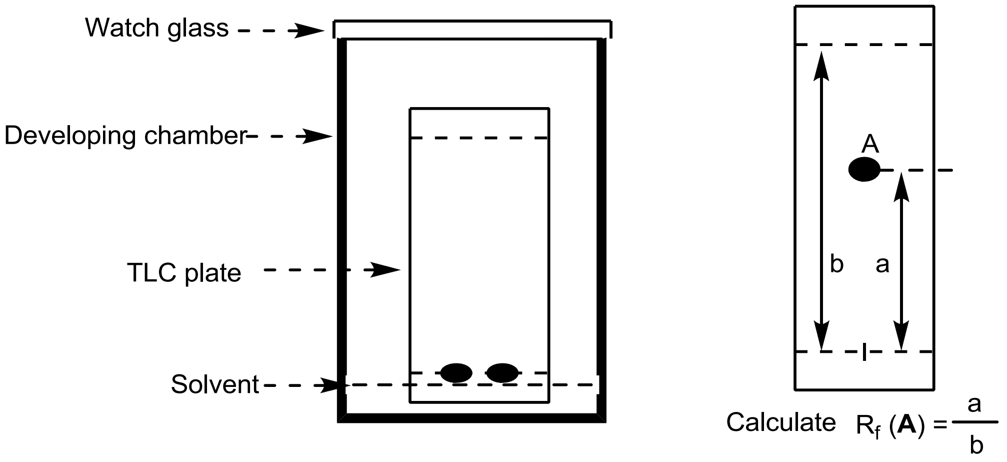


Figure 2.3. A TLC plate placed in the TLC developing chamber and instruction for R_f calculation of compound **A**

5. Insert the TLC plate upright into the TLC developing chamber. Wait until the solvent system reaches the pre-drawn solvent front line. (*Note: You are advised to work on some question below while you wait for the TLC to run.*)
6. When the solvent front reaches the line, remove the TLC plate using the tweezers and then dry the solvent using the hair dryer set at <u>level 1</u>.
7. Dip the piece of cotton wool into the cerium staining reagent, taking care not to let the tweezers come into contact with the solution since the metal stains the plate. Carefully apply the stain to the whole TLC plate.
8. Heat the TLC plate using the hair dryer set at <u>level 2</u> (<u>*Attention: DO NOT set the hair dryer to COLD*</u>) until the blue spots of artemisinin and the product appear on the TLC plate.
9. Ask the lab assistant to take a photo of your final TLC plate together with your student code.
10. Circle all the visualized spots and calculate the R_f values of both artemisinin and the product (*See instruction in Fig. 2.3*). Store your TLC plate in the Petri dish.

Task 2.2 Fill the values of R_f in Table below.

$R_{f,\text{ Artemisinin}}$	$R_{f,\text{ Product}}$	$R_{f\text{ Artemisinin}} / R_{f\text{ Product}}$
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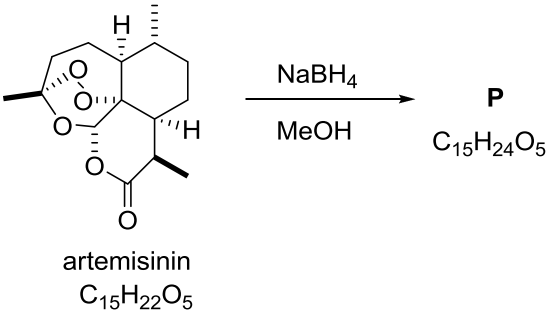
Task 2.*3* Check the total number of developed spots on the TLC plate:

1 ☐	2 ☐	3 ☐	4 ☐	5 ☐

Step 3. Identifying the reaction product P

The reduction of artemisinin leads to the formation of two stereoisomers (**P**). Comparing the ^{1}H-NMR spectrum (in $CDCl_3$) of one of these isomers with the spectrum of artemisinin shows an extra signal at δ_H = 5.29 ppm as a doublet, and also an extra signal as a broad singlet at δ_H = 2.82 ppm.



Task 2.4 Suggest the structure for P.

(You do not need to draw the stereochemistry of the compounds).

Task 2.5 P is mixture of two stereoisomers. What is their stereochemical relationship? Tick the appropriate box below.

Z/E Isomers	Enantiomers	Diastereomers	Constitutional Isomers
☐	☐	☐	☐

PROBLEM 3P (Practical)

Analysis of a hydrated zinc iron(II) oxalate double salt

Zinc iron(II) oxalate double salt is a common precursor in the synthesis of zinc ferrite which is widely used in many types of electronic devices due to its interesting magnetic properties. However, such double salts may exist with different compositions and different amount of water depending on how the sample was synthesized.

You will analyze a pure sample of hydrated zinc iron(II) oxalate double salt (**Z**) in order to determine its empirical formula.

Reagents

- ~ 30 % H_2SO_4, solution in water, 40 cm^3, in a plastic bottle,
- $KMnO_4$,, aqueous solution , c = 1.00×10^{-2} mol dm^{-3}, in 50 cm^3 bottle,
- EDTA, aqueous solution, c = 2.00×10^{-3} mol dm^{-3}, 40 cm^3 in a bottle,
- Buffer aqueous solution, $NH_4Cl + NH_3$, pH = 9 – 10, 40 cm^3 in a bottle
- NaOH, 20 % aqueous solution, 20 cm^3 in a plastic bottle,
- H_3PO_4, solution in water, c = ~3 mol dm^{-3}, 15 cm^3 in a bottle
- Indicator: ETOO, solid in KCl , *ca.* 0.5 g in a plastic bottle

Chemical glass and equipment

- 2 glass beakers, 50-cm^3 (for transferring EDTA and $KMnO_4$ solutions to burettes)
- 1 burette with BLUE graduation marks, 25-cm^3
- 1 burette with BROWN graduation marks, 25-cm^3
- 2 glass beakers, 250 cm^3
- 2 Erlenmeyer flasks, 250 cm^3
- 2 volumetric flasks with stopper, 100 cm^3
- 1 glass graduated measuring cylinder, 10 cm^3
- 1 glass graduated measuring cylinder, 100 cm^3
- burette stand & clamp
- pH paper
- round filter paper for the glass funnel

Procedure

The concentration of the standard $KMnO_4$ is posted on the lab walls.

Bring a clean 250 cm^3 beaker to the lab assistant who will be waiting by the balance. You will receive a pure sample of Z for analysis. Accurately weigh between 0.7 – 0.8 g of the pure sample Z onto the weighing paper (*m*, grams). This should then be immediately quantitatively transferred into your 250 cm^3 beaker for analysis, and its mass recorded in table below.

Task 3.1 Record the mass of the sample of pure Z taken.

Mass of sample, *m* (gram)	Lab assistant's signature
-----------------	--------------------

Analysis of Z

- Using the 100 cm^3 graduated measuring cylinder, measure *ca.* 30 cm^3 of 30 % H_2SO_4 solution and add it into the 250 cm^3 beaker containing your accurately weighed pure sample of **Z**. To speed up the dissolving of your sample you may use the hotplate stirrer to warm up the mixture, **but be careful not to boil** it. *You should not use the digital thermometer as the acid may damage it*. After the solid has dissolved, remove the beaker from the hotplate stirrer and cool it to close to room temperature. After the solution has cooled, quantitatively transfer it into the 100 cm^3 volumetric flask. Add distilled water up to the 100 cm^3- mark. We will now call this solution **C.**
- Use an appropriately labeled beaker to transfer the standardized $KMnO_4$ solution into the burette graduated with **brown** marks.
- Use another appropriately labeled beaker to transfer the standardize **EDTA** solution into the burette graduated with **blue** marks.

Titration with the $KMnO_4$ solution

a) sing the 5 cm^3 graduated pipette add 5.00 cm^3 of the solution **C** into a 250 cm^3 conical flask.

b) To this conical flask add about 2 cm^3 of 30 % H_2SO_4 solution, about 3 cm^3 of H_3PO_4

solution (c = 3.0 mol dm^{-3}), and about 10 cm^3 of distilled water. Heat the mixture on the hot plate stirrer until hot, **but be careful not to boil** it.

c) Titrate the hot solution with the standardized $KMnO_4$ solution, recording your burette readings in the table below. At the end point of the titration, the pink color of the solution appears. Repeat the titration as desired and report your accepted volume of $KMnO_4$ solution consumed (V_1, cm^3) in the table.

Task 3.2 Record volumes of standardized $KMnO_4$ solution consumed

(You DO NOT need to fill in the entire table)

	Titration No			
	1	2	3	4
Initial reading of the burette of $KMnO_4$, cm^3				
Final reading of the burette of $KMnO_4$, cm^3				
Consumed volume of $KMnO_4$, cm^3				

Accepted volume, V_1 = ________ cm^3

Task 3.3 Can aqueous HCl or HNO_3 be used instead of H_2SO_4 for the dissolving of sample Z and the subsequent analyses?

HCl: Yes ☐ No ☐

HNO_3: Yes ☐ No ☐

Titration with EDTA

i) Clean both the 250 cm^3 beakers ready for the next part of the experiment. Pipette 10.00 cm^3 of solution **C** into a 250 cm^3 beaker. Heat and stir the solution on the hotplate stirrer, but be careful not to boil it. Add *ca.* 15 cm^3 of 20 % NaOH solution to the beaker and keep it on the hotplate for *ca*. *3-5* min in order to complete the precipitation of iron hydroxide, and to convert all Zn^{2+} ions into the ionic complex $[Zn(OH)_4]^{2-}$.

ii) Using a glass funnel and the large quantitative filter paper, filter the hot suspension directly into the 250 cm^3 conical flask. From this point take care with the volumes as you will be preparing a standard solution of exactly 100 cm^3 from the filtrate. As it is filtering, prepare some warm distilled water in a 250 cm^3 beaker (*ca*. 50 cm^3). Wash the precipitate on the filter paper (at least 5 times) with small portions (*ca.* 5 cm^3) of the warm distilled water. Cool the filtrate down and then quantitatively transfer it into the 100 cm^3 volumetric flask via a glass funnel. Add distilled water to make up to the 100 cm^3 mark. This will now be referred to as solution D.

iii) Pipette 10.00 cm^3 of solution **D** into a 250 cm^3 conical flask. Add *ca.*10 cm^3 ammonia buffer solution (*pH* = 9 – 10) and a small quantity of the ETOO indicator using the glass spatula spoon. Mix well to obtain a purple solution. Titrate the solution with the standardized EDTA solution (c = 2.00×10^{-3} mol dm^{-3}), recording your burette readings in table below. At the end point, the color of the solution turns blue. Repeat the titration as desired and report your accepted volume of EDTA solution consumed (V_2, cm^3) in the table.

Task 3.4 Record the volumes of EDTA solution consumed

(You do not need to fill in the entire table)

	Titration No			
	1	2	3	4
Initial reading of the volume of EDTA, cm^3				
Final reading of the volume of EDTA, cm^3				
Consumed volume of EDTA, cm^3				

Accepted volume, V_2 = ________ cm^3

Determination of the empirical formula of Z

Task 3.5: Calculate the amount of substance (mol) of Zn^{2+} present in 100 cm^3 of solution C.

Task 3.6: Give the ionic equations for the reduction-oxidation reactions taking place in the titration with $KMnO_4$.

Task 3.7: Calculate the amount o substance (in mol) of Fe^{2+} present in 100 cm^3 of solution C.

Task 3.8: Calculate the amount o substance (in mol) of $C_2O_4^{2-}$ present in 100 cm^3 of solution C.

Task 3.9: Calculate the amount o substance (in mol) of water in tme original sample of Z in tme original sample of Z taken for analysis.

Task 10: Give tme empirical formula of Z.

47th

8 theoretical problems
3 practical problems

THE FORTY-SEVENTH
INTERNATIONAL CHEMISTRY OLYMPIAD
20–29 JULY 2015, BAKU, AZERBAIJAN

THEORETICAL PROBLEMS

PROBLEM 1

New and well-forgotten old refrigerants

The problem of choosing a refrigerant for refrigeration and air conditioning systems attracted the attention of scientists and technologists throughout the last century. It has been suggested that during this time refrigerants progressed through four generations.

Ammonia, which was ascribed to the first generation, had been used in most of the oldest refrigeration units. It was later replaced by chlorofluorocarbons (CFCs) – derivatives of methane and ethane with the hydrogen atoms replaced by fluorine and chlorine.

In Baku, at "Bakkonditsioner" factory, production of the first Soviet serial household air conditioners BK-1500 had been launched. A second-generation refrigerant chlorodifluoromethane CHF_2Cl was used in them. In this problem, we compare various refrigerants in terms of thermodynamics.

First air conditioner of Baku factory in souvenir shop in the Old City (“Icheri Sheher”).

Thermodynamic properties of various refrigerants:

Refrigerant	“Generation”	ΔH_{vap} / kJ mol^{-1} (at 280 K)	$C_{V(gas)}$ / J K^{-1} mol^{-1}
NH_3	1	21.3	26.7

Table continued:

CHF_2Cl	2	20.0	48.8
CF_3CH_2F	3	22.1	79
$CF_3CF=CH_2$	4	19.1	120

Consider a model refrigeration cycle consisting of 4 steps schematically shown below in the pressure (*p*) – internal energy (*U*) coordinates.

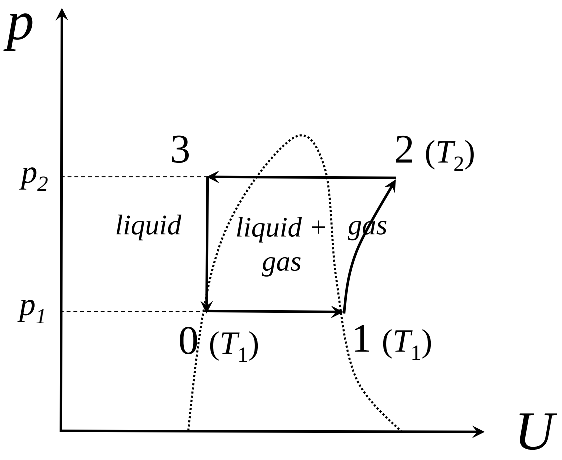


Diagram 1. Dashed line indicates the phase boundaries

During the first step of the cycle (line 0-1 in diagram 1), a liquid refrigerant is boiling at constant pressure p_1 and temperature T_1 (boiling temperature) until it completely evaporates. At this step, the refrigeration unit absorbs heat from surrounding objects. At the second step, the refrigerant undergoes reversible adiabatic compression and heats up to temperature T_2 (line 1-2). After that the compressed refrigerant is cooled in a condenser at constant pressure p_2 (line 2-3) and then returns to the initial state (line 3-0).

Let the cycle involve 1 mole of refrigerant, which is initially (point 0) completely liquid, T_1 = 280 K, T_2 = 380 K, assume that the vapor of any refrigerant behaves like an ideal gas. The thermodynamic characteristics of refrigerants are listed in the table above.

1.1 For each of refrigerants, ammonia and chlorodifluoromethane, calculate the amount of heat *Q* absorbed by refrigeration unit during heat exchange (line 0-1) and the work *W* required to compress its vapor adiabatically (line 1-2).

1.2. Which quantity(ies) remain(s) constant during the adiabatic compression step? Indicate by the circle(s).

U *H* *S* *G* *V*

To compare the energy efficiency of refrigeration cycles with different parameters and refrigerants, the coefficient of performance (*COP*) is used, which is defined as a ratio of heat removed from a cooled system to the work of compressor: $COP = Q/W$.

1.3 Calculate the values of *COP* in a considered cycle for ammonia and chlorodifluoromethane.

1.4 Why was ammonia replaced by CFCs in household refrigeration units? (Choose only one option)

a) to increase the energy efficiency of refrigeration cycles,
b) because the density of ammonia is less than that of air under the same conditions,
c) for user safety reasons.

A search for replacement of CFCs as refrigerants started when it was shown that their use can cause irreparable damage to the protective ozone layer of the atmosphere. The third, ozone-friendly generation of refrigerants came on the scene. Its typical representatives are fluoroalkanes.

1.5 What is the cause of the damage made by CFCs to the ozone layer? (Choose only one option.)

a) Ozone molecule easily adds to C–F bond,
b) C–F bond is easily broken by radiation, which leads to the formation of free radicals,
c) ozone molecule easily adds to C–Cl bond,
d) C–Cl bond is easily broken by radiation, which leads to the formation of free radicals.

1.6 However, under the 1997 Kyoto Protocol, fluoroalkanes also had to be replaced because they accumulate in the atmosphere and rapidly absorb infrared radiation, causing a rise in temperature of the atmosphere (the greenhouse effect). The refrigerants of the fourth generation such as 2,3,3,3-tetrafluoropropene $CF_3CF=CH_2$ have been suggested and are coming into use. Why does this compound enhance the greenhouse effect less than fluoroalkanes? (Choose only one option)

a) It is more reactive and easier to decompose,
b) it easily reacts with ozone,
c) it is better soluble in water.

1.7 Calculate the values of the *COP* in the refrigeration cycle considered above for two refrigerants of the third and fourth generations – CF_3CH_2F and $CF_3CF=CH_2$. Did the energy efficiency improve in comparison with CHF_2Cl? Choose "Yes" or "No".

Unlike household appliances, industrial refrigeration systems are often still using ammonia. It does not contribute to the greenhouse effect nor does it destroy the ozone layer. Industrial units can have a huge size and a large cost. Prior to their construction, they should be carefully modeled taking into account many different factors. In real systems, some part of the refrigerant at the start of the heat exchange with the environment is in the vapor phase (point 0 in the diagram below), and at the end (point 1) it is always overheated above the boiling point.

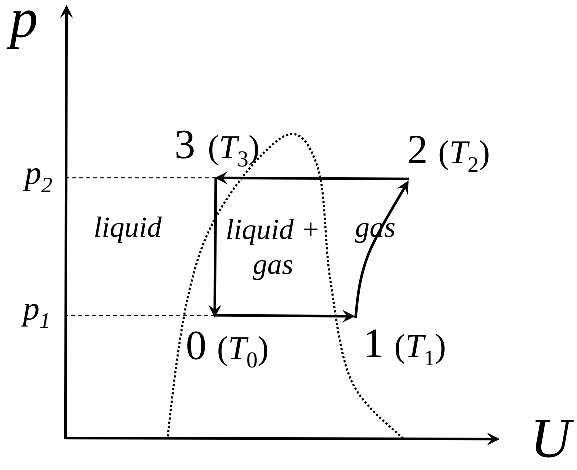


Diagram 2. Dashed line indicates the phase boundaries

Consider a cycle with 1 mole of ammonia. Its thermodynamic properties are the following: enthalpy of vaporization ΔH_{vap} = 23.35 kJ·mol^{-1} at T_{vap} = 239.8 K (boiling temperature at 1 bar pressure). Heat capacity of the liquid phase $C_{V(\text{liq})}$ = 77 J·K^{-1}·mol^{-1}, of the gas phase $C_{V(\text{gas})}$ = 26.7 J·K^{-1}·mol^{-1}. Assume that the heat capacities are temperature-independent and the vapor behaves like an ideal gas. The temperature dependence of the saturated vapor pressure of ammonia can be described by the empirical equation

$$\log (p/\text{bar}) = 4.87 - 1114 / (T/\text{K} - 10.4).$$

During the first step of the cycle (line 0-1 in diagram 2), the equilibrium mixture of liquid refrigerant and its vapor receives heat from the environment at constant pressure p_1 = 3.0 bar. The refrigerant completely evaporates and overheats up to the temperature T_1 = 275 K. In the beginning of the process (point 0), the molar fraction of gaseous ammonia is x = 0.13.

1.8 Calculate the initial temperature of refrigerant T_0, its volume change ΔV and the amount of heat Q absorbed by refrigeration unit during this step. Take into account that the dependence of ΔH_{vap} from the temperature **cannot** be neglected. Then the refrigerant is reversibly and adiabatically compressed. It heats up to the temperature T_2 = 393 K (line 1-2).

1.9 Find the work W required for compression and the *COP* of the system. If you were not able to find Q in 4.1, use Q = 20.15 kJ.

At the next step corresponding to the line 2-3 in diagram, the compressed refrigerant is cooled in a condenser at constant pressure. Then it returns to the initial state through adiabatic expansion with zero work (line 3-0).

1.10 Determine the temperature T_3 at point 3 to which the refrigerant is cooled in a condenser.

In the production of refrigeration units it is necessary to consider climatic factors. If a condenser is cooled by atmospheric air, the temperature T_3 increases as the air temperature increases.

1.11 How will the *COP* change if T_3 increases while T_0, T_1, T_2 remain the same?

a) increase,
b) remain the same,
c) decrease.

SOLUTION

1.1 **Ammonia**

$Q = \text{v}\ \Delta H_{\text{vap}} = 21.3$ kJ;

$W = \text{v}\ C_{V(\text{gas})}(T_2 - T_1) = 2.67$ kJ.

Chlorodifluoromethane

$Q = \text{v}\ \Delta H_{\text{vap}} = 20.0$ kJ;

$W = \text{v}\ C_{V(\text{gas})} \cdot (T_2 - T_1) = 4.88$ kJ.

1.2 U H [✓ S] G V

1.3 **Ammonia:**

$COP = Q / W = 7.98$

Chlorodifluoromethane:

$COP = Q/W = 4.10$

1.4 Correct answer: c)

1.5 Correct answer: d)

1.6 Correct answer: a)

1.7 Calculations:

CF_3CH_2F

$COP = \Delta H_{\text{vap}} / (C_{V(\text{gas})}(T_2 - T_1)) = 2.80$

Correct answer: No

$CF_3CF = CH_2$

$COP = \Delta H_{\text{vap}} / (C_{V(\text{gas})}(T_2 - T_1)) = 1.59$

Correct answer: No

1.8 Calculations:

$T_0 = 10.4 + 1114 / (4.87 - \log p_1) = 264$ K

$\Delta V = (\text{v}RT_1 / p_1) - (x\text{v}RT_0 / p_1) = 6.7\ \text{dm}^3$

$Q = \Delta H = \Delta U + p_1\Delta V = \Delta U$(liquid fraction) + ΔU(gas fraction) + $p_1\Delta V$ =

= ΔU(vaporization of liquid fraction at T_0) + ΔU (heating evaporated liquid fraction up to T_1) + ΔU(gas fraction) + $p_1\Delta V$ =

$= \text{v}\ (1-x)\ (\Delta H_{\text{vap}} - RT_{\text{vap}} + (C_{V(\text{gas})} - C_{V(\text{liq})})(T_0 - T_{\text{vap}})) + \text{v}C_{V(\text{gas})}\ (T_1 - T_0) + p_1\Delta V =$

$= 19.8$ kJ

or

$Q = \text{v}\ (1-x)(\Delta H_{\text{vap}} + (C_{V(\text{gas})} + R - C_{V(\text{liq})})(T_0 - T_{\text{vap}})) + \text{v}(C_{V(\text{gas})} + R)(T_1 - T_0) = 19.8$ kJ

1.9 $W = \text{v}\, C_{V(\text{gas})}\,(T_2 - T_1) = 3.15\ \text{kJ}$
COP = $Q / W = 6.3$

1.10 The internal energies of the refrigerant are equal in points 0 and 3. Thus,
$x\,(\Delta H_{\text{vap}} - RT_{\text{vap}} + (\text{C}_{V(\text{gas})} - \text{C}_{V(\text{liq})})(T_0 - T_{\text{vap}})) + \text{C}_{V(\text{liq})}\,(T_0 - T_3) = 0,$
$T_3 = 298\ \text{K}.$

1.11 Correct answer: c)

Comment: It will decrease because the length of 0 - 1 line decreases or because x (see 1.10) increases and less liquid is in the equilibrium mixture at T_0, so less heat Q is necessary to evaporate it.

PROBLEM 2

Coupling of chemical reactions

I.Prigogine (left)

N. Shilov

W. Ostwald

When in the system one reaction allows another one to proceed they say that these two reactions are coupled. Ilya Prigogine, Nobel prize winner in chemistry (1977) in his books widely used the concept of "coupled reactions". Coupling of reactions is an essential feature of living systems, including human body.

How one reaction makes another one to occur? In this problem we are going to discuss several possible mechanisms of coupling.

(I) "Chemical coupling"

On Chemical coupling" was the title of the dissertation defended by Russian chemist N.Shilov in 1905. N. Shilov was the graduate student of famous professor W. Ostwald. Dr. Shilov described the following set of reactions.

The substance ***A*** does not react with ***Ac***. In the presence of the third reagent (called inductor), ***In***, however, the reaction of ***A*** with ***Ac*** takes place:

$$\boldsymbol{A} + \boldsymbol{Ac} \xrightarrow{\text{In the absence of In}} \text{no reaction} \qquad (1)$$

$$\boldsymbol{A} + \boldsymbol{Ac} \xrightarrow{\text{In the presence of In}} \boldsymbol{P_1} \qquad (2)$$

In is not a catalyst! Its concentration decreases in the course of the reactions.

According to the scheme proposed by Shilov, ***Ac*** reacts not with ***A*** itself, but with the intermediate product ***R*** of the reaction of ***A*** with ***In***. There is another, competing reaction of ***R*** that forms $\boldsymbol{P_2}$.

$$\text{(a) } \alpha\,\boldsymbol{A} + \beta\,\boldsymbol{In} \xrightarrow{k(3a)} \boldsymbol{R}$$

$$\text{(b) } \boldsymbol{R} \xrightarrow{k(3b)} \boldsymbol{P_2} \qquad (3)$$

$$\text{(c) } \boldsymbol{R} + \boldsymbol{Ac} \xrightarrow{k(3c)} \boldsymbol{P_1}$$

α and β are stoichiometric coefficients. Other stoichiometric coefficients and reaction order with respect to all reactants in all three reactions are unity.

In the Shilov's experiments the ratio of the consumed amounts of ***Ac*** and ***In***, $\underline{\boldsymbol{I}} = \Delta n_{Ac} / \Delta n_{In}$ increased up to the constant value with the increasing initial concentration $[\boldsymbol{Ac}]_0$ at $[\boldsymbol{In}]_0$ = const.

2.1 What was this limiting constant value of $\underline{\boldsymbol{I}}$ at $[\boldsymbol{Ac}]_0 \to \infty$, $[\boldsymbol{In}]_0$ = const?

2.2 Derive an expression for $\underline{\boldsymbol{I}}$ using the steady-state approximation if necessary. Plot the graph of $\underline{\boldsymbol{I}}$ vs $[\boldsymbol{In}]_0$ at $[\boldsymbol{Ac}]_0$ = const. Assume that ***In*** was completely consumed and ***Ac*** was in excess..

If Shilov's mechanism is not valid and ***In*** is a conventional catalyst of the reaction (2) then ***In*** reacts simultaneously with ***A*** and its concentration decreases. The reaction scheme in this case is as follows:

(a) $\alpha\,\boldsymbol{A} + \beta\,\boldsymbol{In} \rightarrow \boldsymbol{P_2}$

(b) $\boldsymbol{A} + \boldsymbol{Ac} \xrightarrow{In,\ catalysis} \boldsymbol{P_1}$ (4)

2.3 What is the limiting value of ***I*** for the reaction scheme (4) at $[\boldsymbol{Ac}]_0 \to \infty$, $[\boldsymbol{In}]_0$ = const?

(II) "Kinetic coupling"

The standard Gibbs energy of the gas-phase reaction

$$Br + H_2 \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} HBr + H \qquad (5)$$

is positive, $\Delta G^\circ(5) = 66$ kJ mol^{-1} at $T = 600$ K.

2.4 What is the ratio of the rates of forward and reverse reactions, r_5/r_{-5}, at this temperature, standard pressures of H_2 and HBr and equal pressures of H and Br?

(If you could not answer this question, for further calculations use reference value $r_5 / r_{-5} = 3.14\times10^{-7}$.)

Reaction (5) proceeds in the forward direction due to the reaction (6) which simultaneously occurs in the system:

$$Br + H_2 \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} HBr + H \qquad (5)$$

$$H + Br_2 \xrightarrow{k_6} HBr + Br \qquad (6)$$

k_5, k_{-5}, k_6 are rate constants of forward and reverse reaction (5) and forward reaction (6), respectively.

This is the *kinetic coupling* of two reactions.

Let pressures of neutral molecules keep standard values $p(H_2) = p(Br_2) = p(HBr) = 1$ bar, and pressures of radicals $p(H)$, $p(Br)$ reach steady-state values. Rate constant k_6 is 10 times larger than k_{-5}.

2.5 Calculate $\Delta G(5)$ and r_5/r_{-5} under such conditions.

(III) "Second law of thermodynamics restricts coupling"

According to the Second Law of thermodynamics, two simultaneously occurring chemical reactions should decrease the system's Gibbs energy G_{Syst},

$$\frac{\Delta G_{syst}}{\Delta t} < 0$$

One of these reactions may have positive Gibbs energy and still proceed in the forward direction due to the coupling with the second reaction. This second reaction must have negative Gibbs energy and the requirements of the Second law must be fulfilled! Consider the example.

The synthesis of urea under specific conditions

$$2\ NH_3 + CO_2 \rightarrow (NH_2)_2CO + H_2O \qquad (7)$$

($\Delta G(7) = 46.0$ kJ mol^{-1})

is supposed to be coupled with the complete oxidation of glucose (under the same conditions)

$$1/6\ C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O \qquad (8)$$

$\Delta G(8) = -481.2$ kJ mol^{-1},

$r(8) = 6.0\times10^{-8}$ mol dm^{-3} min^{-1}.

Both reactions are presented schematically. No other reactions are considered.

2.6 What is the maximum rate of the reaction (7) permitted by the Second Law if this reaction is coupled to reaction (8)?

SOLUTION

2.1 Brief explanation

The value of *I* should increase with the increase of [***Ac***]$_0$ at [***In***]$_0$ = const, because the larger fraction of the intermediate product ***R*** will enter the reaction (3c). The maximum value of *I* will be achieved if all ***R*** reacts in (3c), therefore $I_\infty = 1/\beta$.

2.2 Calculations:

Shilov's mechanism includes the initial reaction

$\alpha \mathbf{A} + \beta \mathbf{In} \rightarrow \mathbf{R}$ (3a)

and two competitive reactions:

$\mathbf{R} + \mathbf{Ac} \rightarrow \mathbf{P}_1$ (3c)

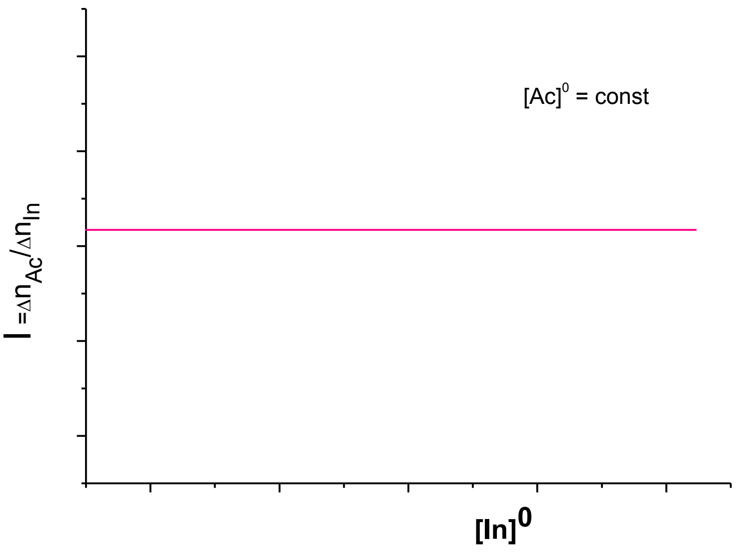
$\mathbf{R} \rightarrow \mathbf{P}_2$ (3b)

The rates of conversion of ***In*** and ***Ac*** are determined by the rates of the reactions (3a) and (3c), respectively:

$$\frac{r(3c)}{r(3a)} = \frac{k(3c)\,[R]\,[Ac]}{k(3a)\,[A]\,[In]} = \frac{k(3c)\,[Ac] \times \dfrac{k(3a)\,[A]\,[In]}{k(3c)\,[Ac] + k(3b)}}{k(3a)\,[A]\,[In]} = \frac{k(3c)\,[Ac]}{k(3c)\,[Ac] + k(3b)}$$

in steady-state approximation for [***R***]. We see that the ratio of two rates does not depend on the initial concentration [***In***]$_0$ and *I* will also not depend on it. This gives the straight line parallel to the [***In***]$_0$ axis on the graph.

Graph



2.3 Brief explanation

In this case ***I*** will permanently increase with the increase of $[\boldsymbol{Ac}]_0 \to \infty$ at $[\boldsymbol{In}]_0$ = const. The rate of the reaction (4b) may be so high that conversion of ***In*** in reaction (4a) will be negligible.

Hence $I \to \infty$ if $[\boldsymbol{Ac}]_0 \to \infty$ at $[\boldsymbol{In}]_0$ = const.

$I_\infty = \infty$ (infinity)

2.4 Calculations:

The standard Gibbs energy of reaction (5) at 600 K is 66 kJ mol^{-1}. The equilibrium constant is

$$K = e^{-66000 / 8.314 / 600} = 1.8\times10^{-6} = k_5 / k_{-5}$$

Reaction is considered at standard pressures of all the reactants and products. The ratio of the rates of forward and reverse reactions is

$$\frac{r_5}{r_{-5}} = \frac{k_5[\mathrm{Br}][\mathrm{H_2}]}{k_{-5}[\mathrm{HBr}][\mathrm{H}]} = \frac{k_5}{k_{-5}} = 1.8\times10^{-6}$$

2.5 Calculations

The steady-state condition is the same for both radicals, e.g. for radical H

$$\frac{d[\mathrm{H}]}{dt} = k_5[\mathrm{Br}][\mathrm{H_2}] - k_{-5}[\mathrm{HBr}][\mathrm{H}] - k_6[\mathrm{H}][\mathrm{Br_2}] = 0$$

$$\frac{[\mathrm{H}]}{[\mathrm{Br}]} = \frac{k_5[\mathrm{H_2}]}{k_{-5}[\mathrm{HBr}] + k_6[\mathrm{Br_2}]}$$

The concentrations of all the neutral molecules are the same (they correspond to the pressure of 1 bar), therefore

$$\frac{[\mathrm{H}]}{[\mathrm{Br}]} = \frac{k_5}{k_{-5} + k_6} = \frac{k_5 / k_{-5}}{1 + k_6 / k_{-5}} = \frac{1.8\times10^{-6}}{1+10} = 1.6\times10^{-7}$$

The Gibbs energy of reaction (5) under such conditions is:

$$\Delta G = \Delta G^0 + RT\ln\frac{[\mathrm{H}]\,[\mathrm{HBr}]}{[\mathrm{Br}]\,[\mathrm{H_2}]} = 66 + 8.314\times10^{-3}\times600\times\ln(1.6\times10^{-7}) = -12\ \mathrm{kJ\ mol^{-1}}$$

The ratio of rates is:

$$\frac{r_5}{r_{-5}} = \frac{k_5\,[\mathrm{Br}]\,[\mathrm{H_2}]}{k_{-5}\,[\mathrm{HBr}]\,[\mathrm{H}]} = \frac{k_5[\mathrm{Br}]}{k_{-5}[\mathrm{H}]} = \frac{k_5}{k_{-5}}\,\frac{1 + k_6 / k_{-5}}{k_5 / k_{-5}} = 1 + \frac{k_6}{k_{-5}} = 11$$

2.6 Calculations

According to the Second law the following condition has to be met:

$$\frac{\Delta G_{\text{syst}}}{\Delta t} = \Delta G(7) \times r_7 + \Delta G(8) \times r_8 \le 0$$

Therefore

$$r_7 \le \frac{-\Delta G(8)}{\Delta G(7)} r_8 = \frac{481.2}{46.0} \times 6.0 \times 10^{-8} = 6.3 \times 10^{-7} \text{ mol dm}^{-3} \text{ min}^{-1}$$

This is the maximum possible rate of the coupled reaction.

$r_7(\text{max}) = 6.3\times10^{-7}$ mol dm^{-3} min^{-1}

PROBLEM 3

Two binding centers – competition or cooperation?

*Ma*ny chemical reactions in living organisms include the formation of “host-guest” complexes where the host molecule reversibly binds one or several guest molecules. Consider a host molecule ***H*** with two binding centers – say, *a* and *b* which have different affinities for the guest molecules ***G***:

$$H + G \rightleftarrows HG_a \qquad K_a = \frac{[HG_a]}{[H]\,[G]}$$

$$H + G \rightleftarrows HG_b \qquad K_a = \frac{[HG_b]}{[H]\,[G]} \qquad K_b \neq K_a$$

where HG_a and HG_b denote a complex where guest is bound to *a* center and *b* center, respectively. K_a and K_b are the binding constants for the centers *a* and *b*, brackets denote molar concentrations.

Attachment of one ***G*** molecule to ***H*** can change the binding ability of the second centre. This change is described by the “interaction factor” β which reflects the influence of one binding center on another and is defined as follows:

$$\boldsymbol{HG_a + G \rightleftarrows HG_2}$$

$$\frac{[HG_2]}{[HG_a]\,[G]} = \beta K_b$$

where $\boldsymbol{HG_2}$ is the completely bound complex.

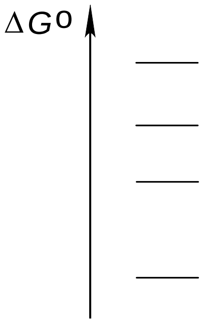
3.1 Determine the range of values (or one value, if necessary) of β which correspond to three possible ways of interaction between binding centers: a) cooperation (binding by one center facilitates subsequent binding); b) competition (first binding complicates the second); c) independence (no interaction).

3.2 Find the equilibrium constant for the process: $\boldsymbol{HG_b + G \rightleftarrows HG_2}$ in terms of binding constant(s) and interaction factor.

3.3 The solution was prepared with the initial concentrations $[\boldsymbol{H}]_0 = 1$ and $[\boldsymbol{G}]_0 = 2$. After the reactions were completed, the concentration of ***H*** decreased by 10 times and that of ***G*** by 4 times. For these host and guest, $K_b = 2K_a$. Determine the concentrations of all other species in the solution and find the binding constant K_a and the factor β.

Note: If you could not answer this question, for further calculations use reference values K_a = 3.14 and β = 2.72.

3.4 Find the correct order of standard molar Gibbs energies of formation of host ***H*** and all host-guest complexes from ***H*** and ***G***. In the scheme below, write the corresponding chemical formula near every line.



3.5 Some amount of ***G*** was added to 1 mole of ***H*** and the mixture was dissolved in water to obtain 1 liter of the solution. The number of the totally bound molecules ***HG*₂** in the solution is equal to the total number of single-bound molecules ***HG***. Find the initial amount of ***G*** (in mol). The constants K_a and K_b and the factor β are the same as in question 3.3.

3.6 What would be the equilibrium composition of the solution if: a) β = 0; b) β is very large ($\beta \to \infty$). The constants K_a and K_b as well as the initial concentrations of ***H*** and ***G*** are the same as in question 2.1.

SOLUTION

3.1 Cooperation: $\beta > 1$

Competition: $0 < \beta < 1$

Independence: $\beta = 1$

3.2

$$K = \frac{[HG_2]}{[HG_b]\,[G]} = \frac{[HG_2]}{[HG_a]\,[G]}\,\frac{[HG_a]}{[HG_b]} = \beta K_b\,\frac{K_a}{K_b} = \beta K_a$$

$\boldsymbol{K} = \beta K_a$

3.3 From $K_b = 2\,K_a$ it follows: $[\boldsymbol{HG_b}] = 2\,[\boldsymbol{HG_a}]$

Material balance with respect to $\boldsymbol{H}$:

$[\boldsymbol{H}] + [\boldsymbol{HG_a}] + [\boldsymbol{HG_b}] + [\boldsymbol{HG_2}] = [\boldsymbol{H}]_0 = 1$

or

$0.1 + 3\,[\boldsymbol{HG_a}] + [\boldsymbol{HG_2}] = 1$

Material balance with respect to $\boldsymbol{G}$:

$[\boldsymbol{G}] + [\boldsymbol{HG_a}] + [\boldsymbol{HG_b}] + 2\,[\boldsymbol{HG_2}] = [\boldsymbol{G}]_0 = 2$

or

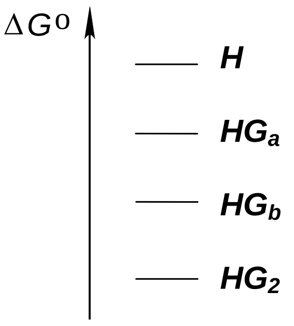
$0.5 + 3\,[\boldsymbol{HG_a}] + 2\,[\boldsymbol{HG_2}] = 2$

Solving the system of two equations, we find: $[\boldsymbol{HG_a}] = 0.1$, $[\boldsymbol{HG_2}] = 0.6$, hence $[\boldsymbol{HG_b}] = 0.2$

$$K_a = \frac{[HG_a]}{[H]\,[G]} = \frac{0.1}{0.1 \times 0.5} = 2$$

$$\beta = \frac{[HG_2]}{[HG_a]\,[G]\,K_b} = \frac{0.6}{0.1 \times 0.5 \times 4} = 3$$

3.4



3.5 **i)** $[HG_2] = [HG_a] + [HG_b] = 3\,[HG_a]$

$$\frac{[HG_2]}{[HG_a][G]} = \beta K_b = 12$$

$$\frac{3}{[G]} = 12$$

$[G] = 0.25$

ii) Material balance with respect to H: $[H] + 3[HG_a] + [HG_2] = 1$

$[H] + 6\,[HG_a] = 1$

$[H] + 12\,[H][G] = 1$

$[H] = 0.25$

iii) $[HG_a] = K_a[H]\,[G] = 0.125$

$[HG_2] = 3[HG_a] = 0.375$

iv) Material balance with respect to G: $[G]_0 = [G] + 3\,[HG_a] + 2\,[HG_2] = 1.375$

$n_0(G) = 1.375$ mol

3.6 $\beta = 0$

Calculations:

In this case, no $\boldsymbol{HG_2}$ is formed.

Material balance with respect to $\boldsymbol{H}$: $[\boldsymbol{H}] + [\boldsymbol{HG_a}] + [\boldsymbol{HG_b}] = 1$ or

$[\boldsymbol{H}] + 3\,[\boldsymbol{HG_a}] = 1$

Material balance with respect to $\boldsymbol{G}$: $[\boldsymbol{G}] + [\boldsymbol{HG_a}] + [\boldsymbol{HG_b}] = 2$ or

$[\boldsymbol{G}] + 3\,[\boldsymbol{HG_a}] = 2$

Equilibrium constant:

$$K_a = \frac{[HG_a]}{[H][G]} = 2$$

Solving the system of three equations, we get:

$[\boldsymbol{H}] = 0.129$ $[\boldsymbol{G}] = 1.129$ $[\boldsymbol{HG_a}] = 0.290$ $[\boldsymbol{HG_b}] = 0.580$ $[\boldsymbol{HG_2}] = 0$

$\beta \to \infty$

Calculations (or arguments):

In this case, formation of $\boldsymbol{HG_2}$ is practically irreversible, so only $\boldsymbol{HG_2}$ is present in the solution.

$[\boldsymbol{H}] = 0$ $[\boldsymbol{G}] = 0$ $[\boldsymbol{HG_a}] = 0$ $[\boldsymbol{HG_b}] = 0$ $[\boldsymbol{HG_2}] = 1$

PROBLEM 4

From one yellow powder to another: A simple inorganic riddle

The yellow binary compound $\mathbf{X_1}$ was completely dissolved in concentrated nitric acid by heating, the gas evolved is 1.586 times denser than air. Upon adding an excess of barium chloride to the solution formed a white solid $\mathbf{X_2}$ precipitates. It was filtered. The filtrate reacts with an excess of silver sulfate solution forming a precipitate of two solids $\mathbf{X_2}$ and $\mathbf{X_3}$, also separated from solution by filtration. To the new filtrate the solution of sodium hydroxide was being added drop-wise until the solution became nearly neutral (about pH 7). At this time a yellow powder $\mathbf{X_4}$ (77.31 wt.% of Ag) crystallized from the solution. The mass of $\mathbf{X_4}$ is nearly 2.4 times larger than that the mass of the first portion of $\mathbf{X_2}$.

4.1 Determine the chemical formulae of $\mathbf{X_1}$ – $\mathbf{X_4}$.

4.2 Determine the chemical formula of the gas and provide equations for all reactions in ionic or non-ionic form.

4.3 In the structural unit of $\mathbf{X_1}$ all atoms of only one element are in equivalent positions. Draw the structure of $\mathbf{X}_1$.

4.4 Predict the products of $\mathbf{X_1}$ interaction with:

a) excess oxygen;

b) excess of hot concentrated sulfuric acid;

c) solid $KClO_3$ with grinding.

Write down the equations of the reactions.

SOLUTION

4.1 The precipitate $\mathbf{X_2}$ formed by addition of barium chloride in acidic medium is barium sulfate $BaSO_4$.

The precipitate $\mathbf{X_3}$ formed by addition of silver sulfate is silver chloride AgCl.

The yellow precipitate $\mathbf{X_4}$ formed by addition of alkali can be mercury oxide HgO or silver phosphate Ag_3PO_4. The ratio of molar masses $\mathbf{X_4}$: $\mathbf{X_2}$ is 0.931 for HgO : $BaSO_4$ which is not valid and 1.798 for Ag_3PO_4 : $BaSO_4$ which gives 2.4 being multiplied by 4/3. So, the molar ratio is 4 Ag_3PO_4 : 3 $BaSO_4$ which corresponds to

P : S = 4 : 3, i.e. to formula P_4S_3 of $\mathbf{X_1}$.

$\mathbf{X_1}$ = P_4S_3 $\mathbf{X_2}$ = $BaSO_4$ $\mathbf{X_3}$ = AgCl $\mathbf{X_4}$ = Ag_3PO_4

4.2 The gas evolved has a molar mass 1.586 × 29 = 46 g mol^{-1}.

Chemical formula of the gas is: NO_2

Dissolution of $\mathbf{X_1}$:

$$P_4S_3 + 38\ HNO_3 = 4\ H_3PO_4 + 3\ H_2SO_4 + 38\ NO_2 + 10\ H_2O$$

Formation of $\mathbf{X_2}$:

$$H_2SO_4 + BaCl_2 = BaSO_4\downarrow + 2\ HCl$$

Formation of $\mathbf{X}_2$ and $\mathbf{X_3}$:

$$Ag_2SO_4 + 2\ HCl = 2\ AgCl\downarrow + H_2SO_4$$

$$BaCl_2 + Ag_2SO_4 = BaSO_4\downarrow + 2\ AgCl\downarrow$$

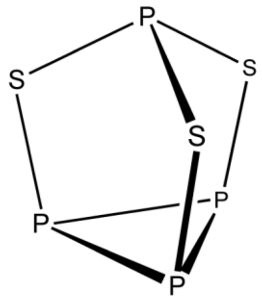
Addition of NaOH and formation of $\mathbf{X_4}$:

$$H_2SO_4 + 2\ NaOH = Na_2SO_4 + 2\ H_2O$$

$$2\ H_3PO_4 + 6\ NaOH + 3\ Ag_2SO_4 = 2\ Ag_3PO_4\downarrow + 3\ Na_2SO_4 + 6\ H_2O$$

(neutralization of H_3PO_4 and subsequent reaction with Ag_2SO_4 can also be accepted).

4.3 Phosphorus sulfide P_4S_3 is a molecular cage



4.4 a) $P_4S_3 + 8\ O_2 = 2\ P_2O_5 + 3\ SO_2$

b) $P_4S_3 + 16\ H_2SO_4 = 4\ H_3PO_4 + 19\ SO_2 + 10\ H_2O$

(oxidation of sulfide to S instead of SO_2 is also acceptable)

c) $3\ P_4S_3 + 16\ KClO_3 = 16\ KCl + 6\ P_2O_5 + 9\ SO_2$

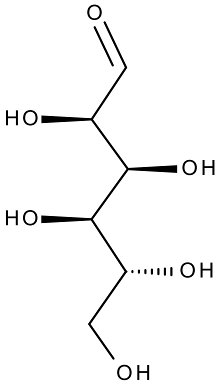
PROBLEM 5

Indispensable glucose

Carbohydrates are the most important providers of energy for living cells. Monosaccharide glucose is a source of energy for the living cell, but for persons who suffer from diabetes glucose may be dangerous. High level of glucose may lead to cardiovascular diseases and even death. That is why people avoid consuming too much carbohydrates and glucose particularly.

A. Determination of reducing sugars in fruit juice

One of the technique for determination of reducing sugars in different samples includes the use of Fehling's reagent. A 10.00 cm^3 aliquot of fruit juice (assuming the initial sample contained only glucose and fructose) was transferred into a titration flask and Fehling's reagent was added. This reagent was prepared by mixing 50.00 cm^3 of copper sulfate solution, c = 0.04000 mol dm^{-3} (solution A) and potassium-sodium tartrate and sodium hydroxide (solution B). Solution C thus obtained, was then heated and red precipitate was formed.



Glucose

5.1 Write the balanced ionic equation of chemical reaction occurring upon heating of the solution C. Use Cu^{2+} for initial copper solution.

After that 10 cm^3 of 10% solution of potassium iodide and sulfuric acid solution (c = = 1 mol dm^{-3}) were added to the flask. The mixture was covered with watch glass and was then placed in a dark place. An excess of iodine was then titrated with sodium thiosulphate solution (c = 0.05078 mol dm^{-3}). A volume of 11.87 cm^3 of the titrant was required to reach the endpoint.

5.2 Write the balanced equation(s) in molecular or ionic form for all the reactions taking place in the flask.

5**.3** Consider that all fructose was transformed into glucose under the experimental conditions. Calculate the total mass concentration of sugars (in g dm^{-3}) in a fruit juice.

M = 180.16 g mol^{-1}.

A new 10.00 cm^3 aliquot of the same juice was treated with a 10.00 cm^3 portion of acidified potassium iodate(V) solution (0.01502 mol dm^{-3}) and 10 cm^3 of 10 % solution of potassium iodide. After the mixture turned brown, an excess of sodium hydroxide solution was added. The flask was then covered with a watch glass and put into a dark place. The obtained solution was acidified and titrated with a solution of sodium thiosulphate (c = 0.01089 mol dm^{-3}). The average titrant volume used for titration was 23.43 cm^3. Note that fructose is not converted into glucose under these conditions.

5.4 Write all the balanced equations for the described reactions in molecular or ionic form.

5.5 Calculate the mass concentration of each sugar (in g dm^{-3}) in the juice.

5.6 One bread exchange unit (1 BEU) corresponds to the content of 12 g of digestible carbohydrates in a product. How many BEU are in one glass (200 cm^3) of juice?

B. Diagnosis of diseases

The derivative of glucose, 2-deoxy-2-(^{18}F)fluoro-D-glucose (FDG), is the most common radiopharmaceutical for diagnosis of cancer using positron emission tomography. The first step of FDG preparation is to produce a radionuclide fluoro-18 by nuclear reaction in a cyclotron. The next step is the radiochemical synthesis. Fluorine-18 is introduced into D-glucose molecule by nucleophilic substitution. 2-deoxy-2-(^{18}F)fluoro-D-glucose once injected into the patient actively accumulates in cells of malignant tumors; this process is accompanied by decomposition of fluorine-18. This radionuclide is a β^+ emitter – nucleus emits a positron (anti-electron). Positron interacts with an electron and after that annihilation occurs, which can be detected. This allows determining precisely the tumor sizes and type.

5.7 Complete the nuclear reactions leading to various fluorine isotopes.

a) $^{18}O + {}^{1}_{1}H \rightarrow ..... + {}^{18}F$

b) $..... + {}^{2}_{1}D \rightarrow {}^{18}F + \alpha$

c) $^{19}F + {}^{2}_{1}D \rightarrow {}^{20}F + ...$

d) $^{16}O + ... \rightarrow {}^{18}F + {}^{1}_{1}H + n$

5.8 The decay mode of unstable light nuclei depends on the ratio between the number of neutrons and protons in them. If this ratio is greater than that for a stable isotope then the nucleus decays in a β^--mode, if it is smaller – in a β^+-mode.

Determine the type of decay for the nuclei in the table:

Nucleus	^{11}C	^{20}F	^{17}F	^{14}C
Decay mode				

When nuclear reaction (a) is used for fluorine-18 preparation, the target material is presented as water enriched with $H_2{}^{18}O$. The presence of usual water $H_2{}^{16}O$ leads to a side nuclear reaction with ^{16}O, leading to the formation of isotope ^{17}F.

5.9 It is known that within five minutes after completion of irradiation of the target the ratio of radioactivities of ^{18}F and ^{17}F is 1.10^5. Assuming that irradiation time is short, the radioactivity of each isotope is proportional to the nuclear reaction yield and the mole fraction of a component in the irradiated target, <u>calculate</u> the mass fraction of $H_2{}^{18}O$ in the target. $t_{1/2}(^{18}F)$ = 109.7 minutes, $t_{1/2}(^{17}F)$ = 65 seconds. The ratio between nuclear reactions yields is $\eta_{^{18}O\,-\,^{18}F} / \eta_{^{16}O\,-\,^{17}F} = 144.7$.

5.10 Calculate the yield of labeling D-glucose with fluorine-18, if initial radioactivity of a fluorine-18 sample was 600.0 MBq and radioactivity of the obtained 2-deoxy-2-(^{18}F)fluoro-D-glucose is 528.2 MBq. Synthesis time is 3.5 minutes.

5.11 Biological half-life (through the excretory organs) of 2-deoxy-2-(^{18}F)fluoro-D-glucose is 120.0 minutes. How much radioactivity (in MBq) will remain in the patient ten hours after injection of FDG with the initial radioactivity of 450.0 MBq.

SOLUTION

5.1 $C_6H_{12}O_6 + 2\ Cu^{2+} + 5\ OH^- \rightarrow C_6H_{11}O_7^- + Cu_2O + 3\ H_2O$

5.2 $2\ CuSO_4 + 4\ KI \rightarrow 2\ CuI + I_2 + 2\ K_2SO_4$

or $2\ Cu^{2+} + 4\ I^- \rightarrow 2\ CuI + I_2$

$KI + I_2 = KI_3$

or $I^- + I_2 = I_3^-$

$C_6H_{11}O_7^- + H_2SO_4 \rightarrow C_6H_{12}O_8 + HSO_4^-$

$2\ Na_2S_2O_3 + I_2 \rightarrow 2\ NaI + Na_2S_4O_6$

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

5.3 The **t**otal amount of copper(II) is 0.05000 dm^3 × 0.04000 mol dm^{-3} = 2.000 mmol.

Obviously, there is an excess of iodine and the remaining iodine was titrated with sodium thiosulphate: 11.87 cm^3 × 0.05078 mol dm^{-3} = 0.6028 mmol.

2.0000 mmol – 0.6028 mmol = 1.3972 mmol of copper(II) was required to oxidize the sugars.

n(sugars) = n(Cu^{2+}) / 2 = 0.6986 mmol in 10.00 cm^3

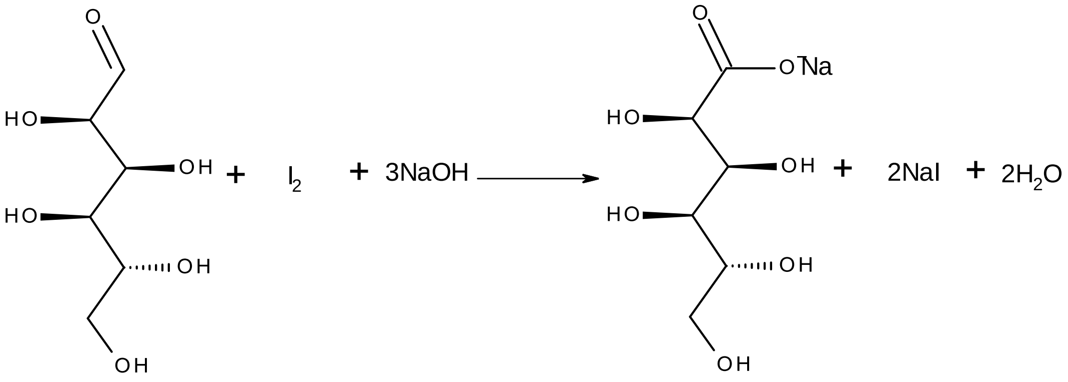
c(sugars) = 0.6986 mmol / 10.00 cm^3 = 0.06986 mol dm^{-3}

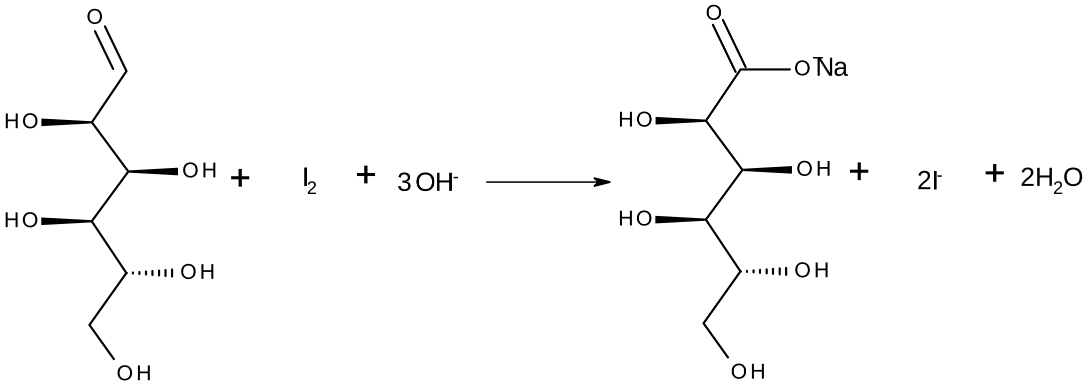
mass concentration = 180.16 g mol^{-1} × 0.06986 mol dm^{-3} = 12.6 g dm^{-3}

5.4 $KIO_3 + 5\ KI + 3\ H_2SO_4 \rightarrow 3\ I_2 + 3\ K_2SO_4 + 3\ H_2O$

$IO_3^- + 5\ I^- + 6\ H^+ \rightarrow 3\ I_2 + 3\ H_2O$

Only glucose was oxidized with iodine





5.5 Total amount $n(I_2) = 3\,n(IO_3^-) = 3 \times 0.01502\ \text{mol dm}^{-3} \times 10.00\ \text{cm}^3 = 0.4506$ mmol

$n(S_2O_3^{2-}) = 23.43\ \text{cm}^3 \times 0.01089\ \text{mol dm}^{-3} = 0.2552$ mmol

$n(S_2O_3^{2-}) / 2 = n(I_2) = 0.1276$ mmol

0.4506 mmol – 0.1276 mmol = 0.3230 mmol of iodine was used to oxidize glucose

c(glucose) = 0.3230 mmol / 10.00 cm^3 = 0.03230 mol dm^{-3}

mass concentration of glucose = 180.16 g mol^{-1} × 0.03230 mol dm^{-3} = 5.82 g dm^{-3}

mass concentration of fructose = 12.6 – 5.82 = 6.78 g dm^{-3}

5.6 0.200 dm^3 × 5.82 g dm^{-3} = 1.16 g of digestible carbohydrates, i e.

or 0.200 dm^3 × 12.6 g dm^{-3} = 2.52 g, i. e. 0.2 BEU

5.7

a) $^{18}O + {}^{1}_{1}H \rightarrow n + {}^{18}F$

b) $^{20}Ne + {}^{2}_{1}D \rightarrow {}^{18}F + \alpha$

c) $^{19}F + {}^{2}_{1}D \rightarrow {}^{20}F + {}^{1}_{1}H$

d) $^{16}O + \alpha \rightarrow {}^{18}F + {}^{1}_{1}H + n$

5.8

Nucleus	^{11}C	^{20}F	^{17}F	^{14}C
Decay mode	β^+	β^-	β^+	β^-

5.9 Radioactivity is:

$A = \lambda N$, where N is the number of atoms, $\lambda = \ln 2 / t_{1/2}$

The initial ratio of radioactivities:

$$\frac{A_0(^{18}F)}{A_0(^{17}F)} = \frac{\lambda\,(^{18}F)}{\lambda\,(^{17}F)} \cdot \frac{\eta\,(^{18}O \rightarrow {}^{18}F)}{\eta\,(^{16}O \rightarrow {}^{17}F)} \cdot \frac{\chi\,(H_2\,{}^{18}O)}{\chi\,(H_2\,{}^{16}O)} = \frac{65/60}{109.7} \cdot 144.7 \cdot \frac{\chi\,(H_2\,{}^{18}O)}{\chi\,(H_2\,{}^{16}O)} = 1.43\,\frac{\chi\,(H_2\,{}^{18}O)}{\chi\,(H_2\,{}^{16}O)}$$

After 5 minutes the ratio changed due to radioactive decay of fluorine:

$$\frac{A_{300}(^{18}\text{F})}{A_{300}(^{17}\text{F})} = \frac{A_0\ (^{18}\text{F})\ \exp\left(-\ \frac{\ln 2}{109.7}\ \times\ 5\right)}{A_0\ (^{17}\text{F})\ \exp\left(-\ \frac{\ln 2}{65}\ \times 300\ \right)} = 23.75\ \frac{A_0(^{18}\text{F})}{A_0(^{17}\text{F})} = 33.94\ .\ \frac{\chi\ (\text{H}_2\ ^{18}\text{O})}{\chi\ (\text{H}_2\ ^{16}\text{O})} = 10^5$$

$$\frac{\chi\ (\text{H}_2\ ^{18}\text{O})}{\chi\ (\text{H}_2\ ^{16}\text{O})} = 2947$$

Mass fraction of $H_2{}^{18}O$ is:

$$\omega(\text{H}_2\ ^{18}\text{O}) = \frac{2947 \times 20}{2947 \times 20\ +\ 18} = 0.9997$$

$\omega(H_2{}^{18}O) = 0.9997 = 99.97\%$.

5.10 During the synthesis, the radioactivity will decrease:

$$A_{3.5} = A_0\ \exp\left(-\ \frac{\ln 2}{109.7}\ \times\ 3.5\right) = 586.9\ \text{MBq}$$

$\eta = 528.2 / 586.9 = 0.900 = 90.0\%$

5.11 Radioactivity is excreted by radioactive decay and through the excretory organs (e.g. kidneys). The excretion process may be considered as two competitive first-order reactions. Activity after one hour is:

$$A_{60} = A_0\ \exp(-\ (\lambda_1\ + \lambda_2)t) = 450\ \exp\left(\ -\left(\frac{\ln 2}{109.7}\ +\ \frac{\ln 2}{120}\right)\times\ 600\right) = 0.32\ \text{MBq}$$

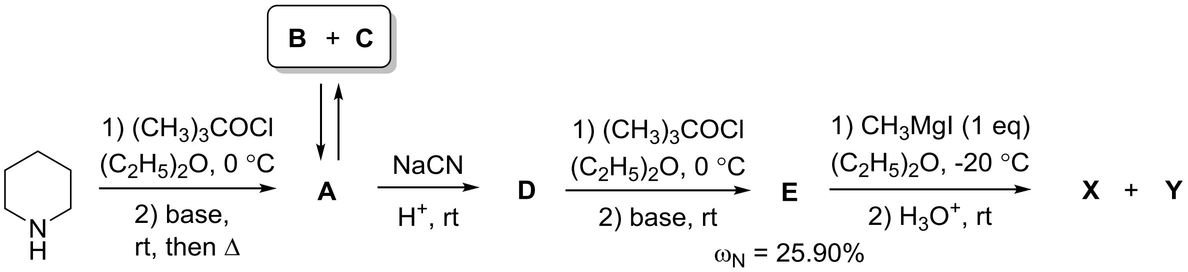
PROBLEM 6

Bread is the stuff of life

When you pass by the bakery, you are stopped by the smell of freshly baked bread. The hero of one of the novels said on a similar occasion: "If you tell me that this is not perfect, you are my enemy forever." The principle bread flavour component was identified in 1969 as compound **X** which occurs in equilibrium with its tautomer **Y** in a 2 : 1 ratio. Unfortunately, both forms are labile, and after some hours bread has no the same nice smell.

This tautomeric mixture of **X** and **Y** was synthesized in 1993 from piperidine by the reaction sequence given in Scheme 1. It is noteworthy that the initial ratio of **X** and **Y** was 1:4; on standing this ratio gradually changed to an equilibrium one.

Scheme 1.



Compound **B** which is characterized by 3-fold axis of symmetry (*i.e.*, rotation by 120° results in a molecule indistinguishable from the original) occurs in equilibrium with its diastereomer **C**. The interconversion of these two forms proceeds *via* intermediate **A** which is also intermediate in **B** and **C** formation as well as their transformation to **D**. Compounds **A**, **B**, and **C** have the same elemental composition: w_C = 72.24 %, w_H = 10.91 %, w_N = 16.85 %.

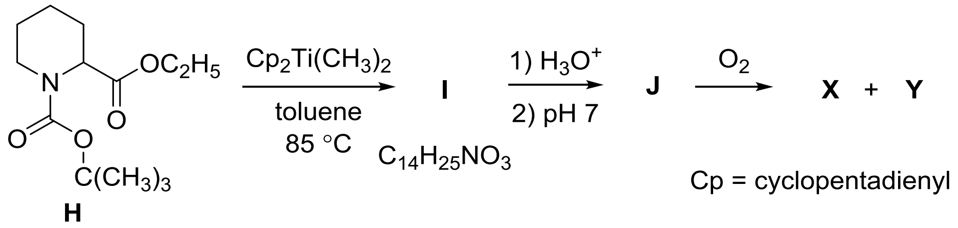
6.1 Write down the structural formulae of compounds **A** - **E**, **X**, **Y**.

Treatment of compound **E** with $CH_3Li \cdot LiBr$ complex in $(C_2H_5)_2O$ at 0 °C failed to produce the target products **X** and **Y**. Instead, a yellow precipitate **F** was initially formed. Aqueous workup of this precipitate led to the mixture of compound **E** and its tautomer **G.**

6.2 Write down the structural formulae of compounds **F** and **G**.

Another approach to compound **X** is based on the use of pipecolinic acid derivative **H**. It was shown that **X** can be synthesized by reaction sequence presented in Scheme 2.

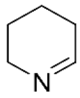
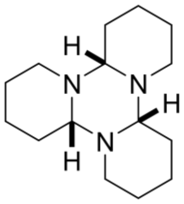
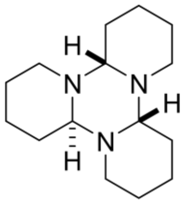
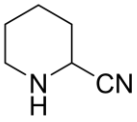
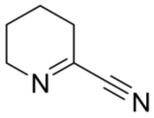
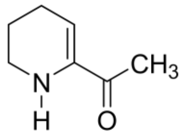
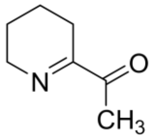
Scheme 2



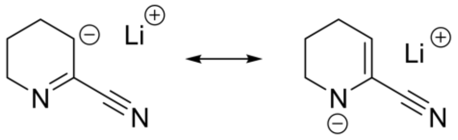
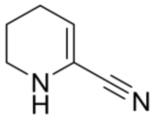
6.3 Write down the structural formulae of compounds **I** and **J**.

SOLUTION

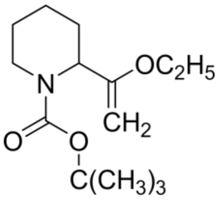
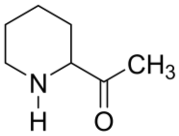
6.1

A	**B**	**C**
		
D	**E**	**X**
		
	Y	
		

6.2

F	**G**
	

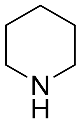
6.3

I	J
	

PROBLEM 7

Not by bread alone

Pomegranate is called in Azerbaijan, which is famous for its vegetables, as the "king of all fruits". Pomegranate is honored in various religions as a "fruit of Paradise", symbol of righteousness, wealth, hope for eternal life.

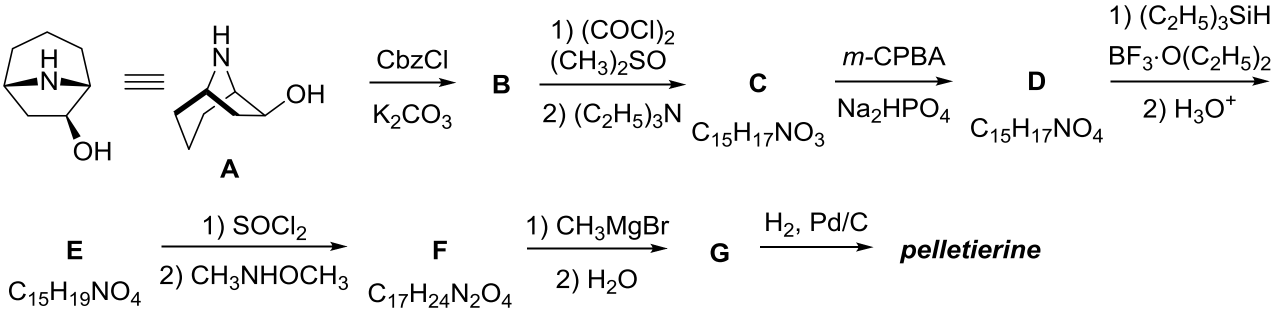


piperidine

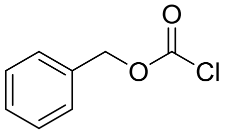
In 1878 alkaloid ***pelletierine*** was isolated from the bark of pomegranate tree (*Punica granatum* L., *Lythraceae*). This alkaloid is traditionally used as an anti-helminthic drug. Initially **X**$_W$ (3-(piperidin-2-yl)propanal) was incorrectly proposed for pelletierine. But now it is accepted that natural pelletierine is (*S*)-1-(piperidin-2-yl)propan-2-one (**X**$_S$).

7.1 Write down the structural formulae of **X**$_W$ and **X**$_S$ (the latter – with the stereochemical information).

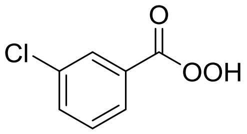
The synthesis of natural pelletierine (**X**$_S$) based on the transformation of nortropanol **A** was recently described.



CbzCl =



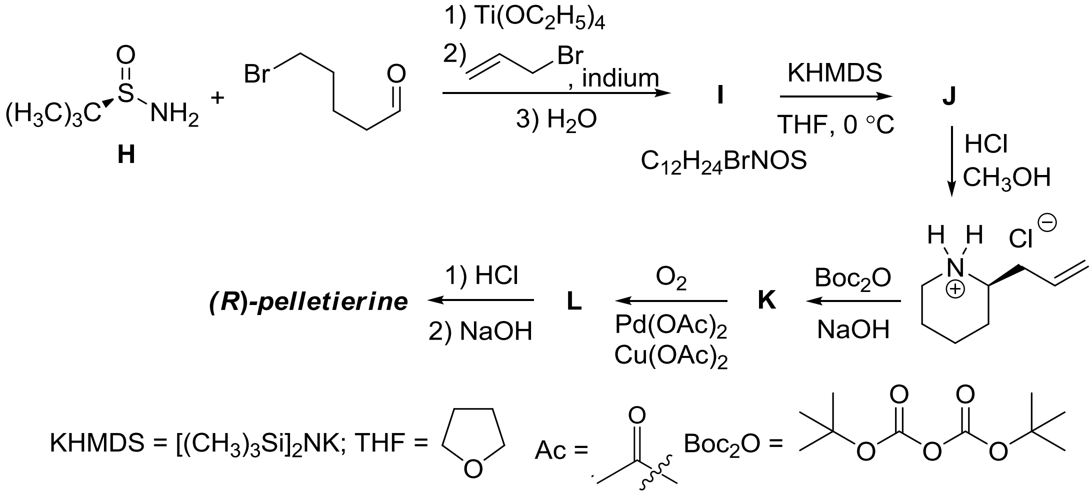
m-CPBA =



7.2 Write down the structural formulae of compounds **B - G** with the stereochemical information.

7.3 Nortropanol **A** was used in this reaction as a single stereoisomer. How many stereoisomers can exist for compound **A** (including **A**)? Ignore nitrogen chirality.

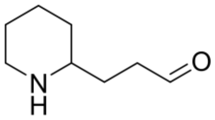
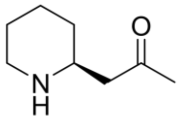
Enantiomer of **X**$_S$ was synthesized using chiral *tert*-butanesulfinamide (**H**):



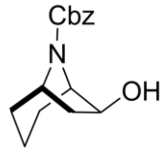
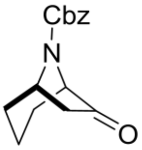
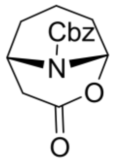
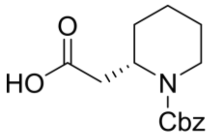
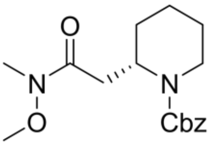
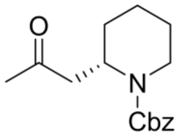
7.4 Write down the structural formulae of compounds **I – L** with the stereochemical information.

SOLUTION

7.1

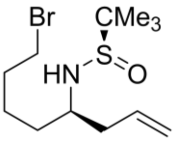
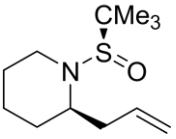
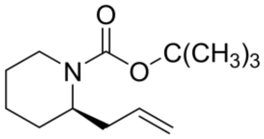
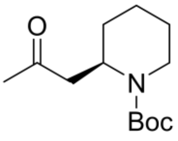
X_W	X_S
(3-(piperidin-2-yl)propanal)	(*S*)-1-(piperidin-2-yl)propan-2-one
	

7.2

B	C	D
		
E	**F**	**G**
		

7.3 The number of possible stereoisomers of **A**: 4 .

7.4

I	J
	
K	**L**
	

PROBLEM 8

Oil for Life and Life after Oil

Azerbaijan is known for its vast oil and gas fields. The first drilling for oil was done in Bibi-Heybat in 1846, 13 years before establishment of the first commercial oil well in Pennsylvania (USA). This remarkable date in the history of Azerbaijan is regarded as a starting point of contemporary oil industry, the leading sector of today's world economy. Currently, on-land and shelf sea oil production is being developed in Azerbaijan. Though serious precautions are taken, there is always a risk of hydrocarbon pollution of the environment during production, transportation, and processing of oil. In this task we will consider diverse technologies of oil spills clean up and specific features of metabolic pathways involved.

Application of complex solvents (dispersants) leading to capture of marine oil spills is among most promising clean up approaches. Organic substance **X** (11.94 % of H by mass) is a typical component of such dispersants. Safety of **X** to human is fiercely debated. **X1** (54.53 % of carbon by mass) composed of three elements and excreted with urine is the major metabolite of **X** in humans. The numbers of atoms of different elements in **X1** are three consecutive terms of a geometric progression (n, nq, nq^2), whereas the sum of these numbers does not exceed 25.

8.1 Decide on the relationship (tick the correct variant) between the numbers of carbon and oxygen atoms in **X1**.

$n(C) > n(O)$	$n(C) < n(O)$	$n(C) = n(O)$	Data insufficient
☐	☐	☐	☐

8.2 Derive the empirical formula of **X1** (hereafter always show your work where required). Be sure you prove the answer by calculations.

The biotransformation of **X** into **X1** occurs in two enzymatically catalyzed steps according to the hereunder reaction balanced equations (NAD$^+$ and NADH are the oxidized and reduced forms of nicotinamide adenine dinucleotide, respectively):

$$\mathbf{X} + NAD^+ \rightarrow \mathbf{X0} + NADH + H^+ \qquad (1)$$

$$\mathbf{X0} + NAD^+ + H_2O \rightarrow \mathbf{X1} + NADH + H^+ \qquad (2)$$

8.3 Derive the molecular formula of **X**.

A minor metabolic transformation of **X** is catalyzed by cytochrome P450-dependent monooxygenase. This reaction leads to two compounds **X2** (51.56 % of oxygen and 9.74 % of hydrogen by mass) and **X3**.

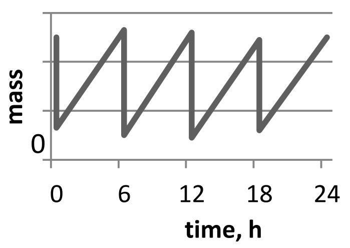
8.4 Derive the molecular formula of **X2** and draw its structure.

X contains only primary and secondary carbon atoms. **X0** and **X3** contain common functional group.

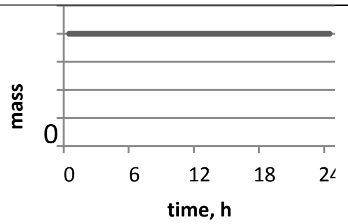
8.5 Draw the structural formulae of **X**, **X1**, and **X3**.

In a medical study, personnel permanently exposed to **X**-based solvents without proper protection was found to have a stationary concentration of **X** in blood.

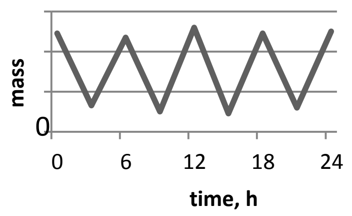
8.6 **X1** is excreted with urine. Choose the graph of **X1** daily <u>mass content</u> in the body of a volunteer participated in this experiment. Write down the number of the correct graph.



1



2



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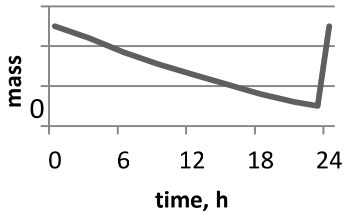

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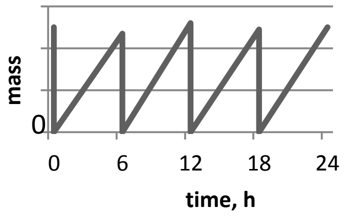

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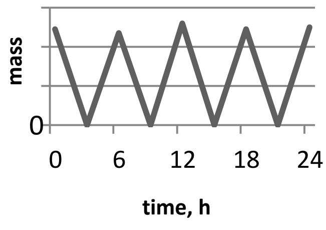
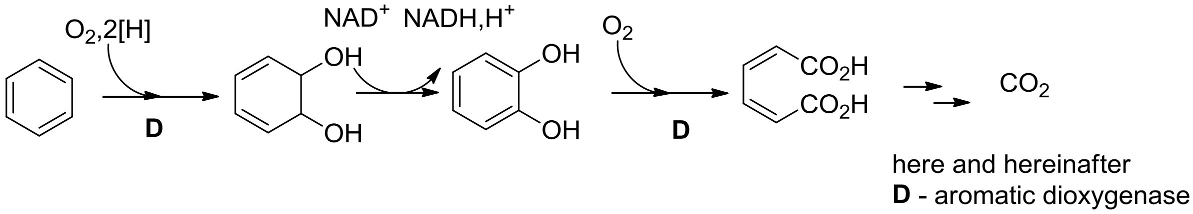
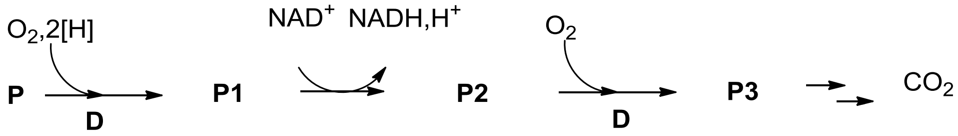


6

The use of different bacteria is also considered as a promising way for the removal of hydrocarbon (even aromatic) contaminants from sea water and soil. Under aerobic conditions, benzene undergoes biodegradation as follows (first three steps are balanced):



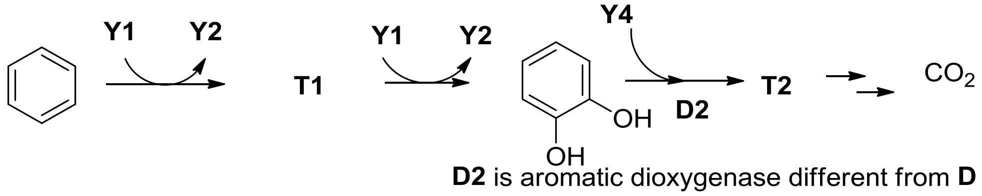
Under the same conditions, a monocyclic aromatic hydrocarbon **P** (91.25 % of carbon by mass) undergoes the following transformation (first three steps are balanced):



P3 gives a positive iodoform test. A 100 mg sample of **P3** requires 6.41 cm^3 of KOH (c = 0.100 mol dm^{-3}) solution for complete neutralization.

8.7 Derive the structures of **P–P3**. Give the most stable tautomer of **P3**.

Microorganisms *Alicycliphilus* are capable of biodegradation of aromatic hydrocarbons even in soil. The process requires a suitable electron acceptor such as inorganic anion **Y1** (first three steps are balanced).



The intermediate anion **Y2** is enzymatically decomposed according to the balanced reaction equation:

$$\mathbf{Y2}(aq) \rightarrow \mathbf{Y3}(aq) + \mathbf{Y4}(g),$$

wherein each of **Y3** and **Y4** is composed of atoms of only one element. **T2** does not contain two identical oxygen-containing functional groups. **T2** gives a precipitate when treated with the ammonia solution of Ag_2O, whereas **Y3** does not.

8.8 Deduce and give formulas of **Y1-Y4**. Draw the structures of **T1-T2**. Give the most stable tautomer of **T2**.

SOLUTION

8.1

n(C) > n(O)	n(C) < n(O)	n(C) = n(O)	Data insufficient
☑	☐	☐	☐

8.2 With regard to 8.1 three variants [n(H)>n(C)>n(O), n(C)>n(H)>n(O), and n(C)>n(O)>n(H)] are possible for **X1**. For each inequality, one can write down the corresponding formula using elements of a geometric progression (q is the progression common ratio), equations for calculation of mass fractions of carbon and its roots

Inequality	Formula	Equation	The first root (q_1)	The second root (q_2)
n(H)>n(C)>n(O)	$C_{qn}H_{q2n}O_n$	$\frac{12.01\,qn}{12.01\,qn + 1.008\,q^2n + 16.00\,n} = 0.5453$	2.00	7.93
n(C)>n(H)>n(O)	$C_{q2n}H_{qn}O_n$	$\frac{12.01\,q^2n}{12.01\,q^2n + 1.008\,qn + 16.00\,n} = 0.5453$	–1.21	1.32
n(C)>n(O)>n(H)	$C_{q2n}H_nO_{qn}$	$\frac{12.01\,q^2n}{12.01\,q^2n + 1.008\,n + 16.00\,qn} = 0.5453$	–0.06	1.66

There is only one positive integer root, thus the empirical formula of **X1** is C_2H_4O.

8.3 Since (1) and (2) are the reaction equations, one can write down the formula of **X** as:

$C_{2n}H_{4n}O_n + 2\ H - 1\ O = C_{2n}H_{4n+2}O_{n-1}$.

With an account for the known mass fraction of hydrogen:

$$\frac{1.008\,(4n + 2)}{12.01 \times 2n + 1.008\,(4n + 2) + 16.00\,(n - 1)} = 0.1194$$

Finally, $n = 3$, and the molecular formula of **X** is $C_6H_{14}O_2$.

8.4 **X2** is formed from **X** composed of three elements (C, H, and O) via a monooxygenase catalyzed reaction:

$$n(\text{C}) : n(\text{H}) : n(\text{O}) = \frac{100 - 51.56 - 9.74}{12} : \frac{9.74}{1.008} : \frac{51.56}{16.00} = 1 : 3 : 1$$

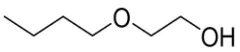
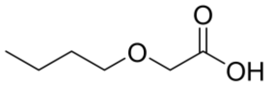
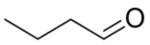
Since the number of hydrogen atom is necessarily even, the molecular formula of **X2** is $C_2H_6O_2$. Other variants with a higher even number of hydrogen are not valid.

Ethylene glycol $HOCH_2CH_2OH$ is the only stable substance with the molecular formula deciphered above.

Ethylene glycol $HOCH_2CH_2OH$ is the only stable substance with the molecular formula deciphered above.

Molecular formula of **X2**: $C_2H_6O_2$	Structure of **X2**: $HO–CH_2–CH_2–OH$

8.5

 **X**	 **X1**	 **X3**

8.6 Number of the correct graph: **1**

8.7 Dioxygenase incorporates two oxygen atoms in vicinal positions of the substrate, which can be followed by chemical bonds reorganization. The empirical formula of the hydrocarbon **P** is C_7H_8

$$C : H = \frac{91.25}{12.01} : \frac{100 - 91.25}{1.008} = 7 : 8$$

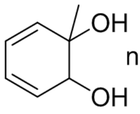
Thus, it is toluene.

The molar mass of **P3** equivalent containing acidic group(s) is

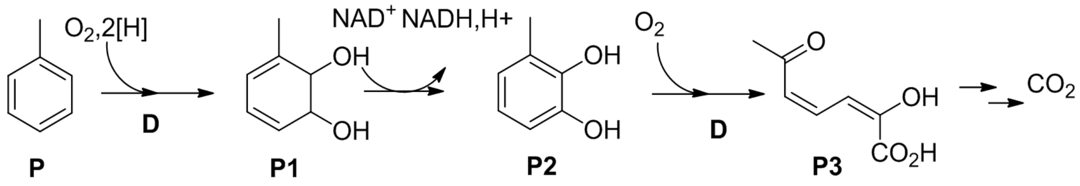
$$\frac{100}{6.41 \times 0.100} = 156 \text{ g mol}^{-1}$$

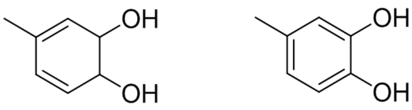
Two dioxygenase steps suggest the composition of $C_7H_8O_4$.

P3 must be a monocarboxylic acid if it still contains seven carbon atoms. Fragments containing a $CH_3CO–$ group (or a $CH_3CH(OH)–$ group further transforming into $CH_3CO–$ one) are involved into the iodoform reaction. This suggests splitting of the benzene moiety during the second oxygenase step at the carbon connected to the methyl group.



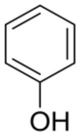
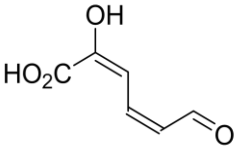
no way to re-aromatization





no way to acetylcarbonic acid

8.8

Y1	Y2	Y3
ClO_3^-	ClO_2^-	Cl^-
Y4	**T1**	**T2**
O_2	 	

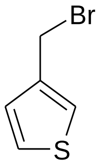
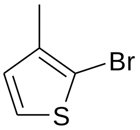
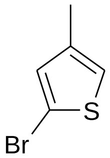
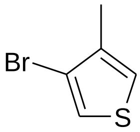
PRACTICAL PROBLEMS

PROBLEM 1P (Practical)

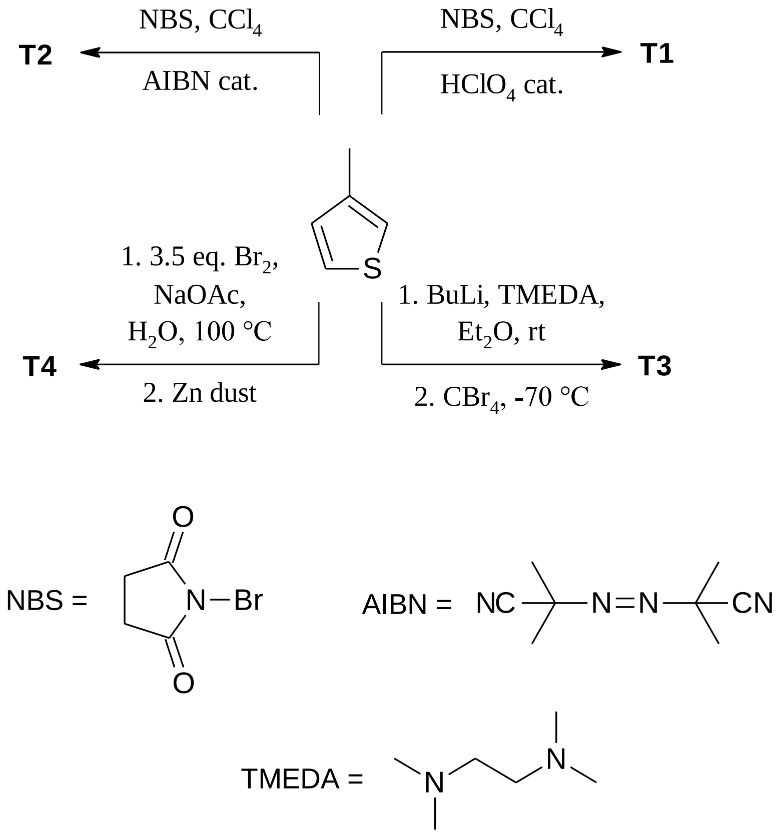
Tuning bromination selectivity by catalysis

Selectivity of chemical reactions is one of the most challenging problems of contemporary research. In many cases, reaction conditions and the catalysts applied are keys to achieving high selectivity of organic reactions. In this problem, you will study one of such cases. 3-Methylthiophene can theoretically be transformed into four monobrominated derivatives **T1–T4**, which have been actually synthesized and characterized in detail. Structures of **T1–T4** and the values of refractive indexes are given in Table 1.

Table 1. Structures and refractive indexes of monobrominated thiophenes.

Designation	**T1**	**T2**	**T3**	**T4**
Structure				
n_D^{20}	1.5961	1.5706	1.5786	1.5795

The selective synthesis of each of **T1-T4** can be performed using 3-methylthiophene as the starting material. **T1** and **T2** can be obtained by direct bromination using different catalysts, whereas **T3** and **T4** are the products of "one pot" multistep synthesis (see Scheme 1).



Scheme 1. Selective synthesis of monobrominated thiophenes.

Task 1.1 Assign the structures given in Scheme 1 with **T1, T2** to the structures given in the Table 1. Fill in the boxes below with one of A - B.

☐ **T1** ☐ **T2**

In this problem you will:

- synthesize a monobrominated thiophene derivative using one of the catalysts from the list below,
- measure the product refractive index (n_D),
- compare the results obtained with literature data and decide on the structure of the product and the catalysts given.

List of possible catalysts

- $HClO_4$ in CCl_4
- AIBN in CCl_4

<u>Chemicals</u>

- 3-Methyl-thiophene, solution in CCl_4, 4g / 8 cm^3
- 1-Bromo-2,5-pyrrolidinedione (NBS), solid, 7.3 g

- Carbon tetrachloride, liquid, 24 cm^3
- Unknown catalyst in CCl_4, in plastic vial, 4 cm^3
- Potassium carbonate, solid, 0.02 g

Chemical Glass and Equipments

- 2 Laboratory stands
- Round-bottom three-necked flask, 100 cm^3
- Reflux condenser, connected to water supply
- 6 Glass ground joint stoppers
- Dropping funnel, 50 cm^3
- Oval magnetic stir-bar (big)
- Pear-shaped round-bottom flask for distillation, 50 cm^3
- Claisen distillation adapter
- Thermometer with fixed ground joint tube
- Buchner type fritted glass filter
- Rubber spacer for vacuum filtration
- Liebig (downward) condenser
- Distilling receiver cow
- 4 Receiver flasks, 10 cm^3
- Receiver flask, 50 cm^3
- Adjustable lab jack lift support
- Oval magnetic stir-bar (small)
- Plastic beaker, 50 cm^3
- Teflon sleeves for ground tapered joints
- Large funnel, 65 mm, with short stem
- 5 Joint clips
- Grey clamp
- Red clamp
- Permanent marker
- Glass beaker, 25 cm^3
- Plastic container labeled “Used glassware”
- Plastic container labeled “Ice bath”
- Digital manometer
- Spatula
- Glass rod

PROCEDURE

Note!

- *Apparatuses used in this problem are shown in Fig. 1 and 2.*
- *Always equip every joint with the Teflon sleeve. Immediately place every piece of the used glassware in the corresponding container. Always keep the container tightly closed.*
- *You can use cotton gloves when handling hot things!*

Step 1. Clamp the three-necked flask on the laboratory stand on top of the hot-plate magnetic stirrer. (Fig.1). Apply the dropping funnel and the reflux condenser to the corresponding necks and put the big magnetic stir-bar into the flask through the open neck. Ask your lab assistant to switch on water supply in the reflux condenser (**Do not do it yourself!**). Transfer NBS quantitatively into the flask using spatula and big plastic funnel. Transfer ~15 cm^3 of CCl_4 into the 25 cm^3 glass beaker. Pour ~2/3 of the solvent volume from the beaker into the flask. Shake the Catalyst and quantitatively add it through the same plastic funnel into the flask. Add the rest of the solvent from the beaker to the flask. Close the open neck with the stopper. Put the flask into the ice bath filled with water and ice to ~ 2/3 of its volume. Start stirring the mixture.

Step 2. Using the big plastic funnel quantitatively transfer the solution of 3-methylthiophene to the dropping funnel with **tap closed**. Apply a piece of the cotton wool to the open end of the dropping funnel and reflux condenser. Under vigorous stirring, add the solution of 3-methylthiophene dropwise during ~ 3 min. Replace the dropping funnel by a glass stopper. Use the Teflon sleeve. Remove the ice bath. Dry the plate and bottom of the flask with napkin.

Step 3. Wrap up the flask with aluminum foil. Switch on the heater (position 3). Bring up the mixture to boiling and boil it for 10 min. Prepare the ice bath (~2/3 of the volume) while the mixture boils.

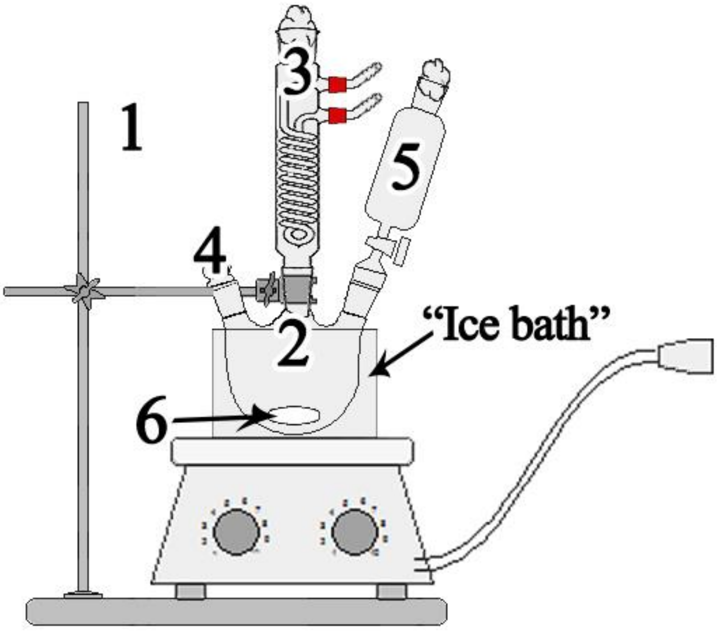


Fig. 1. Set up needed to implement Steps 1-4 of the synthesis.

The particular parts of the apparatus: 1 - laboratory stand, 2 - round-bottom three-necked flask, 3 - reflux condenser, connected to water supply, 4 - glass ground joint stopper, 5 - dropping funnel, 6 - oval magnetic stir-bar (big).

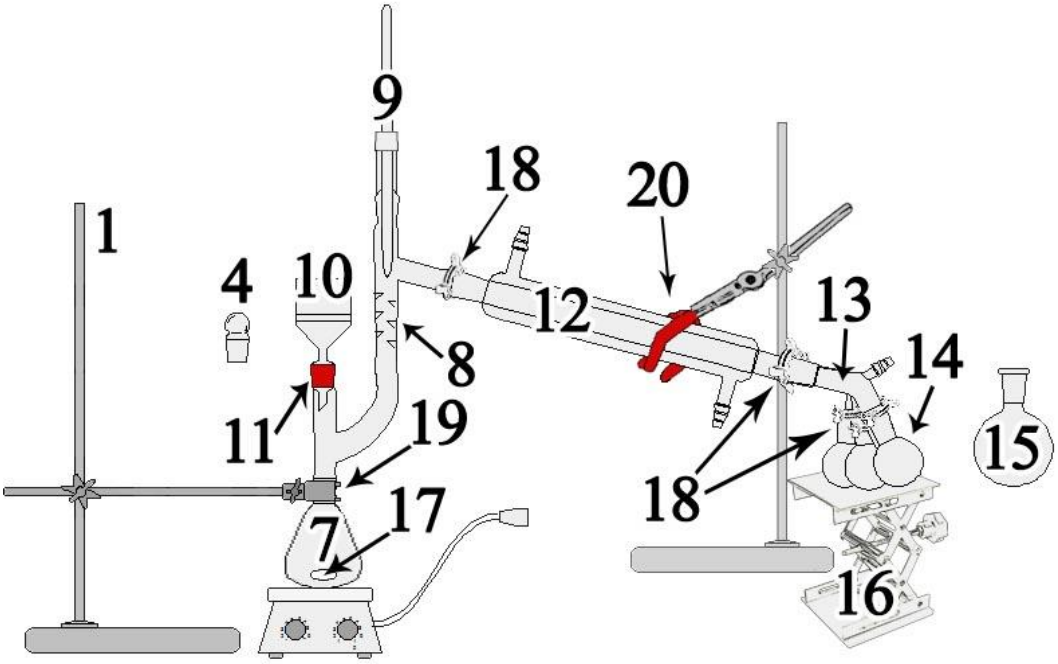


Fig. 2. Set up needed to implement Steps 5-10 of the synthesis.

The particular parts of the apparatus: 1 - laboratory stand, 4 - glass ground joint stopper, 7 - pear-shaped round-bottom flask, 8 - Claisen distillation adapter, 9 - thermometer with fixed ground joint tube, 10 - Buchner type fritted glass filter, 11 - rubber spacer for vacuum filtration, 12 - Liebig condenser, 13 - distilling receiver cow, 14 - receiver flask, 10 cm^3, 15 - receiver flask, 50 cm^3, 16 - lift support, 17 - oval magnetic stir-bar, 18 - joint clips, 19, 20 – clamps.

Step 4. Switch off the heater and carefully **(hot!)** remove the hot-plate magnetic stirrer aside. Dip the flask equipped with the condenser and stoppers into the ice bath for 3-5 min. Keep gently swirling the flask from time to time to provide the faster cooling. Then remove the reflux condenser and load 0.02 g of K_2CO_3 using the big funnel applied to the open neck. Close the neck with a glass stopper and shake the flask several times. Turn off the water supply and unscrew the adaptors of the tubings from the reflux condenser. Let the residual water leak out of the condenser and immediately place it into the container for the used glassware. Remove the clamp keeping the flask in the ice bath.

Step 5. Weigh the 10 cm^3 receiver flask for product with the glass stopper, both marked with your student code. Write down the value in the answer sheet. Put the small magnetic stir-bar in the 50 cm^3 pear-shaped distillation flask. Screw on the adaptors with tubings to the Liebig condenser and fix it on the stand with the red clamp. Turn on the water supply yourself and make sure there is no water leakage.

Step 6. Assemble the distillation apparatus as shown on Fig. 2 supplying all the joints with the teflon sleeves and clips. First, attach two 10 cm^3 and one 50 cm^3 receiver flasks to the distilling receiver cow. Then connect the vacuum hose to the cow and complete assembling. Fix the apparatus over the magnetic stirrer to adjust it on height. Use the adjustable lab jack lift support.

Step 7. Remove the hot-plate magnetic stirrer aside. Insert the fritted glass filter into the Claisen distillation adapter using the rubber spacer. Turn on the water-jet pump and switch on the digital manometer. Remove the three-necked flask from the ice bath and dry it with a napkin. Carefully transfer the reaction mixture from the three-necked flask to the filter (**Attention! If you do it too fast, the mixture can be partially sucked into the curved part of the adaptor**). When finished, turn off the pump and replace the filter with a glass stopper, use the teflon sleeve.

Step 8. Tightly wrap up the flask and distillation adaptor with aluminum foil up to the thermometer joint. Bring back the magnetic stirrer and turn on stirring and heating (position 6). **Do not turn on the water-jet pump!** Collect the distilled solvent into the 50 cm^3 receiver. When the solvent distillation is over, turn off heating and stirring and carefully **(hot!)** remove the hot-plate magnetic stirrer aside. Replace the receiver flask containing the distilled solvent by a new 10 cm^3 receiver. Close the 50 mL flask with a glass stopper and deliver it to your lab assistant.

Step 9. Remove the foil and put the pear-shaped bottom flask into the ice bath for 2-3 min to bring the temperature below ambient. Remove the ice bath; dry the flask with a napkin. Bring back the magnetic stirrer under the flask **(Attention! The hot-plate may be still hot!).** Turn on stirring. Wrap up the flask tightly with aluminum foil. Switch on the water-jet pump. When vacuum is stabilized (follow the reading of the digital manometer), turn on the heater (position 6). Observe the initial stage of the targeted product distillation and collect the first 3-5 drops into an attached receiver flask not labeled with your student code. Then rotate the cow and collect the targeted product into the receiver flask with your student code. Write down the product boiling point and pressure reading from the digital manometer into the answer sheet.

Step 10. When the targeted product is collected, turn off the heater, remove the foil and carefully **(hot!)** remove the hot-plate magnetic stirrer aside. Cool down the apparatus to ambient temperature using the ice bath. **Ask your lab assistant to disconnect the vacuum line.** Disconnect the receiver flask with the targeted product and **immediately** close it with the glass stopper labeled with your student code. Do not attempt to drag the teflon sleeve out if it remains in the receiver. Place the flask into the 50 cm^3 plastic beaker labeled "For the receiver with the product". Immediately attach a new receiver instead of the removed one and apply the joint clip. **Leave the apparatus as it is.**

Step 11. Measure the refraction index **(before weighing)** following the instruction below. Record the temperature from the refractometer.
Weigh the receiver with the targeted product closed with the labeled stopper. Calculate the mass and yield of the product (take the mass of the teflon sleeve equal to 149 mg). The molar masses of 3-metylthiophene and the product equal 98 and 177 g mol^{-1}, respectively.

Task 1.2 Write down all the results in the hereunder Table.

#	Parameter /Characteristics	Value	Units
1	Mass of the receiver flask with the glass stopper, both marked with student code		g
2	Mass of the product		g
3	Yield of the product		%
4	Refraction index for the product		-
5	Temperature recorded from the refractometer		°C

Table continued:

6	Boiling point of the product		°C
7	Pressure at the boiling point		mmHg

Task 1.3 By comparing the obtained and literature data, draw the structure of the product and catalyst given.

Task 1.4 Draw the structure of the 3-methylthiophene-based reactive intermediates behind the selectivity in the case of **T1** and **T2**.

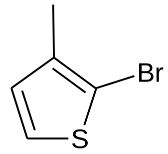
Task 1.5 Write down the product (**T1** or **T2**) formed as a result of direct bromination of 3-methylthiophene with NBS under the given conditions / catalyst used.

Task 1.6 In the synthetic pathways to **T3** and **T4**, draw the structures of the compounds formed in the first steps of each pathways shown on Scheme 1.

SOLUTION

1.1 T1 B T2 A

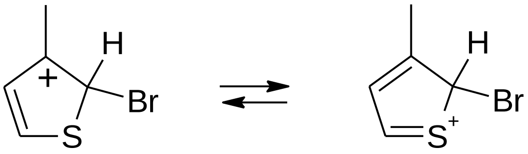
1.3 The product obtained:



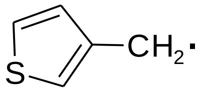
The catalyst given: $HClO_4$

1.4

T1



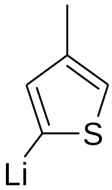
T2



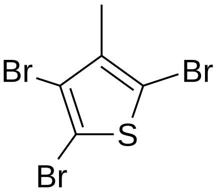
1.5

$ZnBr_2$	**T1**
Dibenzoyl peroxide	**T2**
LiBr in AcOH	**T1**
Visible light or UV light	**T2**

1.6 **T3**



T4



PROBLEM 2P (Practical)

Analysis of the solution of a chromium – vanadium alloy

Antiferromagnetic materials show a good prospect in the development of memory devices for ultra-high-density data storage, the world's smallest magnetic memory bit using only 12 atoms being one of prime examples. Vanadium – chromium alloys exhibit antiferromagnetic properties at subzero temperatures. It is obvious that composition of alloys used in various hi-tech applications should be accurately controlled.

In this problem you will analyze an aqueous solution simulating the product of digestion of vanadium – chromium alloy sample. The task consists of two parts:

I. Oxidation of vanadyl (VO^{2+}) to vanadate (VO_3^-) in the test solution using potassium permanganate, followed by determination **of vanadium** (note that chromium (III) is not oxidized under these conditions).

II. Oxidation of the test solution with ammonium persulfate, followed by titrimetric determination of the total content of vanadium and chromium with Mohr's salt (Ammonium iron(II) sulfate).

Chemicals

- Test aqueous solution containing VO^{2+} and Cr^{3+} (to be determined), 100 cm^3,
- Sulfuric acid, aq., (c = 1 mol dm^{-3}), ~ 500 cm^3,
- Potassium permanganate, aq., (c = 0.03 mol dm^{-3}), 15 cm^3,
- Oxalic acid, aqueous solution, (c = 0.03 mol dm^{-3}), 30 cm^3,
- Phenylanthranilic acid, aqueous solution, 0.1 %, 5 cm^3, indicator in a dropper,
- Ammonium iron(II) sulfate, Mohr's salt, aqueous solution, 100 cm^3, (concentration given on the label),
- Silver nitrate, aqueous solution, 0.3 %, 5 cm^3 in a dropper,
- Ammonium persulfate, aqueous solution, 10 %, 70 cm^3.

Chemical Glass and Equipments

- Laboratory stand
- Clamp for burette
- Plastic beaker, 100 cm^3,
- Glass beaker, 150 cm^3
- Volumetric flask with a stopper, 100 cm^3

- Small funnel, (45 mm)
- Medium-size funnel, (55 mm)
- Watch glass
- Burette, 25.00 cm^3, clamped in the stand
- Volumetric pipette, 10.00 cm^3
- Graduated pipette, 5.00 cm^3
- 2 Erlenmeyer flasks, 150 cm^3
- Graduated cylinder, 100.0 cm^3
- 2 Pasteur pipettes
- White paper sheet
- Refractometer and its operating instructions
- Balances

Procedure

Note!

- The amount of vanadium and chromium should be calculated and reported in mg per 100 cm^3 of the test solution.
- Start doing this task with Part A, since you will need time to oxidize the test solution to be analyzed in Part C.

Part A. Preparation of the solution for determination of vanadium and chromium total content

1. Transfer a 10.00 cm^3 aliquot of your test solution into the 150 cm^3 beaker and add 20 cm^3 of sulfuric acid (c = 1 mol dm^{-3}) using the 25 cm^3 graduated cylinder.
2. Add 6–8 drops of the 0.3% solution of silver nitrate (the catalyst) and heat the mixture on the hotplate to 70 – 80 °C (position 3), until condensate on the beaker wall appears.
3. Add 20 cm^3 of the 10% ammonium persulfate solution to the heated mixture using the 100 cm^3 graduated cylinder.
4. Continue heating and observe the appearance of yellow color, indicating the formation of dichromate.

Note! You can perform the determination of vanadium (Part B, 1 – 6), while the mixture is being heated.

5. Keep heating the mixture for 10 - 15 min (position 3) after appearance of the yellow color to decompose the excess of ammonium persulfate (the decomposition is over when you see no small bubbles in the solution).

6. Cool the solution to ambient temperature.
7. Transfer quantitatively the solution from the 150 cm^3 beaker into the 100 cm^3 volumetric flask, dilute to the mark with distilled water, stopper the flask and mix thoroughly.

Part B. Titrimetric determination of Vanadium

1. Transfer a 5.00 cm^3 aliquot of the test solution into an Erlenmeyer flask using the graduated pipette.
2. Carefully add potassium permanganate solution (c = 0.03 mol dm^{-3}) dropwise, shaking the flask after adding each drop until light pink color appears. Make sure that the light pink color is stable. Remove the excess of potassium permanganate by adding oxalic acid solution (0.03 mol dm^{-3}) dropwise. Shake the flask after each drop until the light pink color changes to pale blue. Let the solution stand for about 1 min to make sure that the pink color has disappeared completely.
3. Transfer 10 cm^3 of H_2SO_4 solution (c = 1 mol dm^{-3}) into the Erlenmeyer flask using the 25 cm^3 graduated cylinder.
4. Add 2–3 (not more!) drops of the indicator into the Erlenmeyer flask and shake it vigorously. Let the flask stand for 2–3 min and observe the purple color appearance.
5. Fill the burette with the Mohr's salt solution. Use the 100 cm^3 plastic beaker labeled "Waste" to drain the excess of Mohr's salt solution from the burette, record the initial reading.
6. Titrate the solution in the Erlenmeyer flask with the Mohr's salt solution until the color changes to pure light green through brownish-grey one.
7. Take the final reading of the burette. Repeat as necessary.

Task 1. Fill in Table 2.

Table 2. Determination of vanadium

Titration №	1	2	3			
Initial reading of the burette, cm^3						
Final reading of the burette, cm^3						
Consumed volume, cm^3						

Accepted volume, V_1 _____cm^3

Part C. Titrimetric determination of vanadium and chromium total content in the test solution

1. Wash the 10.00-cm^3 volumetric pipette with distilled water, rinse with the solution prepared in 100-cm^3 volumetric flask (obtained in part A).
2. Pipette a 10.00-cm^3 aliquot into an Erlenmeyer flask, add 10 cm^3 of H_2SO_4 solution (c = 1 mol dm^{-3}) using the 25-cm^3 graduated cylinder.
3. Add 3–4 drops of the indicator. Vigorously shake the flask and let it stand for 3–4 min. Observe appearance of red color.
4. Fill the burette with the Mohr’s salt solution. Use the 100-cm^3 plastic beaker labeled “Waste” to drain the excess of Mohr’s salt solution from the burette, record the initial reading.
5. Titrate the solution in the flask with the Mohr’s salt solution until the color changes to light yellow-green.
6. Take the final reading of the burette. Repeat as necessary.

Task 2 Fill in Table 3.

Table 3. Determination of vanadium and chromium total content

Titration No	1	2	3			
Initial reading of the burette, cm^3						
Final reading of the burette, cm^3						
Consumed volume, cm^3						

Accepted volume, V_2 _____ cm^3

Part D. Tasks and Data Analysis

Task 3. Write down the balanced chemical equations for the reactions that take place upon:

a) oxidation of the test solution with potassium permanganate

b) titration of vanadate with Mohr’s salt

Task 4. Write down the balanced chemical equations for the reactions that take place upon:

a) oxidation of the test solution with ammonium persulfate
b) titration of the oxidized test solution with Mohr's salt

Task 5 Calculate the concentrations of

a) V(IV),
b) Cr(III)

in the test solution.

c) Calculate the mass of the metals in mg per 100 cm^3 of test solution.

Task 6 This protocol can not be applied to the determination of vanadium and chromium in steels, if the steel was digested by conc. HCl. Give equations of two reactions to explain the reasons behind**.**

SOLUTION

Task 3 a) $2\ KMnO_4 + 10\ VOSO_4 + 12\ H_2O = 2\ MnSO_4 + 10\ HVO_3 + K_2SO_4 + 7\ H_2SO_4$

b) $2\ HVO_3 + 2\ FeSO_4 + 3\ H_2SO_4 = 2\ VOSO_4 + Fe_2(SO_4)_3 + 4\ H_2O$

Task 4 a) $Cr_2(SO_4)_3 + 3\ (NH_4)_2S_2O_8 + 7\ H_2O = H_2Cr_2O_7 + 3\ (NH_4)_2SO_4 + 6\ H_2SO_4$

$2\ VOSO_4 + (NH_4)_2S_2O_8 + 4\ H_2O = 2\ HVO_3 + (NH_4)_2SO_4 + 3\ H_2SO_4$

b) $H_2Cr_2O_7 + 6\ FeSO_4 + 6\ H_2SO_4 = Cr_2(SO_4)_3 + 3\ Fe_2(SO_4)_3 + 7\ H_2O$

$2\ HVO_3 + 2\ FeSO_4 + 3\ H_2SO_4 = 2\ VOSO_4 + Fe_2(SO_4)_3 + 4\ H_2O$

Task 5 a) Calculation for vanadium:

$$c(\mathrm{VO^{2+}}) = \frac{V_1(\mathrm{Fe^{2+}}) \times c(\mathrm{Fe^{2+}})}{V(\mathrm{VO^{2+}})}$$

$$m(\mathrm{V}) = 0.1 \times c(\mathrm{VO^{2+}}) \times M(V) \times 1000 \quad \text{(mg)}$$

b) Calculation for chromium:

$$n(\mathrm{Fe^{2+}\ on\ Cr_2O_7^{2-}}) = \frac{V_2(\mathrm{Fe^{2+}})\ c(\mathrm{Fe^{2+}})}{1000} - 2 \times \frac{V_1(\mathrm{Fe^{2+}})\ c(\mathrm{Fe^{2+}})}{1000} \times \frac{10}{100}$$

$$n(\mathrm{Cr_2O_7^{2-}}) = \frac{1}{6}\left(n(\mathrm{Fe^{2+}})\ \mathrm{on\ Cr_2O_7^{2-}}\right)\ \mathrm{mol}$$

$$c(\mathrm{Cr^{3+}}) = 2 \times \frac{n(\mathrm{Cr_2O_7^{2-}}) \times 100}{10} \times \frac{1000}{100}\ \mathrm{mol\ dm^{-3}}$$

$$m(\mathrm{Cr}) = 0.1 \times c(\mathrm{Cr^{3+}}) \times M(\mathrm{Cr}) \times 1000 \quad \text{(mg)}$$

Task 6 $Fe + 2\ HCl \rightarrow FeCl_2 + H_2\uparrow$

$2\ FeSO_4 + (NH_4)_2S_2O_8 \rightarrow Fe_2(SO_4)_3 + (NH_4)_2SO_4$

$2\ Cl^- + S_2O_8^{2-} \rightarrow Cl_2 + 2\ SO_4^{2-}$

(decrease of the amount of ammonium persulfate due to its reaction with excess of iron(II) in steels)

$Ag^+ + Cl^- \rightarrow AgCl\downarrow$; $AgCl + Cl^- \rightarrow AgCl_2^-$

(reaction between the catalyst and chloride)

PROBLEM 3P (Practical)

Kinetic determination of diclofenac (DCF)

Kinetic methods with spectrophotometric detection for assaying drugs have been intensively developed during the last decade due to a number of obvious advantages, including inherent simplicity, cost-effectiveness, availability in most quality control laboratories, and improved selectivity. In this task you will:

- perform kinetic determination of Diclofenac (DCF) in a medicine by following the progress of the drug oxidation reaction,
- determine the reaction order with respect to DCF.

Task 1. Spectral changes in the course of DCF oxidation with $KMnO_4$ are given in Fig. 1, (1 to 10 reflects the reaction progress). Complete table 1 below suggesting which wavelengths can be applied for photometric kinetic determination of DCF. In each case, indicate the direction of the absorbance changes (denote increasing with ↑ and decreasing with ↓).

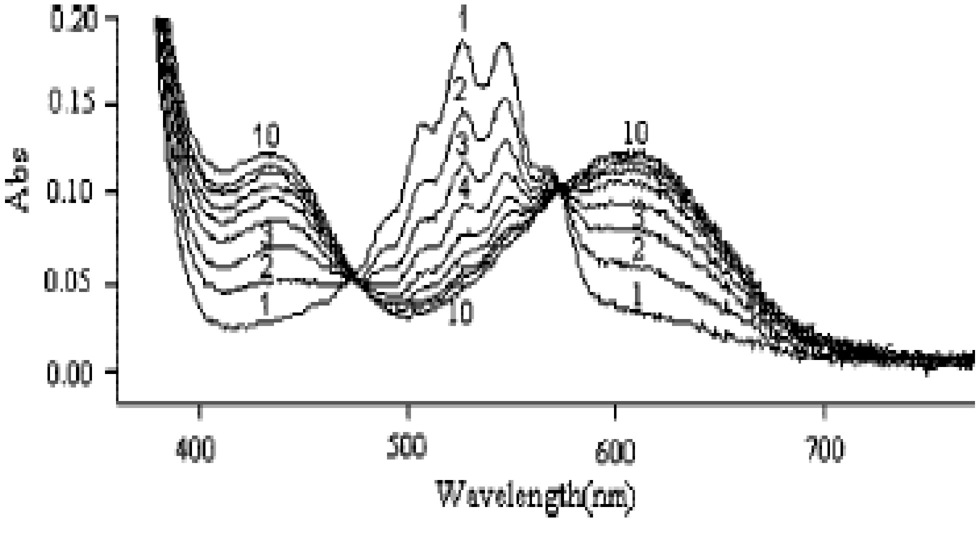


Fig. 1. DCF oxidation with $KMnO_4$

Table 1

#	Wavelength, nm	Yes or No and direction
1	420	
2	480	
3	520	
4	580	
5	610	

Chemical Glass and Equipments

- Photometer, 525 nm
- Thermostat with adaptor
- 2 spectrophotometer cells with a 3.5 cm optical path length
- Magnetic stirrer
- Magnetic stir-bar (medium-size)
- Netbook with adaptor and mouse
- Volumetric flask with a stopper, 100 cm^3
- 2 Graduated pipettes, 2 cm^3
- Memory stick 8 Gb
- Black magnet

Procedure

Part A. Assembling of laboratory equipment

Assemble the laboratory equipment as shown in Fig. 2. Connect the photometer (1), 525 nm (fixed wavelength) and thermostat (2) to the Netbook via USB slots. Connect the thermostat to the cable labeled “Thermo” to the power supply at your work place via the power adapter. Put the optical cuvette (3) on top of the magnetic stirrer (4), pass the cuvette through the photometer from aside (not possible from top down) and place the thermostat over the cuvette from top down (Fig. 2b).

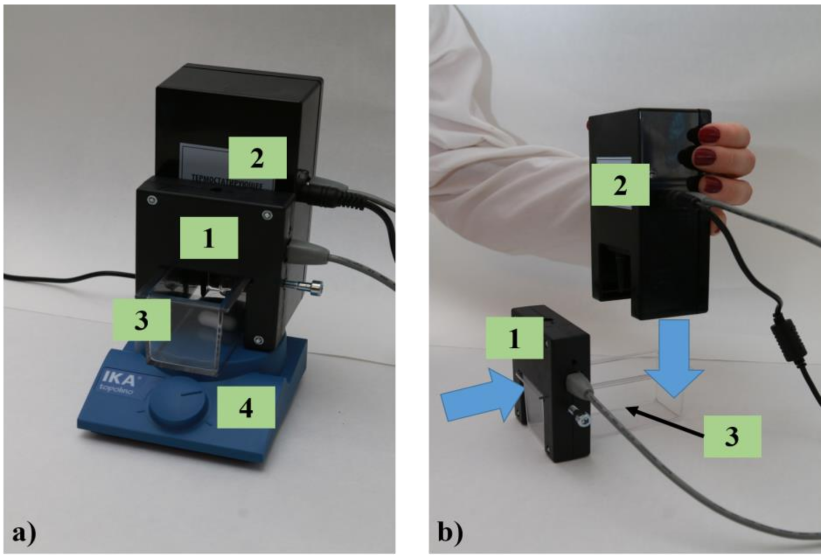


Fig. 2. Laboratory equipment

Hints:

- Plug in your Netbook to the mains before switching on.

- Plug in all the equipment (the photometer and thermostat) before switching on the Netbook. Switch on the mouse.
- If only one window (hereafter referred to as Pattern) instead of two appears after launching the software, quit and re-launch the program.
- Do not unplug ANY device from the USB slot while carrying out the measurements. If it still happens, you will see a warning on the screen. Quit and re-launch the program.
- If your Netbook falls asleep, click the «Setup» button in the Measurements window on the absorbance plot pattern when reverting to the measurements.
- In case you see chaotic temperature changes on the screen, stop and re-start the measurement.

Part B. Plotting of the calibration curve

All measurements needed to plot the calibration curve are carried out at 30 °C with constant initial concentrations of $KMnO_4$ and H_2SO_4. The DCF concentration is varied by using four different aliquots (0.2, 0.4, 0.6, and 0.8 cm^3) of the DCF stock solution.

1. Transfer 5 cm^3 of the H_2SO_4 solution (c = 1 mol dm^{-3}) with a graduated cylinder and 0.2 cm^3 of DCF stock solution using the 2 cm^3 pipette into a 100 cm^3 volumetric flask, dilute up to the mark with distilled water, stopper the flask and mix thoroughly.

2. Carry over the flask contents into the cuvette, put the medium-size stir-bar and switch on the magnetic stirrer. Adjust the stirring speed regulator to the mark shown on Fig. 2a to provide for intensive mixing.

3. Launch the «Chemistry-Practicum» software on the Netbook. The software will detect the external devices (sensors) automatically. You will see two plot patterns (that of absorbance/extinction/optical density, D *vs.* t, (s); and that of temperature, T (°C) *vs.* t, (s) on the display.

4. Set the following parameters in the Menu bars of the corresponding plot patterns (Fig. 3):

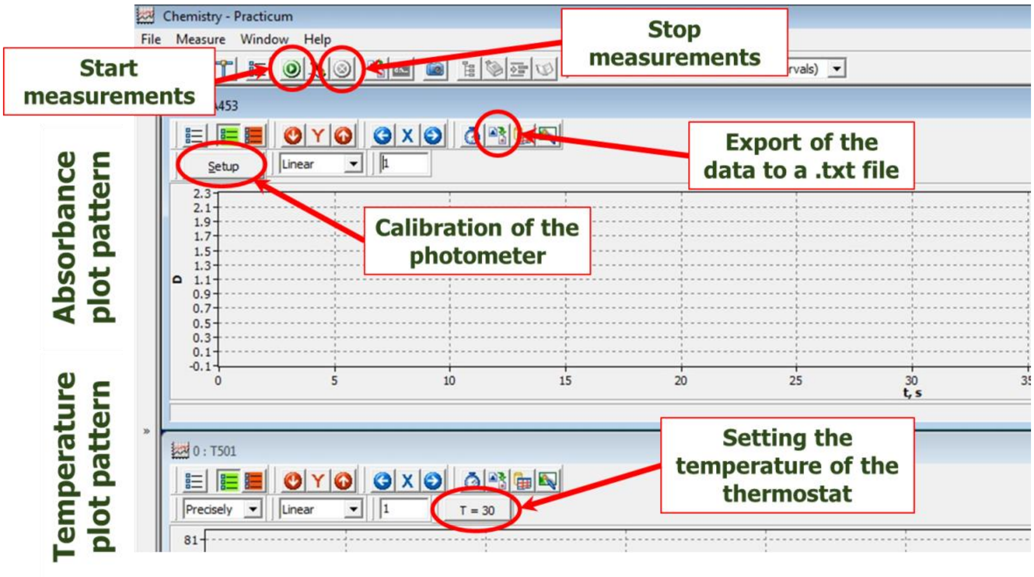


Fig. 3 “Chemistry-Practicum” software interface

- Click the ➡ icon next to the X button («Fixes X-axis maximum on screen») on the absorbance plot pattern. The entire plot will always fit to the screen;
- Click the Y button («Sets the Y range») on the absorbance plot pattern and set the absorbance range (the ordinate axis) from -0.1 to 1.1.
- Type “2” (instead of “1”) in the box of the measurements interval on the absorbance plot pattern.
- Choose «Precisely» in the «Precisely/Roughly» window on the temperature plot pattern, then click on the «T = X» button and set the required temperature of 30 °C in the pop-up window.
- Calibrate the photometer by clicking the «Setup» button in the Measurements window on the absorbance plot pattern.

Note! Setting the parameters (step 4) is needed only prior to the first measurement.

5. Click the ◉ button («Start measure for chosen sensors») to switch on the thermostat and observe the lamp heating up the solution in the cuvette. Follow the current temperature reported in the line above the plot. Wait until the thermostat lamp switches off, reflecting the set up temperature is attained. Stop the measurements by clicking ⊗ button (is activated and turns to red-orange when the measurement is on).

6. Click any part of the absorbance plot pattern to activate it. Take 2 cm^3 of the $KMnO_4$ solution using the 2 cm^3 pipette. Click the ◉ button («Start measure for chosen

sensors») in the Menu bar of the Measurements window and quickly blow out (press the pipette piston) the permanganate solution from the pipette into the cuvette.

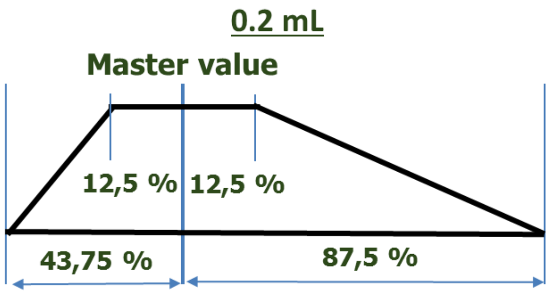
Note! Make sure the temperature in the cuvette equals 30 °C before adding the $KMnO_4$ solution!

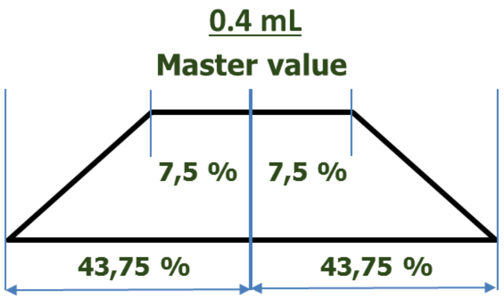
7. Observe the progress of the kinetic curve on the screen. Continue measurement for 50 s after adding the $KMnO_4$ solution, then terminate the measurement by clicking the «Stop measurements» ⊗ button.
8. Save the data by clicking the button («Export all the data collected in an external file») in the Menu bar of the absorbance plot pattern, choose the **Desktop** and type the file name “DCF2” (change the name to “DCF4”, or “DCF6”, or “DCF8” in the subsequent experiments).

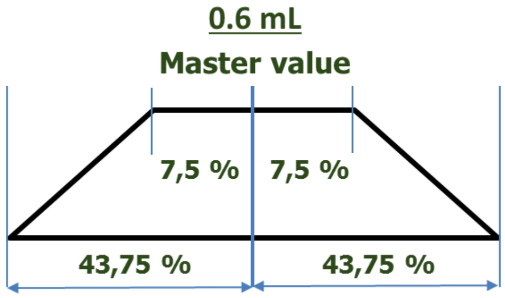
Note!

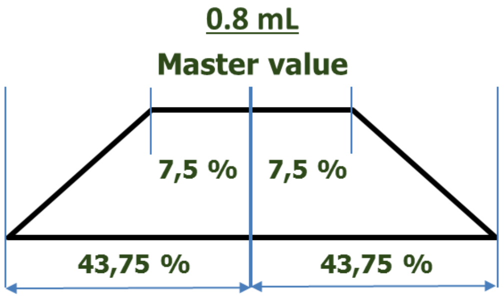
- Use only the names of the given format!
- Always save the data on your Desktop before starting the next experiment, otherwise the current data set will be lost after the next click on the ▶ button.
- Make sure absorbance plot pattern is active when exporting the data. Otherwise, you will export invalid results. In case no pattern is chosen, you will get a warning.

9. Empty the cuvette into the Waste bottle, wash thoroughly the cuvette with distilled water. Use black magnet from the outer side of the cuvette to avoid your stir-bar being dropped into the Waste bottle while washing. Wipe carefully the external surfaces of the cuvette with the napkin. Also, use the napkin to dab the thermostat lamp.
10. Repeat the steps 1, 2, 5 - 9 with the other volumes of the DCF stock solution.









Part C.

I. Studying of the DCF containing medicine ("Control")

i) Wash the volumetric flask and prepare the mixture as described above using a 0.4 cm^3 aliquot of the medicine ("Control") instead of the DCF stock solution.

ii) Repeat the steps 1, 2, 5 - 9 described in Part B. When saving the data, name the file "DCFmed".

iii) Repeat the measurement of the "Control" as necessary.

II. Experimental data analysis

i) Open the Excel file on your memory stick in Excel. One by one open your saved data files in Notepad by double clicking on them on Desktop. Choose Edit/Select All in the Menu bar, then right click and copy the selected data into the Excel sheet with the corresponding name (the volume of DCF added or "DCFmed") and choose Edit/Paste in the Menu bar. You will see the experimental data on the Excel sheet (time, s, in column A, and absorbance in column B).

ii) Ignore the values before the maximum. Select columns A and B, and plot the data. Use the "Insert Scatter" icon shown on Fig 4.

Figure 4. Position of the “Insert Scatter” icon

iii) Choose the initial linear section of the remaining curve (15 to 20 data points), apply linear approximation by adding the linear trend line and bring the parameters to the chart area. Make sure that the R^2 value exceeds 0.98. If needed, decrease the number of the experimental data points plotted removing later data points. Still always search for the most wide range of the experimental data providing for the target R^2 value. Determine the value of the initial rate of absorbance change, v_0.

Note! You will get zero point for this part of the task if less than 12 values are included in the plotted data range.

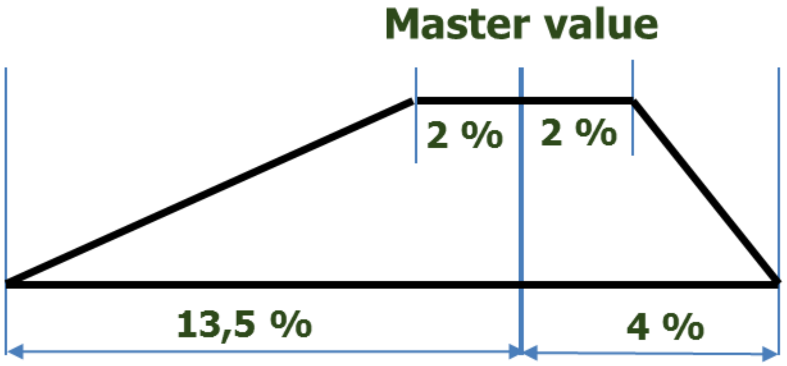
iv) Analyze similarly the experimental data obtained with the other DCF concentrations and with the medicine solution “Control” (“DCFmed” file).

v) Calculate the DCF concentrations in the reaction mixtures (in mg/L). Write down the DCF concentrations and initial rates in appropriate cells of the “Results” Excel sheet.

vi) Plot the calibration graph on the “Results” sheet and use it to determine the DCF concentration in the analyzed mixture prepared from the medicine (“Control”). Fill in the appropriate cells of the “Results” Excel sheet with the coefficients of linear approximation of the calibration graph. Calculate the DCF concentration in the medicine.

vii) Write down the accepted value in the cell F10 of the “Results” sheet.

viii) On the “Results” Excel sheet, graphically determine the reaction order with respect to DCF and write down the exact obtained value in the cell I3.



ix) Once finished, save your file and invite your Lab assistant to demonstrate that you have got experimental data in the Excel file. Sign and get the Lab assistant's signature.

SOLUTION

#	Wavelength, nm	Yes or No and direction
1	420	Yes ↑
2	480	No
3	520	Yes ↓
4	580	No
5	610	Yes ↑

48th

IChO

International Chemistry Olympiad

8 theoretical problems
3 practical problems

THE FORTY-EIGHTH INTERNATIONAL CHEMISTRY OLYMPIAD
JULY 23 – AUG 1, 2016, TBILISI, GEORGIA

THEORETICAL PROBLEMS

PROBLEM 1

Nitrogen trifluoride is a surprisingly stable compound that was first prepared in the melt electrolysis of a mixture of ammonium fluoride and hydrogen fluoride.

1.1 On which electrode does nitrogen trifluoride form? Write a balanced chemical equation for the electrode half reaction for the formation of NF_3.

Interestingly the related fluoroamine (NH_2F) and difluoroamine (NHF_2) are very unstable materials; decomposition of either pure substance can even be explosive. This is dangerous as they are formed in the electrolysis as side products.

1.2 Which of NF_3, NHF_2 or NH_2F compound is expected to condense at the lowest temperature?

The N-F bond lengths in these molecules were determined to be 136, 140 and 142 pm. The change in the bond lengths can be explained with a simple electrostatic model taking into account the partial charges on the atoms.

1.3 Assign the N-F bond lengths (136, 140, 142 pm) to the molecules.

When NHF_2 is bubbled through a solution of KF in HF, a binary nitrogen – fluorine compound can be obtained as a mixture of two geometric isomers.

1.4 Write a balanced chemical equation for the formation of the binary nitrogen-fluorine compound.

Tetrafluoroammonium ion (NF_4^+) and its corresponding salt can form from NF_3 with elementary fluorine in the presence of an appropriate reagent.

1.5 Propose a suitable reagent and write a balanced chemical equation for the reaction.

NF_4^+ ions form stable salts with a number of anions. These are very sensitive to humidity, because NF_4^+ ion hydrolyzes forming NF_3 and O_2. Interestingly nitrogen trifluoride always forms quantitatively, while the quantity of oxygen is often less than expected due to side reactions.

1.6 Write a balanced chemical equation for the hydrolysis of NF_4^+ Write a balanced chemical equation for a possible side reaction that can decrease the theoretically expected O_2:NF_3 mole ratio.

Tetrafluoroammonium salts were investigated for use as solid rocket fuels, because NF_3 and F_2 are released from them on heating. One of them has a fluorine content of 65.6 *m/m*%, all of which is converted into NF_3 and F_2 upon decomposition. During the decomposition 2.5 times as many moles of F_2 are formed as of NF_3.

1.7. Determine the formula of the salt in question.

SOLUTION

1.1 ☑ anode

$NH_4^+ + 3\ F^- \rightarrow NF_3 + 4\ H^+ + 6\ e^-$ or

$NH_4F + 2\ HF \rightarrow NF_3 + 6\ H^+ + 6\ e^-$

1.2 ☑ NF_3

1.3

Molecule	NH_2F	NHF_2	NF_3
N-F bond length (pm)	142	140	136

1.4 $2\ NHF_2 + 2\ KF \longrightarrow N_2F_2 + 2\ KHF_2$ or $2\ NHF_2 \longrightarrow N_2F_2 + 2\ HF$

1.5 $NF_3 + F_2 + SbF_5 \longrightarrow NF_4^+ + SbF_6^-$ any strong fluoride acceptor (AsF_5, BF_3)

1.6 a) $2\ NF_4^+ + 2\ H_2O \longrightarrow 2\ NF_3 + O_2 + 2\ HF + 2\ H^+ \Rightarrow n(O_2) : n(NF_3) = 1 : 2$

b) e.g.: $NF_4^+ + 2\ H_2O \longrightarrow NF_3 + H_2O_2 + HF + H^+$ HOF, O_3, OF_2 also accepted.

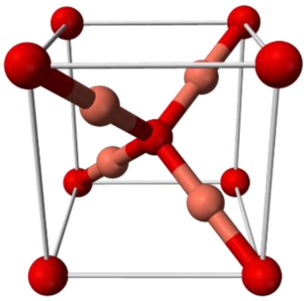
1.7 From the $NF_3 : F_2$ ratio it is clear that the anion also contains fluorine. Moreover, the starting NF_4^+: liberated F_2 ratio is 1 : 2, and all fluorine content is released. With a $(NF_4)_xAF_y$ composition, $x : y = 1 : 4$.

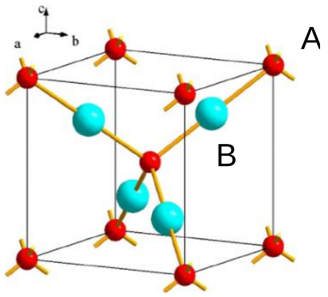
$$\frac{8\ M(F)}{8\ M(F)\ +\ x\ M(N)\ +\ M(A)} = 0.656 \Rightarrow \frac{M(A)}{x} = 65.7\ \text{g mol}^{-1}$$

With $x = 1$, the atomic mass of **A** is close to zinc, but not all fluorine would be released with Zn. If $x = 2$, then the element is xenon, and the formula is $(NF_4)_2XeF_8$

PROBLEM 2

One of the first materials used in solid state electronics was red copper(I) oxide. Interest is renewed nowadays because it could be a non-toxic and cheap component of solar cells.





The two figures above depict the cubic unit cell of the Cu_2O crystal. The lattice constant of the structure is 427.0 pm.

2.1.1 Which of the atoms (A or B) is copper?

Which basic structure (primitive cubic, face centered cubic, body centered cubic, diamond) is formed by the A atoms and which structure is formed by the B atoms?

What are the coordination numbers of the atoms?

2.1.2 Calculate the smallest O-O, Cu-O and Cu-Cu distances in the structure?

2.1.3 What is the density of pure copper(I) oxide?

A common defect in this crystal is some copper atoms missing with the oxygen lattice unchanged. The composition of one such crystal sample was studied, and 0.2% of all copper atoms were found to be in oxidation state +2.

2,2 What percentage of normal copper sites are empty in the crystal sample? What is x in the empirical formula $Cu_{2-x}O$ of the crystal?

Copper(I) oxide is insoluble in water. It is stable in dry air, but humidity in the air catalyses a transformation (Reaction 1).When copper(I) oxide is dissolved in dilutesulfuric acid, a blue solution containing a precipitate is formed without evolution of a gas (Reaction 2). When hot, concentrated sulfuric acid is used, no precipitate remains, but an odorous gas forms (Reaction 3). The same gas forms when the precipitate from reaction 2 is dissolved in hot concentrated sulfuric acid.

2.3 Write balanced chemical equations for reactions (1-3).

Copper (I) oxide can be produced in a number of ways. Heating copper in air is a common method in the synthesis of semiconductor Cu_2O. In a pure oxygen atmosphere, the three species containing copper (Cu(s), Cu_2O(s) or CuO(s)) can potentially interconvert.

Suppose that the $\Delta_f H^o$ and S^o data given for 10^5 Pa are independent of temperature:

Compound	$\Delta_f H^o$ / kJ mol^{-1}	S^o / J mol^{-1} K^{-1}
Cu(s)	0	65
O_2(g)	0	244
CuO(s)	−156	103
Cu_2O(s)	−170	180

2.4. Determine the temperature ranges, if any, of thermodynamic stability of copper and its oxides between 500 and 1500 K in a 10^5 Pa oxygen atmosphere.

Important data are given for 298 K. Use this temperature in the following calculations:

$K_{sp}(Cu(OH)_2) = 2 \times 10^{-19}$

$Cu_2O(s) + H_2O(l) + 2e^- \longrightarrow 2\ Cu(s) + 2\ OH^-(aq)$ $E^o = -0.360$ V

$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$ $E^o = +0.159$ V

$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ $E^o = +0.337$ V

One possibility for producing Cu_2O is the anodic oxidation of copper. Electrolysis of an aqueous basic solution (e.g. NaOH) with a copper anode and platinum cathode can lead to formation of copper(I) oxide on the anode.

2.5 Write the half reaction equations for the electrode processes during the anodic production of Cu_2O in NaOH solution with a platinum cathode and copper anode.

Electrolytic reduction of copper(II) ions in solution is another possibility.

2.6.1 Write the half reaction equation of the cathode process giving Cu_2O in acidic medium.

Let us use 0.100 mol dm^{-3} Cu^{2+} solution and carry out electrolysis with platinum electrodes.

2.6.2 **W**hat is the maximum pH of this solution at which the concentration of copper(II) can be maintained at 0.100 mol dm^{-3}?

If the pH is too low, reduction to metallic copper is preferred to the formation of copper(I) oxide.

2.6.3 What is the minimum pH at which the cathodic production of Cu_2O in a Cu^{2+} solution (c = 0.100 mol dm^{-3}) is still possible?

SOLUTION

2.1.1 There are 2 A atoms and 4 B atoms in the cell. Cu: B

	pr. cubic	fcc	bcc	diamont
A			✓	
B		✓		

B: fcc A: bcc

The coordination numbers of the atoms A and B: B: 2 A: 4

2.1.2 The smallest O-O, Cu-O and Cu-Cu distances in the structure:

O-O: $1/2 \times 427.0 \text{ pm} \times \sqrt{3} = 369.8 \text{ pm}$

Cu-O: 1/4 of the cell body diagonal: $1/4 \times 427.0 \text{ pm} \times \sqrt{3} = 184.9 \text{ pm}$

Cu-Cu: 1/2 of the face diagonal: $1/2 \times 427.0 \text{ pm} \times \sqrt{2} = 301.9 \text{ pm}$

2.1.3 The density of the pure copper(I) oxide?

The volume of the unit cell is $(427.0 \text{ pm})^3$.

The mass of the unit cell is $(4\,M(\text{Cu}) + 2\,M\text{o}) / N_A$. The density is 6.106 g cm^{-3}.

2.2 From 1000 coppers atoms 998 are Cu(I) and two atoms are Cu(II). In order to balance the charge of the anions there has to be 2 vacant Cu sites. The percentage of empty sites is: 2 / 1002 ≈ 0.2 %.

The value of x in the empirical formula $Cu_{2-x}O$ of the crystal:

0.2 % of 2 coppers is missing. That is 0.004.

2.3 (1): $2\,Cu_2O + O_2 \rightarrow 4\,CuO$

(2) $Cu_2O + 2\,H^+ \rightarrow Cu + Cu^{2+} + H_2O$

(3) $Cu_2O + H_2SO_4 + 4\,H^+ \rightarrow 2\,Cu^{2+} + SO_2 + 3\,H_2O$

2.4 $\Delta_f G(CuO) = -156000 \text{ J mol}^{-1} + 84 \text{ J mol}^{-1}\text{K}^{-1}\,T$

$\Delta_f G(Cu_2O) = -170000 \text{ J mol}^{-1} + 72 \text{ J mol}^{-1}\text{ K}^{-1}\,T$

Both Gibbs energies of formation are negative in the range 500-1500 K, so the oxides are more stable than the elements. Cu is not stable.

Looking at the conversion process: $2\,CuO = Cu_2O + 0.5\,O_2$

$\Delta_rG = 142000\ J\ mol^{-1} - 96\ J\ mol^{-1}\ K^{-1}\ T$

The Gibbs energy of the reaction is negative above 1480 K. CuO is stable below 1480 K, Cu_2O above 1480 K.

2.5 Cathode: $2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$

Anode $2\,Cu + 2\,OH^- \rightarrow Cu_2O + H_2O + 2\,e^-$

2.6.1 $2\,Cu^{2+} + H_2O + 2\,e^- \rightarrow Cu_2O + 2\,H^+$

2.6.2 If the pH is too high, $Cu(OH)_2$ precipitates

$K_{sp} \geq 0.1\,[OH^-]^2$ ⇨ pH ≤ 5.15

2.6.3 The potential of the cathodic process ($2\,Cu^{2+} + H_2O + 2\,e^- = Cu_2O + 2\,H^+$) depends on the pH.

The standard potential of the cathodic process can be calculated from:

$Cu_2O(s) + H_2O(l) + 2\,e^- \rightarrow 2\,Cu(s) + 2\,OH^-(aq)$ $\Delta G^o_1 = -\,2\,F\,(-0.36\ V)$

$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$ $\Delta G^o_2 = -\,2\,F\,(+0.337\ V)$

$H_2O(l) \rightarrow H^+(aq) + OH^-(aq)$ $\Delta G^o_3 = -RT\ln K_w$

For $2\,Cu^{2+}(aq) + H_2O(l) + 2\,e^- \rightarrow Cu_2O(s) + 2\,H^+(aq)$:

$\Delta G^o = -\Delta G^o_1 + 2\,\Delta G^o_2 + 2\,\Delta G^o_3$

$E^o = -\Delta G^o / 2F = 0.36\ V + 2 \times 0.337\ V - (RT/F)\cdot\ln K_w = 0.208\ V$

The concentration dependence of the cathodic Cu_2O production potential:

$E = 0.208\ V + 0.059 / 2\ \log\,([Cu^{2+}]^2 / [H^+]^2)$

This potential has to be higher than the potential of the reduction of Cu^{2+}.

$0.337 + (0.059 / 2)\log\,[Cu^{2+}] = 0.208 + (0.059 / 2)\log\,([Cu^{2+}]^2 / [H^+]^2)$

$[H^+]^2 = [Cu^{2+}] / 23600$ pH = 2.69

PROBLEM 3

Iodine deficiency is of special concern in Georgia because it occupies a region where iodine is scarce in soil and water. Iodine deficiency can be effectively and inexpensively prevented if salt for human consumption is fortified with small amounts of iodine. Methods for analyzing salt for iodine content are thus important. Current regulations in Georgia are that iodized salt must contain between 25 - 55 ppm iodine (1 ppm = 1 mg iodine/kg salt).

Most salt is iodized by fortification with potassium iodate (KIO_3). Iodate content can be determined in salt samples using iodometric titration. In a typical procedure, 10.000 g of an iodized salt sample is dissolved in 100 cm^3 aqueous HCl (c = 1.0 mol dm^{-3}) to which 1.0 g KI has been added. The solution is then titrated with aqueous sodium thiosulfate solution (c = 0.00235 mol dm^{-3}) to a starch endpoint; this requires 7.50 cm^3 of titrant.

3.1.1 Write a balanced net ionic equation for the reaction when iodate reacts with excess iodide in acidic solution.

3.1.2 Write a balanced net ionic equation for the reaction taking place during the titration with thiosulfate.

3.1.3 Calculate the iodization level, in ppm, of this salt sample.

A less common agent for iodizing salt is potassium iodide, which cannot be easily measured by iodometric titration.

One possible method for analyzing iodide in the presence of chloride is potentiometric titration. However, this method is not very precise in the presence of large amounts of chloride. In this method, a silver wire is immersed in the solution (containing iodide and chloride) to be analyzed and silver ion is gradually added to the solution. The potential of the silver wire is measured relative to a reference electrode consisting of a silver wire in a solution of $AgNO_3$ (c = 1.000 mol dm^{-3}). The measured potentials are negative and the absolute values of these potentials are reported. The solution to be analysed has a volume of 1.000 dm^3 (which you may assume does not change as silver ion is added) and t = 25.0 °C.

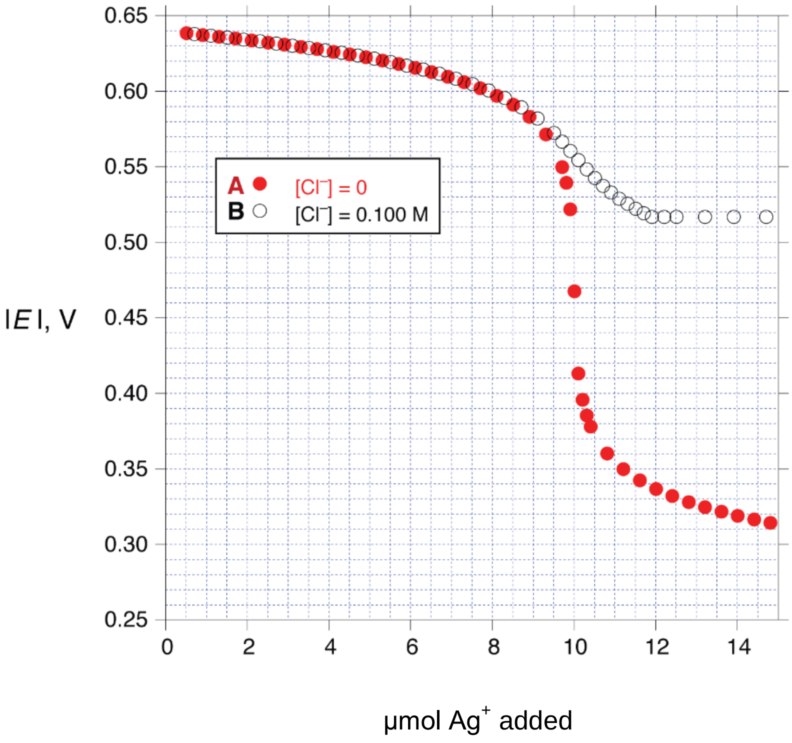
The results of this experiment are governed by three equilibria: the solubility of AgI(s) [K_{spI}] and AgCl(s) [K_{spCl}] and the formation of $AgCl_2^-$(aq) [K_f]. (Iodide also forms complex ions with silver but this may be neglected at the very low concentrations of iodide present in this experiment).

$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$ K_{spI}

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ K_{spCl}

$Ag^+(aq) + 2\,Cl^-(aq) \rightleftharpoons AgCl_2^-(aq)$ K_f

Below are shown the results of two experiments measuring the observed potential as a function of added number of moles of silver ion. Experiment **A** (solid circles) was carried out with 1.000 dm^3 of iodide solution with concentration 1.00×10^{-5} mol dm^{-3} and containing no chloride ion. Experiment **B** (open circles) was done using 1.000 dm^3 of solution with a concentration of iodide 1.00×10^{-5} mol dm^{-3} and that of chloride equal to 1.00×10^{-1} mol dm^{-3}.



μmol Ag^+ added	|*E*|, V exp. **A**	|*E*|, V exp. **B**
1.00	0.637	0.637
3.00	0.631	0.631
5.00	0.622	0.622
7.00	0.609	0.610
9.00	0.581	0.584
10.0	0.468	0.558
11.0	0.355	0.531
12.0	0.337	0.517
13.0	0.327	0.517
15.0	0.313	0.517

3.2.1 Select an appropriate data from the experiments and use it to calculate the solubility product of AgI, ($K_{spI.}$).

3.2.2 Select an appropriate data from the experiments and use it to calculate the solubility product of AgCl, ($K_{spCl.}$).

3.2.3 Select an appropriate data from the experiments and use it to calculate K_f. You may need to use values of K_{spI} or K_{spCl} to do this calculation. If you were unable to carry out the calculations in **3.2.1** or **3.2.2** you may use the arbitrary values of $K_{spI} = 1.00\times10^{-15}$ and $K_{spCl} = 1.00\times10^{-9}$ without penalty.

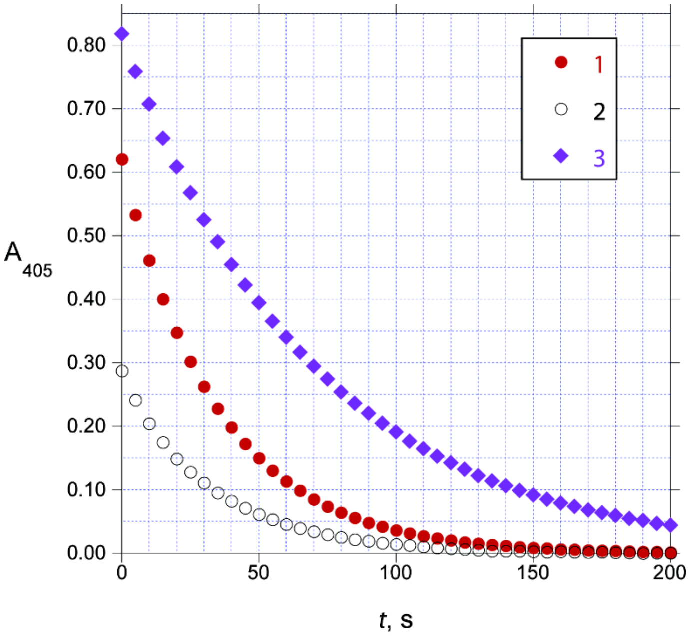
An analytical method that is more practical, because it is not sensitive to the presence of chloride, uses the Sandell-Kolthoff reaction. This is the reaction of H_3AsO_3 with Ce(IV) to give Ce(III) in acidic solution, which is strongly catalyzed by iodide ion.

3.3.1 Write balanced net ionic equations for the reaction of cerium(IV) with H_3AsO_3 in acidic solution, as well as reactions of cerium(IV) with a species containing the element iodine and H_3AsO_3 with a species containing the element iodine, that could reasonably account for the catalysis of the net reaction by iodide.

The reaction of Ce(IV) with H_3AsO_3 can be monitored by measuring the absorbance at 405 nm, as Ce(IV) is orange and absorbs significantly at 405 nm, while the other reactants and products are colorless and do not absorb appreciably. Three runs were carried out, all in 0.50 mol dm^{-3} H_2SO_4 at 25.0°C using the following initial concentrations:

Run	$[H_3AsO_3]_0$, (mol dm^{-3})	$[Ce(IV)]_0$, (mol dm^{-3})	$[I^-]_0$, (mol dm^{-3})
1	0.01250	0.00120	$1.43\cdot10^{-6}$
2	0.00625	0.00060	$1.43\cdot10^{-6}$
3	0.01250	0.00120	$7.16\cdot10^{-7}$

An analyst initiated the reactions by mixing the reagents in a cuvette. After a short variable delay absorbance measurements were started, with the first measurement recorded at t = 0 s. The data obtained are shown below:



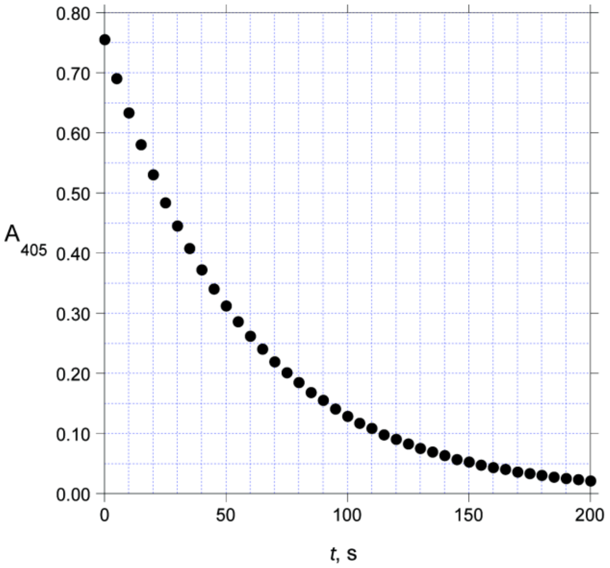
t, s	A_{405} Run 1	A_{405} Run **2**	A_{405} Run **3**
0	0.621	0.287	0.818
20	0.348	0.149	0.608
40	0.198	0.083	0.455
60	0.113	0.046	0.340
80	0.064	0.025	0.254
100	0.037	0.014	0.191

Under these conditions (0.5 mol dm^{-3} H_2SO_4, 25.0°C), the rate law for the reaction can be written as

Rate = $k[H_3AsO_3]^m[Ce(IV)]^n[I^-]^p$ where m, n and p are integers.

3.3.2. Determine the values of m, n, and p and calculate the value of k (be sure to specify its units).

A 1.000 g sample of iodized salt is dissolved in water to give 10.00 cm^3 of solution. A 0.0500 cm^3 aliquot of this solution is added to a mixture of 1.000 cm^3 0.025 mol dm^{-3} H_3AsO_3 in 0.5 mol dm^{-3} H_2SO_4 and 0.800 cm^3 0.5 mol dm^{-3} H_2SO_4. To this mixture is added 0.200 cm^3 0.0120 mol dm^{-3} $Ce(NH_4)_2(NO_3)_6$ in 0.5 mol dm^{-3} H_2SO_4 and the absorbance at 405 nm is measured as a function of time at 25.0°C:



t, s	A_{405}
0	0.756
20	0.531
40	0.373
60	0.262
80	0.185
100	0.129

3.3.3. Calculate the iodization level, in ppm, of this salt sample.

SOLUTION

3.1.1 $IO_3^- + 8\ I^- + 6\ H^+ \rightarrow 3\ I_3^- + 3\ H_2O$ or

$IO_3^- + 5\ I^- + 6\ H^+ \rightarrow 3\ I_2 + 3\ H_2O$

3.1.2 $I_3^- + 2\ S_2O_3^{2-} \rightarrow 3\ I^- + S_4O_6^{2-}$ or

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

3.1.3 $n(S_2O_3^{2-}) = 0.00750\ dm^3 \times 0.00235\ mol\ dm^{-3} = 1.76\times10^{-5}\ mol\ S_2O_3^{2-}$

$(1.76\times10^{-5}\ mol\ S_2O_3^{2-}) \times (1\ mol\ IO_3^- / 6\ mol\ S_2O_3^{2-}) = 2.94\times10^{-6}\ mol\ IO_3^-$

$(2.94\cdot10^{-6}\ mol\ IO_3^-)\cdot(126.90\ g\ mol^{-1}) = 3.73\times10^{-4}$ g iodine

$\{(3.73\times10^{-4}$ g iodine)/(10.00 g salt)$\} \times10^6$ ppm = 37.3 ppm iodine

3.2.1 In the experiments, $|E| = -(RT/nF)\ \ln([Ag^+]cell / [Ag^+]ref) = -0.0591\cdot\log[Ag^+]$

There is a sharp endpoint at n(added Ag^+) = n (I^- initially present) in experiment ***A***($[Cl^-] = 0$), so precipitation of AgI(s) must be essentially complete at any point in the titration curve. If one considers, for example,

5.0 μmol added Ag^+, then

$[I^-] = [I^-]_0 - 5.0\times10^{-6}\ mol\ dm^{-3} = 5.0\times10^{-6}\ mol\ dm^{-3}$

$|E| = 0.622\ V = -0.0591 \times \log[Ag^+] \Rightarrow [Ag^+] = 3.2\times10^{-11}\ mol\ dm^{-3}$

$K_{sp} = [Ag^+][I^-] = 1.6\times10^{-16}$

3.2.2 In the titration with $[Cl^-] = 0.100\ mol\ dm^{-3}$ (experiment **B**), the fact that the potential stops changing at n(added Ag^+) ≥ 11.8 μmol must be due to the precipitation of AgCl(s) (the high concentration of chloride therefore effectively fixes the $[Ag^+]$ in the solution). So in this regime:

$|E| = 0.517\ V = -0.0591\ \log[Ag^+] \Rightarrow [Ag^+] = 1.6\times10^{-9}$

$K_{spl} = [Ag^+][Cl^-] = 1.6\times10^{-10}$

3.2.3 There are a number of good approaches to this problem.

One can use the point at which AgCl(s) first precipitates (estimated at 11.8 μmol Ag^+ added) to calculate K_f. At this point, $[Ag^+] = 1.6\times10^{-9}$, $[Cl^-] = 0.100$ (see above).

Almost all of the originally present iodide ($1.0\times10^{-5}\ mol\ dm^{-3}$) has been precipitated out as 9.9 μmol AgI, since $[I^-] = K_{sp} / [Ag^+] = 1.0\times10^{-7}$.

Total Ag in solution = 11.8 μmol – 9.9 μmol = 1.9 μmol

$[AgCl_2^-] = 1.9\times10^{-6}$ (since free $[Ag^+]$ is only 1.6×10^{-9}).

$$K_f = \frac{[AgCl_2^-]}{[Ag^+][Cl^-]^2} = \frac{1.9\times10^{-6}}{1.6\times10^{-9}\times0.100^2} = 1.2\times10^5 \quad (1.9\times10^{-4}\text{ given constant})$$

The same approach works for 11 μmol Ag^+ added.

An alternative approach is to look at the equivalence point, where

$E = 0.558\text{ V} = -0.0591\log[Ag^+] \;\Rightarrow\; [Ag^+] = 3.62\times10^{-10}$

Since AgI(*s*) is present, $[I^-] = K_{spI} / [Ag^+] = 4.42\times10^{-7}$. The amount of dissolved iodine and silver is equivalent:

$[I^-] = [Ag^+] + [AgCl_2^-] \;\Rightarrow\; [AgCl_2^-] = 4.42\times10^{-7}$

$$K_f = \frac{[AgCl]}{[Ag^+][Cl^-]^2} = \frac{4.42\times10^{-7}}{3.62\times10^{-10}\times0.100^2} = 1.2\times10^5\,[7.6\times10^5\text{ given const.}]$$

3.3.1 Net reaction of cerium(IV) with H_3AsO_3 in acidic solution:

$2\,Ce^{4+} + H_3AsO_3 + H_2O \rightarrow 2\,Ce^{3+} + H_3AsO_4 + 2\,H^+$

Reaction of cerium(IV) with an iodine-containing species:

$2\,Ce^{4+} + 2\,I^- \rightarrow 2\,Ce^{3+} + I_2$

Reaction of cerium(IV) with an iodine-containing species:

$H_3AsO_3 + I_2 + H_2O \rightarrow H_3AsO_4 + 2\,I^- + 2\,H^+$

3.3.2 The limiting reactant is Ce(IV) which is < 10% of the concentration of H_3AsO_3, so only the concentration of Ce(IV) changes appreciably over the course of the reaction. (I^- is a catalyst and is not consumed.) So the order in Ce(IV) can be judged by the time course of the reaction. By eye, it appears to be first order.

This can be verified by calculating $-\ln(A/A_0)\cdot(1/t)$, which should be a constant (k_{obs}) if the reaction is first-order:

t, s	k_{obs}, s^{-1}, Run 1	k_{obs}, s^{-1}, Run **2**	k_{obs}, s^{-1}, Run **3**
20	0.0290	0.0328	0.0148
40	0.0286	0.0310	0.0147
60	0.0284	0.0305	0.0146
80	0.0284	0.0305	0.0146
100	0.0282	0.0302	0.0145
avg.	0.0285	0.0310	0.0146

So $n = 1$.

Since k_{obs} is unchanged (within 10%) from run **1** to run **2** despite decreasing [H_3AsO_3] by a factor of two, $m = 0$.

In contrast, decreasing [I^-] by a factor of two from run **1** to run **3** results in a decrease in observed rate constant of a factor of two, so $p = 1$.

$k = k_{obs}$ / [I^-], giving values of 1.99×10^4, 2.17×10^4, and 2.04×10^4 $dm^3\ mol^{-1}\ s^{-1}$ for runs **1-3**; average $k = 2.07 \times 10^4$ $dm^3\ mol^{-1}\ s^{-1}$.

3.3.3

t, s	$-\ln(A/A_0) \times (1/t)$, s^{-1}
20	0.0177
40	0.0177
60	0.0177
80	0.0176
100	0.0177

So $k_{obs} = 0.0177\ s^{-1} = k[I^-] = (2.07 \times 10^4\ dm^3\ mol^{-1}\ s^{-1})\ [I^-]$

$[I^-] = 8.55 \cdot 10^{-7}$ mol/dm^3

Since the salt solution was diluted by a factor of (2.05 cm^3) / (0.050 cm^3) = 41, the concentration in the original salt solution was

$41 \times (8.55 \times 10^{-7}$ mol/dm$^3) = 3.51 \times 10^{-5}$ mol/dm^3.

$(3.51 \times 10^{-5}$ mol dm$^{-3})(0.01000$ dm$^3) = 3.51 \times 10^{-7}$ mol I in the salt sample

$(3.51 \times 10^{-7}$ mol iodine)(126.90 g/mol) $= 4.45 \times 10^{-5}$ g iodine

$\{(4.45 \times 10^{-5}$ g iodine)/(1.000 g salt)$\} \times 10^6$ ppm = 44.5 ppm I

PROBLEM 4

Application of kinetic studies in water treatment

Industrial waste is a major cause of water pollution and kinetic studies are carried out in a laboratory to design effluent treatment. 1,4-dioxane, more commonly known as dioxane ($C_4H_8O_2$), an industrial solvent and by-product, is a significant water contaminant. It can be oxidised to hazard free chemicals using oxidants such as peroxodisulfate, ozone or hydrogen peroxide.

The data obtained in the kinetic study of oxidation of dioxane with potassium peroxodisulfate ($K_2S_2O_8$) as oxidant and $AgNO_3$ as catalyst at T = 303.15 K are given below. The reaction was monitored by the estimation of unreacted peroxodisulfate. The concentration of $AgNO_3$ used in this study was $1.00 \cdot 10^{-3}$ mmol dm^{-3}.

Trial	Dioxane mmol·dm^{-3}	$K_2S_2O_8$ mmol·dm^{-3}	Initial rate mmol·dm^{-3}·min^{-1}
1	0.0100	2.50	$1.661 \cdot 10^{-2}$
2	0.0100	5.10	$3.380 \cdot 10^{-2}$
3	0.00500	13.8	$9.200 \cdot 10^{-2}$
4	0.0110	13.8	$9.201 \cdot 10^{-2}$

In many countries the accepted maximum level of dioxane in drinking water is specified as 0.35 µg dm^{-3}.

A water sample contains an initial dioxane concentration of 40.00 µg dm^{-3}. Assume that 1 mol dioxane requires 1 mol of peroxodisulfate for oxidation. The concentration of $AgNO_3$ used in this study was 1.00×10^{-3} mmol·dm^{-3}.

4.1.1. Calculate the time in minutes the oxidation process has to continue in order to reach the accepted level of dioxane at 303.15 K if the initial concentration of $K_2S_2O_8$ is 5.0×10^{-6} mol dm^{-3}. Assume that the rate law obtained from the data above is valid under these conditions.

Various mechanisms have been proposed for the peroxodisulfate oxidation of dioxane. Misra and Ghosh (1963) proposed the following mechanism:

$$S_2O_8^{2-} + Ag^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Ag^{3+} + 2\ SO_4^{2-}$$

$$Ag^{3+} + D\ (\text{dioxane}) \xrightarrow{k_3} D'\ (\text{dioxane oxidized}) + 2\ H^+ + Ag^+$$

4.1.2 Assuming Ag(III) to be in steady state, deduce the rate equation for the oxidation of dioxane.

4.1.3 Which of the following is/are correct?

A) The rate equation based on the mechanism given in **4.1.2**, at very high concentrations of dioxane, is consistent with the experimental data in **4.1.1.**

B) The rate equation based on the mechanism given in **4.1.2**, at very low concentrations of dioxane, is consistent with the experimental data in **4.1.1.**

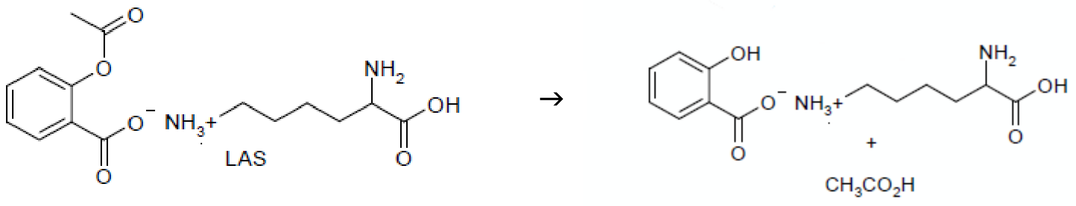
C) The units of the observed rate constant are $dm^3 \cdot mol^{-1} \cdot s^{-1}$ at very high concentrations of dioxane.

D) The units of the observed rate constant are $dm^3 \cdot mol^{-1} \cdot s^{-1}$ at very low concentrations of dioxane.

Degradation of pharmaceutical products – a kinetic overview

Kinetic studies are important in deciding the shelf life of a pharmaceutical product. Several chemical reactions can affect the shelf life of pharmaceutical products and the rates of these reactions depend on conditions such as pH, temperature, humidity.

Lysine acetylsalicylate (LAS) is prescribed as a pain killer and anti-inflammatory drug under the brand name Aspegic. LAS on hydrolysis forms lysine salicylate and acetic acid.



Hydrolysis of LAS can proceed via three different pathways (a) acid catalysed, (b) uncatalysed and (c) base catalysed.

If [LAS] denotes the concentration of LAS at time *t*, the overall rate of the hydrolysis reaction can be written as

$$-\frac{d[\mathrm{LAS}]}{dt} = k_\mathrm{H}\,[\mathrm{LAS}][\mathrm{H^+}] + k_\mathrm{O}\,[\mathrm{LAS}] + k_\mathrm{OH}\,[\mathrm{LAS}][\mathrm{OH^-}]$$

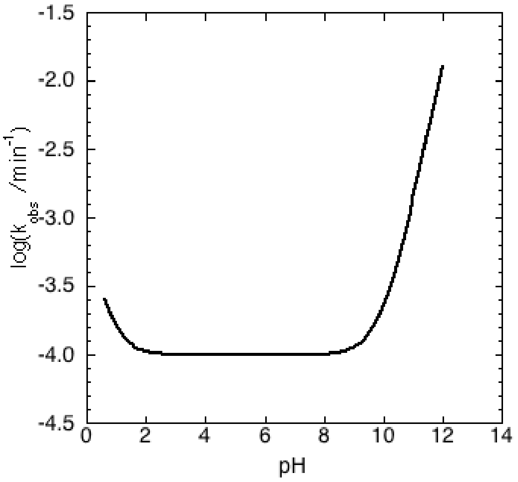
where k_H, k_O and k_OH are the rate constants of the acid catalysed, uncatalysed and base catalysed pathways of hydrolysis, respectively. The overall rate constant is defined as:

$$-\frac{d[\mathrm{LAS}]}{dt} = k_{obs}\,[\mathrm{LAS}]$$

4.2.1 <u>Write</u> an expression for k_obs in terms of k_H, k_O, k_OH and [H$^+$].

Hydrolysis of LAS was carried out at 298.15 K at various pH values (0.50 to 13.0). A very low initial concentration of LAS ensured that the pH did not change during the course of the reaction.

The following graph shows the pH dependence of the hydrolysis of LAS.



4.2.2 Which of the following is/are correct?

A) $k_\mathrm{obs} \approx k_0$ at pH = 12

B) $k_\mathrm{obs} \approx k_0$ at pH = 5.0

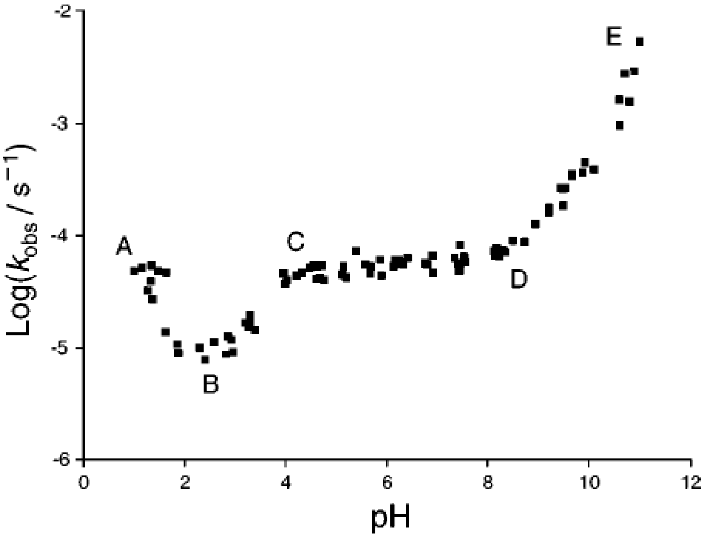
C) The rate of the reaction increases when the pH is changed from 0.50 to 1.0.

D) The rate of the reaction increases when the pH is changed from 10 to 12.

4.2.3 Using the diagram and the data given below, calculate k_H, k_0 and k_{OH}. Make sure to specify the units.

pH	1.300	5.300	12.180
log (k_{obs}/min^{-1})	−3.886	−4.000	−1.726

Acetylsalicylic acid, more commonly known as aspirin is a medicine often used for reducing fever, pain and inflammation. Like LAS, the hydrolysis of aspirin can also take different pathways depending on the pH. The pH rate profile of aspirin hydrolysis at 333.15 K is given below:



The following are possible reactions for the hydrolysis of aspirin. Depending on the pH, one or more of these reactions will predominate.

I. $CH_3COOC_6H_4COOH + H_3O^+ \longrightarrow HOC_6H_4COOH + CH_3COOH + H^+$

II. $CH_3COOC_6H_4COOH + H_2O \longrightarrow HOC_6H_4COOH + CH_3COOH$

III. $CH_3COOC_6H_4COOH + OH^- \longrightarrow HOC_6H_4COOH + CH_3COO^-$

IV. $CH_3COOC_6H_4COO^- + H_3O^+ \longrightarrow HOC_6H_4COOH + CH_3COOH$

V. $CH_3COOC_6H_4COO^- + H_2O \longrightarrow HOC_6H_4COOH + CH_3COO^-$

VI. $CH_3COOC_6H_4COO^- + OH^- \longrightarrow HOC_6H_4COO^- + CH_3COO^-$

4.3.1 Using the pH-rate profile diagram and the reactions given above, state which of the following statements is/are correct. (pK_a of aspirin = 3.57 at 333.15 K)

a) In the region C-D, reaction IV is predominant
b) In the region C-D, reaction V is predominant
c) In the region D-E reaction VI is predominant
d) In the region A-B, reaction II is predominant

The plot of k_{obs} *vs* pH for the hydrolysis of aspirin has been confirmed to show a minimum at a particular pH. At 290.15 K the following rate constants for reactions I, II and III were determined:

k_H (reaction I)	k_0 (reaction II)	k_{OH} (reaction III)
1.99 $dm^3 \cdot mol^{-1} \cdot day^{-1}$	2.29×10^{-4} day^{-1}	3.18×10^9 $dm^3 \cdot mol^{-1} \cdot day^{-1}$

The ionic product of water at 290.15 K can be taken as 1.0×10^{-14}.

4.3.2 Assuming that only reactions I, II and III occur, calculate the value of the pH at the minimum.

SOLUTION

4.1.1 Trial 1 and 2 ⇒ the rate doubles when concentration of $K_2S_2O_8$ is doubled.

Order with respect to $K_2S_2O_8$ = 1.

Trial 3 and 4 ⇒ the rate does not change with concentration of dioxane. Order with respect to dioxane = 0.

Initial rate = k [$K_2S_2O_8$] Average $k = 6.65\times10^{-3}$ min^{-1}

Change in dioxane concentration: (40.00 − 0.35) μg dm^{-3} / 88.1 g mol^{-1} = 0.450 μmol dm^{-3}

$[K_2S_2O_8]_0 = 5.00$ μmol dm^{-3}; $[K_2S_2O_8]_t = 4.55$ μmol dm^{-3}

$4.55 = 5.00 \exp(-6.65\times10^{-3}\, t)$

t = 14.2 minutes

4.1.2 $k_1[S_2O_8^{2-}][Ag^+] - k_2[SO_4^{2-}]^2\,[Ag^{3+}] - k_3[Ag^{3+}]\,[D] = 0$

$$[Ag^{3+}] = \frac{k_1\,[S_2O_8^{2-}][Ag+]}{k_2\,[SO_4^{2-}] + k_3[D]}$$

$$\text{rate of oxidation} = \frac{k_1\,k_3[S_2O_8^{2-}][D][Ag+]}{k_2\,[SO_4^{2-}] + k_3[D]}$$

4.1.3 A, C

4.2.1

$$k_{obs} = k_H[H^+] + k_0 + k_{OH}\frac{K_w}{[H^+]}$$

4.2.2 B, D

4.2.3 At pH = 5.30, k_0 is dominant

$\log(k_{obs}/\text{min}^{-1}) = -4.000$ ⇒ $k_{obs} = k_0 = 1.00\times10^{-4}$ min^{-1}

At pH = 12.18, $[OH^-] = 0.01514$ mol dm^{-3}

$\log(k_{obs}/\text{min}^{-1}) = -1.726$ ⇒ $k_{obs} = 1.88\times10^{-2}$ min^{-1}

$k_{obs} = k_0 + k_{OH}[OH^-]$ k_0 can be neglected

$k_{OH} = k_{obs} / [OH^-] = 1.24$ dm^3 mol^{-1} min^{-1}

At pH = 1.30, $[H^+] = 0.0501$ mol dm^{-3}

$\log(k_{obs}/\text{min}^{-1}) = -3.886$ ⇒ $k_{obs} = 1.30\times10^{-4}$ min^{-1}

$k_{obs} = k_H[H^+] + k_0$ k_0 cannot be neglected

$$k_H = \frac{k_{obs} - k_0}{[H^+]} = \frac{3.0\times10^{-5}\ \text{min}^{-1}}{0.0501\ \text{mol dm}^{-3}}$$

$k_H = 6.0\times10^{-4}$ dm^3 mol^{-1}min^{-1}

4.3.1 b, c

4.3.2

$$k_{obs} = k_H[H^+] + k_0 + k_{OH}\frac{K_w}{[H^+]}$$

This is a minimum if

$$\frac{d\,k_{obs}}{d\,[H^+]} = k_H - k_{OH}\frac{K_w}{[H^+]} = 0$$

$$[H^+]_{min} = \sqrt{\frac{k_{OH}\;K_w}{k_H}} \qquad pH_{min} = \frac{1}{2}\,pK_w + \frac{1}{2}\log\frac{k_H}{k_{OH}} = 2.40$$

or see alternative solution without calculus:

k_{obs} is a minimum if

$$k_H[H^+] + k_{OH}\frac{K_w}{[H^+]}$$

is minimal.

The minimum is reached when the two terms are equal. So at minimum:

$$k_H[H^+] = k_{OH}\frac{K_w}{[H^+]}$$

$$pH_{min} = \frac{1}{2}\,pK_w + \frac{1}{2}\log\frac{k_H}{k_{OH}} = 2.40$$

PROBLEM 5

5500 years ago in ancient Egypt people learned for the first time how to synthesize a blue pigment. Now we know this pigment as Egyptian blue. About 2000 years later in ancient China another pigment was widely used, which is now referred to as Chinese blue. The two pigments are similar in structure, but have different elemental compositions.

Ushabti figurines from Egyptian pharaoh tomb covered with Egyptian blue
and a Chinese blue soap dinspenser sold at Alibaba

The ancient method of preparation for these pigments can easily by reproduced in a modern laboratory.

When considering the amounts, assume that all of the compounds in this task are pure, and the yields are quantitative.

To make Egyptian blue, one should heat 10.0 g of mineral **A** with 21.7 g of SiO_2 and 9.05 g of mineral **B** at 800 – 900°C for a prolonged time. A volume of 16.7 dm^3 of a mixture of two gaseous products are released (the volume is measured at 850°C and 1.013×10^5 Pa (1.013 bar) pressure. In result, 34.0 g of the pigment was obtained. No other products are formed. As the gas mixture is cooled, one component of the mixture condenses. As the remaining gas is further cooled to 0°C, the gaseous volume reduces to 3.04 dm^3.

5.1.1 Calculate the mass of the gaseous mixture formed upon heating of **A** with **B** and SiO_2.

5.1.2 Determine the quantitative composition of this gas mixture.

When 10.0 g of mineral **A** is heated with 21.7 g of SiO_2 in the absence of **B**, it forms 8.34 dm^3 of gaseous products at a temperature of 850°C and pressure of $1.013 \cdot 10^5$ Pa (= 1.013 bar). Mineral **A** contains only one metal.

5.1.3 Calculate the molar mass and determine the formula of mineral **B**. Hint: it is an ionic solid insoluble in water and containing no water of crystallization.

In order to obtain **Chinese blue**, one should take 17.8 g of mineral **C** instead of mineral **B** (keeping the amounts of mineral **A** and SiO_2 same as for Egyptian blue), and run the reaction at higher temperatures. Besides the pigment, the same gaseous products in the same quantities are formed as in the preparation of Egyptian blue.

5.1.4 Determine the formula of mineral **C**.

5.1.5 Determine the formulae of Egyptian blue and Chinese blue.

5.1.6 Determine the formula of mineral **A**.

Elemental analysis of some samples of Chinese blue shows traces of sulfur. This led to a conclusion that those were synthesized using another common mineral instead of **C**.

5.2.1 Suggest a formula for the mineral used in place of **C**.

5.2.2 Could the temperature of synthesis of Chinese blue be decreased if this mineral is used instead of **C**?

If during the synthesis of Chinese blue we take a smaller amount of silica than in the process above, we will obtain a purple pigment: Chinese violet. It was used, in particular, for coloring the famous Terracotta army soldiers.

Terracotta army from Xian, China and reconstruction of its original coloring.

5.3 Write down the formula of a binary compound that forms under the conditions required for Chinese violet and is responsible for the change of the color.

SOLUTION

5.1.1 m = 10.0 + 21.7 + 9.05 – 34.0 = 6.75 g

5.1.2 At 850°C, the number of moles of gaseous products is:

$$n_1 = \frac{p\,V}{R\,T} = \frac{101325\text{ kPa} \times 0.0167\text{ m}^3}{8.314\text{ J mol}^{-1}\text{K}^{-1} \times (850 + 273)\text{ K}} = 0.181\text{ mol}$$

while at 0 °C

$$n_2 = \frac{p\,V}{R\,T} = \frac{101325\text{ kPa} \times 0.00304\text{ m}^3}{8.314\text{ J mol}^{-1}\text{K}^{-1} \times 273\text{ K}} = 0.136\text{ mol}$$

The difference of 0.045 moles is probably water that has condensed. Hence, the mass of the gas at 0 °C is m = 6.75 – 0.045×18 = 5.94 g, and the molar mass is m/n_2 ≈ 44 g mol^{-1}. Taken into account that we dealt with minerals, and the temperature was high, we can conclude that the rest of the gas is CO_2.

The gas formed at 850°C contains 0.045 mol of H_2O and 0.136 mol of CO_2.

5.1.3 Heating of mineral **A** with SiO_2 alone produces half of the gases evolved in the presence of **B**. Thus, **B** should form the rest 0.181 / 2 = 0.0905 moles of gases and is a carbonate of some metal. If it forms pure CO_2, the molar mass of **B** per carbonate group is 9.05 g / 0.0905 mol = 100 g mol^{-1}. The molar mass of CO_3 group is 60 g mol^{-1}, so the mass of metal per carbonate group is 40 g mol^{-1}. This corresponds to Ca, **B** – $CaCO_3$.

5.1.4 Similar to the previous question, the molar mass of **C** per carbonate group is:
17.8 g / 0.0905 mol = 197 g mol^{-1}.
The mass of metal per carbonate group is 137 g mol^{-1}.
This corresponds to Ba, **C** – $BaCO_3$.

5.1.5 Taking into account the molar ratios of known compounds, we can write a general equation of formation of Egyptian blue:

$$\mathbf{A} + 2\,CaCO_3 + 8\,SiO_2 = \text{pigment} + 3\,CO_2 + H_2O$$

The composition of Egyptian blue can be written as 2 CaO × 8 SiO_2 × n Me_xO_y. Oxide Me_xO_y is formed from mineral **A**. Let us find the molar mass of n Me_xO_y:

$$M(\text{pigment}) = M(2\,CaO \cdot 8\,SiO_2) + M\,(n\,Me_xO_y)$$

$$M(\text{pigment}) = 2\,M(\text{CaCO}_3)\,\frac{m(\text{pigment})}{m(CaCO_3)}$$

$$M(\text{nMe}_x\text{O}_y) = 2\,M(\text{CaCO}_3)\,\frac{34.0\text{ g}}{9.05\text{ g}} - M(2\text{Ca}O.8\text{ SiO}_2) = 159\text{ g mol}^{-1}$$

Trying different values (at least from 1 to 3) of *n*, *x*, and *y*, we ensure that the only possibility is *n* = 2, *x* = *y* = 1, Me is Cu. This is supported by a blue color of a pigment.

The formula of Egyptian blue is then $CaCuSi_4O_{10}$.

The formula of Chinese blue is $BaCuSi_4O_{10}$.

5.1.6 Upon heating **A** turns into 2 CuO, 1 CO_2 and 1 H_2O. It means that **A** is malachite, $Cu_2CO_3(OH)_2$.

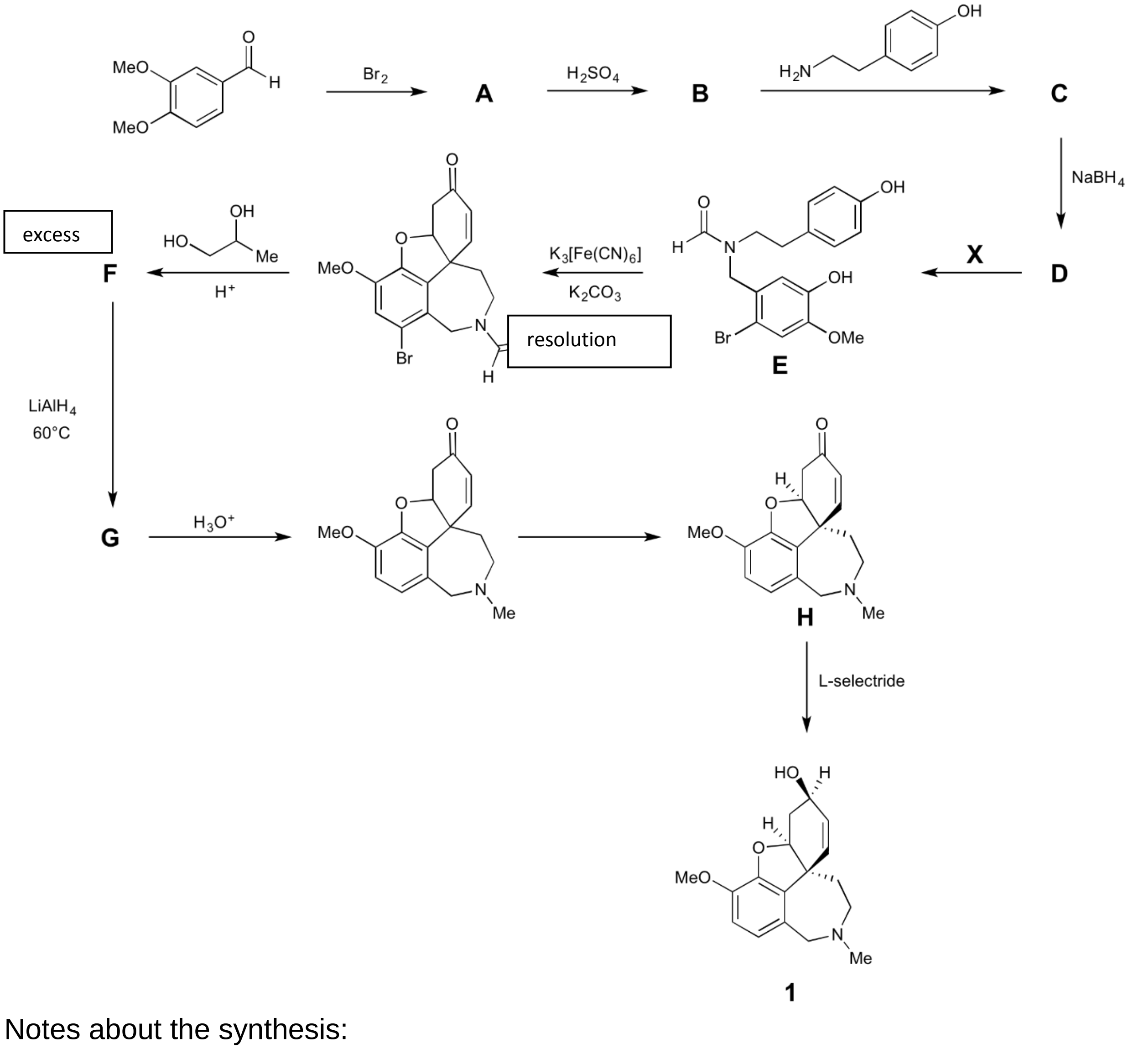
5.2.1 $BaSO_4$ (the most stable compound containing Ba and S, mineral barite).

5.2.2 No. $BaSO_4$ is more stable than $BaCO_3$.

5.3 Cu_2O (mixing red with blue gives purple).

PROBLEM 6

Although there is currently no known cure for Alzheimer's disease, there are medications available to manage the neurodegenerative disorder. Among these are acetylcholinesterase inhibitors, of which galantamine **1** is an example. This molecule can be isolated from the Caucasian snowdrop, a plant native to Georgia; however, the large amounts needed for therapy require a synthetic route. Shown below is the route used to prepare galantamine industrially.



Notes about the synthesis:

- ^{1}H NMR of **A** indicates 2 aromatic protons in a *para* arrangement.

- **C** is labile in aqueous conditions, so it is not isolated, but rather reacted immediately with $NaBH_4$ to convert it to **D**.

6.1.1 Suggest structures for **A**, **B**, **C**, **D**, **F**, and **G**. None of the reactions except for the final transformation with L-selectride are stereoselective. Therefore, stereochemistry does not need to be indicated in your answers.

6.1.2 Give the formula for a possible reagent, **X**, to convert compound **D** to **E**.

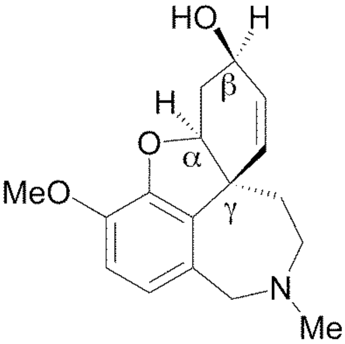
The optical rotation of the material obtained by resolution was –400° $cm^2 g^{-1}$, while that of the enantiomerically pure compound is –415° $cm^2 g^{-1}$ when measured under the same conditions. You may assume that the only optical impurity is the other enantiomer.

One way of describing optical purity is enantiomeric excess (*ee*). It is defined as the difference in the percentages of the enantiomers in a mixture. For example in a mixture of 70% *R* and 30% *S*, the *ee* is 40%.

6.2.1 What is the enantiomeric excess of the resolved compound as prepared by the industrial route?

L-selectride is a commercial reagent that performs the final reaction stereoselectively.

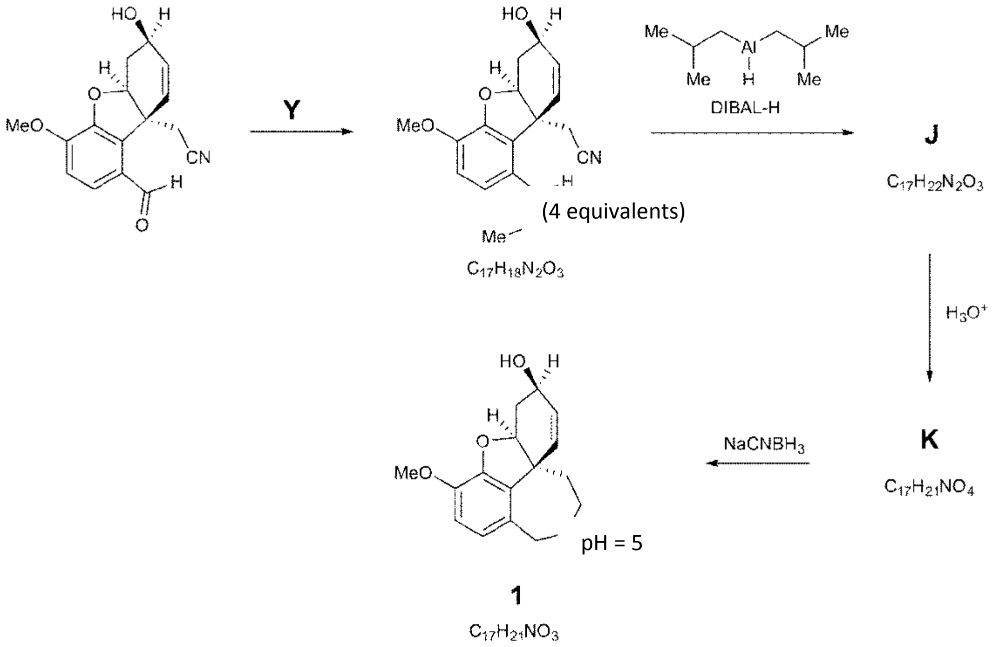
6.2.2 Assign the labelled stereocentres (α, β, γ) in (–)-**1** as *R* or *S*.



(–)-1

6.2.3 Give the formula for a reagent that carries out the same reaction as L-selectride, converting **H** to **1**. You need not worry about stereoselectivity.

An alternative route to galantamine occurs with the seven-membered ring being the last ring to form.

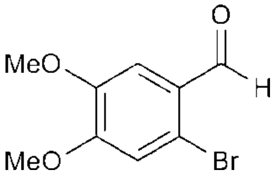


6.3.1 Give the formula for compound **Y** to carry out the first step of the route.

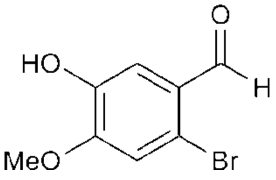
6.3.2 Suggest structures for **J** and **K**.

SOLUTION

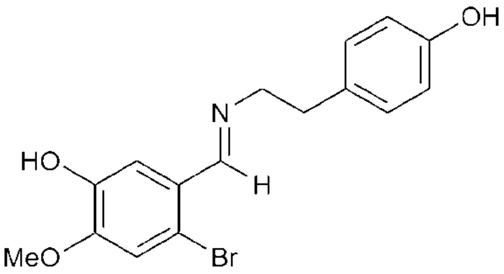
6.1.1 **A**



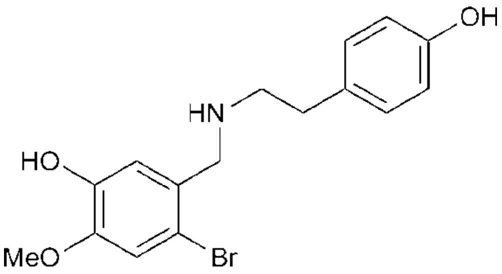
B



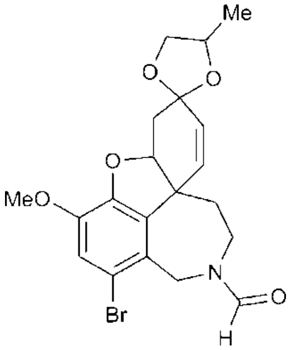
C



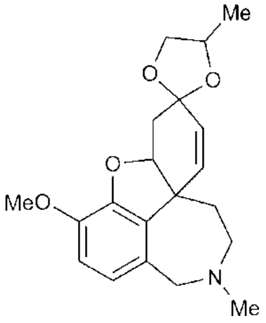
D



E



G



6.1.2 **X:** CH_3CH_2OCOH or any other reasonable reagent.

6.2.1 If *x* is the percentage of the (−)enantiomer:

$x(-415) + (1 - x)(415) = -400$

$x = 815 / 830$

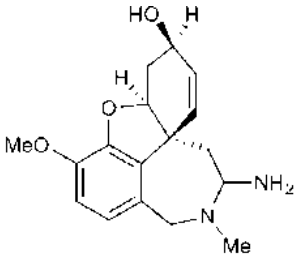
ee = (815 / 830) – (15 / 830) = 800 / 830 = 0.964 or 96.4%

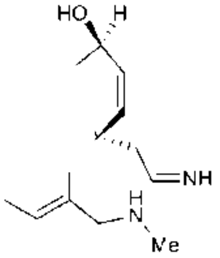
6.2.2 α – S; β – R; γ – S

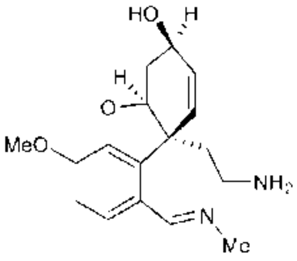
6.2.3 $NaBH_4$, $LiAlH_4$, etc.

6.3.1 **Y:** **CH_3NH_2**

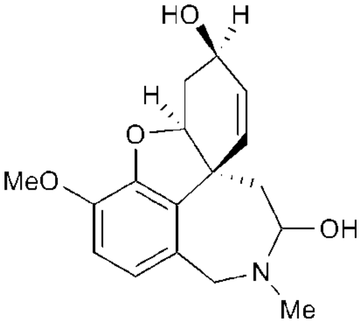
6.3.2 **J:**





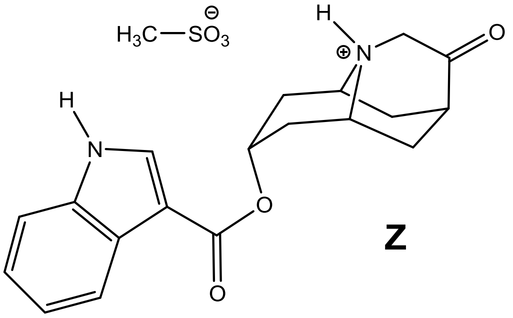


K:

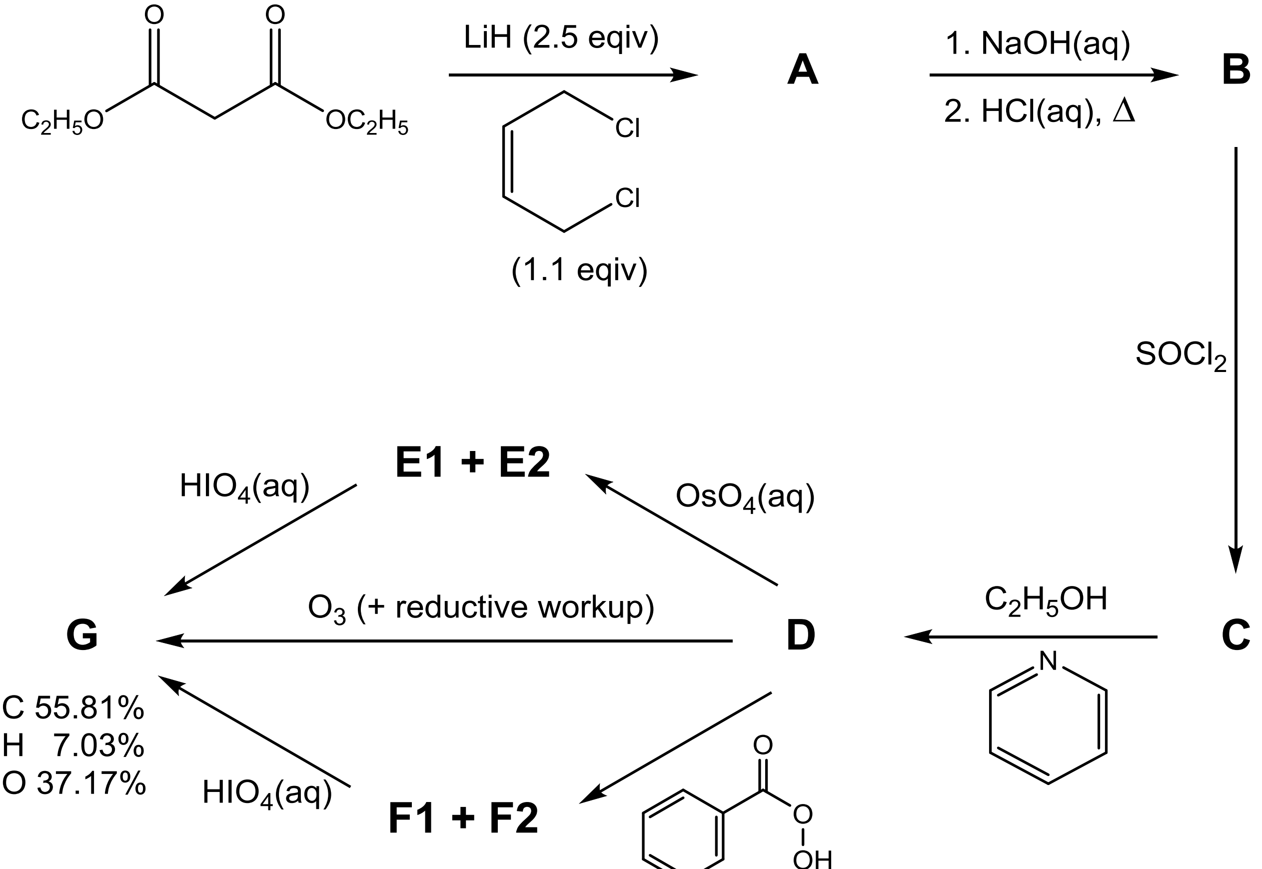


PROBLEM 7

This question looks at the synthesis of *dolasetron mesylate*, **Z** (shown right), a drug sold under the tradename *Anzemet* and used to treat post-operative nausea and vomiting.



The synthesis begins as shown below.



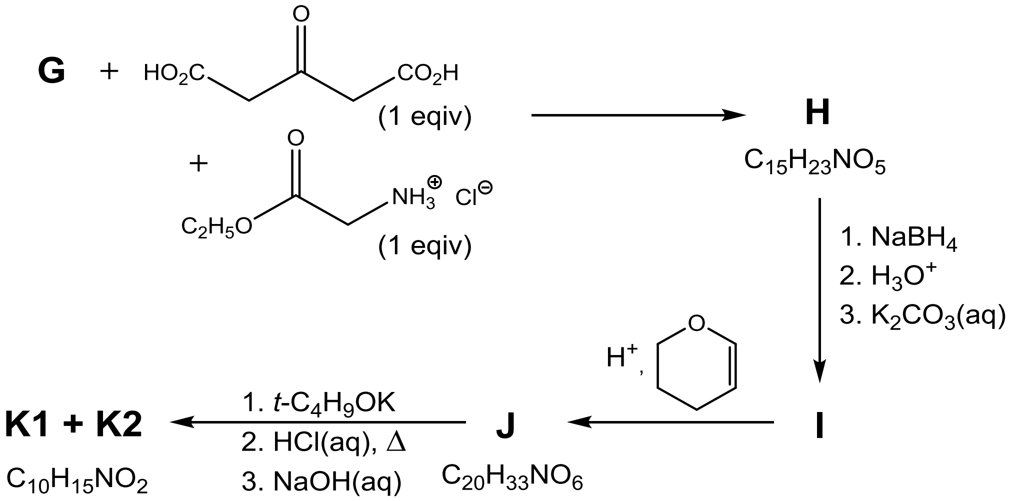
C 55.81%
H 7.03%
O 37.17%

First cyclic compound **A** is made, which contains C, H, and O only. Compound **G** is achiral and can be prepared directly from **D** using ozone under reductive conditions, or via stereoisomers **E1** and **E2** using OsO_4, or via stereoisomers **F1** and **F2** using the peracid shown.

7.1 Determine the empirical formula of **G** from the percentage masses given.

7.2 **Give** the structures of **A**, **B**, **C**, **D**, **E1**, **E2**, **F1**, **F2** and **G**.

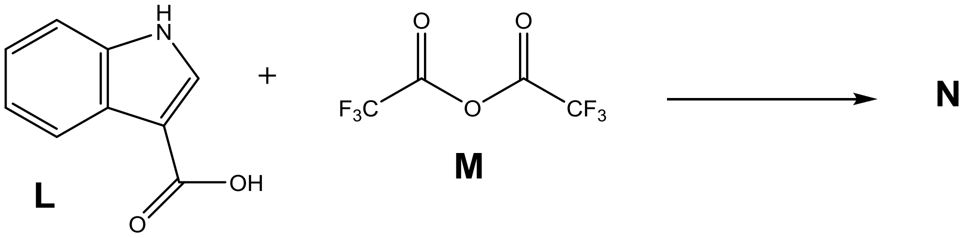
Compound **G** is used in the next stage of the synthesis, under buffered conditions, to form **H** (as a mixture of two achiral diastereoisomers). Reduction of **H** with $NaBH_4$ gives alcohol **I** (as a mixture of four achiral diastereoisomers). **I** reacts with acidified dihydropyran to form **J** (as a mixture of even more diastereoisomers). **J** is then treated first with *t*-butoxide base, then refluxed with acid before finally extracting under weakly basic conditions to form **K** as a mix of two diastereomers, **K1** (major product) and **K2** (minor product). These could be separated, and **K1** was used in the final stages of the synthesis.



7.3.1 Give the structures of **H**, **I**, and **J**. There is no need to show the different diastereoisomers formed.

7.3.2 Give the structures of diastereoisomers **K1**, and **K2**.

In the final stage of the synthesis, **L** and **M** react to form intermediate **N**. **N** then reacts with **K1** to form, after extraction, the neutral amine which gives the target compound upon protonation with CH_3SO_3H.



$$\mathbf{K1} \xrightarrow[\text{2. } CH_3SO_3H]{\text{1. } \mathbf{N}} \mathbf{Z}$$

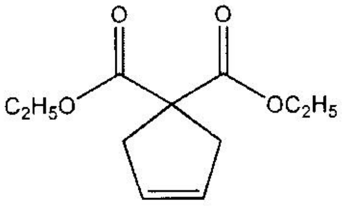
7.4 Give the structure of **N**.

SOLUTION

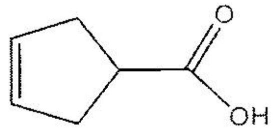
7.1 C_2H_3O

7.2

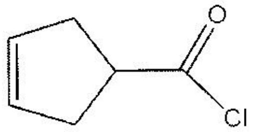
A



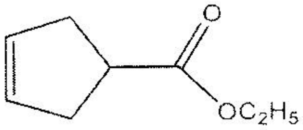
B



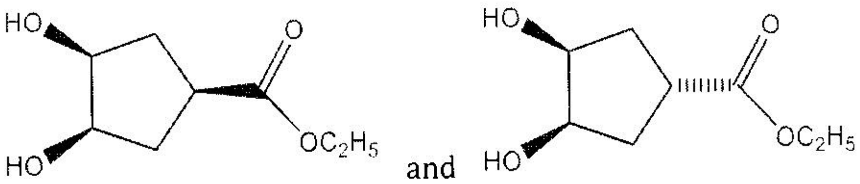
C



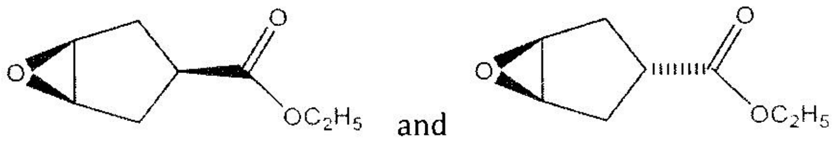
D



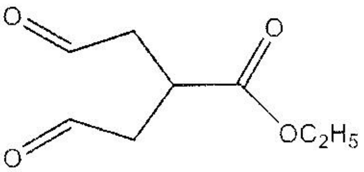
E_1 + E_2

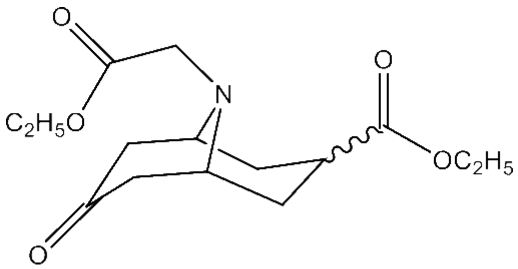


F_1 + F_2



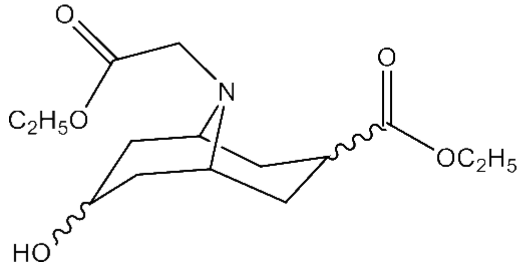
G:



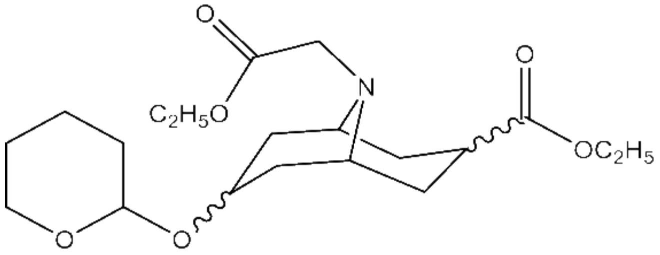


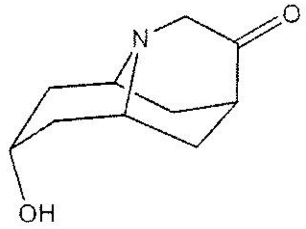
H

I:

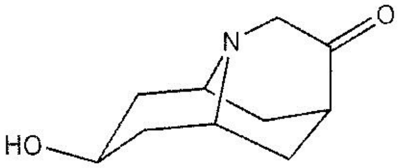


J:

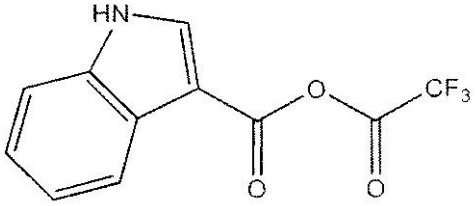




K₁



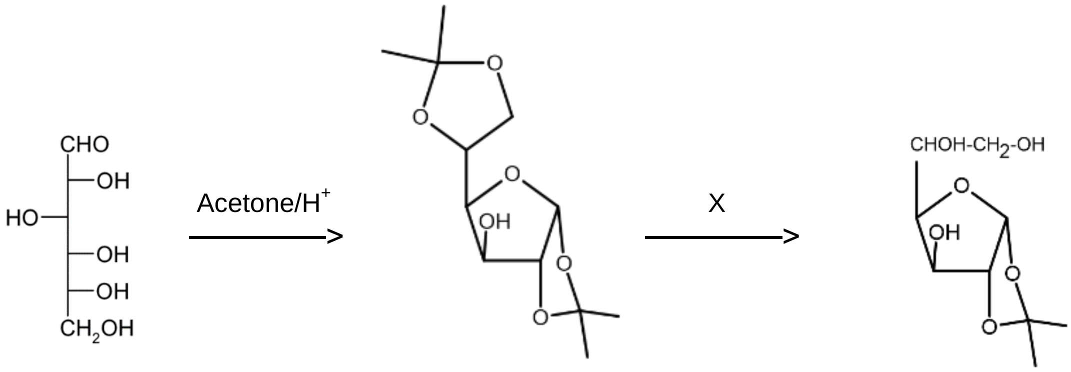
K₂



N

PROBLEM 8

An exotic, but biologically relevant sugar analogue can be prepared from D-glucose in the following manner. Heating a mixture of D-glucose and acetone with a few drops of concentrated acid results in the formation of a diacetonide **A**. Then **A** can be hydrolyzed selectively to **B**.



D-glucose

A

B

8.1.1 Which of the following sentences is true? (Tick the relevant boxes.)

☐ **A** is an α isomer.

☐ **A** is a β isomer.

☐ **A** is neither α nor β.

☐ **A** is a mixture of α and β isomers.

Give your chosen answers to the questions on the answer sheet.

8.1.2 Which of the following sentences is true?

☐ We can get product **A** only if we use α-D glucose as starting material.

☐ We can get product **A** only if we use β-D glucose as starting material.

☐ We can get product **A** either from α- or from β-D glucose as starting material.

8.1.3 Which one of these reagents can be utilized as **X** for the selective hydrolysis of **A**?

☐ 50% acetic acid

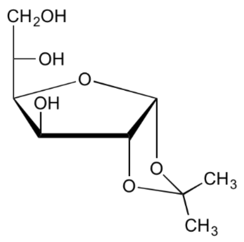
☐ HCl in water (6 mol dm^{-3})

☐ HCl in acetic acid (6 mol dm^{-3})

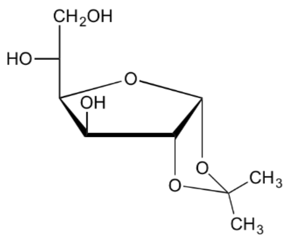
☐ concentrated H_2SO_4

☐ NaOH aqueous solution (1 mol dm^{-3})

8.1.4 Which is the stereochemically correct structure for compound **B**?



☐



☐

Neither of these

☐

B is treated with sodium metaperiodate to get **C**. **C** is then reacted with an aqueous solution of NaCN, then heated with 10% NaOH solution to get a mixture of two diastereomeric compounds $\mathbf{D}_1$ and $\mathbf{D}_2$. These compounds can be separated by column chromatography.

$$\mathbf{B} \xrightarrow{IO_4^-} \underset{188.2\ \text{g mol}^{-1}}{\mathbf{C}} \xrightarrow[\text{2. NaOH/}H_2O]{\text{1. NaCN}} \mathbf{D}_1 \text{ and } \mathbf{D}_2$$

Reaction of $\mathbf{D}_1$ with $LiAlH_4$ followed by heating with 1M HCl solution gives sugar **F** that is the hydrolysis product of the most abundant natural polysaccharide.

$$\mathbf{D_1} \xrightarrow{\text{LiAlH4}} \mathbf{E} \xrightarrow{\text{1M HCl/}H_2O} \mathbf{F}$$

8.2.1 Draw the structures of **C**, $\mathbf{D}_1$, $\mathbf{D}_2$, **E** and **F** including stereochemical information. Show **F** as the more stable 6-membered ring containing isomer using the ring skeleton. Indicate with a wavy line if absolute chirality around a carbon is not known.

8.2.2 The reaction sequence from glucose to **F** does not seem to be useful. In some cases, however, this is the most economical way to produce **F**. In which case?

☐ ^{13}C labelling at carbon 6 of **F**
☐ ^{13}C labelling at carbon 5 of **F**
☐ ^{13}C labelling at carbon 1 of **F**
☐ ^{15}O labelling at glycosidic OH of **F**
☐ synthesis of an uncommon isomer of **F**

Neutralization of $\mathbf{D_2}$ with HCl followed by heating in toluene results in dehydration and formation of **G**, which has a tricyclic structure in water-free solvents. Boiling **G** in HCl solution (c = 1 mol dm^{-3}) gives **H** ($C_6H_{10}O_7$), which is a natural sugar derivative containing a 6 membered ring. **H** is a building block of heparin, an anticoagulant polysaccharide produced by our bodies.

$$\mathbf{D_2} \xrightarrow[\mathbf{-\,H_2O}]{\substack{\text{1. Equimolar HCl} \\ \text{2. Heat, toluene}}} \mathbf{G} \xrightarrow{\text{1 M HCl/}H_2O} \mathbf{H}$$

8.3.1 Draw the structure of **G** including the stereochemistry.

Draw **H** as the more stable 6-membered ring containing isomer using the ring skeleton. Indicate with a wavy line if absolute chirality around a carbon is not known.

8.3.2 How are the rings of **G** fused together?

☐ both junctions cis,

☐ one cis and one trans junction,

☐ both junctions trans.

8.3.3 Which of the following is true for **H**? (You can choose more than one option.)

☐ **H** is a reducing sugar (reacts with Fehling’s reagent)

☐ **H** is an aldaric acid (dicarboxylic derivative of an aldose)

☐ **H** is an aldonic acid (α-carboxyl derivative of an aldose)

☐ **H** is a uronic acid (ω-carboxyl derivative of an aldose)

☐ **H** is a ketose

☐ **H** is a lactone

☐ **H** is a D sugar

☐ **H** is achiral

☐ **H** is a meso compound

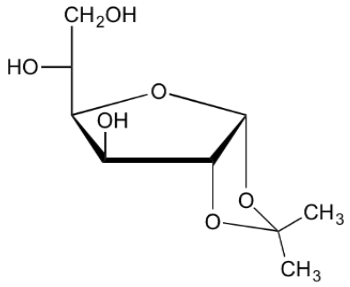
SOLUTION

8.1.1 ☑ **A** is an α isomer.

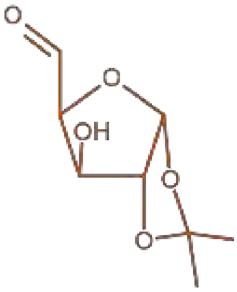
8.1.2 ☑ We can get product **A** either from α- or from β-D glucose as starting material.

8.1.3 ☑ 50% acetic acid

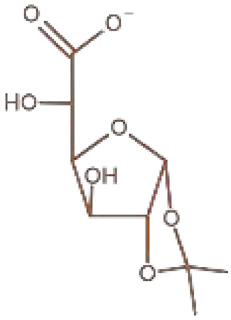
8.1.4 ☑



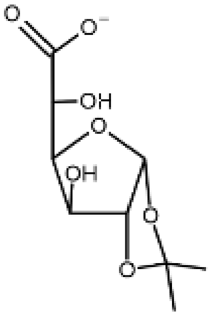
8.2.1 **C:**



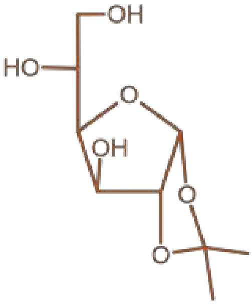
D$_1$:



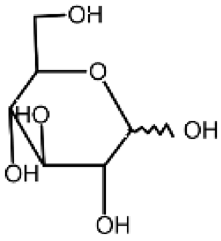
D$_2$:



E:

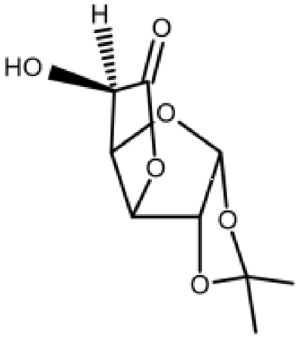


F:

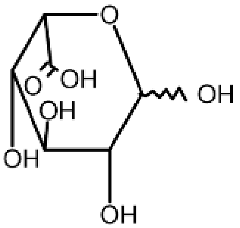


8.2.2 ☑ ^{13}C labelling at carbon 6 of **F**

8.3.1 **G:**



H:



8.3.2 ☑ both junctions cis,

8.3.3 ☑ **H** is a reducing sugar (reacts with Fehling's reagent)

☑ **H** is a uronic acid (ω-carboxyl derivative of an aldose)

PRACTICAL PROBLEMS

PROBLEM 1P (Practical)

Identification of compounds

You have 10 different compounds dissolved in water in 5 unknown solutions. Each numbered container contains two of the following compounds in aqueous solution (every compound is used, and each compound is used only once):

$AgNO_3$, $Al_2(SO_4)_3$, $Ba(NO_3)_2$, $Fe(NO_3)_3$, KI, KIO_3, Na_2CO_3, Na_2SO_3, $MgCl_2$, NH_3

You are given HNO_3 solution, NaOH solution, hexane and the aqueous solutions of the 10 pure compounds listed above. You can use empty test tubes and any of the liquids provided (including the unknowns) to identify the unknown samples. A funnel and filter paper can be used for separation.

Identify the compounds in the solutions 1 – 5**. Give the number of the solution that contains the individual compounds on the answer sheet. Indicate two** observations caused by a chemical reaction for each compound in your unknown mixtures by giving the letter code of the appropriate observation (choose one or more from the list), and write appropriate balanced ionic equation(s) that explain the observation. At least one of the reactions has to be specific for clearly identifying the compound from this selection of unknowns.

Labware

- 1 Test tube rack (60 holes)
- 1 Glass stirring rod, 20 cm
- 1 Glass stirring rod, 20 cm
- 1 Polypropylene funnel, diam. 3.5 cm
- Caps for polystyrene test tubes
- Rack for centrifuge tubes (21 holes)
- Paper filters in zip-bag
- 20 Pasteur pipettes
- 35 Polystyrene test tubes, (10 cm^3)

Chemicals

- hexane, liquid, 25 cm^3
- sodium hydroxide, aqueous solution, (c = 1 mol dm^{-3}), 80 cm^3
- nitric acid, aqueous solution, (c = 2 mol dm^{-3}), 150 cm^3
- 5 unknowns, aqueous solutions,
- silver nitrate, aq. (c = 0.1 mol dm^{-3}), 25 cm^3,
- aluminium sulfate, aq. (c = 0.3 mol dm^{-3}), 25 cm^3,
- barium nitrate, aq. (c = 0.25 mol dm^{-3}), 25 cm^3,
- iron(III) nitrate, aqueous acidic (HNO3) solution, (c = 0.2 mol dm^{-3}), 25 cm^3
- potassium iodide, aqueous solution, (c = 0.1 mol dm^{-3}), 25 cm^3
- potassium iodate, aqueous solution, (c = 0.1 mol dm^{-3}), 25 cm^3
- magnesium chloride, aqueous solution, (c = 0.2 mol dm^{-3}), 25 cm^3
- sodium carbonate, aqueous solution, (c = 0.2 mol dm^{-3}), 25 cm^3
- sodium sulfite, aqueous solution, (c = 0.2 mol dm^{-3}), 25 cm^3
- ammonia, aqueous solution, (c = 1 mol dm^{-3}), 25 cm^3

Only fill out the following table when you are ready with all your assignments. Use the following observation codes:

A - Formation of white precipitate
B - Formation of colored precipitate (red, brown, yellow, black, etc.)
C - Dissolution of precipitate
D - Color change in the solution
E - Formation of colored solution
F - Brown color in the organic phase
G - Purple color in the organic phase
H - Formation of colored gas
I - Formation of colorless and odorless
J - Formation of colorless and odorous
K – Change in the color of precipitate

Table:

Compound	No. of unknown	Formula of the reaction partner(s)	Observation code(s)	Balanced net ionic equation(s)
NH_3				
$Fe(NO_3)_3$				
$Al_2(SO_4)_3$				
$AgNO_3$				
KIO_3				
Na_2CO_3				
$MgCl_2$				
Na_2SO_3				
$Ba(NO_3)_2$				
KI				

SOLUTION

Characteristic reactions are marked with bold letters. One of these or equivalent has to be shown on the answer sheet.

NH_3

$AgNO_3$, B)	$2 Ag^+ + 2 OH^- = Ag_2O + H_2O$ *(if* Ag^+ *is not mixed with* Fe^{3+}*)*
C)	$Ag_2O + H_2O + 4 NH_3 = 2 [Ag(NH_3)_2]^+ + 2 OH^-$ *(if* Ag^+ *is not with* Fe^{3+}*)*
$Fe(NO_3)_3$, B)	$Fe^{3+} + 3 OH^- = Fe(OH)_3$
$Al_2(SO_4)_3$, A)	$Al^{3+} + 3 OH^- = Al(OH)_3$ or $[Al(H_2O)_6]^{3+} + 3 OH^- = Al(OH)_3 + 6 H_2O$)
$MgCl_2$, A)	$Mg^{2+} + 2 OH^- = Mg(OH)_2$
NaOH, J)	$NH_4^+ + OH^- = NH_3 + H_2O$
$(KIO_3) + AgNO_3$, C)	$AgIO_3 + 2 NH_3 = [Ag(NH_3)_2]^+ + IO_3^-$

$Fe(NO_3)_3$

NaOH, B)	$Fe^{3+} + 3 OH^- = Fe(OH)_3$
NH_3, B)	$Fe^{3+} + 3 OH^- = Fe(OH)_3$
KI, D) or E)	$2 Fe^{3+} + 2 I^- = 2 Fe^{2+} + I_2$
$MgCl_2$, E)	$Fe^{3+} + Cl^- = [FeCl]^{2+}$ (or $Fe^{3+} + 3 Cl^- = FeCl_3$ etc.)

$Al_2(SO_4)_3$

NaOH, A)	$Al^{3+} + 3 OH^- = Al(OH)_3$ (or $[Al(H_2O)_6]^{3+} + 3 OH^- = Al(OH)_3 + 6 H_2O$)
C)	$Al(OH)_3 + OH^- = [Al(OH)_4]^-$
(NaOH +HNO_3 A)	$[Al(OH)_4]^- + H^+ = Al(OH)_3 + H_2O$
$Ba(NO_3)_2$, A)	$Ba^{2+} + SO_4^{2-} = BaSO_4$
Na_2CO_3, A)	$Al^{3+} + 3 OH^- = Al(OH)_3$ (or $[Al(H_2O)_6]^{3+} + 3 OH^- = Al(OH)_3 + 6 H_2O$)

$AgNO_3$

NaOH, B)	$2 Ag^+ + 2 OH^- = Ag_2O + H_2O$
KI, B)	$Ag^+ + I^- = AgI$
NH_3, B)	$2 Ag^+ + 2 OH^- = Ag_2O + H_2O$ *(if* Ag^+ *is not mixed with* Fe^{3+}*)*
C)	$Ag_2O + H_2O + 4 NH_3 = 2 [Ag(NH_3)_2]^+ + 2 OH^-$ *(if* Ag^+ *is not with* Fe^{3+}*)*
$MgCl_2$, A)	$Ag^+ + Cl^- = AgCl$
Na_2CO_3, A) or B)	$2 Ag^+ + CO_3^{2-} = Ag_2CO_3$
Na_2SO_3, A)	$2 Ag^+ + SO_3^{2-} = Ag_2SO_3$
C)	$Ag_2SO_3 + 3 SO_3^{2-} = 2 [Ag(SO_3)_2]^{3-}$
KIO_3, A)	$Ag^+ + IO_3^- = AgIO_3$

KIO_3

Na_2SO_3 + HNO_3, B) or E) (+ hexane, G)	$5\ SO_3^{2-} + 2\ IO_3^- + 2\ H^+ = I_2 + 5\ SO_4^{2-} + H_2O$
KI + HNO_3, B) or E) (+ hexane, G)	$5\ I^- + IO_3^- + 6\ H^+ = 3\ I_2 + 3\ H_2O$
$AgNO_3$, A)	$Ag^+ + IO_3^- = AgIO_3$
$Ba(NO_3)_2$, A)	$Ba^{2+} + 2\ IO_3^- = Ba(IO_3)_2$

Na_2CO_3

HNO_3, I)	$O_3^{2-} + 2\ H^+ = H_2O + CO_2$
$Ba(NO_3)_2$, A)	$Ba^{2+} + CO_3^{2-} = BaCO_3$
+ HNO_3, C), I)	$BaCO_3 + 2\ H^+ = Ba^{2+} + H_2O + CO_2$
$AgNO_3$, A) or B)	$2\ Ag^+ + CO_3^{2-} = Ag_2CO_3$
+ HNO_3, C), I)	$Ag_2CO_3 + 2\ H^+ = 2\ Ag^+ + H_2O + CO_2$
$MgCl_2$, A)	$Mg^{2+} + CO_3^{2-} = MgCO_3$
+ HNO_3, C), I)	$MgCO_3 + 2\ H^+ = Mg^{2+} + H_2O + CO_2$

$MgCl_2$

NaOH, A)	$Mg^{2+} + 2\ OH^- = Mg(OH)_2$
NH_3, A)	$Mg^{2+} + 2\ OH^- = Mg(OH)_2$
$AgNO_3$, A)	$Ag^+ + Cl^- = AgCl$
Na_2CO_3, A)	$Mg^{2+} + CO_3^{2-} = MgCO_3$
$Fe(NO_3)_3$, E)	$Fe^{3+} + Cl^- = [FeCl]^{2+}$ (or $Fe^{3+} + 3\ Cl^- = FeCl_3$ etc.)

Na_2SO_3

HNO_3, J)	$SO_3^{2-} + 2\ H^+ = H_2O + SO_2$
KIO_3 + HNO_3, B) or E) (+hexane, G)	$5\ SO_3^{2-} + 2\ IO_3^- + 2\ H^+ = I_2 + 5\ SO_4^{2-} + H_2O$
$Ba(NO_3)_2$, A)	$Ba^{2+} + SO_3^{2-} = BaSO_3$
+ HNO_3, C)	$BaSO_3 + 2\ H^+ = Ba^{2+} + SO_2 + H_2O$
$AgNO_3$, A)	$2\ Ag^+ + SO_3^{2-} = Ag_2SO_3$
C)	$Ag_2SO_3 + 3\ SO_3^{2-} = 2\ [Ag(SO_3)_2]^{3-}$
KI + KIO_3 , D)	$I_2 + SO_3^{2-} + H_2O = 2\ I^- + SO_4^{2-} + 2\ H^+$

$Ba(NO_3)_2$

$Al_2(SO_4)_3$, A)	$Ba^{2+} + SO_4^{2-} = BaSO_4$
KIO_3, A)	$Ba^{2+} + 2\ IO_3^- = Ba(IO_3)_2$
Na_2CO_3, A)	$Ba^{2+} + CO_3^{2-} = BaCO_3$
Na_2SO_3, A)	$Ba^{2+} + SO_3^{2-} = BaSO_3$
+ HNO_3, C)	$BaSO_3 + 2\ H^+ = Ba^{2+} + SO_2 + H_2O$

KI

$Fe(NO_3)_3$, E) orD)	$2\ Fe^{3+} + 2\ I^- = 2\ Fe^{2+} + I_2$
$AgNO_3$, B)	$Ag^+ + I^- = AgI$
KIO_3, + HNO_3, B) or E) (+hexane, G)	$5\ I^- + IO_3^- + 6\ H^+ = 3\ I_2 + 3\ H_2O$

PROBLEM 2P (Practical)

Determination of fluoride and chloride content in mineral water

Georgia is world famous for its splendid mineral waters. Many of these are used to cure various diseases. Manufacturers have to carefully control the ionic composition of waters, fluoride and chloride being among the most important ions.

2.1 Visual colorimetric detection of fluoride

The method of fluoride determination is based on the decrease in the color intensity of zirconium(IV)-Alizarin Red S complex in the presence of fluoride ions due to formation of a more stable colorless complex. The equilibrium is achieved in about 20 minutes after the reagent addition. The fluoride concentration is determined visually by comparing the color developed in the sample with those in the calibration solutions.

Procedure:

Transfer 9.0 cm^3 of mineral water from the sample into the plastic test tube labeled “X”.

Calculate the volume of the standard fluoride solution with a concentration of 9.0 mg dm^{-3}) you will need to prepare a set of calibration solutions with the following fluoride ion mass concentrations (mg dm^{-3}): 0.0; 1.0; 2.0; 3.5; 5.0; 6.5; 8.0 (calculate for 9.0 cm^3 of each solution).

Using the 1.0 cm^3 and 10.0 cm^3 graduated pipettes, add the calculated amounts of the standard fluoride solution to the test-tubes, then add 1.0 cm^3 of Zirconyl Alizarin indicator into each test tube, and bring the volume in each calibration test tube to the 10.0 cm^3 mark with distilled water (the mark is shown in the figure with the arrow).

2.1.1 Report the fluoride volumes used in your dilutions.

Mix the obtained solutions in the test tubes. Set the tube rack aside for at least 20 minutes.

2.1.2 Compare the colour of the sample and the calibration solutions looking on them from the top down and from the front. Select the concentration of the standard that is closest to the fluoride concentration of the water sample.

Note: The rack with the test tubes will be photographed by the lab staff after the whole exam is finished.

2.2 Standardization of silver nitrate solution by the Mohr method

Transfer 10.0 cm^3 of the standard NaCl solution (c = 0.0500 mol dm^{-3}) into an Erlenmeyer flask using the bulb (Mohr) pipette. Add approximately 20 cm^3 of distilled water and 10 drops of 10% aqueous K_2CrO_4 solution. Fill a burette with the silver nitrate solution. Titrate the contents of the flask with the silver nitrate solution while vigorously mixing the solution containing the precipitate formed. The final titrant drops are added slowly with vigorous swirling of the flask. The titration is complete when the faint color change visible on titrant addition does not disappear in the pure yellow suspension. Take the final burette reading. Repeat the titration as necessary.

2.2.1 Report your volumes on the answer sheet.

2.2.2 Write balanced chemical equations for the titration of NaCl with $AgNO3$ and for the end-point indication reaction.

2.2.3 Calculate the concentration of the $AgNO3$ solution from your measurement.

2.2.4 The Mohr titration method requires a neutral medium. Write down equations for the interfering reactions that take place at lower and at higher pH.

2.3 Chloride determination by the Volhard method

Wash the bulb (Mohr) pipette with distilled water. Wash the Erlenmeyer flasks first with a small portion of the ammonia solution left over from Task 1 to help removing the silver salt precipitate and then with distilled water. (In case you used up all the ammonia solution in the first task, you can get a refill without penalty.)

Transfer a 10.0 cm^3 aliquot of the mineral water from the sample into an Erlenmeyer flask using the bulb (Mohr) pipette. Add 5 cm^3 of nitric acid (c = 2 mol dm^{-3}) using a graduated cylinder. Add 20.00 cm^3 of the silver nitrate solution from the burette and mix well the suspension. Add approximately 2 cm^3 of the indicator (Fe^{3+}) solution with the Pasteur pipette.

Fill the second burette with the standard ammonium thiocyanate solution (see the exact concentration on the label). Titrate the suspension with this solution while vigorously swirling. At the end point one drop produces a faint brown colour that is stable even after intense mixing. Take the final burette reading. Repeat the titration as necessary.

Note. The AgCl precipitate exchanges Cl^- ions with SCN^- ions from the solution. If you titrate too slowly or with breaks, the brown color disappears with time, and too much titrant is spent for the titration. Therefore when approaching the endpoint you should add the titrant at a constant slow rate swirling the flask constantly so that the suspension would stay white. The appearance of faint brown color will mean reaching the endpoint.

2.3.1 Report your volumes on the answer sheet.

2.3.2 Write down balanced chemical equations for the back titration with NH4SCN and that for the end-point indication reaction.

2.3.3 Calculate the chloride concentration (in mg/dm^3) in the water sample from your measurements.

2.3.4 If Br^-, I^-, and F^- ions are present in the sample in addition to chloride, the concentration of which ion(s) will contribute to the result of the Volhard titration?

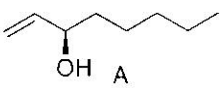
2.3.5 When trying to determine the concentration of Cl^- in the presence of other halides, an analyst added some potassium iodate and sulfuric acid to the sample and boiled the solution. Afterwards he reduced the excess of iodate to iodine by boiling the sample with phosphorous acid H_3PO_3. What interfering anions were removed by this operation? Write the chemical equations for the reactions of these ions with iodate.

PROBLEM 3P (Practical)

Identifying flavors and fragrances

Tourists coming to Georgia admire many specialties, local cuisine occupying one of the top positions in the list of adventures. Excellent meat, fresh vegetables and greens, ripe fruits, home-made jams… What else is needed to satisfy true gourmets? Of course, unique flavors and fragrances!

You are given 8 samples of unknown organic compounds (labeled 1 to 8), which are industrially used as flavors and fragrances. All samples are pure individual compounds. Their possible structures are found among **A**-**M** given here.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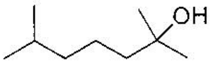
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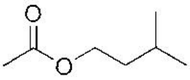
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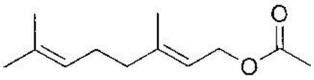
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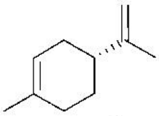
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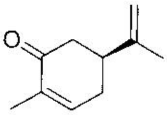
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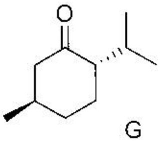
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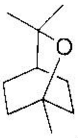
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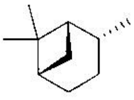
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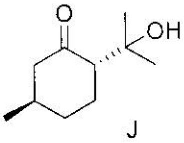
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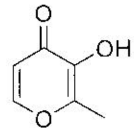
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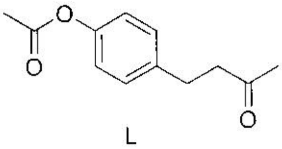
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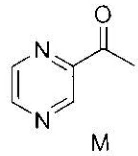

M

The organic compounds in your unknown samples are readily soluble in ether, and insoluble in dilute aqueous NaOH and HCl. These compounds, but the unknown No. 6. are insoluble in water, the latter being slightly soluble (3.5 g dm^{-3}).

3.1. Perform test reactions described below to identify the samples **1**-**8**. Indicate the results of the tests by giving the Roman numeral of the appropriate observation (choose one or more from the list). Fill in all cells of the table. Use **+** and **–** to indicate positive and negative tests.

3.2. Identify the unknowns based on the test results and the information given above.

3.3. Write the structure codes (of **A** to **M**) of the identified samples in the appropriate box.

Test procedures

KMnO$_4$ test (Baeyer test)

Place approximately 1 cm^3 of 95% ethanol in a plastic test tube and add 1 drop of an unknown. Add 1 drop of KMnO$_4$ solution and shake the mixture. Treat the test as positive if the permanganate color disappears immediately after shaking.

3.4. Write the reaction scheme for a positive Baeyer test with one of the compounds **A** - **M**.

Cerium(IV) nitrate test

Place 2 drops of the **Ce(IV) reagent** into a glass test tube, add 2 drops of acetonitrile and then 2 drops of an unknown (the sequence is important!). Shake the mixture. In the case of positive test the mixture color promptly changes from yellow to orange-red.

Note 1. Use only glass test tubes to perform the test. In case you need to wash the glass test tubes, carefully choose the appropriate solvent. Use caps to prevent the strong odor.

Note 2. Comparison with blank (no unknown) and reference (with ethanol) tests is recommended for adequate interpretation.

Note 3. Ce(IV) ions initially form brightly colored coordination compounds with alcohols. Complexes formed from primary or secondary alcohols react further (within 15 seconds to 1 hour) with the disappearance of the color.

2,4-dinitrophenylhydrazine (2,4-DNPH) test

Add only 1 drop of an unknown to 1 cm^3 of 95% ethanol in a plastic test tube. Add 1 cm^3 of the DNPH reagent to the prepared solution. Shake the mixture and let it stand for 1-2 min. Observe formation of yellow to orange-red precipitate if the test is positive.

3.5. Write the reaction scheme for a positive 2,4-DNPH test with one of the compounds **A**-**M**.

Ferric hydroxamate test

Ask a lab assistant to light up your alcohol lamp. Mix 1 cm^3 of 0.5 mol dm^{--3} ethanolic hydroxylamine hydrochloride solution with 5 drops of 6 mol dm^{--3} sodium hydroxide aqueous solution in a glass test tube. Add 1 drop of an unknown and use the alcohol lamp to heat the mixture to boiling while gently swirling the test tube to avoid splashes of the reaction mixture. Allow it to cool down slightly and add 2 cm^3 of 1 mol/dm^3 HCl solution. Add 1 drop of 2.5% iron(III) chloride solution. Observe appearance of magenta color if the test is positive. Close the alcohol lamp with the cap when finished.

Note 1. Use glass test tubes only to perform the test; use the test tube holder when heating. In case you need to wash the glass test tubes, use an appropriate

solvent. Stopper the test tubes with a green cap after completing the test to prevent a strong odor.

Note 2. Fe(III) ions form a colored 1:1 complex with hydroxamic acids (R-CO-NHOH).

3.6. Write the reaction scheme for a positive ferric hydroxamate test with one of the compounds **A**-**M**.

49^{th}

11 theoretical problems
3 practical problems

THE FORTY-NINETH
INTERNATIONAL CHEMISTRY OLYMPIAD
6–15 JULY 2017, NAKHON PATHOM, THAILAND

THEORETICAL PROBLEMS

PROBLEM 1

Production of propene using heterogeneous catalysts

Propene or propylene is one of the most valuable chemicals for the petrochemical industry in Thailand and around the world. One good example of the commercial use of propene is for the production of polypropylene (PP).

Part A.

Propene can be synthesized via a direct dehydrogenation of propane in the presence of a heterogeneous catalyst. However, such a reaction is not economically feasible due to the nature of the reaction itself. Provide a concise explanation to each of the questions below. Additional information: H_{bond}(C=C) = 1.77H_{bond}(C-C), H_{bond}(H-H) = 1.05H_{bond}(C-H), and H_{bond}(C-H) = 1.19H_{bond}(C-C), where H_{bond} refers to average bond enthalpy of the indicated chemical bond.

1.1 What is the enthalpy change of the direct dehydrogenation of propane? Show your calculation and express your answer in terms of H_{bond}(C-C).

1.2 It is difficult to increase the amount of propene by increasing pressure at constant temperature. Which law or principle can best explain this phenomenon? Select your answer by marking "✓" in **one** of the open circles.

☐ Boyle's law
☐ Charles' law
☐ Dalton's law
☐ Raoult's law
☐ Le Chatelier's principle

1.3 Initially, the system is in equilibrium. Consistent with question **1.1**, what is/are correct set(s) of signs for the following thermodynamic variables of the system for the direct dehydrogenation of propane? Select your answer(s) by marking „✓" in any of the open square(s).

	ΔH	ΔS	ΔG	T^*
☐	-	+	+	lower
☐	-	+	-	higher
☐	-	-	+	lower
☐	-	-	-	higher
☐	+	+	+	lower
☐	+	+	-	higher
☐	+	-	+	lower
☐	+	-	-	higher

☐ None of the above is correct

[*] Relative to the initial temperature at the same partial pressure.

Part B.

A better reaction to produce large quantity of propene is the *oxidative dehydrogenation (ODH)* using solid catalysts, such as vanadium oxides, under molecular oxygen gas. Although this type of reaction is still under intense research development, its promise toward the production of propene at an industrial scale eclipses that of the direct dehydrogenation.

1.4 The overall rate of propane consumption in the reaction is

$$r_{C_3H_6} = \frac{1}{\dfrac{p^0}{k_{red}\, p_{C_3H_6}} + \dfrac{p^0}{k_{ox}\, p_{O_2}}}$$

where k_{red} and k_{ox} are the rate constants for the reduction of metal oxide catalyst by propane and for the oxidation of the catalyst by molecular oxygen, respectively, and p^o is the standard pressure of 1 bar. Some experiments found that the rate of oxidation of the catalyst is 100,000 times faster than that of the propane oxidation. The experimental

$$r_{C_3H_6} = k_{obs}\,\frac{p_{C_3H_6}}{p^0}$$

where k_{obs} is the observed rate constant (0.062 mol s^{-1}). If the reactor containing the catalyst is continuously passed through with propane and oxygen at a total pressure of 1 bar, determine the value of k_{red} and k_{ox} when the partial pressure of propane is 0.10 bar. Assume that the partial pressure of propene is negligible.

Part C.

The metal oxide catalyst contains oxygen atoms on its surface that serve as active sites for the ODH. Denoting red* as a reduced site and O(*s*) as an oxygen atom on the surface of the catalyst, one of the proposed mechanisms for the ODH in the presence of the catalyst can be written as follows:

$$C_3H_8(g) + O(s) \xrightarrow{k_1} C_3H_6(g) + H_2O(g) + \text{red*} \qquad (1)$$

$$C_3H_6(g) + 9\,O(s) \xrightarrow{k_2} 3\,CO_2(g) + 3\,H_2O(g) + 9\,\text{red*} \qquad (2)$$

$$O_2(g) + 2\,\text{red*} \xrightarrow{k_3} 2\,O(s) \qquad (3)$$

Given $\beta = \dfrac{\text{number of reduced sites}}{\text{total number of active sites}}$

The rate laws for the above 3 steps are:

$r_1 = k_1\,p_{C_2H_8}(1 - \beta)$

$r_2 = k_2\,p_{C_3H_6}(1 - \beta)$

and $r_3 = k_3\,p_{O_2}\,\beta$

1.5 Assuming that the amount of oxygen atoms on the surface stays constant at any time of reaction, calculate β as a function of

$$k_1,\ k_2,\ k_3,\ p_{C_2H_8},\ p_{C_3H_6},\ \text{and } p_{O_2}.$$

SOLUTION

1.1 $\Delta H_{rxn} = -\{H_{bond}(C{=}C) + H_{bond}(C\text{-}C) + 6H_{bond}(C\text{-}H) + H_{bond}(H\text{-}H)\}$

$+\{2H_{bond}(C\text{-}C)+8H_{bond}(C\text{-}H)\}$

$= -\{1.77H_{bond}(C\text{-}C) + H_{bond}(C\text{-}C) + 6(1.19H_{bond}(C\text{-}C) + 1.05(1.19H_{bond}(C\text{-}C)\}$

$+\{2H_{bond}(C\text{-}C)+8(1.19H_{bond}(C\text{-}C)\} = +0.360H_{bond}(C\text{-}C)$

1.2 ☑ Le Chatelier's principle

1.3

	ΔH	ΔS	ΔG	T^*
☑	+	+	+	lower
☑	+	+	–	higher

1.4 From the information given, the oxidation step is much faster than the propane reduction. Thus,

$$\frac{1}{k_{red}\, p_{C_3H_8}} >> \frac{1}{k_{ox}\, p_{O_2}}$$

We then have $r_{C_3H_8} = k_{red}\, p_{C_3H_8}$

Therefore, $k_{obs} = k_{red} = 0.062$ mol s^{-1}.

Since $k_{ox}\, p_{O_2} = 100{,}000\; k_{red}\, p_{C_3H_8}$

$k_{ox} = 100{,}000\ (0.062 \text{ mol s}^{-1})\ (0.10) / (0.90) = 6.9\times10^{2} \text{ mol s}^{-1}$.

1.5 $r_1 + 9\, r_2 = 2\, r_3$

$k_1\, p_{C_3H_8}(1 - \beta) + 9\, k_2 p_{C_3H_6}(1 - \beta) = 2\, k_3 p_{O_2}\beta$

$k_1\, p_{C_3H_8} + 9\, k_2 p_{C_3H_6} - \beta(k_1\, p_{C_3H_8} + 9\, k_2 p_{C_3H_6}) = 2\, k_3 p_{O_2}\beta$

$\beta(k_1\, p_{C_3H_8} + 9\, k_2 p_{C_3H_6} + 2\, k_3 p_{O_2}) = k_1\, p_{C_3H_8} + 9\, k_2 p_{C_3H_6}$

$$\text{Thus, } \beta = \frac{k_1\, p_{C_3H_8} + 9\, k_2 p_{C_3H_6}}{k_1\, p_{C_3H_8} + 9\, k_2 p_{C_3H_6} + 2\, k_3 p_{O_2}}$$

PROBLEM 2

Kinetic isotope effect (KIE) and zero-point vibrational energy (ZPE)

Calculation of ZPE and KIE

Kinetic isotope effect (KIE) is a phenomenon associated with a change in rate constant of the reaction when one of the atoms is replaced by its isotope. KIE can be used to confirm whether a particular bond to hydrogen is broken in the reaction. Harmonic oscillator model is used to estimate the difference in the rate between C-H and $\overset{1}{\text{C}}$-D bond activation (D – deuterium).

The vibrational frequency (ν) represented by harmonic oscillator model is

$$v = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

where k is the force constant and μ is the reduced mass.

The vibrational energies of the molecule are given by

$$E_n = \left(n + \frac{1}{2}\right) hv$$

where n is vibrational quantum number with possible values of 0, 1, 2, ... The energy of the lowest vibrational energy level (E_n at n = 0) is called **zero-point vibrational energy (ZPE)**.

2.1 Calculate the reduced mass of C-H (μ_{CH}) and C-D (μ_{CD}) in atomic mass unit. Assume that the mass of deuterium is twice that of hydrogen.

Note: If a student is unable to calculate the values for μ_{CH} and μ_{CD} he/she can use μ_{CH} = 1.008 and μ_{CD} = 2.016 for the subsequent parts of the question. The given values are not necessarily be close to the correct values.

2.2 Given that the force constant (k) for C-H stretching is the same as that for the C-D stretching and the C-H stretching frequency is 2900 cm^{-1}, find the corresponding C-D stretching frequency (in cm^{-1}).

2.3 According to the C-H and C-D stretching frequencies in question **2.2**, calculate the zero-point vibrational energies (ZPE) of C-H and C-D stretching in kJ mol^{-1}.

Note: If a student is unable to calculate the values for *ZPE* in **2.3**, he/she can use use ZPE_{CH} = 7.23 kJ mol^{-1} and ZPE_{CD} = 2.15 kJ mol^{-1} for the subsequent parts of the question. The given values are not necessarily be close to the correct values.

Kinetic isotope effect (KIE)

Due to the difference in zero-point vibrational energies, a protonated compound and its corresponding deuterated compounds are expected to react at different rates.

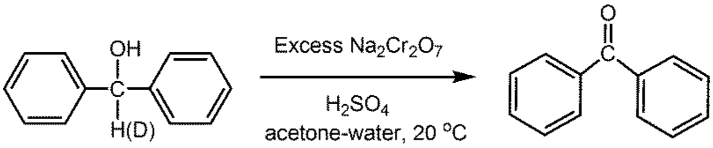
For the C-H and C-D bond dissociation reactions, the energies of both transition states and both products are identical. Then, the isotope effect is controlled by the difference in the ZPE's of the C-H and C-D bonds.

2.4 Calculate the difference in the bond dissociation energy (BDE) between C-D bond and C-H bond ($\text{BDE}_{\text{CD}} - BDE_{CH}$) in kJ mol^{-1}.

2.5 Assume that the activation energy (E_a) for the C-H/C-D bond cleavage is approximately equal to the bond dissociation energy and the Arrhenius factor is the same for both C-H and C-D bond cleavage. Find the relative rate constant for the C-H/C-D bond cleavage (k_{CH}/k_{CD}) at 25 °C.

Using KIE to study reaction mechanism

The oxidation of nondeuterated and deuterated diphenylmethanol using an excess of chromic acid was studied.



2.6 Let C_0 be the initial concentration of either nondeuterated diphenylmethanol or deuterated diphenylmethanol and C_t its concentration at time t. The experiment led to two plots (Figure 2a and Figure 2b), from which the first-order rate constant can be determined.

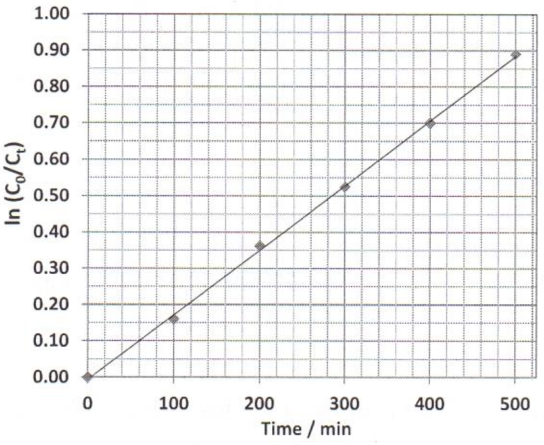


Figure 2a

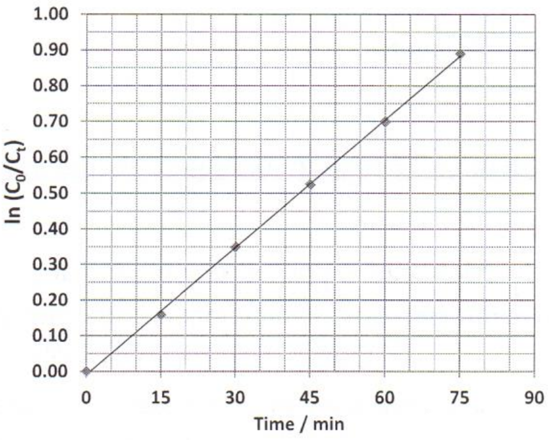


Figure 2b

Which plot should be for the oxidation of nondeuterated diphenylmethanol and which one is for the oxidation of deuterated diphenylmethanol?

For each statement, select your answer by marking "✓" in **one** of the square.

The oxidation of nondeuterated diphenylmethanol:

☐ Figure 2a

☐ Figure 2b

The oxidation of deuterated Figure 2b

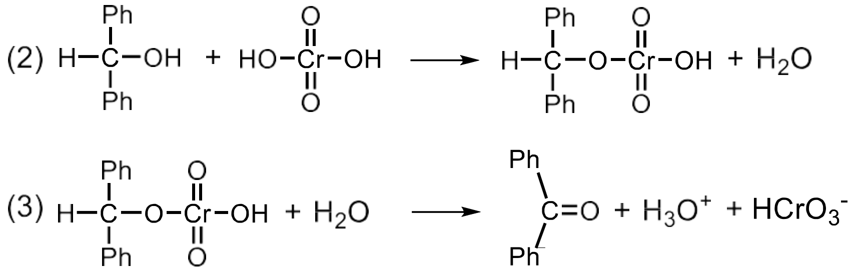
☐ Figure 2a

☐ Figure 2b

2.7 Determine k_{CH}, k_{CD} (in min^{-1}), and the k_{CH}/k_{CD} of this reaction from the plots in question **2.6.**

2.8 The mechanism has been proposed as follows:

$$(1)\quad Cr_2O_7^{2-} + H_2O + 2H^+ \rightleftharpoons 2H_2CrO_4$$



$$(2)\quad Ph_2CH{-}OH + HO{-}CrO_2{-}OH \longrightarrow Ph_2CH{-}O{-}CrO_2{-}OH + H_2O$$

$$(3)\quad Ph_2CH{-}O{-}CrO_2{-}OH + H_2O \longrightarrow Ph_2C{=}O + H_3O^+ + HCrO_3^-$$

According to the information in **2.6** and **2.7**, which step should be the rate determining step?

Select your answer by marking “✓” in **one** of the corresponding squares:

☐ Step (1)

☐ Step (2)

☐ Step (3)

SOLUTION

2.1

$$\mu_{CH} = \frac{m_C\, m_H}{m_C + m_H} = \frac{(12.01)\,(1.008)}{12.01 + 1.008} = \frac{12.11}{13.02} = 0.9299 \text{ amu}$$

$$\mu_{CD} = \frac{m_C\, m_D}{m_C + m_D} = \frac{(12.01)\,(2\times 1.008)}{12.01 + (2\times 1.008)} = \frac{24.21}{14.03} = 1.726 \text{ amu}$$

2.2 1. Use the correct reduced mass.

$$\nu_{CH} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{CH}}}$$

$$\nu_{CD} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu_{CD}}}$$

$$\frac{\nu_{CH}}{\nu_{CD}} = \sqrt{\frac{\mu_{CD}}{\mu_{CH}}} = \sqrt{\frac{1.726}{0.9299}} = \sqrt{1.856} = 1.362$$

$$\nu_{CD} = \frac{\nu_{CH}}{1.362} = \frac{2900}{1.362} = 2129 \text{ cm}^{-1}$$

2. Use the reduced mass given.

$$\frac{\nu_{CH}}{\nu_{CD}} = \sqrt{\frac{\mu_{CD}}{\mu_{CH}}} = \sqrt{\frac{2.016}{1.008}} = \sqrt{2.000} = 1.414$$

$$\nu_{CD} = \frac{\nu_{CH}}{1.414} = \frac{2900}{1.414} = 2051 \text{ cm}^{-1}$$

2.3 $E_n = (n + 1/2)\, h\nu$, $n = 0, 1, 2, \ldots$

ZPE = $E_{n=0}$ = 1/2 $h\nu$

ZPE$_{CH}$ = 1/2 $h\nu_{CH}$ =

= 1/2 (6.6261×10^{-34} J s) (2900 cm^{-1}) (2.9979×10^{10} cm s^{-1}) (6.0221×10^{23} mol^{-1}) (10^{-3} kJ)

= 17.35 kJ mol^{-1}

Either 1. or 2. below is accepted.

1. Use the correct reduced mass.

ZPE$_{CD}$ = 1/2 $h\nu_{CD}$ =

= 1/2 (6.6261×10^{-34} J s) (2129 cm^{-1}) (2.9979×10^{10} cm s^{-1}) (6.0221×10^{23} mol^{-1})(10^{-3} kJ) =

= 12.73 kJ mol^{-1}

2. Use the given reduced mass.

ZPE$_{CD}$ = 1/2 $h\nu_{CD}$ =

$= 1/2\ (6.6261\times10^{-34}\ \text{J s})\ (2051\ \text{cm}^{-1})\ (2.9979\times10^{10}\ \text{cm s}^{-1})\ (6.0221\times10^{23}\ \text{mol}^{-1})\ (10^{-3}\ \text{kJ})$

$= 12.27\ \text{kJ mol}^{-1}$

2.4 From the ZPE_{CH} and ZPE_{CD} in question **2.3**

1. Use the correct reduced mass.

$$BDE_{CD} - BDE_{CH} = ZPE_{CH} - ZPE_{CD}$$

$$\square \qquad = (17.35 - 12.73)\ \text{kJ mol}^{-1}$$

$$\square \qquad = 4.62\ \text{kJ mol}^{-1}$$

2. Use the given reduced mass.

$$BDE_{CD} - BDE_{CH} = ZPE_{CH} - ZPE_{CD}$$

$$\square \qquad = (17.35 - 12.27)\ \text{kJ mol}^{-1}$$

$$\square \qquad = 5.08\ \text{kJ mol}^{-1}$$

3. Use the given ZPE.

$$BDE_{CD} - BDE_{CH} = ZPE_{CH} - ZPE_{CD}$$

$$= 7.23 - 2.15\ \text{kJ mol}^{-1}$$

$$= 5.08\ \text{kJ mol}^{-1}$$

2.5 **1.** Use the correct reduced mass.

$$\frac{k_{CH}}{k_{CD}} = e^{-(ZPE_{CD} - ZPE_{CH})\,/\,RT}$$

$$= e^{-(-4.62\times10^{3}\ \text{J mol}^{-1})\,/\,8.314\ \text{J K}^{-1}\ \text{mol}^{-1}\times298.15\ \text{K}} = e^{1.86} = 6.45$$

2. Use the given reduced mass or the given ZPE.

$$\frac{k_{CH}}{k_{CD}} = e^{-(ZPE_{CD} - ZPE_{CH})\,/\,RT}$$

$$= e^{-(-5.08\times10^{3}\ \text{J mol}^{-1})\,/\,8.314\ \text{J K}^{-1}\ \text{mol}^{-1}\times298.15\ \text{K}} = e^{2.05} = 7.77$$

2.6 The oxidation of nondeuterated diphenylmethanol: ☑ Figure 2b

The oxidation of deuterated diphenylmethanol: ☑ Figure 2a

2.7

$$\ln\frac{C_0}{C_t} = k_{CH}\,t \qquad \ln\frac{C_0}{C_t} = k_{CD}\,t$$

k_{CH} = 0.012 min^{-1} (from the slope of the plot in Figure 2b)

Example:

$$k_{CH} = \frac{0.70 - 0.35}{60 - 30} = 0.012 \text{ min}^{-1}$$

k_{CD} = 0.0018 min^{-1} (from the slope of the plot in Figure 2a)

Example:

$$k_{CD} = \frac{0.70 - 0.35}{400 - 200} = 0.0018 \text{ min}^{-1}$$

$$\frac{k_{CH}}{k_{CD}} = \frac{0.012}{0.0018} = 6.7$$

2.8 ☑ Step (3)

PROBLEM 3

Thermodynamics of chemical reactions

Part A.

Methanol is produced commercially by using a mixture of carbon monoxide and hydrogen over zinc oxide/copper oxide catalyst:

$CO(g) + 2\ H_2(g) \rightarrow CH_3OH(g)$.

The standard enthalpy of formation (ΔH_f^o) and the absolute entropy (S^o) for each of the three gases at room temperature (298 K) and at a standard pressure of 1 bar are given as follows.

Gas	ΔH_f^o (kJ mol^{-1})	S^o (J K^{-1} mol^{-1})
$CO(g)$	-111	198
$H_2(g)$	0	131
$CH_3OH(g)$	-201	240

3.1 Calculate ΔH^0, ΔS^0, ΔG^0, and K_p for the reaction at 298 K.

(If you are unable to calculate K_p at 298 K in problem 3.1, use $K_p = 9\times10^5$ later on.)

3.2 A commercial reactor is operated at a temperature of 600 K. Calculate the value of K_p at this temperature, assuming that ΔH^o and ΔS^o are independent on temperature.

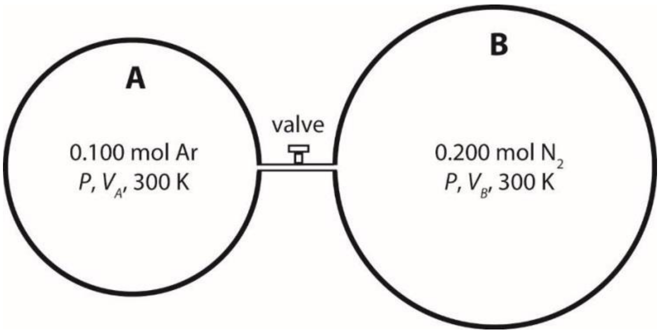
(If you are unable to calculate K_p at 600 K in problem 3.2, use $K_p = 1.0\times10^{-2}$ later on.)

3.3 Production of methanol in industry is based on flowing of the gas comprising 2.00 moles of H_2 for each mole of CO into the reactor. The mole fraction of methanol in the exhaust gas from the reactor was found to be 0.18. Assuming that equilibrium is established, what is the total pressure in the reactor at a high temperature of 600 K?

Part B.

3.4 Consider the following closed system at 300 K. The system comprises 2 compartments, separated by a closed valve, which has negligible volume (see next figure). At the same pressure P, compartment A and compartment B contain 0.100

mol argon gas and 0.200 mol nitrogen gas, respectively. The volumes of the two compartments, V_A and V_B, are selected so that the gases behave as ideal gases.



After opening the valve slowly, the system is allowed to reach equilibrium. It is assumed that the two gases form an ideal gas mixture. Calculate the change in Gibbs free energy at 300 K, ΔG .

If you are unable to calculate K_p at 298 K in problem **3.1**, use $K_p = 9\times10^5$ later on.

SOLUTION

3.1 $\Delta H^o\text{ (reaction)} = \Delta H_f^o\,(CH_3OH) - \Delta H_f^o\,(CO) - 2\,\Delta H_f^o(H_2)$ (kJ)

$= -201 - (-111) - 2(0)$ (kJ)

$= 90$ kJ

$\Delta S^o\text{ (reaction)} = S^o\,(CH_3OH) - S^o\,(CO) - 2\,S^o(H_2)$ (J K^{-1})

$= 240 - 198 - (2 \times 131)$

$= -220\ \text{J K}^{-1}$

$\Delta G^o = \Delta H^o - T\,\Delta S^o$ (kJ)

$= -90- [\,(298)(-220)\,/1000]$

$= -24$ kJ

$K_p = \exp(-\Delta G^o/RT) = \exp\,[24000 / (8.3145)(298)] = \exp(9.69)$

$K_p = 1.6\times10^4$

3.2 To find the value of K_p at 600 K we use the van't Hoff isochore

$$\ln K_p = \frac{-\Delta H^0}{R\,T} + constant$$

It follows that

$$\ln K_p(600) = \ln K_p(298) + \frac{\Delta H^0}{R}\left(\frac{1}{298\ K} - \frac{1}{600\ K}\right)$$

$$\ln K_p(1.6\times10^4) + \frac{-90\times10^3\ \text{J mol}^{-1}}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{298\ K} - \frac{1}{600\ K}\right)$$

$K_p = 1.8\times10^{-4}$

or $K_p = 1\times10^{-2}$ (if using $K_{p,\,298\,K} = 9\times10^5$ ⇨ fake value)

3.3 It is helpful to consider the amounts of different species present before the reaction and during the equilibrium.

	$CO(g)$	+	$2\ H_{2(}(g)$	⇆	$CH_3OH(g)$
Before reaction:	1 mol		2 mol		0 mol
At equilibrium:	1–y mol		2–2y mol		y mol

The amount of methanol, y moles, can be found from the fact that the mole fraction of methanol is 0.18, so

$$0.18 = \frac{n(CH_3OH)}{n(H) + n(CO) + n(CH_3OH)} = \frac{y}{3 - 2y}$$

Thus, y = 0,40 mol

From the above expressions it is possible to find the mole fractons x of different species.

$$x(CH_3OH) = \frac{0.40}{3 - (2 \times 0.40)} = 0.18$$

$$x(CO) = \frac{1 - 0.40}{3 - (2 \times 0.40)} = 0.27$$

$$x(H_2) = \frac{2 - (2 \times 0.40)}{3 - (2 \times 0.40)} = 0.55$$

The corresponding partial pressures are:

$p(CH_3OH) = 0.18 \times p_{tot}$

$(CO) = 0.27 \times p_{tot}$

$p(H_2) = 0.55 \times p_{tot}$

where p_{tot} is the total pressure.

Since the reactor operates at 600 K,

$$K_p = 1.8 \times 10^{-4}) = \frac{p(CH_3OH)}{p(CO)\,p(H_2O)} = \frac{0.18\, p_{tot}}{0.27\, p_{tot} \times 0.55\, p_{tot}}$$

Solving this equation gives p_{tot} = 111 bar (or 15 bar if $K_p = 1.0 \times 10^{-2}$ is used).

4.1 At constant T, $\Delta U = 0$ and $\Delta H = 0$.

ΔS of the process can be found as described below.

For an irreversible process (at constant pressure), $q = -w = p\,\Delta V$, while $q = - w = nRT \ln V_2/V_1$ for a reversibile process (at a constant temperature). The change in the entropy can be find from:

$$\Delta S = \frac{q_{rev}}{T} = \frac{nRT \ln \frac{V_2}{V_1}}{T} = nR \ln\frac{V_2}{V_1}$$

Therefore, for this process:

$$\Delta S = n_A R \ln\frac{(V_A + V_B}{V_A} + n_B R \ln\frac{(V_A + V_B}{V_B}$$

$$= 0.100\ R \ln\frac{3}{1} + 0.200\ R \ln\frac{3}{2} = 1.59\ \text{J K}^{-1}$$

Lastly the change in Gibbs free energy can be found as follows:

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

$= - 300´1.59 = - 477$ J

$\Delta G = n_A RT \ln x_A + n_B RT \ln x_B = - 477$ J

PROBLEM 4

Electrochemistry.

Part A. Galvanic cell

The experiment is performed at 30.00ºC. The electrochemical cell is composed of a hydrogen half-cell [Pt(*s*)│H2(*g*)│H$^+$(*aq*)] containing a metal platinum electrode immersed in a buffer solution under a pressure of hydrogen gas. This hydrogen half-cell is connected to a half-cell of a metal (**M**) strip dipped in an unknown concentration of **M^{2+}**(*aq*) solution. The two half-cells are connected *via* a salt bridge as shown in Figure 1.

Note: The standard reduction potentials are given in Table 1.

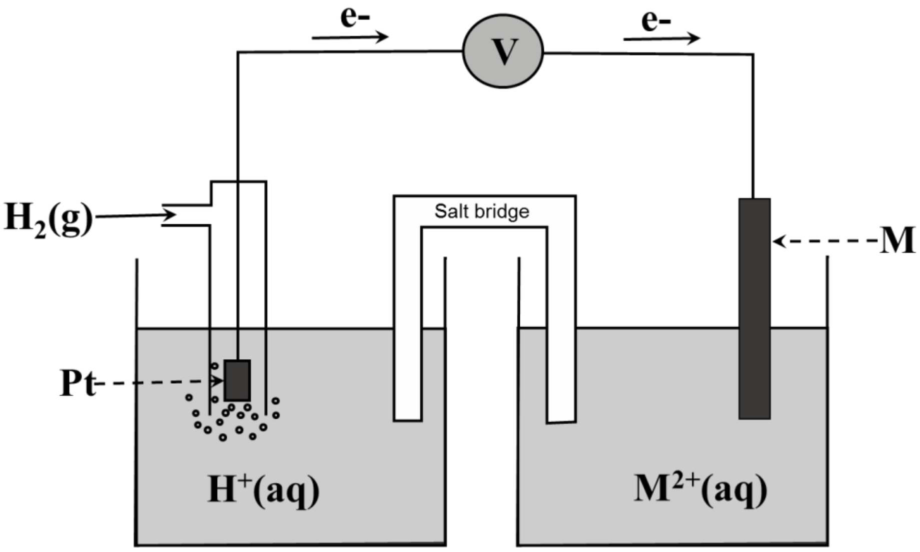


Figure 1 The galvanic cell

Table 1. Standard reduction potential (range 298-308 K)

Half-reaction	E° (V)-
$Ba^{2+}(aq) + 2\ e^- \rightarrow Ba(s)$	-2.912
$Sr^{2+}(aq) + 2\ e^- \rightarrow Sr(s)$	2.899
$Ca^{2+}(aq) + 2\ e^- \rightarrow Ca(s)$	-2.868
$Er^{2+}(aq) + 2\ e^- \rightarrow Er(s)$	-2.000
$Ti^{2+}(aq) + 2\ e^- \rightarrow Ti(s)$	-1.630

$Mn^{2+}(aq) + 2\ e^- \rightarrow Mn(s)$	-1.185
$V^{2+}(aq) + 2\ e^- \rightarrow$;$V(s)$	-1.175
$Cr^{2+}(aq) + 2\ e^- \rightarrow Cr(s)$	-0.913
$Fe^{2+}(aq) + 2\ e^- \rightarrow Fe(s)$	-0.447
$Cd^{2+}(aq) + 2\ e^- \rightarrow Cd(s)$	-0.403
$Co^{2+}(aq) + 2\ e^- \rightarrow Co(s)$	-0.280
$Ni^{2+}(aq) + 2\ e^- \rightarrow Ni(s)$	-0.257
$Sn^{2+}(aq) + 2\ e^- \rightarrow Sn(s)$	-0.138
$Pb^{2+}(aq) + 2\ e^- \rightarrow Pb(s)$	-0.126
$2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$	0.000
$Sn^{4+}(aq) + 2\ e^- \rightarrow Sn^{2+}(aq)$	+0.151
$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$	+0.153
$Ge^{2+}(aq) +2\ e^- \rightarrow Ge(s)$	+0.240
$VO^{2+}(aq) + 2\ H^+(aq) + e^- \rightarrow V^{3+}(aq) + H_2O(l)$	+0.337
$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$	+0.340
$Tc^{2+}(aq) + 2\ e^- \rightarrow Tc(s)$	+0.400
$Ru^{2+}(aq) + 2\ e^- \rightarrow Ru(s)$	+0.455
$I_2(s) + 2\ e^- \rightarrow 2\ I^-(aq)$	+0.535
$UO_2^{2+}(aq) + 4\ H^+(aq)+ 2\ e^- \rightarrow U^{4+}(aq) + 2\ H_2O(l)$	+0.612
$PtCl_4^{2-}(aq) + 2\ e^- \rightarrow Pt(s) + 4\ Cl^-(aq)$	+0.755
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.770
$Hg_2^{2+}(aq) + 2\ e^- \rightarrow 2\ Hg(l)$	+0.797
$Hg^{2+}(aq) + 2\ e^- \rightarrow Hg(l)$	+0.851
$2Hg^{2+}(aq) + 2\ e^- \rightarrow Hg_2^{2+}(aq)$	+0.920
$Pt^{2+}(aq) + 2\ e^- \rightarrow Pt(s)$	+1.180
$MnO_2(s) + 4\ H^+(aq) + 2\ e^- \rightarrow Mn^{2+}(aq) + 2\ H_2O(l)$	+1.224
$Cr_2O_7^{2-}(aq)+ 14\ H^+(aq) + 6\ e^- \rightarrow 2\ Cr^{3+}\ (aq) + 7\ H_2O\ (l)$	+1.360
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+1.920
$S_2O_8^{2-}(aq) + 2\ e^- \rightarrow 2\ SO_4^{2-}(aq)$	+2.010

4.1 If the reaction quotient (Q) of the whole galvanic cell is equal to 2.18×10^{-4} at 30.00 °C, the electromotive force is +0.450 V. Calculate the value of standard reduction potential (E°) and identify the metal "**M**".

Note: $\Delta G = \Delta G^o + RT \ln Q$

4.2 Write the balanced equation of the spontaneous redox reaction of the galvanic cell.

4.3 The unknown concentration of **M**$^{2+}$(*aq*) solution in the cell (Figure 1) can be analyzed by a iodometric titration. A 25.00 cm^3 aliquot of **M**$^{2+}$(*aq*) solution is added into a conical flask and an excess of KI is added. A volume of 25.05 cm^3 of a sodium thiosulfate solution with a concentration of 0.800 mol dm^{-3} is required to reach the equivalent point. Write all the redox reactions associated with this titration and calculate the concentration of **M**$^{2+}$(*aq*) solution.

Note: If a student cannot find the answer, the student can use 0.950 mol dm^{-3} as the concentration of **M**$^{2+}$ for further calculations.

4.4 In Figure 1, if the hydrogen half-cell is under 0.360 bar hydrogen gas and the platinum electrode is immersed in a 500 cm^3 buffer solution containing 0.050 mol lactic acid ($HC_3H_5O_3$) and 0.025 mol sodium lactate ($C_3H_5O_3Na$), the electromotive force of tme galvanic cell measured is +0.534 V. Calculate the pH of the buffer solution and the dissociation constant (K_a) of lactic acid at 30.00 °C.

Note: If a student cannot find the answer, the student can use 3.46 as the buffer pH for further calculations.

SOLUTION

4.1 $E_{cell} = E^0_{cell} - (RT / nF) \ln Q$

$$0.450 = E^0_{cell} - \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 303.15 \text{ K}}{2 \times 96485 \text{ C mol}^{-1}} \ln 2.18 \times 10^{-4}$$

$0.450 = E^0_{\text{cell}} + 0.110$ and

E^0_{cell} 0.450 V – 110 V = 0.340 V

Therefore,

$E^0_{cell} = E^0_{cathode} - E^0_{anode}$

0.340 V = $E^0_{cathode}$ – 0,000 V thus: $E^0_{cathode}$ = 0.340 V

The standard reduction potential o M is +340 V.

Therefore, the metal „M“ strip is Cu(s).

4.2 $H_2(g) + Cu^{2+}(aq) \rightarrow 2\ H^+(aq) + Cu(s)$

4.3 Iodometric titration of copper is based on the oxidation of iodide to iodine by copper (II) ions.

Reactions taking place:

$2\ Cu^{2+}(aq) + 4\ I^-(aq) \rightarrow 2\ CuI(s) + I_2(aq)$

This is followed during the titration by the reaction of iodine with thiosulfate:

$2\ Na_2S_2O_3(aq) + I_2(aq) \rightarrow Na_2S_4O_6(aq) + 2\ NaI(aq)$

At the equivalent point:

$n(Cu^{2+}) = n(S_2O_3^{2-})$

$c(Cu^{2+})\ V(Cu^{2+}) = c(S_2O_3^{2-})\ V(S_2O_3^{2-})$

$c(Cu^{2+}) = c(S_2O_3^{2-}) \times V(S_2O_3^{2-}) / V(Cu^{2+}) =$

$= (0{,}800 \text{ mol dm}^{-3} \times 0.02505 \text{ dm}^3) / 0.02500 \text{ dm}^3 = 0.802 \text{ mol dm}^{-3}$

4.4 From the Nernst’s equation:

$E_{\text{cell}} = E^0_{\text{cell}} - (RT/\text{n}F) \ln ([\text{H+}]^2 / p(\text{H}_2) \times [\text{Cu}^{2+}]$

$$0.534 \text{ V} = 0.340 \text{ V} - \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 303.15 \text{ K}}{2 \times 96485 \text{ C mol}^{-1}} \ln \frac{[\text{H}^+]^2}{0.360 \text{ bar} \times 0.802 \text{ mol dm}^{-3}}$$

$$-14.9 = \ln \frac{[\text{H}^+]^2}{0.360 \text{ bar} \times 0.802 \text{ mol dm}^{-3}}$$

$[\text{H+}] = 3.19 \times 10^{-4}$

pH = 3.50

Calculations of the dissociation constant (K_a) of lactic acid

The buffer solution composes of $HC_3H_5O_3$ and $C_3H_5O_3Na$,

The pH of the solution can be calculated from the Henderson-Hasselbalch equation.

$$[C_3H_5O_3Na] = \frac{0.050 \text{ mol} \times 1.000 \text{ dm}^3}{0.500 \text{ dm}^3} = 0.10 \text{ mol dm}^{-3}$$

$$[HC_3H_5O_3] = \frac{0.025 \text{ mol} \times 1.000 \text{ dm}^3}{0.500 \text{ dm}^3} = 0.050 \text{ mol dm}^{-3}$$

$pH = pK_a + \log ([C_3H_5O_3Na] / [HC_3H_5O_3])$

$3.50 = pK_a + \log (0.050/0.10)$

$pK_a = 3.80$

$K_a = 1.58 \times 10^{-4}$

PROBLEM 5

Phosphate and silicate in soil

Distribution and mobility of phosphorus in soil are usually studied by sequential extraction. Sequential extraction is performed by the use of acid or alkaline reagents to fractionate inorganic phosphorus in soil. Soil sample was extracted and analyzed as follows:

Part A. Determination of total phosphate (PO_4^{3-}) and silicate (SiO_4^{4-})

A 5.00 gram of soil sample is digested to give a final volume of 50.0 cm^3 digesting solution which dissolves total phosphorus and silicon. The extract is analyzed for the total concentrations of phosphorus and silicon. The concentrations of phosphorus and silicon are found to be 5.16 mg dm^{-3} and 5.35 mg dm^{-3}, respectively.

5.1.1 Determine the mass of PO_4^{3-} in mg per 1.00 g of soil.

5.1.2 Determine the mass of PO_4^{3-} in mg per 1.00 g of soil.

Part B. Determination of available PO_4^{3-} in acid extract

Phosphate can be analyzed by using molybdenum blue method. One mole of phosphate is converted into one mole of molybdenum blue compound. This method is used for determination of phosphate in the acid extract. Absorbance (A) and transmittance (T) are recorded at 800 nm. The molar absorptivity of the molybdenum blue compound is 6720 dm^3 mol^{-1} cm^{-1} and all measurement is carried out in a 1.00-cm cuvette.

Transmittance and absorbance are given by the following equations:

$$T = I / I_o$$

$$A = \log (I_o / I)$$

where I is the intensity of the transmitted light and I_o is the intensity of the incident light.

5.2.1 When the sample containing high concentration of phosphate is analyzed, a reference solution of 7.5×10^{-5} mol dm^{-3} of molybdenum blue compound is used for adjusting zero absorbance. The transmittance of the sample solution is then measured to be 0.55. Calculate the concentration of phosphate (mol dm^{-3}) in the sample solution.

Part C. Determination of PO_4^{3-} and SiO_4^{4-} in alkaline extract

Both phosphate and silicate ions can react with molybdate in alkaline solution, producing the yellow molybdophosphate and molybdatosilicate. Further reduction with ascorbic acid produces intense color molybdenum blue compounds. Both complexes exhibit maximum absorption at 800 nm. Addition of tartaric acid helps preventing interference from silicate in the determination of phosphate.

Two series of phosphate standard are treated with and without tartaric acid whereas a series of silicate standard is not treated with tartaric acid. Linear equations obtained from those calibration curves are as follows:

Conditions	Linear equations
Phosphate with and without tartaric acid	$y = 6720\ x_1$
Silicate without tartaric acid	$y = 868\ x_2$

y is absorbance at 800 nm,

x_1 is concentration of phosphate as mol dm^{-3},

x_2 is concentration of silicate as mol dm^{-3}

Absorbance at 800 nm of the alkaline fraction of the soil extract after treated with and without tartaric acid are 0.267 and 0.510, respectively.

5.3.1 Calculate the phosphate concentration in the alkaline soil extract in mol dm^{-3} and calculate the corresponding phosphorous in mg dm^{-3}.

5.3.2 Calculate the silicate concentration from the soil sample in t the alkaline fraction in mol dm^{-3} and calculate the corresponding silicon in mg dm^{-3}.

Part D. Preconcentration of ammonium phosphomolybdate

A 100 cm^3 of aqueous sample of ammonium phosphomolybdate ($(NH_4)_3PMo_{12}O_{40}$) compound is extracted with 5.0 cm^3 of an organic solvent. The organic-water partition coefficient (K_{ow}) is defined as the ratio of the concentration of the compound in the organic phase (c_o) to that in the water phase (c_w). K_{ow} of the ammonium phosphomolybdate is 5.0.

The molar absorptivity of ammonium phosphomolybdate in the organic phase is 5000 dm^3 mol^{-1} cm^{-1}.

5.4 If the absorbance in the organic phase is 0.200, calculate the total mass of phosphorus (in mg unit) in the original aqueous sample solution. The optical pathlength of the cuvette is 1.00 cm.

SOLUTION

5.1.1 30.97 g of P from 94.97 g of PO_4^{3-}

5.16 mg of P from PO_4^{3-} (94.97/30.97) × 5.16 = 15.82 mg dm^{-3}

In 50 cm^3 solution, PO_4^{3-} = (15.82/1000) × 50 = 0.791 mg

5 g of soil contains PO_4^{3-} 0.791 mg

1 g of soil contains 0.158 mg of PO_4^{3-} .

5.1.2 28.09 g of Si from 92.09 g of SiO_4^{4-}

5.35 mg of Si from SiO_4^{4-} (92.09/28.09) × 5.35 = 17.539 mg dm^{-3}

In 50 cm^3 solution, SiO_4^{4--} = (17.539/1000) × 50 = 0.877 mg

5 g of soil contains 0.877 mg of SiO_4^{4--}

1 g of soil contains 0.175 mg of SiO_4^{4--} .

5.2.1 Calculations:

At a given wavelength: $A_{total} = A_1 + A_2$

$-\log (T_{\text{total}}) = -\log(T_1) + -\log(T_2) = -\log(T_1T_2)$

$T_1 = T_{solution\ for\ adjusting\ zero\ absorbance} = 10^{-\varepsilon\, b\, c} =$

$= 10^{-(6720\ \text{dm}^3\text{mol}^{-1}\text{cm}^{-1})(1\ \text{cm})(7.5 \times 10^{-5}\ \text{mol dm}^{-3})} = 10^{(-0.504)} = 0.3133$

$T_2 = T_{measured} = 0.55$

Method 1: $T_{sample} = T_{solution\ for\ adjusting\ zero\ absorbance}\ T_{measured}$

$= 0.313 \times 0.55 = 0.1723$

$-\log T = \varepsilon\, b\, c$

$C = -\log 0.1723 / (6720\ \text{dm}^3\text{mol}^{-1}\text{cm}^{-1})(1\ \text{cm})$

$= 1.136 \times 10^{-4}\ mol\ dm^{-3}$

Method 2: If $T = 0.313$, $A = -\log T = 0.504$

If $T = 0.55$, $A = -\log T = 0.2596$

$A_{sample} = A_{measured} + A_{solution\ for\ adjusting\ zero\ absorbance} =$

$= 0.2596 + 0.504 = 0.7636\ C =$

$= 0.7636 / (6720\ \text{dm}^3\ \text{mol}^{-1}\text{cm}^{-1})(1\ \text{cm}) = 1.136 \times 10^{-4}\ \text{mol dm}^{-3}$

concentration of an unknown sample = 1.14×10^{-4} mol dm^{-3}

5.3.1 $c(PO_4^{3-}) = 0.267 / 6720 = 3.97\times10^{-5}$ mol dm^{-3}

Mass concentration of P = (3.97×10^{-5} mol dm^{-3}) (30.97 g mol^{-1}) (1000 mg g^{-1}) =

= 1.23 mg dm^{-3}

5.3.2 Abs of PO_4^{3-} = (3.97×10^{-5} mol dm^{-3})(6720) = 0.267

Abs of $SiO_4^{4-}{}_{\text{in sample}}$ = 0.510 – 0.267 = 0.243

$c(SiO_4^{4})$ = (0.243 / 868) = 2.80×10^{-4} mol dm^{-3}

mass concentration of Si = (2.80×10^{-4} mol dm^{-3}) (28.09 g mol^{-1}) (1000 mg g^{-1}) =

= 7.87 mg dm^{-3}

5.4 $c_o = 0.200/5000 = 4\times10^{-5}$ mol dm^{-3}

The volume of the organic phase is 5.0 cm^3, therefore ammonium phosphor-molybdate in the organic phase:

= (4×10^{-5} mol dm^{-3}) (5 cm^3) / 1000 cm^3 dm^{-3} = 2×10^{-7} mol

From $K_{ow} = c_o / c_w = 5.0$

c_w = (4×10^{-5} mol dm^{-3}) / 5 = 8×10^{-6} mol dm^{-3}

The volume of the aqueous solution is 100 cm^3, therefore ammonium phosphor-molybdate in the aqueous solution

= (8×10^{-6} mol dm^{-3})(100 cm^3) / 1000 cm^3 dm^{-3}

= 8×10^{-7} mol

Therefore, the total amount of substance of ammonium phosphomolybdate =

= (2×10^{-7}) + (8×10^{-7}) mol = 1×10^{-6} mol

Total mass of P = (1×10^{-6} mol) × (30.97 g mol^{-1}) × (1000 mg g^{-1}) = 0.031 mg

PROBLEM 6

Iron

Iron (Fe) is the fourth most abundant element in the Earth's crust and has been used for more than 5,000 years.

Part A.

Pure iron is easily oxidized, which limits its utilization. Element **X** is one of the alloying elements that is added to improve the oxidation resistance property of iron.

6.1 Below is some information about the element **X**:

(1) In first ionization, an electron with quantum numbers $n_1 = 4 - l_1$ is removed.
(2) In second ionization, an electron with quantum numbers $n_2 = 5 - l_2$ is removed.
(3) The atomic mass of **X** is lower than that of Fe.

What is the element **X**?

(Answer by writing the proper symbol according to the periodic table.)

6.2 Both Fe and **X** crystallize in the body centered cubic structure. Approximating the Fe atoms as hard-spheres, the volume taken up by the Fe atoms inside the unit cell is 1.59×10^{-23} cm^3. The volume of the unit cell of **X** is 0.0252 nm^3. A complete substitutional solid solution usually occurs when

$$\Delta R = \left(\frac{|R_X - R_{Fe}|}{R_{Fe}} \right) \times 100$$

is less than or equal to 15, where R_X and R_{Fe} are the atomic radii of **X** and Fe, respectively. Can **X** and Fe form a complete substitutional solid solution?

Tick the relevant box ☐ YES ☐ NO.

Show your calculation. The volume of sphere is $4/3\pi r^3$.

Part B.

Iron in natural water is in the form of $Fe(HCO_3)_2$, which ionizes to Fe^{2+} and HCO_3^-. To remove iron from water, $Fe(HCO_3)_2$ is oxidized to an insoluble complex $Fe(OH)_3$, which can be filtered out of the water.

6.3 Fe^{2+} can be oxidized by $KMnO_4$ in a basic solution to yield $Fe(OH)_3$ and MnO_2 precipitates. Write the balanced ionic equation for this reaction in a basic solution.

6.4 Under this condition, HCO_3^- ions are converted to CO_3^{2-}. Write the balanced ionic equation for this reaction in a basic solution.

6.5 A covalent compound **A** which contains more than 2 atoms and, a potential oxidizing agent, can be prepared by the reaction between diatomic halogen molecule (**X**$_2$) and Na**Q**O$_2$

$\mathbf{X}_2 + x\,\mathrm{Na}\mathbf{X}\mathrm{O}_2 \rightarrow y\,\mathbf{A} + z\,\mathrm{Na}\mathbf{X}$ where $x + y + z \le 7$

where x, y and z are the coefficients for the balanced equation. Among the binary compounds between hydrogen and halogen, H**X** has the lowest boiling point. Identify **X** and if **A** has an unpaired electron, draw a Lewis structure of compound **A** with zero formal charge on all atoms.

6.6 Compound **D** is an unstable oxidizing agent that can be used to remove $Fe(HCO_3)_2$ from natural water. It consists of elements **G**, **Z** and hydrogen and the oxidation number of **Z** is +1. In this compound, hydrogen is connected to the element having the higher electronegativity among them. Below is some information about the elements **G** and **Z**:

(1) **G** exists in its normal state as a diatomic molecule, **G**$_2$.

(2) **Z** has one proton fewer than that of element **E**. **E** exists as a gas under standard conditions. **Z**$_2$ is a volatile solid.

(3) The compound **EG**$_3$ has a pyramidal shape.

Identify the elements **G** and **Z** and draw a molecular structure of compound **D**.

Part C.

^{59}Fe is a radiopharmaceutical isotope which is used in the study of iron metabolism in the spleen. This isotope decays to ^{59}Co as follows:

$${}^{59}_{26}\mathrm{Fe} \rightarrow {}^{59}_{27}\mathrm{Co} + \mathbf{a} + \mathbf{b} \qquad (1)$$

6.7 What are **a** and **b** in equation (1)? (Mark ✓ in the appropriate boxes.)

proton	neutron	beta	positron	alpha	gamma

6.8 Consider equation (1), if the ^{59}Fe isotope is left for 178 days which is *n* times of its half- life ($t_{1/2}$), the mole ratio of ^{59}Co to ^{59}Fe is 15 : 1. If *n* is an integer, what is the half-life of ^{59}Fe in day(s)? Show your calculation.

SOLUTION

6.1 Answer: Cr

6.2 **The correct answer:** ☑ YES (since $\Delta R \leq 15$)

Calculation

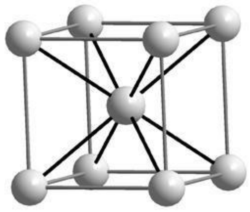
For Fe:

$V = 2\,(4/3)\pi r^3$ (the bcc unit cell contains 2 atoms of Fe)

$r^3 = (3\,V/\,(8\,\pi) = (3 \times 1.59 \times 10^{-23}\ \text{cm}^3)\ /\ (8\pi) = 1.90 \times 10^{-24}\ \text{cm}^3$

$r = 1.24 \times 10^{-8}$ cm i. e. $r = 0.124$ nm

For X:



$$V = a^3 \quad \Rightarrow \quad a = \sqrt[3]{V} = \sqrt[3]{0.0252} = 0.293 \text{ nm}$$

$$r = \left(a\,\sqrt[3]{3}\right)/4 = \left(0.293 \text{ nm} \times \sqrt[3]{3}\right)/\,4 = 0.127 \text{ nm}$$

$$\Delta R = \left(\frac{|R_X - R_{Fe}|}{R_{Fe}}\right) \times 100 = \left(\frac{|\,0.127 \text{ nm} - 0.124 \text{ nm}\,|}{0.124 \text{ nm}}\right) \times 100 = 2.42$$

(less than 15)

$R_{Fe} = 0.124$ nm

$R_X = 0.127$ nm

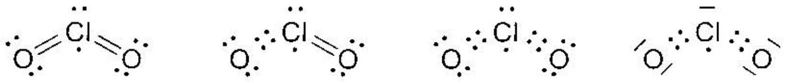
$\Delta R = 2.42$

6.3 $3\,Fe^{2+} + MnO_4^- + 5\,OH^- + 2\,H_2O \rightarrow 3\,Fe(OH)_3 + MnO_2$

6.4 $HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$

6.5 X = Cl

Lewis structure of compound **A:**

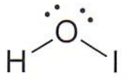


(All are correct answers. Student draws only one structure.)

The molecular geometry of compound A: The correct answer: ☑ bent

6.6 **G** = O **Z** = I

Molecular structure of compound **D**



Hydrogen is connected to the element having the highest electronegativity.

The oxidation number of Z in compound D is I (+1).

6.7

proton	neutron	beta	positron	alpha	gamma
		✓			✓

6.8 $t = 0$ ^{59}Fe = N_0 and ^{59}Co = 0

t = 178 d ^{59}Fe = N_t and ^{59}Co = $N_0 - N_t$

The ratio of ^{59}Co to ^{59}Fe at t = 178 d is 15 = $(N_0 - N_t) / N_t$

Thus, $N_t = N_0 / (15+1)$

At 178 day ⇨ $N_t = N_o / (15+1)$

$= N_0 / 16 = 0.0625\, N_0$

Suppose that N_0 = 100 %. Then N_t = 6.25 %

$t = 0$ ⇨ N_0 = 100 %

$t = 1(t_{1/2})$ ⇨ N_t = 50 %

$t = 2(t_{1/2})$ ⇨ N_t = 25 %

$t = 3(t_{1/2})$ ⇨ N_t = 12.5 %

$t = 4(t_{1/2})$ ⇨ N_t = 6.25 %

So, n = 4 and $t_{1/2}$ = 178 / 4 = 44.5 days

$$\ln(N_t / N_o) = -kt \ \ln[(N_0 / 16) / N_0] = -k(178\text{ d})\ \ln(1/16) = -k(178\text{ d})$$

$$k = [\ln(1/16)] / (-178)\ \text{d}^{-1}$$

$t_{1/2}$ = ln 2 / k = 44.5 days

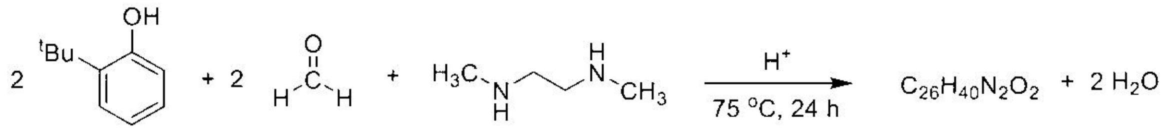
Half-life of ^{59}Fe = 44.5 days

PROBLEM 7

Chemical Structure Puzzles

Titanium complexes have been investigated for their antitumor activity. Many factors including isomerism and sizes have shown to affect the potency of the complexes. This question deals with the synthesis and characterization of some titanium complexes.

7.1 A reaction of 2 equivalents of 2-*tert*-butylphenol, 2 equivalents of formaldehyde, and *N,N'*-dimethylethylene-1,2-diamine under acidic conditions at 75 °C affords three major products with the same chemical formula of $C_{26}H_{40}N_2O_2$, as shown in the equation below. Draw the structure of each product.



7.2 If 2,4-di-*tert*-butylphenol is used as a substrate instead of 2-*tert*-butylphenol using the same stoichiometry as that in **7.1**, only one product **X** was obtained. Draw the structure of **X**.

A reaction between **X** from **7.2** and $Ti(O^iPr)_4$ [^iPr = isopropyl] in diethyl ether under an inert atmosphere resulted in the six-coordinate Ti complex **Y**, as a yellow crystalline solid and isopropanol at room temperature.

$$a\,\mathbf{X} + b\,Ti(O\,^iPr)_4 \xrightarrow{Et_2O} d\,\mathbf{Y} + c\,^iPrOH \qquad \text{(equation 1)}$$

UV-VIS spectra of **X**, $Ti(O^iPr)_4$, and **Y** reveal that only the product **Y** has an absorption at λ = 370 nm. By varying the volumes of **X** and $Ti(O^iPr)$, each with the concentration of 0.50 mol dm^{-3}, and using benzene as the solvent, the absorbance data at λ = 370 nm are given below:

Volume of X (cm^3)	**Volume of $Ti(O^iPr)_4$ (cm^3)**	**Volume of benzene (cm^3)**	**Absorbance**
0	1.20	1.80	0.05
0.20	1.00	1.80	0.25
0.30	0.90	1.80	0.38
0.50	0.70	1.80	0.59
0.78	0.42	1.80	0.48
0.90	0.30	1.80	0.38

1.10	0.10	1.80	0.17
1.20	0	1.80	0.02

7.3 Fill in appropriate values in the table provided below.

$\dfrac{\text{mol of X}}{\text{mol of }\mathbf{X}\text{ + mol of Ti(O}^{i}\text{Pr)}_4}$	**Absorbance**
	0.05
	0.25
	0.38
	0.59
	0.48
	0.38
	0.17
	0.02

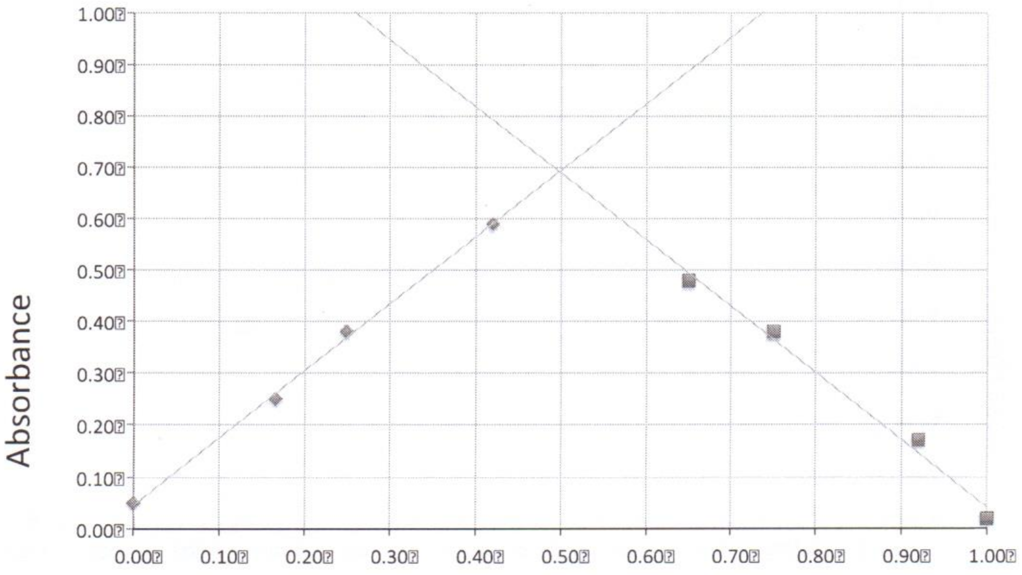
Next figure: Plot a graph showing a relationship between

$$\frac{\text{mole of }\mathbf{X}}{\text{mole of }\mathbf{X}\text{ + mole of Ti(}O^{i}\text{Pr)}_4}$$

and absorbance in the space provided below.

The value of

$$\frac{\text{mole of }\mathbf{X}}{\text{mole of }\mathbf{X}\text{ + mole of Ti(}O^{i}\text{Pr)}_4}$$



which maximizes the amount of the product **Y** represents the stoichiometry of **X** in the chemical formula of **Y**. Based on the graph above, show what is the molar ratio Ti : **X** in the complex **Y**.

Volume of X (cm^3)	**Volume of $Ti(O^iPr)_4$ (cm^3)**	**Volume of benzene (cm^3)**	**Absorbance**
0	1.20	1.80	0.05
0.20	1.00	1.80	0.25
0.30	0.90	1.80	0.38
0.50	0.70	1.80	0.59
0.78	0.42	1.80	0.48
0.90	0.30	1.80	0.38
1.10	0.10	1.80	0.17
1.20	0	1.80	0.02

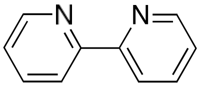
Fill in appropriate values in the table provided below.

$\frac{\text{mol of X}}{\text{mol of }\mathbf{X}\text{ + mol of }Ti(O^iPr)_4}$	**Absorbance**
	0.05
	0.25
	0.38
	0.59
	0.48
	0.38
	0.17
	0.02

7.4 The titanium complex **Y** is six-coordinated. The IR spectrum of **Y** does not contain a broad absorption band in the range of 3200 – 3600 cm^{-1}. **Y** exists as three diastereomers. Ignoring stereochemistry at N atoms, draw clearly the structures of all three diastereomers.

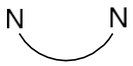
Note that you do not need to draw the complete structure of the ligand. Only identify donor atoms that involve in coordination with titanium and the ligand framework between the donor atoms can be drawn as follows:

For example:

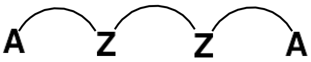


(2,2'-bipyridine)

can be drawn as:



If you did not get a structure of **X from **7.2**, use the following ligand symbol to represent **X** (**A** and **Z** are donor atoms):

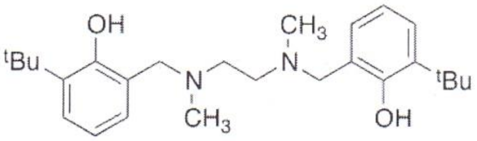


7.5 Under certain conditions, the reaction shown in **equation 1** affords only one diastereomer of **Y**. Given that structures of **Y** are "fixed" (no intramolecular movement), the ^{1}H NMR spectrum of **Y** in $CDCl_3$ shows four singlet resonances at δ 1.25, 1.30, 1.66, and 1.72 corresponding to the *tert*-butyl groups. Draw a structure of the only possible diastereomer of **Y**.

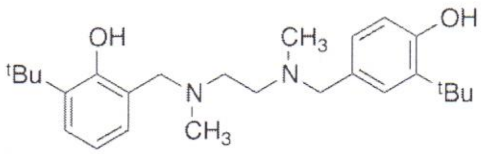
(You do not need to draw the complete structure of the ligand. Only identify donor atoms that involve in coordination and the ligand framework between the donor atoms can be drawn as shown in **7.4).**

SOLUTION

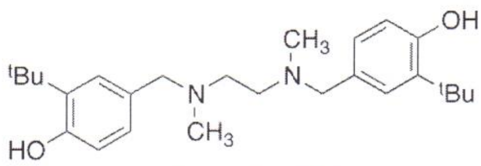
7.1



(*o*,*o*-substituted)

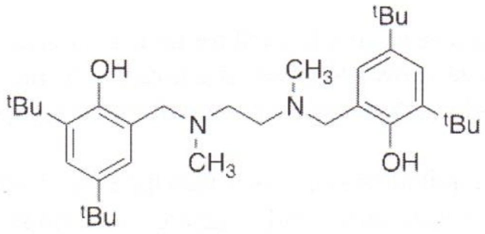


(*o*,*p*-substituted)



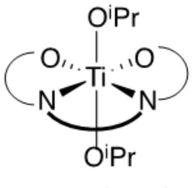
(*p*,*p*-substituted)

7.2



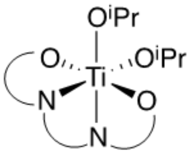
7.3 The molar ratio between Ti:**X** in the complex **Y** is 1:1.

7.4



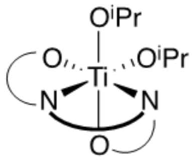
trans(O^{i}Pr,O^{i}Pr)

A



cis(O^{i}Pr,O^{i}Pr)
trans(O,O)

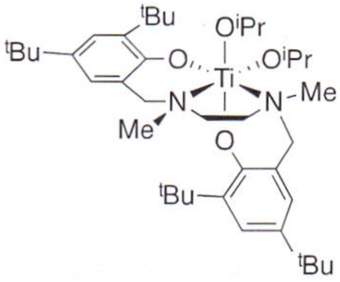
B



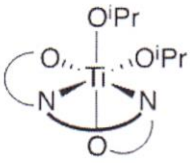
cis(O^{i}Pr,O^{i}Pr)
cis(O,O)

C

7.5



or



cis(O^{i}Pr,O^{i}Pr)
cis(O,O)

PROBLEM 8

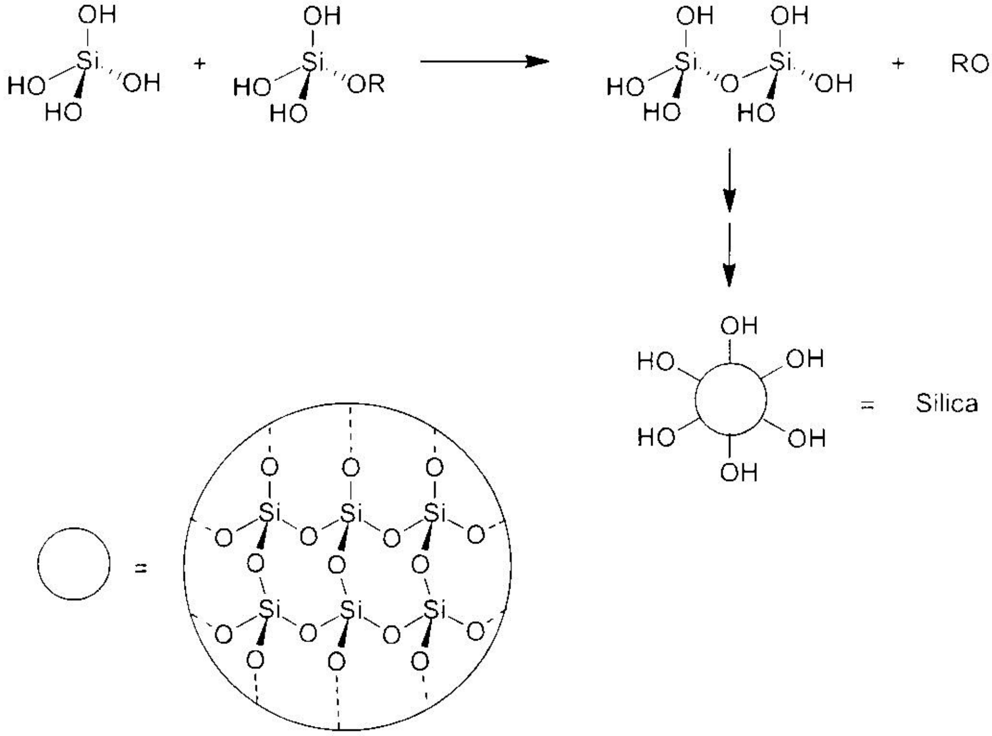
Silica Surface

Silica exists in various forms like amorphous and crystalline. Silica can be synthesized *via* sol- gel process by using silicon alkoxides like tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) as the details below:

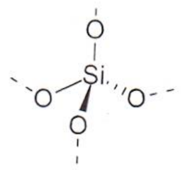
a. Hydrolysis

b. Water condensation

c. Alcohol condensation

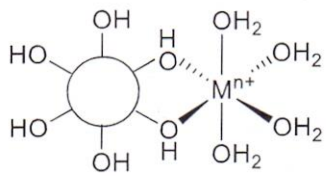


In bulk silica, all silicon atoms are tetrahedrally bonded to four oxygen atoms giving three-dimensional solid network. The silicon environments found inside silica is presented below:

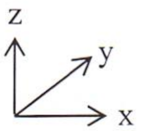


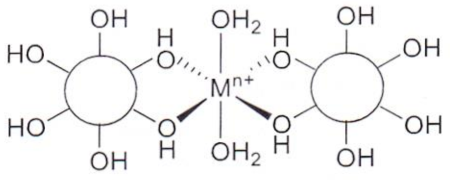
8.1 Three silicon atom environments (similar to the example above) are commonly observed at the silica **surface**. The three structures of the silicon environments must be **drawn** in the provided boxes.

Silica can be used as an effective metal ion adsorbent in water. The proposed structure for metal-silica complex is as follows:



I





II

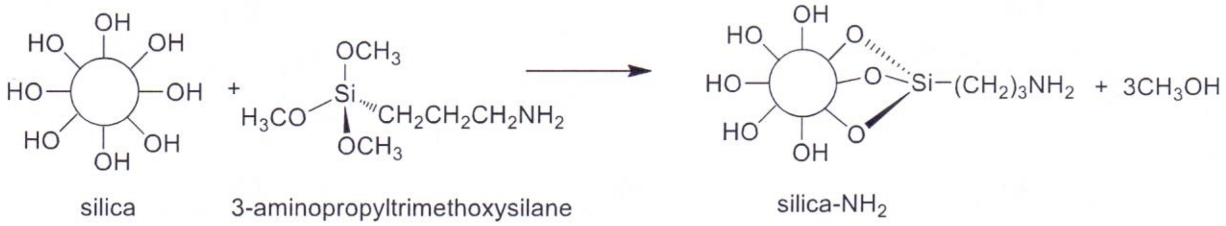
8.2 After Cu^{2+} is being adsorbed, the color of silica changes from white to pale blue. The visible spectrum shows a broad absorption band (with a shoulder) at $\lambda_{max} = 550$ nm.

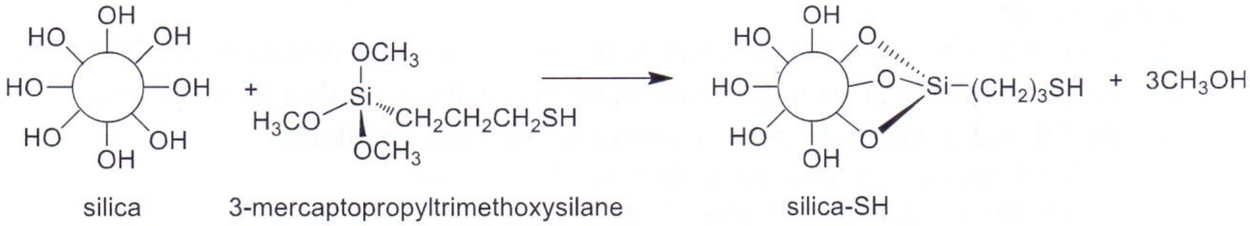
If Cu^{2+} can bind with silica and adopt the structure similar to **II**, draw the splitting diagram of the *d*- orbitals of Cu^{2+} ion including the label of the *d* orbitals in the complex and **specify** the corresponding electronic transition(s) for the visible absorption.

8.3 If the first row transition metal ions form complexes with silica analogous to Cu^{2+}, which metal ion(s) do(es) have the analogous to electronic transition(s) to Cu^{2+}?

The metal ion(s) must be in +2 or +3 oxidation state. Please note that the silanol groups (Si-OH) and water are weak field ligands.

However, silica is randomly bonded to various types of metal ion. To increase the selectivity, modification of silica surface has been performed by grafting with various organic molecules like 3-aminopropyltrimethoxysilane and 3-mercaptopropyltrimethoxysilane.





8.4 If Hg^{2+} is only bonding to sulfur binding sites in silica-SH, the **symmetric** complex of $[Hg(silica\text{-}SH)_2]^{2+}$ is formed. Draw the structure of $[Hg(silica\text{-}SH)_2]^{2+}$, specify the direction of the bond axes, and draw the corresponding *d*-orbital splitting. (You may use R-SH instead of drawing the whole structure of silica-SH.).

The structure: *d*-orbital splitting diagram :

8.5 Specify whether the following statements are true or false:

a) *d*-*d* transition is found in $[(Hg(silica\text{-}SH)x)]^{2+}$

☐ True ☐ False

b) The $[Cu(silica\text{-}NH_2)_x]^{2+}$ in a similar geometry, is expected to have a color similar to other copper(II) amine complexes.

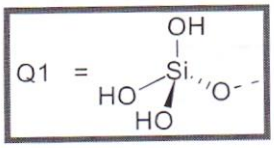
☐ True ☐ False

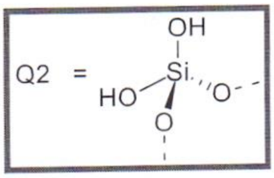
c) In the visible absorption spectra, □max of $[Cu(silica\text{-}NH2)x]^{2+}$ is greater than that of $[Cu(silica\text{-}OH)x]^{2+}$.

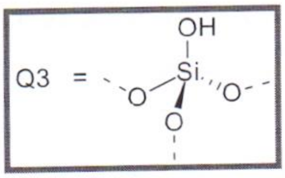
☐ True ☐ False

SOLUTION

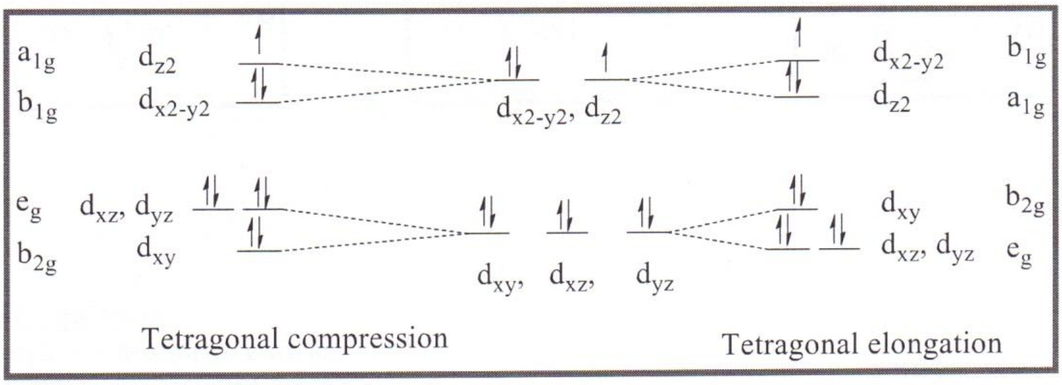
8.1







8.2



Electronic Transition:

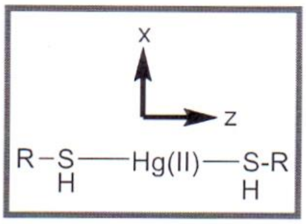
1. Tetragonal compression: $d_{xy} \rightarrow d_{z2}$ and d_{xz} , $d_{yz} \rightarrow d_{z2}$
2. Tetragonal elongation: d_{xz} , $d_{yz} \rightarrow d_{x2-y2}$ and $d_{xy} \rightarrow d_{x2-y2}$

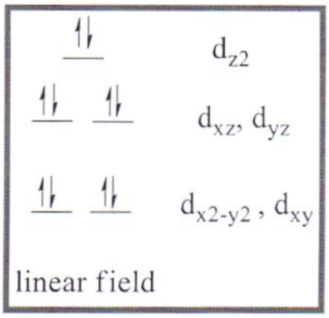
Cu^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

Cu^{2+}-complex → tetragonal distortion → Tetragonal elongation or tetragonal compression

8.3 Cr^{2+}, Mn^{3+}

8.4





8.5 **a)** *d*-*d* transition is found in silica-SH-Hg^{2+}.

☐ True ☑ False

Explanation : Hg^{2+} is a d^{10}- metal ion in which *d*-*d* transition is **not** found.

b) The $[(Cu(silica\text{-}NH_2)_x]^{2+}$ is expected to have a color similar to other copper(II) amine complexes.

☑ True ☐ False

Explanation: Various copper amine complexes like $[Cu(en)(H_2O)_4]^{2+}$, $[Cu(en)_2(H_2O)_2]^{2+}$ and $[Cu(en)_3]^{2+}$ have deep blue color. $[(Cu(silica\text{-}NH_2)_x]^{2+}$ containing similar ligands to these copper complexes is expected to have a similar color.

c) In the visible absorption spectra, l_{max} of $[(Cu(silica\text{-}NH_2)_x]^{2+}$ is greater than that of $[(Cu(silica\text{-}OH)_x]^{2+}$.

☐ True ☑ False

Explanation: R-NH_2 is **a stronger** field ligand as compared to R-OH. This results in a larger energy gap or a smaller λ_{max} of $[(Cu(silica\text{-}NH_2)_x]^{2+}$ as compared with that of $[(Cu(silica\text{-}OH)_x]^{2+}$.

PROBLEM 9

Into the Unknown

Organic compound **A** is **chiral** and contains only three elements with the molecular weight (MW) of 149 (rounded to an integer).

^{1}H NMR spectrum of compound **A** shows among others, three types of aromatic protons, and its ^{13}C NMR spectrum shows eight signals, of which four signals are in the range of 120-140 ppm.

Compound **A** can be prepared by treating a carbonyl compound with methylamine followed by $NaBH_3CN$.

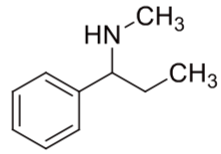
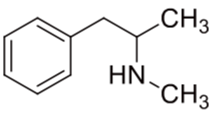
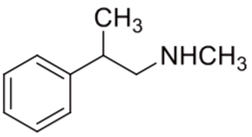
9.1 Write all possible structural formulae of compound **A**. No stereochemistry is required, and **do not** include stereoisomers.

9.2 One of the position isomers of compound **A** (structure **A1**, **A2** or **A3**) can be synthesized from compound **B** or **C** and **D** as shown in the diagram below. Write down the structural formulae of compounds **B**-**F**, and the position isomer of compound A.

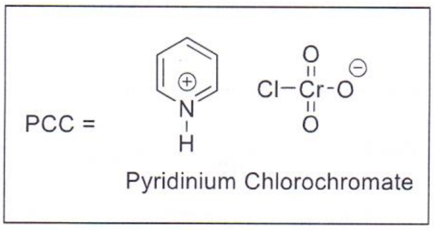
9.3 Compound **A** is the (*R*)-form of one of structures **A1– A3**. It can be prepared from vicinal diols **X** and **Y** as shown in the diagram below. Both diols are structural isomers, and each structure contains one carbon less than that of compound **A**. Write down the structural formulae of compounds **G**-**N**, **X**, **Y** and the (*R*)-form of compound **A**. You must show stereochemistry of all compounds.

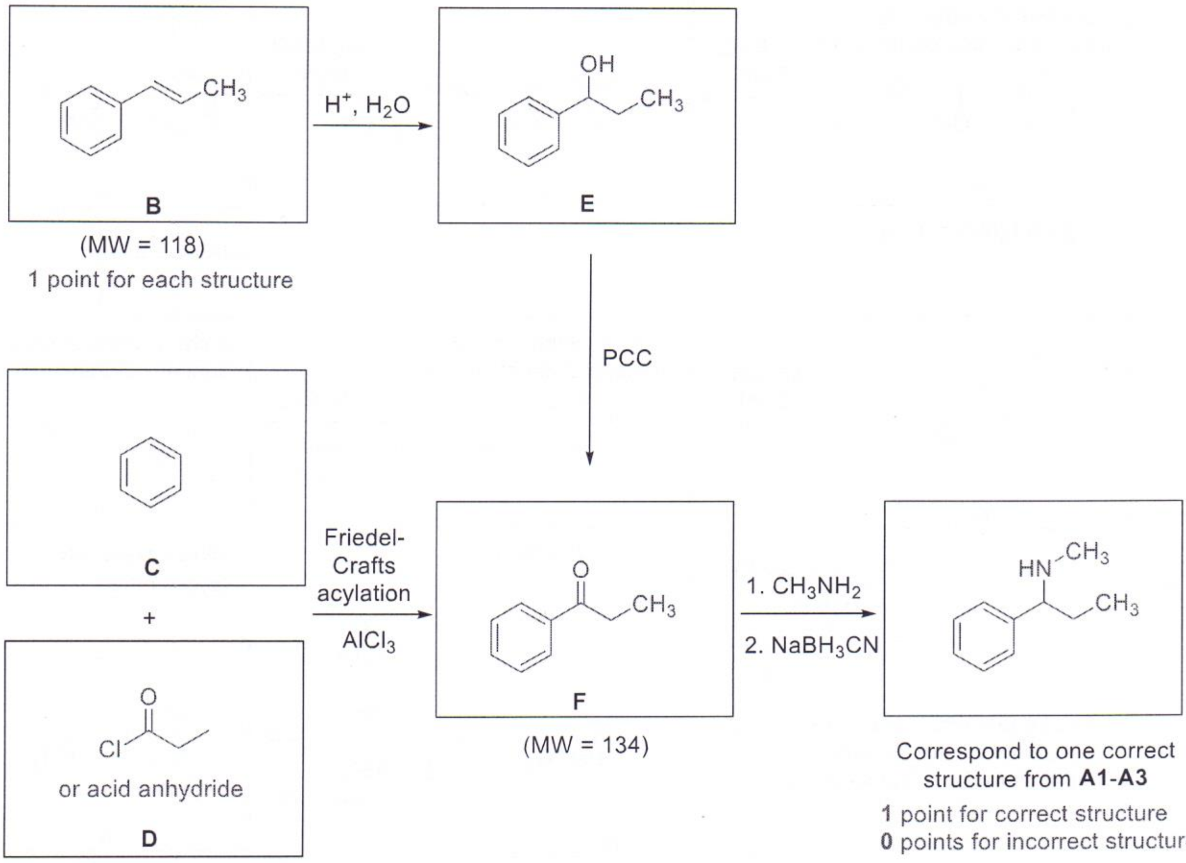
SOLUTION

9.1

		
A1	**A2**	**A3**

9.2



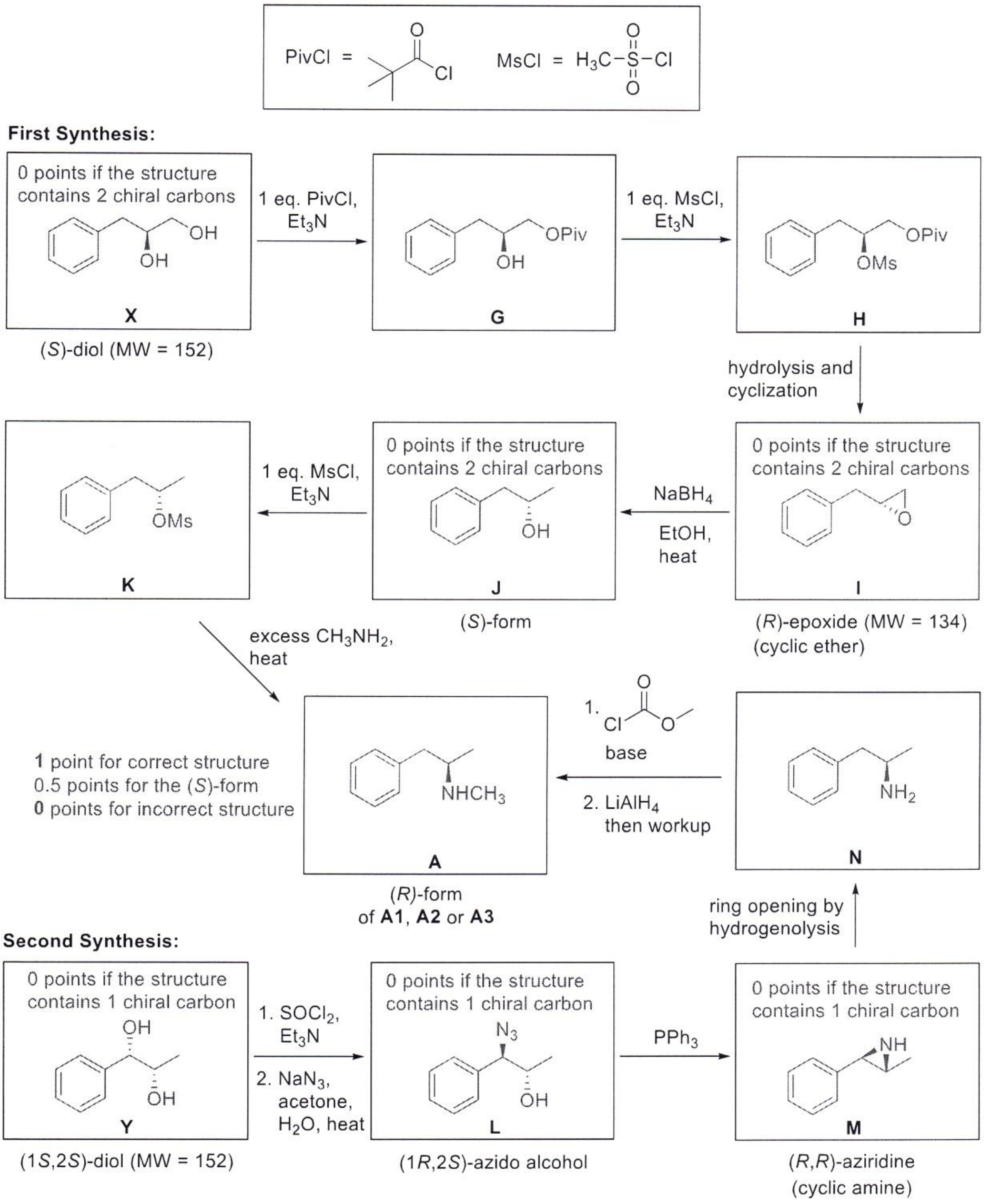


(MW = 118)
1 point for each structure

(MW = 134)

Correspond to one correct structure from **A1-A3**
1 point for correct structure
0 points for incorrect structure

9.3


PivCl =
MsCl = $H_3C-S(=O)_2-Cl$
First Synthesis:
0 points if the structure contains 2 chiral carbons
X
(S)-diol (MW = 152)
1 eq. PivCl, Et_3N
G
1 eq. MsCl, Et_3N
H
hydrolysis and cyclization
0 points if the structure contains 2 chiral carbons
I
(R)-epoxide (MW = 134)
(cyclic ether)
$NaBH_4$
EtOH, heat
0 points if the structure contains 2 chiral carbons
J
(S)-form
1 eq. MsCl, Et_3N
K
excess CH_3NH_2, heat
1 point for correct structure
0.5 points for the (S)-form
0 points for incorrect structure
A
(R)-form of A1, A2 or A3
1. base
2. $LiAlH_4$ then workup
N
ring opening by hydrogenolysis
Second Synthesis:
0 points if the structure contains 1 chiral carbon
Y
(1S,2S)-diol (MW = 152)
1. $SOCl_2$, Et_3N
2. NaN_3, acetone, H_2O, heat
0 points if the structure contains 1 chiral carbon
L
(1R,2S)-azido alcohol
PPh_3
0 points if the structure contains 1 chiral carbon
M
(R,R)-aziridine
(cyclic amine)
OH
OPiv
OMs
O
NHCH₃
NH₂
N₃
NH
Cl

PROBLEM 10

Total Synthesis of Alkaloids

Alkaloids are a class of nitrogen-containing natural products. Their tructural complexity and potent biological activities has drawn attentions. Two representative examples of alkaloids – sauristolactam and pancratistatin are highlighted in following questions.

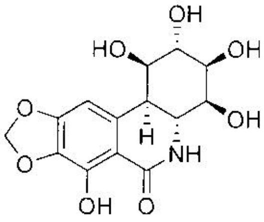
Part A

Sauristolactam possesses excellent cytotoxicity against various cancer cell lines. It could be prepared by following synthetic sequence on the page. (^{1}H-NMR spectra were recorded in $CDCl_3$ at 300 MHz.)

10.1 Draw the structures of **A**-**G** in the sequence.

Part B

Pancratistatin, isolated from a Hawaiian native plant, spider lily, exhibits potent in vitro and in vivo inhibitory activity of cancer cell growth in addition to its excellent antiviral activity.



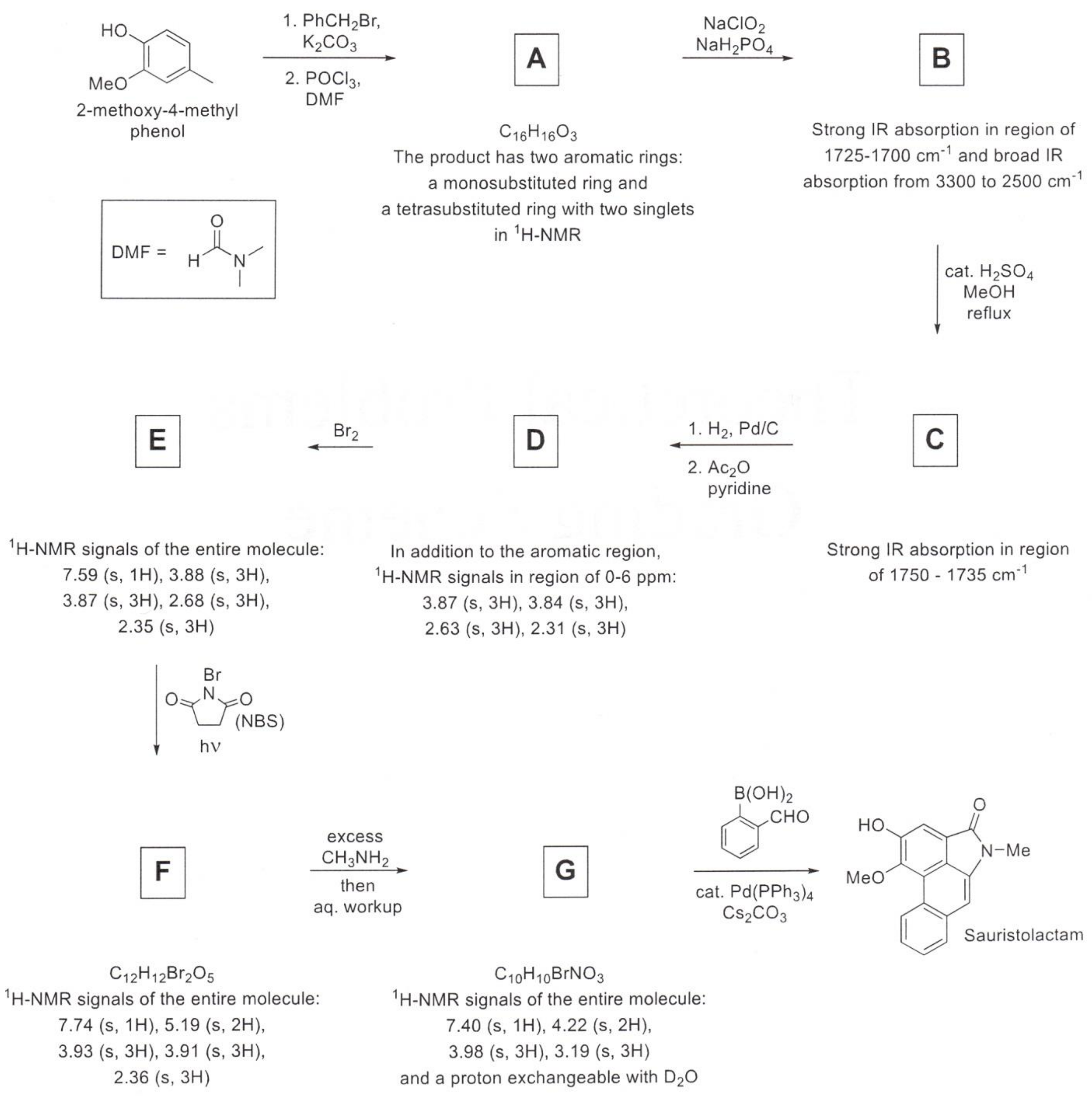
Pancratistatin

Pancratistatin could be successfully synthesized via intermediates **X1** and **X2**. The synthesis of these intermediates are shown in the attached scheme.

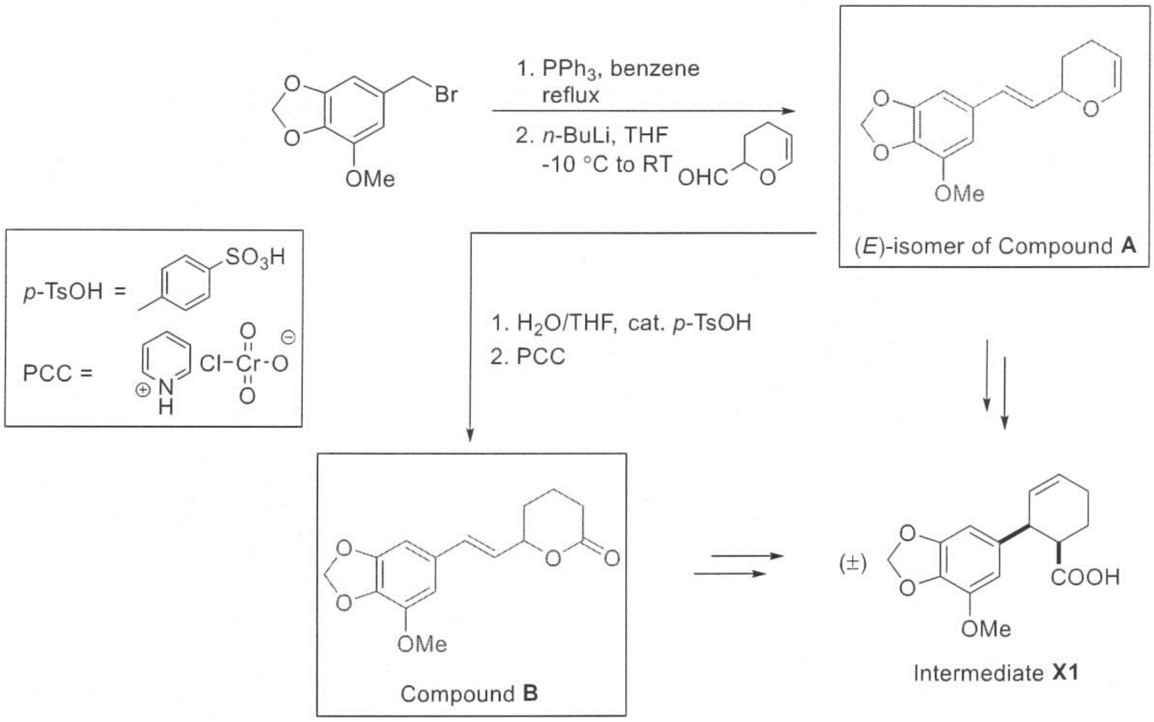
10.2 Draw the structures of **A** and **B**.

10.3 Intermediate **X1** (a single enantiomer with the stereochemistry shown) is labeled with deuterium with configuration as indicated below, <u>propose</u> the 3-D chair structure of compound **E** and the structure of compound **F**, with stereochemistry. Is **Y** a proton (^{1}H) or a deuterium (^{2}H)?

Syntetic sequence:

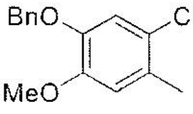


Scheme of the synthesis of Pancratistatin and structures of compound A and B:

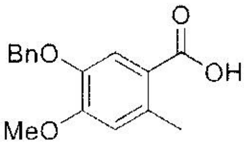


SOLUTION

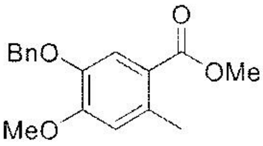
10.1 The structures of A – G:



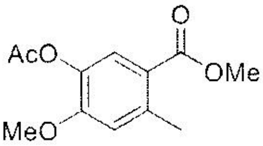
A



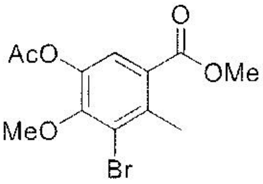
B



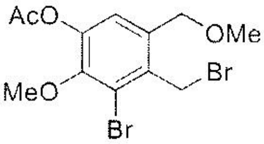
C



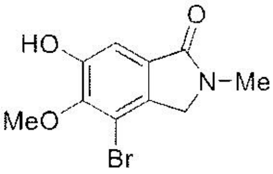
D



E

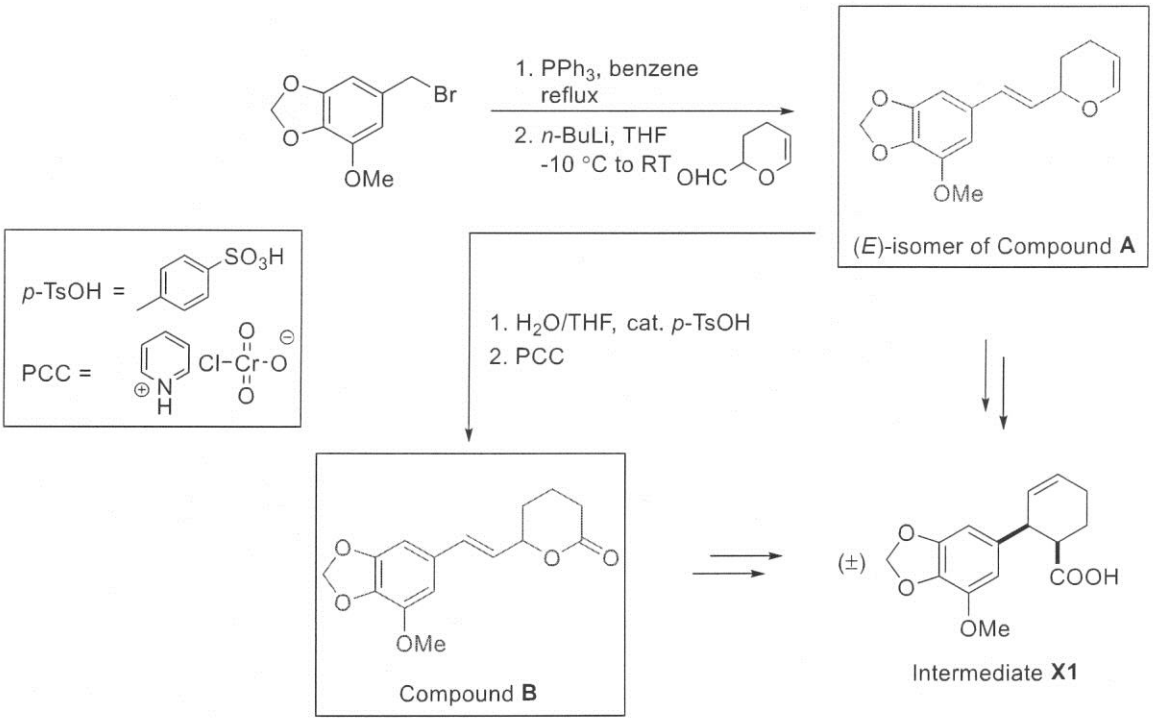


F

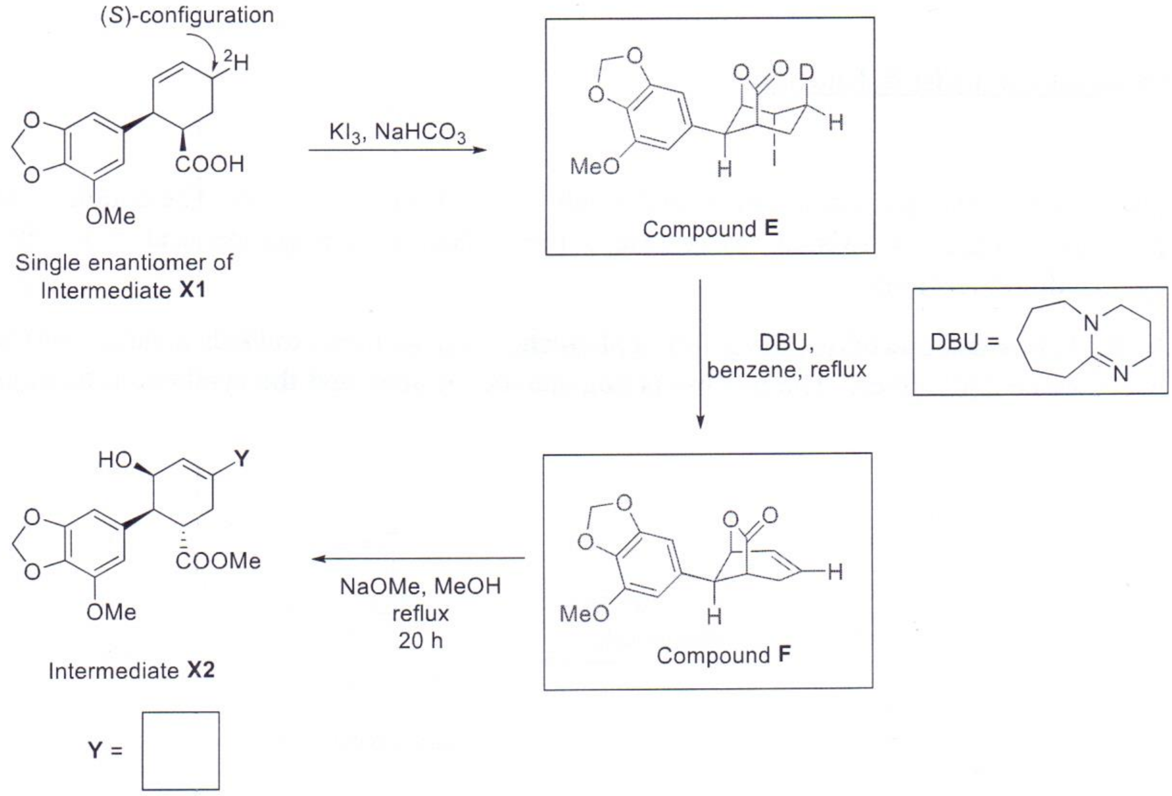


G

10.2 Scheme of the synthesis of Pancratistatin and structures of compound A and B:



10.3 The structures of **E** and **F**

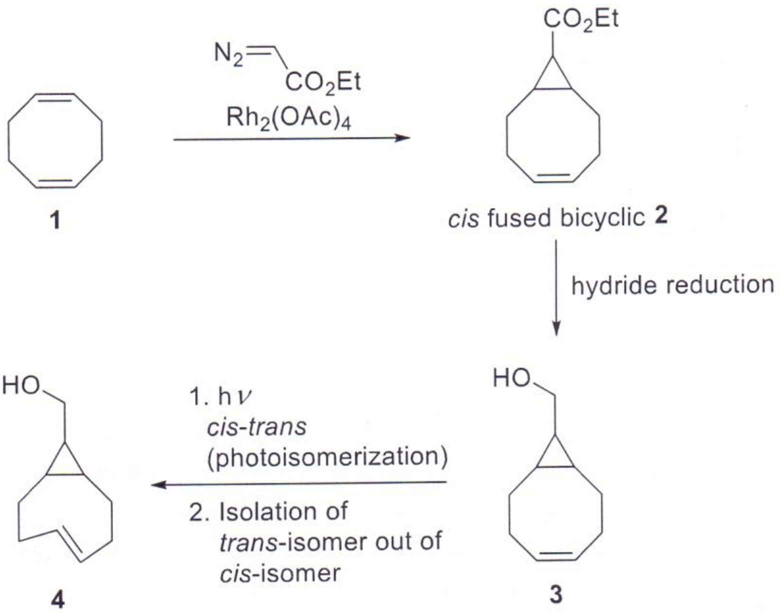


PROBLEM 11

Twist & Chirality

trans-Cyclooctene has a chiral plane and a high barrier for racemization. The double bond of *trans*-cyclooctene is twisted, as a result, the molecule displays unusual reactivity in cycloaddition reactions.

In 2011, Fox and coworkers developed a photochemical synthesis towards a variety of *trans*- cyclooctene derivatives. The process is non-stereocontrolled and the synthetic scheme is as follow.



11.1 Draw all possible stereoisomers of compound **3** that could be obtained from the reduction of compound **2.** Not necessary to assign *R*,*S* configuration.

11.2 i) If one of the stereoisomers of compound **3** is converted to compound **4**, how many stereoisomeric form(s) of compound **4** will be obtained?

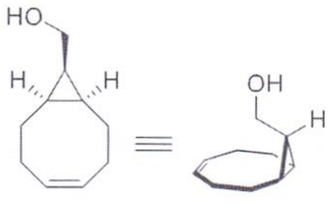
ii) The number of possible stereoisomeric form(s) of compound **4** =

iii) If there are more than one stereoisomer, is it possible to separate the obtained stereoisomers of compound **4** by achiral chromatography? Tick the relevant circle.

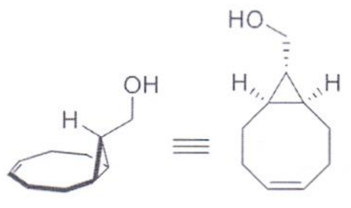
○ Yes ○ No

SOLUTION

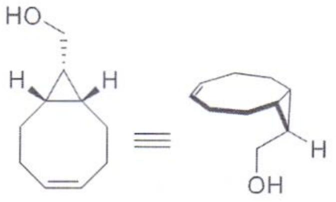
11.1



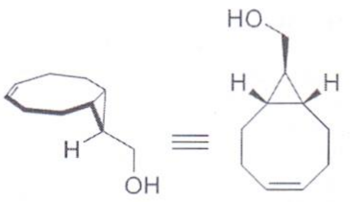
A



B



C



D

11.2 There can exist 2 stereoisomeric forms of compound 4.

The correct answer is: ☑ No

PRACTICAL PROBLEMS

PROBLEM 1P (Practical)

Acid-base indicator and its application for pH measurements

Acid-base indicators are week acids (or bases) that exhibit different colors when they are present in solution as their acidic form (HIn, color 1) or as their basic form (In^- color 2). They undergo the following reaction in dilute aqueous solution.

$$HIn \leftrightarrows H^+ + In^-$$

As the pH of a solution containing the indicator changes, the equilibrium shown above will be driven either to reactants (HIn) or products (In^-) causing the solution color to change depending on the concentration of each form present. In a strongly acidic solution most of the indicator will be present in the HIn form (color 1) and in strongly basic solutions, most of the indicator will be in the In^- form (color 2). At intermediate pH values the color of the solution will be a mix of color 1 (absorption at wavelength 1) and color 2 (absorption at wavelength 2), depending on the relative amount of HIn and In^- present.

By monitoring the absorbance values at two wavelengths the concentrations of HIn and In^- can be calculated by using the following expressions:

$$A^{\lambda 1}_{total} = A^{\lambda 1}_{HIn} + A^{\lambda 1}_{In^-}$$
$$= \varepsilon^{\lambda 1}_{HIn}\, b[HIn] + \varepsilon^{\lambda 1}_{In^-}\, b[In^-]$$
$$A^{\lambda 2}_{total} = A^{\lambda 2}_{HIn} + A^{\lambda 2}_{In^-}$$
$$= \varepsilon^{\lambda 2}_{HIn}\, b[HIn] + \varepsilon^{\lambda 2}_{In^-}\, b[In^-]$$

where b is pathlength of solution and ε is the molar absorptivity.

At a certain pH value the relative amounts of HIn and In^{-in} in solution are related to the acid dissociation constant (K_a) of the indicator, as shown in the following equation.

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

Therefore, for a given pH value acid dissociation constant K_a of the indicator can be calculated when the relative amounts of HIn and In^- in solution are known.

Experimental setup

Instructions for using a spectrophotometer are given and they can differentiate according to spectrophotometer used. Students are suggested to check the spectrophotometer before use by measuring the absorbance values of the instrument check solution at two different wavelengths, for instance at 430 and 620 nm, respectively.

Chemical and materials

- Instrument check solution, 80 cm^3 in a plastic bottle,
- Methyl orange indicator solution, $c = 2.00 \times 10^{-4}$ mol dm^{-3}, 30 cm^3 in a wide mouth glass bottle,
- Bromothymol blue indicator solution, $c = 1.00 \times 10^{-3}$ mol dm^{-3}, 30 cm^3 in a wide mouth glass bottle,
- Methyl red indicator solution, 10 cm^3 in a wide mouth glass bottle,
- HCl, aqueous solution, 1 mol dm^{-3}, 30 cm^3 in a plastic bottle,
- NaOH, aqueous solution, 1 mol dm^{-3}, 30 cm^3 in a plastic bottle,
- Buffer solution A, 110 cm^3 in a plastic bottle,
- Unknown solution X, 50 cm^3 in a plastic bottle.
- Unknown solution Y, 50 cm^3 in a plastic bottle.
- Unknown solution Z, 50 cm^3 in a plastic bottle.

Equipment and labwares:

- UV–Visible sapectrophotometer
- 2 beakers, 25 cm^3
- 9 volumetric flasks, 25.00 cm^3
- 2 measuring pipettes, 2.00 cm^3
- 3 measuring cylinders, 10.0 cm^3
- 6 Pasteur pipettes,
- 6 rubber bulbs for Pasteur pipette
- Pipette filler bulb (3-way)
- 6 test tubes (13 x 100 mm)

Experimental part

Absorbance measurement of an acid-base indicator (methyl orange) in a strong acid and a strong base

i. Pipette 1.50 cm^3 of 2.00×10^{-4} mol dm^{-3} methyl orange indicator solution into a 25.00-cm^3 volumetric flask, add 2.5 cm^3 of 1 mol dm^{-3} HCl into the flask and make up to the volume using distilled water. Record the absorbance at 470 and 520 nm.

ii. Pipette 2.00 cm^3 of methyl orange indicator solution (c = 2.00×10^{-4} mol dm^{-3}) into a 25.00-cm^3 volumetric flask, add 2.5 cm^3 of NaOH solution (1 mol dm^{-3}) into the flask and make up to the volume using distilled water. Record the absorbance at 470 and 520 nm.

iii. Calculate the molar absorptivities at 470 and 520 nm of acidic and basic forms of methyl orange.

1.1 Record the absorbance values of methyl orange in acid and basic solutions.

(You do not need to fill the entire table.)

methyl orange in acidic form	A (at 470 nm)	A (at 520 nm)
Replicate 1		
Replicate 2		
Replicate 3		
Accepted value		

methyl orange in basic form	A (at 470 nm)	A (at 520 nm)
Replicate 1		
Replicate 2		
Replicate 3		
Accepted value		

1.2 Calculate the molar absorptivities of both the acidic form and the basic form of methyl orange (unit, dm^3 mol^{-1} cm^{-1})

The molar absorptivities of methyl orange are as follows: (unit, dm^3 mol^{-1} cm^{-1})

	ε, acidic form (HIn)		ε, basic form (In$^-$)	
methyl orange	λ = 470	λ = 520	λ = 470	λ = 520

Part b

Absorbance measurement of an acid-base indicator (bromothymol blue) in buffer solution

Bromothymol blue is an acid-base indicator which shows yellow color when it is present as an acidic form (HIn) and it shows blue color when it is present as a basic form (In^-). The absorption maximum of the bromothymol blue in the acidic form is at 430 nm and that in the basic form is at 620 nm. The molar absorptivities of bromothymol blue in the acidic form are 16,600 dm^3 mol^{-1} cm^{-1} and 0 dm^3 mol^{-1} cm^{-1} at 430 nm and 620 nm, respectively. The molar absorptivities of bromothymol blue in the basic form are 3,460 dm^3 mol^{-1} cm^{-1} and 38,000 dm^3 mol^{-1} cm^{-1} at 430 nm and 620 nm, respectively.

i. Pipette 1.00 cm^3 of bromothymol blue indicator solution (1.00×10^{-3} mol dm^{-3}) into a 25.00-cm^3 volumetric flask, and make up to the volume using solution A. (Note: solution A is a buffer solution pH = 7.00).

ii. Record the absorbance at 430 and 620 nm.

iii. Calculate the concentrations of the acidic form and basic form of bromothymol blue indicator solution in the volumetric flask.

iv. Calculate the acid dissociation constant of bromothymol blue.

1.3 Record the absorbance values of bromothymol blue in buffer solution

(You do not need to fill the entire table.)

bromothymol blue in buffer solution	*A* (at 430 nm)	*A* (at 620 nm)
Replicate 1		
Replicate 2		
Replicate 3		
Accepted value		

1.4 Calculate the concentrations of the acidic and basic forms, respectively, of bromothymol blue indicator in the resulting solution.

The concentrations of the acidic form and basic form of bromothymol blue in the resulting solution are as follows:

[HIn], mol dm^{-3}	[In$^-$], mol dm^{-3}
____________________	____________________

1.5 Calculate the acid dissociation constant of bromothymol blue from this experiment.

The acid dissociation constant of bromothymol blue from this experiment is as

The acid dissociation constant =

follows:

Part c

Determination of solution pH by using acid-base indicator (methyl red)

Methyl red is an acid-base indicator which shows reddish-pink color when it is present as an acidic form (HIn) and it shows yellow color when it is present as a basic form (In$^-$). The molar absorptivities of methyl red in the acidic form are 9,810 dm^3 mol^{-1} cm^{-1} at 470 nm and 21,500 dm^3 mol^{-1} cm^{-1} at 520 nm. The molar absorptivities of methyl red in the basic form are 12,500 dm^3 mol^{-1} cm^{-1} at 470 nm and 1,330 dm^3 mol^{-1} cm^{-1} at 520 nm. The pKa of methyl red is 4.95.

Note: There is no need to accurately measure the volumes used in this part, as it does not affect the accuracy of the results obtained.

i. Fill a test tube to one quarter with solution of unknown pH X. Add three drops of methyl red into the solution and mix thoroughly. Record the color.

ii. Fill a test tube to one quarter with solution of unknown pH Y. Add three drops of methyl red into the solution and mix thoroughly. Record the color.

iii. Fill a test tube to one quarter with solution of unknown pH Z. Add three drops of methyl red into the solution and mix thoroughly. Record the color.

1.6 Record the color change of the indicator in sample solutions

Indicator	Color observed		
	in sample X	in sample Y	in sample Z

1.7 Select one solution from the three sample solutions, of which the pH can be determined spectrophotometrically by using methyl red as an indicator.

☐ Sample X ☐ Sample Y ☐ Sample Z

iv. Use a measuring cylinder to transfer 10 cm^3 of the selected unknown solution into a beaker. Add three drops of methyl red indicator into the solution and mix thoroughly. Record the absorbance at 470 and 520 nm.

v. Calculate the concentration ratio of basic form and acidic form of methyl red in the solution.

vi. Calculate the pH of the selected unknown solution.

1.8 Record the absorbance values of the resulting solution

selected unknown solution	*A* (at 470 nm)	*A* (at 520 nm)

1.9 Calculate the concentration ratio of the basic form and acidic form of methyl red indicator in an unknown solution and the pH value of the unknown solution. The results are as follows:

sample	$[In^-] / [HIn]$	pH

PROBLEM 2P

Calcium iodate

Calcium iodate is an inorganic salt composed of calcium and iodate ions. $Ca(IO_3)_2$ is sparingly soluble in water. Equilibrium is established between the undissolved salt and saturated solution of the salt.

$$Ca(IO_3)_2(s) \leftrightarrows Ca^{2+}(aq) + 2\ IO_3^-(aq)$$

Titration data will be used to determine the concentration of iodate ions in a saturated solution of $Ca(IO_3)_2$ ans then to determine the value of K_{sp} for $Ca(IO_3)_2$.

The concentration of will be determined by titration with a standard solution of sodium thiosulfate ($Na_2S_2O_3$) in the presence of potassium iodide (KI). Starch will be used as an indicator.

Part a is associated with the standardization of $Na_2S_2O_3$ solution. **Part b** is the determination of K_{sp} for $Ca(IO_3)_2$.

In Part C solid $Ca(IO_3)_2$.is dissolved in an unknown dilute KIO_3 solution. After standing for 3 days equilibrium is also established between the undissolved salt and saturated solution of the salt. The concertation of iodate ions will be determined using the same titrimetric method, and then used to calculate the concertation of the dilute KIO_3 solution.

Experimental part

Chemicals and materials:

- Solution A (KIO_3, 10.7042 g in 5.00 dm^3), 60 cm^3
- Solution B (saturated $Ca(IO_3)_2$ solution, 50 cm^3
- Solution C (saturated $Ca(IO_3)_2$ in unknown dilute KIO_3 solution), 50 cm^3
- $Na_2S_2O_3$, aqueous solution, 200 cm^3
- KI, aqueous solution, 10 %, 100 cm^3
- HCl, aqueous solution, c = 1 mol dm^{-3}
- Starch solution, 0.1 %, 30 cm^3 in a dropping glass bottle

Equipment and labwares

- 2 beakers, 100 cm^3
- beaker, 250 cm^3
- 9 Erlenmeyer flasks, 125 cm^3
- 2 pipettes, 5.00 cm^3
- pipette, 10.00 cm^3

- measuring cylinder, 10.0 cm^3
- 2 measuring cylinders, 25.0 cm^3
- Pasteur pipette
- Rubber bulb for Pasteur pipette
- 2 glass funnels, diameter 7.5 cm
- plastic funnel, diameter 5.5 cm
- 3 filter papers in a zipped bag
- burette, 50.0 cm^3

Part a

Standardization of $Na_2S_2O_3$

i. Fill the burette with $Na_2S_2O_3$ solution,

ii. Pipette 10.00 cm^3 of standard KIO_3 solution (provided as solution A, KIO_3, 10.7042 g in 5.00 dm^3) into an Erlenmeyer flask. Add 10 cm^3 of 10 % KI solution and 10 cm^3 of HCl solution (c = 1 mol dm^{-3}) into a flask. The solution should turn dark brown as I_2 is formed.

iii. Titrate with $Na_2S_2O_3$ solution until the solution has turned pale yellow. Add 2 cm^3 of 0.1 % starch solution. The solution should turn dark blue. Titrate carefully to the colorless endpoint. Record the volume of $Na_2S_2O_3$ solution.

2.1 Balance the relevant chemical equations:

$IO_3^-(aq) + I^-(aq) + H_3O^+(aq) \rightarrow I_2(aq) + H_2O(l)$

$I_2(aq) + S_2O_3^{2-}(aq) \rightarrow I^-(aq) + S_4O_6^{2-}(aq)$

2.2 Record volume of $Na_2S_2O_3$ solution.

(You do not need to fill in the entire table)

	Titration No.		
	1	2	3
Initial reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Final reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Consumed volume of $Na_2S_2O_3$ solution, cm^3			

Accepted volume , (cm^3); V_1 =

2.3 Calculate the concentration of the $Na_2S_2O_3$ solution.

(If one cannot find the concentration of $Na_2S_2O_3$, the concentration of 0.0700 mol dm^{-3} can be used for further calculations.)

Part B

Determination of K_{sp} of $Ca(IO_3)_2$

i. You are provided with the filtrate of the filtered saturated solution of $Ca(IO_3)_2$. (Solution B)

ii. Pipette 5.00 cm^3 of the filtrate into an Erlenmeyer flask. Add 10 cm^3 of 10% (w/v) KI and 10 cm^3 of 1 mol dm^{-3} HCl into a flask.

iii. Titrate with $Na_2S_2O_3$ solution until the solution has turned pale yellow. Add 2 cm^3 0.1% (w/v) starch solution. The solution should turn dark blue. Titrate carefully to the colorless endpoint. Record the volume of $Na_2S_2O_3$ solution.

2.4 Record volume of $Na_2S_2O_3$ solution.

(You do not need to fill in the entire table)

	Titration No.		
	1	2	3
Initial reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Final reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Consumed volume of $Na_2S_2O_3$ solution, cm^3			

Accepted volume, (cm^3); V_1 =

2.5 Calculate the concentration of the IO_3^- solution.

2.6 Calculate value of K_{sp} for $Ca(IO_3)_2$.

(If the student cannot find K_{sp}, the value of 7×10^{-7} can be sused for further calculations.)

Part C

Determination of concentration of unknown dilute KIO_3 solution.

i. You are provided with the filtrate of the filtered saturated solution of $Ca(IO_3)_2$ dissolved in the unknown dilute KIO_3 (provided as solution C).

ii. Pipette 5.00 cm^3 of the filtrate solution into an erlenmeyer flask. Add 10 cm^3 of 10% (w/v) KI and 10 cm^3 of solution (c = 1 mol dm^{-3} HCl) into a flask.

iii. Titrate with $Na_2S_2O_3$ solution until the solution has turned pale yellow. Add 2 cm^3 0.1% (w/v) starch solution. The solution should turn dark blue. Titrate carefully to the colorless endpoint. Record the volume of $Na_2S_2O_3$ solution.

2.7 Record volume of $Na_2S_2O_3$ solution.

(You do not need to fill in the entire table)

	Titration No.		
	1	2	3
Initial reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Final reading of the burette of $Na_2S_2O_3$ solution, cm^3			
Consumed volume of $Na_2S_2O_3$ solution, cm^3			

Accepted volume, (cm^3); V_1 =

2.8 Calculate the concentration of the IO_3^- in solution C.

2.9 Calculate the concentration of the unknown dilute KIO_3 sample.

PROBLEM 3P (Practical)

Elaborating Carbon Framework

The core structure of organic molecules is mostly based on carbon-carbon skeleton. Carbon-carbon bond formations have played a vital role in the construction of complex structures from smaller starting materials. Therefore, the synthetic transformations to efficiently achieve carbon-carbon bond formation has long been of interest. In this experiment, you are required to transform commercially available p-chlorobenzaldehyde and 3-pentanone to a more elaborated structure.

Important Notes:

- Ethanol can be refilled with no penalty.
- All weighing processes require verification from lab supervisor. The supervisor will need to sign in the student's answer sheet for grading. No mark will be given for unverified values.
- Total score will be based on the quality and quantity of the product submitted. We could not give any score on this part if the product is not submitted for grading.
- ^{1}H-NMR and melting point determination techniques will be used by the grader to verify the quality of your product.

Part a

a) Take the vial containing 3-pentanone (A) (Code Axxx, For example: A305) and unwrap the parafilm. Weigh the vial with caps. Record the weight in the answer sheet question a1.

b) Setup a water bath by filling water in the 250 cm^3 crystallizing dish and heat to 55 ± 2°C. Add paper clip into the water bath and let it stir so that the heat could be distributed evenly.

c) Ensure a magnetic stirring bar is in the 100-cm^3 round bottom flask. Transfer the pre-weighed 3-pentanone (labeled as A) and p-chlorobenzaldehyde (labeled as B) to the flask. Add 50 cm^3 ethanol to the mixture and swirl to dissolve.

d) Measure 15 cm^3 of NaOH solution (c = 2 mol dm^{-3}) using a measuring cylinder and add to the reaction mixture. Be careful not to wet the ground joint with NaOH solution.

e) Setup the reaction as shown in Figure 1. The reaction flask is placed in the 55 ± 2 °C water bath. Attach the air condenser to the reaction flask with plastic joint clip. Heat the reaction mixture while stirring for 30 minutes using the water bath.

f) Remove the reaction flask from the water bath. (Be careful! The flask might be hot.) Place the flask on the rubber supporting ring.

g) Detach the probe from the hotplate/stirrer to avoid over-heating of the hotplate in the recrystallizing steps. After you detach the probe, inform the supervisor to check and submit the probe to the supervisor.

h) Prepare the ice bath by replacing the warm water in the 250 cm^3 crystalizing dish with ice and small amount of water. Place the reaction flask on the ice bath to cool down the reaction. Solid should be observed. (Suggestion: If you do not observe any solid within 5 minutes, you may use a stirring rod to scratch the side of the flask. This could induce precipitation.)

i) Keep the mixture cool for approximately 20 minutes to allow complete precipitation.

j) Set up the suction filtration equipment (Figure 2). Connect the suction flask to the water aspirator. Place a Buchner funnel fitted with a rubber adapter onto the suction flask. Place a filter paper at the center of the funnel. Filter the precipitate via suction filtration and wash the precipitate with small amount of cold ethanol. Let air suck through the precipitates for 2-3 minutes to dry the product.

Figure 2: Set up needed for suction filtration.

k) Disconnect the vacuum (before turning off the water aspirator). Bring your equipment back to your space and keep the common area clean. Collect the crude precipitates from the filter paper and transfer to the Erlenmeyer flask. Careful not to scrape the paper too hard as you may obtain small pieces of paper as contaminant. Student may use Ethanol to rinse the Buchner funnel.

l) Place ethanol in a separate Erlenmeyer flask and heat it gently on a hotplate. (Student may set the temperature mark at 100-120 °C) Before heating, please make sure that the temperature probe is detached from the hotplate.

m) Recrystallize the product from hot ethanol. You can follow the procedure below.

Add small amount of hot ethanol to the flask containing crude solid while swirling. Continue addition of hot ethanol (swirling after each addition) until the solid is completely dissolved. During the dissolution process, keep the flask hot at all times by resting it on the hotplate. Be careful that the flask may be hot. You may use paper towels or towels provided to wrap around the flask while swirling. Once the dissolution is complete, set the flask containing the dissolved compound on a benchtop and let the flask cool down to room temperature without disturbance. The crystalline product should be observed. If not, you may use the stirring rod to scratch the side of the flask to induce crystallization. Place the flask into the ice bath to complete crystallization.

n) Filter the recrystallized product via suction filtration (See step 10 for suction filtration protocol) and wash the product with small amount of cold ethanol. Let air suck through the precipitates for 2-3 minutes. Disconnect the vacuum. Let the purified product air-dry on the benchtop for at least 15 minutes.

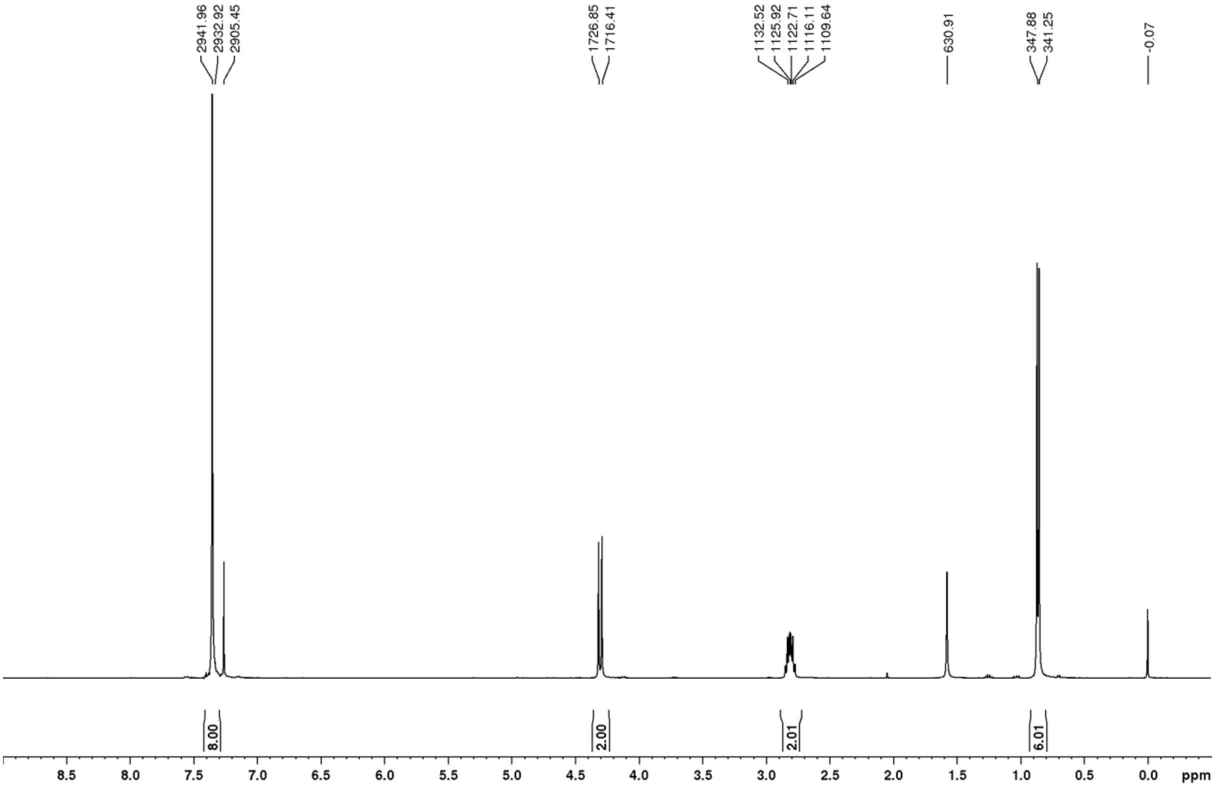
o) Weigh the vial (without cap) labeled with your student code provided. Record the value in the answer sheet question a1.

p) Transfer the recrystallized product to the pre-weighed vial. Determine and record the mass of the purified product.

3.1 Write the mass of the recrystallized product. :

3,2 Write 4 plausible aromatic compounds that may occur from this reaction. Stereoisomers are excluded.

3.3 **T**he 400 MHz ^{1}H-NMR (in $CDCl_3$) of the product is given below. Write the structure of the product.



Integrals are for all protons presented in the molecule.

50th

8 theoretical problems
3 practical problems

THE FIFTIETH
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19–29 JULY 2018, BRATISLAVA (Slovakia),
PRAGUE (Czech Republic)

THEORETICAL PROBLEMS

PROBLEM 1

DNA

Palindromic sequences are an interesting class of DNA. In a palindromic double-stranded DNA (dsDNA) species, the sequence of one strand read in the 5′→3′ direction matches the 5′→3′ reading on the complementary strand. Hence, a palindromic dsDNA consists of two identical strands that are complementary to each other. An example is the so-called

Drew–Dickerson dodecanucleotide (**1**):

```
5′-CGCGAATTCGCG-3′
   | | | | | | | | | | | |
3′-GCGCTTAAGCGC-5′
```

(**1**)

1.1 How many different palindromic double-stranded DNA dodecanucleotides (i. e. dsDNA species with twelve base pairs) exist?

1.2 How many different palindromic double-stranded DNA undecanucleotides (i.e., dsDNA species with eleven base pairs) exist?

The melting temperature of dsDNA, T_m is defined as the temperature at which 50% of the original amount of DNA double strands are dissociated into separate strands.

1.3 Consider the Drew–Dickerson dodecanucleotide (**1**). Assume that a G–C nucleobase pair contributes to the DNA duplex stability more than an A–T pair does.

What is the probability that its T_m increases when a single randomly selected base pair is replaced by a G–C pair?

Let us analyze the thermodynamics of formation of double-helical DNA from single strands, and its dependence on the length of the DNA and on the temperature. The equilibrium constant of association of single strands to form dsDNA differs for palindromic and non-palindromic dsDNA.

A solution of dsDNA with the initial concentration of $c_{\text{init}} = 1.00 \times 10^{-6}$ mol dm^{-3} was heated to T_{m} and equilibrium was reached.

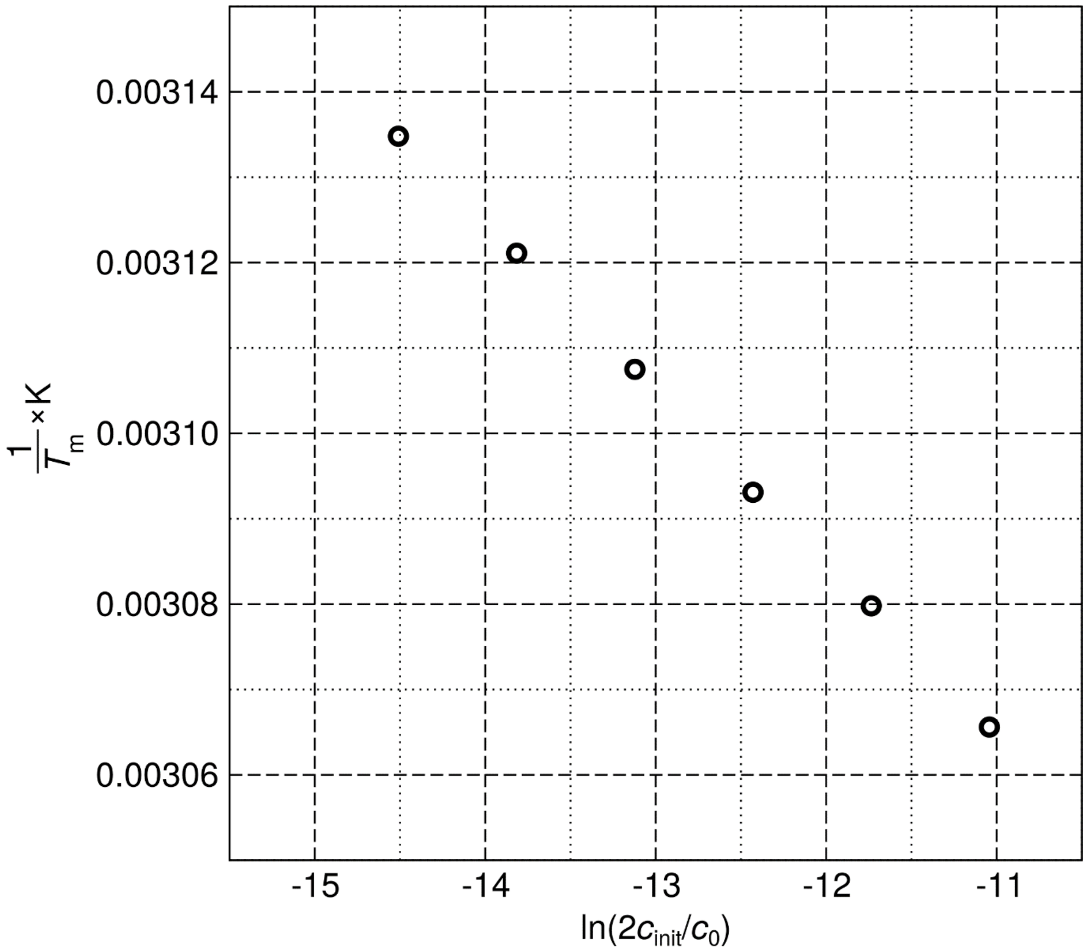
1.4 Calculate the equilibrium constant of **association** of single strands at T_{m} for both non-palindromic and palindromic DNA.

The mean contributions to the Gibbs energy of association of two single strands to form dsDNA were estimate over a certain range of experimental conditions, and they amount to −6.07 kJ mol^{-1} per one G–C pair, and −1.30 kJ mol^{-1} per one A–T pair present in a dsDNA.

1.5 How many base pairs are there in the **shortest** dsDNA oligonucleotide that has T_{m} above 330 K? At this T_{m}, consider the following values of the equilibrium constant of association of single strands to form a dsDNA: $K_{\text{np}} = 1.00 \times 10^6$ for a non-palindromic dsDNA, $K_{\text{p}} = 1.00 \times 10^5$ for a palindromic dsDNA. Is the shortest oligonucleotide palindromic or non-palindromic?

Finally, let us leave the simplified idea of base pairs contributing individually to the **association** of DNA strands. The Gibbs energy of this process may be considered explicitly dependent on temperature. The dependence of the inverse T_{m} of the Drew–Dickerson dodecanucleotide (**1**) on the logarithm of the initial duplex concentration c_{init} is shown below. (*Note*: a standard concentration c_0 = 1 mol dm^{-3} is introduced.)

c_{init} / 10^{-6} mol dm^{-3}	0.25	0.50	1.00	2.0	4.0	8.0
T_{m} / K	319.0	320.4	321.8	323.3	324.7	326.2



1.6 Calculate the standard enthalpy Δ*H*° and the standard entropy Δ*S*° of the association of DNA single strands to form the palindromic double-stranded Drew–Dickerson dodecanucleotide (**1**). Assume that Δ*H*° and Δ*S*° do not vary with temperature.

SOLUTION

1.1 The choice of the first, second, third, fourth, fifth and sixth nucleotide in one strand is arbitrary; the seventh through twelfth nucleotides in the same strand are determined by the condition of self-complementarity. There are always 4 options (C, G, A, T) for the first through six nucleotide. Hence, the total number of palindromic DNA hexanucleotides is $4 \times 4 \times 4 \times 4 \times 4 \times 4 = 4^6 = 4\,096$.

1.2 There is no palindromic dsDNA with an odd number of base pairs.

1.3 The thermodynamic stability, and thus the melting temperature increases whenever an A–T pair is replaced by a G–C pair. The probability of randomly drawing one of the 4 A–T pairs from the Drew–Dickerson dodecanucleotide containing 12 base pairs is **4/12** = **1/3** ~ **0.333** ~ **0.33** or **33.3% ~ 33%**

1.4 Non-palindromic dsDNA

Calculation:

The association reaction of a non-palindromic dsDNA reads

$$\text{ssDNA1} + \text{ssDNA2} \rightleftharpoons \text{dsDNA}$$

and the equilibrium constant of association takes the form

$$K_{np} = \frac{\dfrac{[\text{dsDNA}]}{c_0}}{\dfrac{[\text{ssDNA1}]}{c_0} \times \dfrac{[\text{ssDNA2}]}{c_0}}$$

where c_0 is the standard concentration of 1.00 mol dm^{-3} and the lower index *np* stands for “non-palindromic”.

At T_m, one half of the initial dsDNA concentration has melted to ssDNA, so

$$[\text{dsDNA}] = [\text{ssDNA1}] = [\text{ssDNA2}] = 1/2\ c_{init}$$

which yields

$$K_{np}(T_m) = \frac{\dfrac{1/2\ c_{init}}{c_0}}{\dfrac{1/2\ c_{init}}{c_0} \times \dfrac{1/2\ c_{init}}{c_0}} = \frac{c_0}{1/2\ c_{init}} = \frac{1.00\ \{\text{mol dm}^{-3}\}}{1/2 \times 1.00 \times 10^{-6}\ \{\text{mol dm}^{-3}\}} = \mathbf{2.00 \times 10^6}$$

Palindromic dsDNA

Calculation:

The association reaction of a palindromic dsDNA reads

$$2\ \text{ssDNA} \rightleftharpoons \text{dsDNA}$$

and the equilibrium constant of association is

$$K_p = \frac{\frac{[\text{dsDNA}]}{c_0}}{\left(\frac{[\text{ssDNA}]}{c_0}\right)^2}$$

where c_0 is the standard concentration, and the lower index p stands for "palindromic".

At T_m, one half of the initial dsDNA concentration has melted into two ssDNAs with identical sequences, so

$$[\text{dsDNA}] = 1/2\ c_{\text{init}}$$

$$[\text{ssDNA}] = 2 \times [\text{dsDNA}] = c_{\text{init}}$$

which yields K_p:

$$K_p(T_m) = \frac{\frac{1/2\ c_{\text{init}}}{c_0}}{\left(\frac{c_{\text{init}}}{c_0}\right)^2} = \frac{1/2\ c_0}{c_{\text{init}}} = \frac{1/2 \times 1 \times 1.00\ \text{mol dm}^{-3}}{1.00 \times 10^{-6}\ \text{mol dm}^{-3}} = \mathbf{5.0 \times 10^5}$$

1.6 Calculation of the number of base pairs:

K is related to the association Gibbs energy as $\Delta G^\circ_{np} = -RT \ln K_{np}$, so the Gibbs energy at T_m is

$$\Delta G^0{}_{np}(T_m) = -RT \ln K_{np}(T_m) =$$

$$= -8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 330\ \text{K} \times \ln(1.00\times10^6) = -37.9\ \text{kJ mol}^{-1}$$

The shortest oligonucleotide will be obtained if C–G-only dsDNA is considered, because C–G pairs are more stable than A–T pairs.

Then, the smallest number of base pairs is obtained by dividing the Gibbs energy by the contribution of one C–G pair, which for a non-palindromic dsDNA is:

$$n_{np} = \frac{-37.9\ \text{kJ mol}^{-1}}{-6.07\ \text{kJ mol}^{-1}} = 6.2$$

The needed length of a non-palindromic dsDNA: **7**

For a palindromic dsDNA, the Gibbs energy at T_m is

$$\Delta G^0{}_p(T_m) = -RT \ln K_p T_m =$$

$$= -8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 330\ \text{K} \times \ln(1.00\times10^5) = -31.6\ \text{kJ mol}^{-1}$$

and the number of base pairs is

$$n_\text{p} = \frac{-31.6 \text{ kJ mol}^{-1}}{-6.07 \text{ kJ mol}^{-1}} = 5.2$$

The needed length of a palindromic dsDNA: **6**

The shortest oligonucleotide is

☐ palindromic (P)

☐ non-palindromic (NP).

A smaller number of base pairs was obtained under the assumption of a palindromic dsDNA. Therefore, we conclude that the shortest dsDNA that has T_m above 330 K has a palindromic sequence of 6 C–G pairs.

Calculation:

Start from the definition of $\Delta G°$ and its relation to the equilibrium constant:

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0$$

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

Combination of the expressions leads to

$$\Delta H^0 - T\,\Delta S^0 = -RT \ln K$$

Division by $T \times \Delta H°$ yields

$$\frac{1}{T} = \frac{\Delta S^0}{\Delta H^0} - \frac{R}{\Delta H^0} \ln K_m$$

so that, specifically for T_m

$$\frac{1}{T_m} = \frac{\Delta S^0}{\Delta H^0} - \frac{R}{\Delta H^0} \ln K_m$$

where K_m is the equilibrium constant at the melting temperature.

For the palindromic Drew–Dickerson dodecanucleotide, the concentrations of dsDNA and ssDNA at the melting temperature may be expressed in terms of the initial duplex concentration c_init

$$[\text{dsDNA}] = 0.5\, c_\text{init}$$

$$[\text{ssDNA}] = c_\text{init}$$

and the equilibrium constant at the melting temperature follows as

$$K_m = \frac{0.5\frac{c_{init}}{c_0}}{\left(\frac{c_{init}}{c_0}\right)^2} = \frac{1}{2\frac{c_{init}}{c_0}}$$

This may be cast into the equation above for the inverse melting temperature, yielding a linearized concentration dependence (note the "plus" sign), which corresponds to the plot in this task directly:

$$\frac{1}{T_m} = \frac{\Delta S^0}{\Delta H^0} + \frac{R}{\Delta H^0}\ln\left(2\frac{c_{init}}{c_0}\right)$$

The slope $R/\Delta H°$ and the intercept $\Delta S°/\Delta H°$ may be obtained

- either graphically from the plot – **method 1**,
- or by solving a system of 2 linear equations using any 2 data points – **method 2**.

Method 1:

The dependence in the plot is strongly linear, and it is very easy to draw a straight line passing the centre of each of the circles representing data points. Then, values of the linear function may be read, e.g., at $\ln(2\frac{c_{init}}{c_0}) = -15$, ca. 0.003145 K^{-1}, and at $\ln(2\frac{c_{init}}{c_0}) = -11$, ca. 0.003065 K^{-1}. From these numerical values, the slope follows as

$$\text{slope} = \frac{0.003065\ \text{K}^{-1} - 0.003145\ \text{K}^{-1}}{-11-(-15)} = -\,0.000020\ \text{K}^{-1}$$

and the intercept has to be re-calculated to abscissa equal to zero, e.g., as

$$\text{intercept} = 0.003065\ \text{K}^{-1} + (0-(-11)) \times (-0.000020\ \text{K}^{-1}) = 0.002845\ \text{K}^{-1}$$

Method 2:

For instance, considering the first and the last point, we obtain:

The first point:

$$\frac{1}{T_m} = \frac{1}{319.0\ \text{K}} = 3.135\times10^{-3}\ \text{K}^{-1} \qquad \ln\left(\frac{c_{init}}{c_0}\right) = \ln(2 \times 0.25\times10^{-6}) = -14.5$$

the last point:

$$\frac{1}{T_m} = \frac{1}{326.2\ \text{K}} = 3.066\times10^{-3}\ \text{K}^{-1} \qquad \ln\left(\frac{c_{init}}{c_0}\right) = \ln(2 \times 8.0\times10^{-6}) = -11.0$$

A system of two linear equations follows as

$$3.135\times10^{-3}\ K^{-1} = \frac{\Delta S^0}{\Delta H^0} - 14.5 \times \frac{R}{\Delta H^0}$$

$$3.066\times10^{-3}\ K^{-1} = \frac{\Delta S^0}{\Delta H^0} - 11.0\times \frac{R}{\Delta H^0}$$

which yields the solution

$$\frac{\Delta S^{\circ}}{\Delta H^{\circ}} = 2.849 \times 10^{-3}\ \text{K}^{-1} \quad \text{and} \quad \frac{R}{\Delta H^{\circ}} = -2.0 \times 10^{-5}\ \text{K}^{-1}$$

Common to Methods 1 and 2:

The desired thermodynamic quantities follow from there:

$$\Delta \boldsymbol{H}^{\circ} = \frac{R}{\text{slope}} = \frac{8.314}{-0.000020}\ \text{J mol}^{-1}\ \mathbf{= -416\ kJ\ mol^{-1}}$$

$$\Delta \boldsymbol{S}^{\circ} = R \times \frac{\text{intercept}}{\text{slope}} = 8.314 \times \frac{0.002845}{-0.000020}\ \text{J K}^{-1}\ \text{mol}^{-1}\ \mathbf{= -1.18\ kJ\ K^{-1}\ mol^{-1}}$$

Alternative route:

It is also possible to consider the linearized dependence implicitly.

After the combination of equalities for $\Delta G°$, K_m may be expressed in terms of c_{init}:

$$\Delta H^{\circ} - T_m \Delta S^{\circ} = RT_m \ln\left(2\frac{c_{init}}{c_0}\right)$$

Then, a set of 2 such equations for 2 different concentrations

$$\Delta H^{\circ} - T_{m1} \Delta S^{\circ} = RT_{m1} \ln\left(2\frac{c_{init,1}}{c_0}\right)$$

$$\Delta H^{\circ} - T_{m2} \Delta S^{\circ} = RT_{m2} \ln\left(2\frac{c_{init,2}}{c_0}\right)$$

may be solved for 2 unknowns, $\Delta H°$ and $\Delta S°$.

For instance, multiplication of the equations with T_{m2} and T_{m1}, respectively, followed by the subtraction of equations leads to

$$\Delta H^{\circ} = R\,\frac{T_{m1}T_{m2}}{T_{m2} - T_{m1}}\ \ln\frac{c_{init,1}}{c_{init,2}}$$

and a plain subtraction of equations leads to

$$\Delta S^{\circ} = R\,\frac{T_{m1} \ln\left(2\frac{c_{init,1}}{c_0}\right) - T_{m2} \ln\left(2\frac{c_{init,2}}{c_0}\right)}{T_{m2} - T_{m1}}$$

Or, $\Delta S°$ may be obtained by casting $\Delta H°$ into one of the equations being solved:

$$\Delta S^{\circ} = \frac{\Delta H^{\circ}}{T_{m1}} + R\ \ln 2\frac{c_{init,1}}{c_0}$$

The desired quantities follow as:

$\Delta H^{\circ} = -420$ kJ mol^{-1} and $\Delta S^{\circ} = -1.2$ kJ mol^{-1} K^{-1}.

PROBLEM 2

Repatriation of remains in the middle ages

At ambient temperatures, racemization is a slow reaction. As such, it can be used for dating biological objects and, moreover, for studying their thermal history. Let us take L-isoleucine (L-Ile) ((2*S*,3*S*)-2-amino-3-methylpentanoic acid) as an example. It isomerizes on the α-carbon and forms (2*R*,3*S*)-2-amino-3-methylpentanoic acid, also known as D-*allo*-isoleucine. As the configuration changes on only one of the two stereogenic centres, this process is called epimerization rather than racemization.

2.1 Choose all true statements.

☐ D-*allo*-isoleucine and L-isoleucine have the same values of specific optical rotation but they have different melting points.

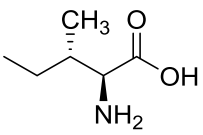
☐ D-*allo*-isoleucine has an identical absolute value of specific optical rotation as L-isoleucine but the sign is opposite. The melting point is the same for both isomers.

☐ D-*allo*-isoleucine and L-isoleucine have different values of specific optical rotation but they have the same melting points.

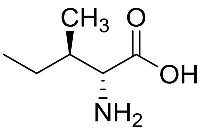
☐ D-*allo*-isoleucine and L-isoleucine have different values of specific optical rotation and different melting points.

☐ D-*allo*-isoleucine is not optically active.

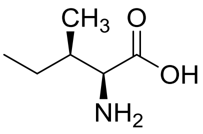
2.2 Assign the absolute configurations for each stereoisomer of isoleucine.



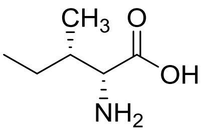
A



B



C



D

☐ 2*S*,3*R* (L-*allo*-isoleucine)

☐ 2*R*,3*S* (D-*allo*-isoleucine)

☐ 2*S*,3*S* (L-isoleucine)

☐ 2*R*,3*R* (D-isoleucine)

2.3 The equilibrium constant K_{ep} for L-isoleucine epimerization has the value of 1.38 (at 374 K). If we set molar Gibbs free energy of L-isoleucine G^{o}_{m} = 0 kJ mol^{-1} determine the Gibbs free energies for all structures **A**–**D** from question 2.2 at 374 K.

2.4 If we take into account stereoisomerism at all stereocentres, what is the maximum possible number of the stereoisomers of the tripeptide Ile-Ile-Ile?

At the start of the epimerization, we can neglect the reverse reaction. The epimerization then follows the first-order kinetics:

$$\text{L-isoleucine} \xrightarrow{k_1} \text{D-}\textit{allo}\text{-isoleucine}$$

The value of the rate constant at 374 K is $k_1(374\ \text{K}) = 9.02\times10^{-5}\ \text{h}^{-1}$ and that at 421 K is $k_1(421\ \text{K}) = 1.18\times10^{-2}\ \text{h}^{-1}$.

In the following calculation, shorten the concentration of L-isoleucine to [L] and of D-*allo*-isoleucine to [D].

We can define a quantity *de* (diastereomeric excess):

$$de = \frac{[\text{L}] - [\text{D}]}{[\text{L}] + [\text{D}]} \times 100(\%).$$

2.5 Let us boil L-isoleucine for 1 943 hours at 374 K. What is the value of *de* (with three significant figures) for L-isoleucine a) before boiling and b) after boiling?

2.6 How long does it take to convert 10% of L-isoleucine to D-*allo*-isoleucine at 298 K?

In fact, the reverse reaction cannot be neglected. The correct kinetic scheme is expressed as

$$\text{L-isoleucine} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{D-}\textit{allo}\text{-isoleucine}$$

Let us define the deviation of concentration from its equilibrium value $[\text{L}]_{eq}$

$$x = [\text{L}] - [\text{L}]_{eq}$$

It is possible to derive that x evolves with time according to the following equation:

$$x = x(0) \times e^{-(k_1 + k_2)t},$$

where $x(0)$ is the deviation from equilibrium at t = 0 h.

2.7 Let us boil 1.00 mol dm^{-3} L-isoleucine solution for 1 943 hours at 374 K. The rate constant for the forward reaction is $k_1(374\ \text{K}) = 9.02 \times 10^{-5}\ \text{h}^{-1}$, K_{ep} for L-isoleucine epimerization has the value of 1.38 (at 374 K). In the following calculation, shorten the concentration of L-isoleucine to [L] and of D-*allo*-isoleucine to [D]. Evaluate (with three significant figures)

a) $[L]_{eq}$,

b) diastereomeric excess (*de*) after boiling.

Amino acids with a single chiral centre undergo racemization, e.g. L-arginine racemizes:

$$\text{L-arginine} \underset{k_1}{\overset{k_1}{\rightleftharpoons}} \text{D-arginine}$$

e

The time evolution of concentrations is governed by

$$\ln\frac{1+\frac{[D]}{[L]}}{1-\frac{[D]}{[L]}} = 2k_1 t + C$$

Here [D] and [L] are concentrations of D- and L-arginine at time t, k_1 is the rate constant, and the term C is set according to the initial concentrations.

Holy Roman Emperor Lothar III passed away during his journey to Sicily in 1137. To facilitate the repatriation of the remains, his body was, immediately after his death, boiled in water (373 K) for a certain time. Let us try to estimate the boiling time with the help of chemical kinetics. We know that the rate constant k_1 of arginine racemization within the protein at 373 K and pH = 7 has the value of 5.10×10^{-3} h^{-1}.

In order to analyse the isomeric composition of arginine in Lothar's bones, we need to start with transferring arginine into solution. Lothar's bones were hydrolyzed in a highly acidic environment for 4 hours at 383 K. The ratio of the optical isomers was $\frac{[D]}{[L]} = 0.090$. Lothar's wife Richenza was not boiled after her death. Her bones were hydrolyzed using the same procedure and in this case the ratio was $\frac{[D]}{[L]} = 0.059$. (Note that the racemization also takes place during the hydrolysis, with the rate constant $k_1^{'}$, different from k_1).

2.8 How long was the Holy Roman Emperor Lothar III boiled in water in 1137?

Note: The racemization of arginine is an extremely slow process at temperatures typically encountered in graves. As both bodies are only some 880 years old, we can neglect the natural racemization during this time.

SOLUTION

2.1 The correct answer:

D-*allo*-isoleucine and L-isoleucine have different values of specific optical rotation and different melting points.

2.2

C	2*S*,3*R*	(L-*allo*-isoleucine)
D	2*R*,3*S*	(D-*allo*-isoleucine)
A	2*S*,3*S*	(L-isoleucine)
B	2*R*,3*R*	(D-isoleucine)

2.3 **A:** $G^{\mathrm{o}}_{\mathrm{m}} = 0\ \mathrm{kJ\ mol^{-1}}$ (L-isoleucine)

B: $G^{\mathrm{o}}_{\mathrm{m}} = 0\ \mathrm{kJ\ mol^{-1}}$ (**B** is a mirror image of **A** with identical physical properties)

C: $G^{\mathrm{o}}_{\mathrm{m}} = -RT \ln K_{\mathrm{ep}} = -1.00\times10^{3}\ \mathrm{J\ mol^{-1}}$

D: $G^{\mathrm{o}}_{\mathrm{m}} = -\ 1.00\times10^{3}\ \mathrm{J\ mol^{-1}}$ (**D** is a mirror image of **C** with identical physical properties)

2.4 The number of stereoisomers is 2^N, where N is the number of stereogenic centres.

For Ile-Ile-Ile, $N = 6$, so there are $2^6 = 64$ stereoisomers.

2.5 a) Before boiling, the *de* is:

$$de = \frac{[\mathrm{L}]_0 - [\mathrm{D}]_0}{[\mathrm{L}]_0 + [\mathrm{D}]_0} \times 100(\%)$$

Because $[\mathrm{D}]_0 = 0$, the *de* of native L-isoleucine before boiling is 100%.

b) After boiling:

First, we have to calculate the concentration ratio $[\mathrm{L}]/[\mathrm{L}_0]$ from the first-order rate equation

$$\frac{[\mathrm{L}]}{[\mathrm{L}]_0} = \mathrm{e}^{-k_1 t} = 0.839$$

so $[\mathrm{D}] = 0.161\ [\mathrm{L}]_0$

and

$$de = \frac{0.839\ -\ 0.161}{0.839\ +\ 0.161} \times 100\ \% = 67.8\ \%$$

2.6 We need to evaluate the rate constant at 298 K. It can be evaluated from the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT}$$

We get ln A and E_a from the values of k at two temperatures (374 K and 421 K)

$$\ln k\ (374\ \text{K}) = \ln 9.02 \times 10^{-5}\ [\text{h}^{-1}] = -\,9.313 = \ln A - \frac{E_a}{R \times 374}$$

$$\ln k\ (421\ \text{K}) = \ln 1.18 \times 10^{-2}\ [\text{h}^{-1}] = -\,4.444 = \ln A - \frac{E_a}{R \times 421}$$

It follows that

$$\ln A = -\,9.313 + \frac{E_a}{R \times 374} = -\,4.444 + \frac{E_a}{R \times 421}$$

from which $E_a = 136\ \text{kJ mol}^{-1}$.

ln A is from the equation at 374 K

$$\ln (A[\text{h}^{-1}]) = -\,9.313 + \frac{E_a}{R \times 374} = 34.4$$

For k at 298 K we then have:

$$\ln(k\,(298\ \text{K})[\text{h}^{-1}]) = \ln A - \frac{E_a}{R \times 298} = 34.4 - \frac{136 \times 10^3}{R \times 298} = -\,20.5$$

$$k(298\ \text{K}) = 1.25{\times}10^{-9}\ \text{h}^{-1}$$

It follows from the rate equation that

$$\ln \frac{[\text{L}]}{[\text{L}]_0} = -\,kt$$

$$\ln 0.90 = -\,1.25{\times}10^{-9}\ t$$

$$t = 8.42{\times}10^{7}\ \text{h} = 9610\ \text{years}$$

2.7 a) Calculation:

From the definition and mass balance we know that

$$x = [\text{L}] - [\text{L}]_{eq} = [\text{D}]_{eq} - [\text{D}]$$

We can derive the formulae for $[\text{L}]_{eq}$ (and also for $[\text{D}]_{eq}$) in terms of $[\text{L}]_0$

$$[\text{L}]_0 = [\text{L}]_{eq} + [\text{D}]_{eq}$$

$$[\text{D}]_{eq} = [\text{L}]_0 - [\text{L}]_{eq}$$

We also know that

$$K_{ep} = \frac{k_1}{k_2} = \frac{[\text{D}]_{eq}}{[\text{L}]_{eq}}$$

from which

$$[D]_{eq} = \frac{k_1}{k_2}[L]_{eq}$$

The substitution for $[D]_{eq}$ in $[D]_{eq} = [L]_0 – [L]_{eq}$ yields

$$[L]_{eq} = \frac{k_2}{k_1 + k_2}[L]_0$$

The rate constant k_2 is calculated from the epimerization constant K_{ep} as

$$k_2 = \frac{k_1}{K_{ep}} = \frac{9.02 \times 10^{-5}\ h^{-1}}{1.38} = 6.54 \times 10^{-5}\ h^{-1}$$

After the substitution of the numerical values, we get (with three significant digits)

$$[L]_{eq} = \frac{6.54 \times 10^{-5}\ h^{-1}}{9.02 \times 10^{-5}\ h^{-1} + 6.54 \times 10^{-5}\ h^{-1}} \times 1\ mol\ dm^{-3} = 0.420\ mol\ dm^{-3}$$

b) Calculation:

de is defined as

$$de = \frac{[L] - [D]}{[L] + [D]} \times 100(\%)$$

We can express *de* in terms of the equilibrium values as

$$de = \frac{[L]_{eq} + x - [D]_{eq} + x}{[L]_{eq} + x + [D]_{eq} - x} \times 100(\%) = \frac{[L]_{eq} - [D]_{eq} + 2x}{[L]_0} \times 100(\%)$$

We already have the formula for $[L]_{eq}$ from task a). $[D]_{eq}$ in terms of $[L]_0$ is then

$$[D]_{eq} = \frac{k_1}{k_2}[L]_{eq} = \frac{k_1}{k_1 + k_2}[L]_0$$

Finally, we need to evaluate x in terms of $[L]_0$. We know that $x(0) = [D]_{eq}$, so

$$x = [D]_{eq} \times e^{-t(k_1 + k_2)} = \frac{k_1}{k_1 + k_2}[L]_0 \times e^{-t(k_1 + k_2)}$$

We can now express *de* as

$$de = \frac{\frac{k_2}{k_1 + k_2}[L]_0 - \frac{k_1}{k_1 + k_2}[L]_0 + 2\frac{k_1}{k_1 + k_2}[L]_0 e^{-t(k_1 + k_2)}}{[L]_0} \times 100(\%) = \frac{k_2 - k_1 + 2k_1 e^{-t(k_1 + k_2)}}{k_1 + k_2} \times 100(\%)$$

$$de = \frac{6.54 \times 10^{-5} - 9.02 \times 10^{-5} + 2 \times 9.02 \times 10^{-5} e^{-1\,943\,(9.02 \times 10^{-5} + 6.54 \times 10^{-5})}}{9.02 \times 10^{-5} + 6.54 \times 10^{-5}} \times 100(\%) = 69.8\%$$

2.8 Calculation:

Let us assume the following schemes for Lothar and Richenza:

Lothar: $0 \xrightarrow{k_1} 1 \xrightarrow{k_1'} 2$

Richenza: $0 \xrightarrow{k_1'} 3$

where 0 is the state before boiling with [D]/[L] ratio X_0, 1 corresponds to the Lothar's state after boiling in water in 1137 with the [D]/[L] ratio X_1, 2 is the Lothar's state after the acidic hydrolysis with the [D]/[L] ratio X_2, and 3 is the Richenza's state after the hydrolysis with the [D]/[L] ratio X_3. k_1 is the rate constant for racemization at 373 K, k_1' is the rate constant for acid-catalyzed racemization at 383 K.

We can write the following equations:

$$\ln\frac{1+X_3}{1-X_3} = 2\,k_1' t_{\text{hydrolysis}} \quad \text{(eq. 1)}$$

$$\ln\frac{1+X_1}{1-X_1} = 2\,k_1 t_{\text{boiling}} \quad \text{(eq. 2)}$$

$$\ln\frac{1+X_2}{1-X_2} = 2\,k_1' t_{\text{hydrolysis}} + \ln\frac{1+X_1}{1-X_1} \quad \text{(eq. 3)}$$

Combining the equations leads to

$$\ln\frac{1+X_2}{1-X_2} = \ln\frac{1+X_3}{1-X_3} + 2\,k_1 t_{\text{boiling}}$$

From which the time of boiling t_{boiling} is

$$\ln\frac{(1+X_2)\,(1-X_3)}{(1-X_2)\,(1+X_3)} = 2\,k_1 t_{\text{boiling}}$$

Using the values $X_2 = 0.090$ and $X_3 = 0.059$ we get

$$t_{\text{boiling}} = \frac{1}{2\times 5.10\times 10^{-3}}\ln\frac{(1+0.090)\,(1-0.059)}{(1-0.090)\,(1+0.059)} = 6.11\text{ h}$$

PROBLEM 3

Emerging electro-mobility

Contemporary means of transportation rely on burning fossil fuels, although the efficiency of real combustion engines is inherently limited and typically ranges between 20 and 40%.

3.1 Mark the factors that can make the efficiency of a heat engine higher:

☐ Increasing the friction in the mechanical parts of the engine

☐ Increasing the burning temperature of the fuel in the engine

☐ Narrowing the working temperature interval of the engine

☐ Increasing the working pressure of the gas

Fuel cells represent a way to improve the engine efficiency for future vehicles. The engine efficiency can be improved by using hydrogen-based fuel cells.

3.2 The standard enthalpy of formation of liquid water is $\Delta_f H°(H_2O,l) = -285.84$ kJ mol^{-1}, and the standard combustion enthalpy of isooctane is $\Delta_c H°(C_8H_{18},l) = -5\,065.08$ kJ mol^{-1} (both at 323.15 K). Calculate the values of specific (per unit of mass) combustion enthalpy at 232.15 K of pure liquid isooctane and pure gaseous hydrogen.

3.3 Calculate the standard electromotive force (EMF) of a fuel cell using gaseous oxygen and hydrogen, both ideal gases at 100 kPa and 323.15 K, to produce liquid water.

Use the following entropy data for 323.15 K: $S°(H_2O,l) = 70$ J K^{-1} mol^{-1},
$S°(H_2,g) = 131$ J K^{-1} mol^{-1},
$S°(O_2,g) = 205$ J K^{-1} mol^{-1}.

3.4 Determine the ideal thermodynamic efficiency (η) of a fuel cell producing liquid water at 353.15 K. At this temperature, the enthalpy of formation of water is $\Delta_f H°(H_2O,l) = -281.64$ kJ mol^{-1} and the corresponding reaction Gibbs energy change is $\Delta_r G° = -225.85$ kJ mol^{-1}.

3.5 A polymer membrane electrolyzer facility operates at the voltage of 2.00 V and is powered by a 10.0 MW wind turbine plant which was running at full power from 10 pm to 6 am. The electrolysis yielded 1 090 kg of pure hydrogen. Calculate the electrolysis yield defined as the mass of produced hydrogen divided by its theoretical produced mass.

3.6 Calculate the mass of hydrogen required to drive the distance between Prague and Bratislava (330 km) at the average speed of 100 km h^{-1} with a car fitted with a 310 kW electric engine running on average at a 15% rate of its maximum power. Assume that the efficiency of the hydrogen cell producing electrical energy is 75%, the efficiency of the electric engine is 95%, and the Gibbs energy change for combustion of hydrogen fuel is $\Delta_r G = -226$ kJ mol^{-1}.

The low efficiency of hydrogen production and the safety issues connected with its storage impede spreading the hydrogen-based transportation technology. Hydrazine (N_2H_4) fuel cells might be a suitable alternative.

The following standard reduction potentials for aqueous hydrazine systems are available:

$N_2(g) + 5\ H^+(aq) + 4\ e^- \rightarrow N_2H_5^+(aq)$ $E^0 = -0.23$ V

$N_2H_5^+(aq) + 3\ H^+(aq) + 2\ e^- \rightarrow 2\ NH_4^+(aq)$ $E^0 = +1.28$ V

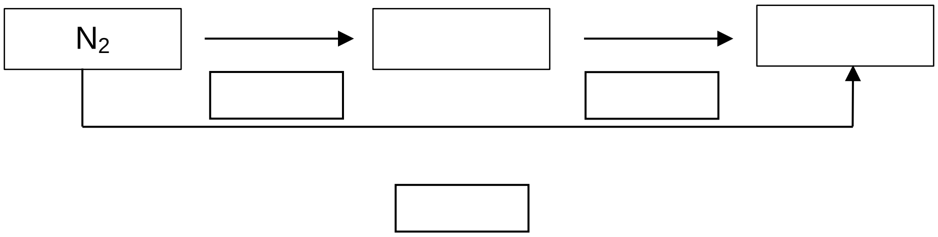
$N_2(g) + 4\ H_2O(l) + 4\ e^- \rightarrow N_2H_4(aq) + 4\ OH^-(aq)$ $E^0 = -1.16$ V

$N_2H_4(aq) + 2\ H_2O(l) + 2\ e^- \rightarrow 2\ NH_3(aq) + 2\ OH^-(aq)$ $E^0 = +0.10$ V

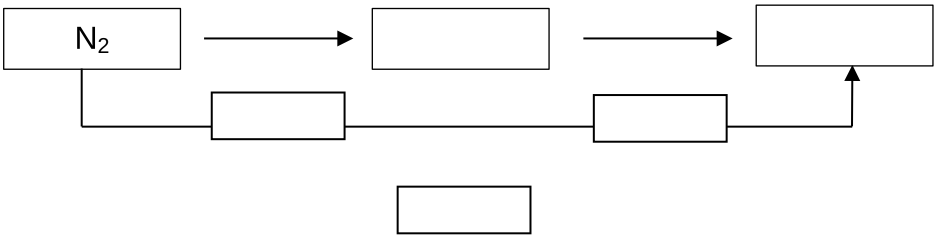
$2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$ $E^0 = -0.83$ V

3.7 Fill in the following Latimer diagrams with the forms of hydrazine and ammonia prevailing at the given conditions and write the redox potential value for each arrow representing the electrochemical half-reaction. Record all the necessary calculations.

a) Acidic environment (pH = 0)



b) Basic environment (pH = 14)



Due to the toxicity, odour and its environmental impact, it is extremely unfavourable to produce ammonia in fuel cells.

3.8 Write down the net reaction for the decomposition of hydrazine under basic conditions to:

(i) ammonia and nitrogen,

(ii) nitrogen and hydrogen.

Calculate the corresponding equilibrium constants at T = 298.15 K.

Rechargeable lithium-based batteries are an alternative to fuel cells. Lithium-ion batteries commonly use graphite for one of the electrodes, in which lithium clusters intercalate in between the graphite sheets. The other electrode is made of lithium cobalt oxide, which can reversibly absorb lithium ions moving from one electrode to the other during the charge and discharge processes. The half-reactions relevant for the system can be formally written as:

$$(C)_n + Li^+ + e^- \rightarrow Li(C)_n \qquad E^\circ = -3.05\ V,$$
$$CoO_2 + Li^+ + e^- \rightarrow LiCoO_2 \qquad E^\circ = +0.19\ V.$$

3.9 Using the formalism given above, write down the overall chemical reaction occurring in the battery during the **discharge** process. Give the oxidation states of the cobalt atom.

3.10 Tick the boxes to get the correct statements which are valid for the **discharge** of the lithium-based battery described in 3.9:

$Li(C)_n$ electrode is	☐	cathode	☐	because lithium ions are reduced here.
	☐	anode	☐	because lithium atoms are oxidized here.
$LiCoO_2$ electrode is	☐	cathode	☐	because cobalt ions are reduced here.
	☐	anode	☐	because cobalt ions are oxidized here.

3.11 Assume that a C_6 unit, a CoO_2 unit and Li atom form the active battery mass required to transfer one electron between the electrodes. Using the corresponding standard EMF, calculate the theoretical specific reversible charge capacity (in mAh g^{-1}) and the energy density (in kWh kg^{-1}) of such a model lithium ion battery related to the whole active battery mass.

SOLUTION

3.1 The correct answers:

☒ Increasing the burning temperature of the fuel in the engine

☒ Increasing the working pressure of the gas

3.2 $\Delta_c H_s°(C_8H_{18})$ =

$$\Delta_c H_s°(C_8H_{18}) = \frac{\Delta_c H°(C_8H_{18})}{M(C_8H_{18})} = \frac{-5\,065.08 \times 10^3 \text{ J mol}^{-1}}{114.23 \times 10^{-3} \text{ kg mol}^{-1}} = -44.34 \text{ MJ kg}^{-1}$$

$\Delta_c H_s°(H_2)$ = H

$$\Delta_c H_s°(H_2) = \frac{\Delta_c H°(H_2)}{M(H_2)} = \frac{-285.84 \times 10^3 \text{ J mol}^{-1}}{2.02 \times 10^{-3} \text{ kg mol}^{-1}} = -141.50 \text{ MJ kg}^{-1}$$

3.3 The oxidation of molecular hydrogen requires the transfer of $z = 2$ electrons according to the equation: $H_2 + ½\, O_2 \rightarrow H_2O$

$$\Delta_r S° = S°(H_2O,l) - \left(S°(H_2,g) + \frac{1}{2} S°(O_2,g)\right) = -164 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r G° = \Delta_r H° - T\Delta_r S° =$$

$$= -285.84 \times 10^3 \text{ J mol}^{-1} + 323.15 \text{ K} \times 164 \text{ J K}^{-1} \text{ mol}^{-1} = -233 \text{ kJ mol}^{-1}$$

$$EMF = -\frac{\Delta_r G°}{|z|F} = -\frac{-233 \times 10^3 \text{ J mol}^{-1}}{2 \times 96\,485 \text{ C mol}^{-1}} = 1.21 \text{ V}$$

3.4

$$\eta = \frac{\Delta_r G°}{\Delta_f H°} = \frac{-225.85 \text{ kJ mol}^{-1}}{-281.64 \text{ kJ mol}^{-1}} \times 100\% = 80.19\%$$

3.5 Electric energy produced:

$$W = P \times \tau = 10 \times 10^6 \text{ W} \times 8 \times 3\,600 \text{ s} = 2.88 \times 10^{11} \text{ J}$$

is sufficient to transfer the charge:

$$Q = \frac{W}{U} = \frac{2.88 \times 10^{11} \text{ J}}{2 \text{ V}} = 1.44 \times 10^{11} \text{ C}$$

between the electrodes. Water formation is a two-electron process. Thus, the theoretical mass of hydrogen produced is:

$$m_{\text{theory}} = \frac{Q\,M}{|z|\,F} = \frac{1.44 \times 10^{11} \text{ C}}{2 \times 96\,485 \text{ C mol}^{-1}} \times 2.02 \times 10^{-3} \text{ kg mol}^{-1} = 1\,507 \text{ kg}$$

The efficiency of the electrolysis can be evaluated as the ratio:

$$\eta_{\text{electrolysis}} = \frac{m_{\text{real}}}{m_{\text{theory}}} \times 100\% = \frac{1\,090}{1\,507} \times 100\% = 72.3\%.$$

3.6 Driving time:

$$\tau = \frac{s}{v} = \frac{330 \text{ km}}{100 \text{ km h}^{-1} / 3\,600 \text{ s}} = 11\,880 \text{ s}$$

determines the ideal amount of energy required to cover the given distance:

$$W_{\text{ideal}} = P \times f \times \tau = 310 \times 10^3 \text{ W} \times 0.15 \times 11\,880 \text{ s} = 5.52 \times 10^8 \text{ J.}$$

Assuming the overall non-unity efficiency, the real energy required is:

$$W_{\text{real}} = \frac{W_{\text{ideal}}}{\eta_{\text{electrolysis}} \times \eta_{\text{engine}}} = \frac{5.52 \times 10^8 \text{ J}}{0.75 \times 0.95} = 7.75 \times 10^8 \text{ J.}$$

This can be combined with the standard Gibbs energy of liquid water formation to yield the amount of hydrogen:

$$m = \frac{W_{\text{real}}}{|\Delta_r G°|} \times M = \frac{7.75 \times 10^8 \text{ J}}{2.26 \times 10^5 \text{ J mol}^{-1}} \times 2.02 \times 10^{-3} \text{ kg mol}^{-1} = 6.93 \text{ kg.}$$

3.7 Acidic environment:

$$\begin{tikzcd} \boxed{N_2} \arrow[r, "-0.23"'] \arrow[rr, bend right, "+0.27"'] & \boxed{N_2H_5^+} \arrow[r, "+1.28"'] & \boxed{NH_4^+} \end{tikzcd}$$

Basic environment:

:

$$\begin{tikzcd} \boxed{N_2} \arrow[r, "-1.16"'] \arrow[rr, bend right, "-0.74"'] & \boxed{N_2H_4} \arrow[r, "+0.10"'] & \boxed{NH_3} \end{tikzcd}$$

Calculations:

Redox potentials for N_2 to NH_4^+ and N_2 to NH_3, respectively, are calculated as follows:

$$E°(N_2/NH_4^+) = \frac{4\,E°(N_2/N_2H_5^+) + 2\,E°(N_2H_5^+/NH_4^+)}{6} = \frac{4 \times (-\,0.23) + 2 \times 1.28}{6}\ \text{V} = 0.27\ \text{V}$$

$$E°(N_2/NH_3) = \frac{4\,E°(N_2/N_2H_4) + 2\,E°(N_2H_4/NH_3)}{6} = \frac{4 \times (-\,1.16) + 2 \times 0.10}{6}\ \text{V} = -\,0.74\ \text{V}$$

3.8 Equations for hydrazine decomposition:

$N_2H_4(aq) \rightarrow N_2(g) + 2\ H_2(g)$

$3\ N_2H_4(aq) \rightarrow 4\ NH_3(aq) + N_2(g)$

Calculations:

$$\Delta_r G° = -\,RT \ln K = -\,|z|FE° \rightarrow\ K = \exp\left(\frac{|z|FE°}{RT}\right)$$

Hydrazine decomposition to NH_3 and N_2 in a basic environment:

$$E° = E°(N_2H_4/NH_3) + \left(-\,E°(N_2/N_2H_4)\right) = (0.10 + 1.16)\ \text{V} = 1.26\ \text{V}$$

$$K = \exp\left(\frac{|z|FE°}{RT}\right) = \exp\left(\frac{4 \times 96\,485\ \text{C mol}^{-1} \times 1.26\ \text{V}}{8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298.15\ \text{K}}\right) = 1.6 \times 10^{85}$$

Hydrazine decomposition to H_2 and N_2 in a basic environment:

$$E° = E°(H_2O/H_2) + \left(-\,E°(N_2/N_2H_4)\right) = (-\,0.83 + 1.16)\ \text{V} = 0.33\ \text{V}$$

$$K = \exp\left(\frac{|z|FE°}{RT}\right) = \exp\left(\frac{4 \times 96\,485\ \text{C mol}^{-1} \times 0.33\ \text{V}}{8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298.15\ \text{K}}\right) = 2.1 \times 10^{22}$$

3.9 Because $E°_{\text{lower}} > E°_{\text{upper}}$ the upper reaction occurs spontaneously in the opposite direction. Therefore, the discharge of the battery occurs when lithium leaves the graphite structure and its ions intercalate in the cobalt oxide:

$$Li(C)_n + Co^{IV}O_2 \rightarrow LiCo^{III}O_2 + (C)_n$$

3.10

$Li(C)_n$	☐	cathode	☐	because lithium ions are reduced here.
electrode is	✓	anode	✓	because lithium atoms are oxidized here.

LiCoO$_2$ electrode is	☑	cathode	☑	because cobalt ions are reduced here.
	☐	anode	☐	because cobalt ions are oxidized here.

3.11 **S**pecific charge capacity:

The transfer of 1 mol of electrons requires at least the molar mass of the active ingredients M_{total} = 169.94 g mol^{-1}, meaning that the specific charge capacity is:

$$c_{q,s} = \frac{F}{M} = \frac{96\,485\text{ C mol}^{-1}}{169.94\text{ g mol}^{-1}} = 567.76\text{ C g}^{-1} \approx 567.76\text{ A s g}^{-1} \approx 157.71\text{ mAh g}^{-1}$$

Energy density of the battery:

Assuming the standard EMF (voltage) of the battery is:

$$U = E°(\text{Li}_{x1}\text{CoO}_2/\text{Li}_{x2}\text{CoO}_2) - E°(\text{Li}^+/\text{Li}^0) = 0.19 + 3.05\text{ V} = 3.24\text{ V}\ ,$$

the energy density of the battery can be calculated as:

$$\rho_{\text{el}} = U \times c_{q,s} = 3.24\text{ V} \times 567.76\text{ C g}^{-1} = 1\,839.6\text{ W s g}^{-1} \approx\ 0.511\text{ kWh kg}^{-1}$$

PROBLEM 4

Column chromatography of radioactive copper

^{64}Cu for positron emission tomography is prepared by the bombardment of a zinc target with deuterium nuclei (further referred to as the activated target).

4.1 Write down the balanced equation for the ^{64}Zn nucleus bombardment with deuterium nuclei, giving ^{64}Cu. Specify the corresponding atomic and mass numbers of all species. Disregard the charges.

The activated target is dissolved in concentrated hydrochloric acid (HCl (aq)) to give a mixture containing Cu^{2+} and Zn^{2+} ions and their respective chlorido complexes.

4.2 Calculate the mole fraction of negatively charged copper species with respect to the amount of copper prepared by zinc target activation. Assume [Cl$^–$] = 4 mol dm$^{–3}$. For the overall complexation constants, β, see Table 1.

Before you start the calculation, write down the charges in the upper right boxes:

Cu☐ [CuCl]☐ [$CuCl_2$]☐ [$CuCl_3$]☐ [$CuCl_4$]☐

Table 1. Overall complexation constants β of Cu species (charges were omitted in the formula).

$$\beta_i = \frac{[CuCl_i]}{[Cu] \times [Cl]^i}$$

i in [CuCl$_i$]	1	2	3	4
β_i	2.36	1,49	0.690	0.055

The mixture containing Cu^{2+} and Zn^{2+} ions and their respective chlorido complexes was separated with an anion exchange resin. Dry resin in OH$^–$ form was dispersed in water and the suspension was transferred into a column. To occupy all sites with Cl$^–$ ions (i.e. to obtain resin in a Cl$^–$ form), the resin was washed with hydrochloric acid and then with deionized water to wash out all the unbound Cl$^–$ ions.

4.3 Everything was initially at laboratory temperature before washing with hydrochloric acid. Does the column temperature change during the washing with hydrochloric acid?

☐ No.
☐ Yes, the temperature decreases.
☐ Yes, the temperature increases.

The mixture containing Cu^{2+} and Zn^{2+} ions and their respective chlorido complexes was transferred onto the resin-filled column. Hydrochloric acid solution was used as an eluent.

Using the simple experimental formula below, you can calculate quantities that determine average elution properties of both copper species and zinc species on the column.

The retention volume V_R (the mobile phase volume at which 50% of the compound has been eluted from the column) can be calculated as follows:

$$V_R = D_g \times m_{\text{resin,dry,OH form}} + V_0$$

4.4 Using the average mass distribution coefficients D_g (D_g(Cu species) = 17.4 cm^3 g^{-1}, D_g(Zn species) = 78.5 cm^3 g^{-1}), calculate the retention volumes V_R in cm^3 of both copper species and zinc species. The mass of dry resin in OH^- form $m_{\text{resin,dry,OH form}}$ = 3.72 g and the void volume of a column V_0 = 4.93 cm^3.
(If you cannot find the answer, use V_R(Cu species) = 49.9 cm^3 and V_R(Zn species) = 324 cm^3 for further calculations.)

Using the simple experimental formula, separation of two sets of species, **A** and **B**, can be considered complete if

$$\boldsymbol{V}_{0.001}(\mathbf{A}) - \boldsymbol{V}_{0.999}(\mathbf{B}) > 10\boldsymbol{V}_c$$

where $\boldsymbol{V}_{0.001}$ is the mobile phase volume at which 0.1% of **A** has been eluted from the column, and $V_{0.999}$ is the mobile phase volume at which 99.9% of **B** has been eluted from the column.

$$V_{0.001}(\mathbf{A}) = V_R(\mathbf{A}) \times (1 - 6.91\sqrt{d_p/L_c})$$

$$V_{0.001}(\mathbf{B}) = V_R(\mathbf{B}) \times (1 - 6.91\sqrt{d_p/L_c})$$

$$V_{0.999}(\mathbf{B}) = 2\, V_R(\mathbf{B}) - \mathrm{V}_{0.001}(\mathbf{B})$$

4.5 Based on a calculation, decide whether copper species were separated completely from zinc species. The volume of the column filled with the swollen resin V_c = 10.21

cm^3, the resin particle diameter d_p = 0.125 mm, and the height of the wet resin in a swollen state in the column L_c = 13.0 cm.

4.6 Calculate the theoretical value of the total ion exchange mass capacity of the dry resin used in this problem, $Q_{m,theor}$, in mmol g^{-1}. Consider tetralkylammonium groups were the only ones responsible for ion exchange of the resin. No other nitrogen containing groups were present. The mass fraction of nitrogen in the dry resin was 4.83%.

(If you cannot find the answer, use $Q_{m,theor}$ = 4.83 mmol g^{-1} for further calculations.)

In reality, not all tetraalkylammonium groups are involved in the ion exchange. To determine the total ion exchange volume capacity, Q_v, the column filled with 3.72 g dry resin converted to the Cl^- form was washed with the excess of sodium sulfate solution. The effluent was collected in a 500 cm^3 volumetric flask, which was then filled with water to the mark. An aliquot of 100 cm^3 was potentiometrically titrated with 0.1027 mol dm^{-3} silver nitrate. The silver nitrate solution volume at the equivalence point was 22.20 cm^3. The volume of the column filled with the swollen resin, V_c, was 10.21 cm^3.

4.7 Calculate the Q_v of the swollen resin in mmol of active tetraalkylammonium groups per cm^3 of the swollen resin.

(If you cannot find the answer, use Q_v = 1.00 mmol cm^{-3} for further calculations.)

4.8 Calculate the mole fraction (x) of the tetraalkylammonium groups actively involved in the ion exchange.

SOLUTION

4.1

$$^{64}_{30}\mathrm{Zn} + ^{2}_{1}\mathrm{H} \rightarrow ^{64}_{29}\mathrm{Cu} + 2\,^{1}_{1}\mathrm{p}$$

4.2 $Cu\boxed{2+}$ $[CuCl]\boxed{+}$ $[CuCl_2]\boxed{0}$ $[CuCl_3]\boxed{-}$ $[CuCl_4]\boxed{2-}$

Calculation of the mole fraction:

The mole fraction is the sum of the distribution coefficients of $[CuCl_3]^-$ and $[CuCl_4]^{2-}$:

$([[CuCl_3]^-] + [[CuCl_4]^{2-}]) / c(Cu^{2+}) =$

$= (\beta_3\,[Cl^-]^3 + \beta_4\,[Cl^-]^4) / (1 + \beta_1\,[Cl^-] + \beta_2\,[Cl^-]^2 + \beta_3\,[Cl^-]^3 + \beta_4\,[Cl^-]^4) =$

$= (0.690\times4^3 + 0.055\times4^4) / (1 + 2.36\times4 + 1.49\times4^2 + 0.690\times4^3 + 0.055\times4^4) =$

$= 58.24 / 92.52 = 0.63$

Mole fraction: 0.63

(answer with 2 digits after decimal point)

4.3 ☒ Yes, the temperature increases.

4.4 $V_R(\text{Cu species}) = 17.4\ \text{cm}^3\ \text{g}^{-1} \times 3.72\ \text{g} + 4.93\ \text{cm}^3 = 69.7\ \text{cm}^3$

$V_R(\text{Zn species}) = 78.5\ \text{cm}^3\ \text{g}^{-1} \times 3.72\ \text{g} + 4.93\ \text{cm}^3 = 297\ \text{cm}^3$

4.5 According to the retention volumes (V_R), $V_{0.001}(A)$ corresponds to $V_{0.001}(\text{Zn species})$ and $V_{0.999}(B)$ corresponds to $V_{0.999}(\text{Cu species})$

$V_{0.001}(A) = 297\ \text{cm}^3 \times (1 - 6.91 \times \sqrt{0.125\ \text{mm}/130\ \text{mm}}) = 233\ \text{cm}^3$

$V_{0.999}(B) = 2 \times 69.7\ \text{cm}^3 - 54.8\ \text{cm}^3 = 84.6\ \text{cm}^3$

where $V_{0.001}(\text{Cu species}) = 69.7\ \text{cm}^3 \times (1 - 6.91 \times \sqrt{0.125\ \text{mm}/130\ \text{mm}}) = 54.8\ \text{cm}^3$

It is possible to separate copper species from zinc species.

☒ True ☐ False

4.6 $Q_{m,theor} = w(N) / M(N) = 0.0483 / (14.01\ \text{g mol}^{-1}) = 3.45\ \text{mmol g}^{-1}$

4.7 $Q_v = V(AgNO_3) \times c(AgNO_3) \times V_{flask} / (V_{aliquot} \times V_c) =$

$= 0.0222\ \text{dm}^3 \times 0.1027\ \text{mol dm}^{-3} \times 0.500\ \text{dm}^3 / (0.100\ \text{dm}^3 \times 0.01021\ \text{dm}^3) =$

$= 1.12\ \text{mmol cm}^{-3}$

4.8 $x = Q_v \times V_c / (Q_{m,teor} \times m_{resin}) = 1.12\ \text{mmol cm}^{-3} \times 10.21\ \text{cm}^3 / (3.45\ \text{mmol g}^{-1} \times 3.72\ \text{g})$

$= = 0.891$

PROBLEM 5

Bohemian garnet

Bohemian garnet (pyrope) is a famous Czech blood coloured semi-precious stone. The chemical composition of natural garnets is expressed by the general stoichiometric formula of $A_3B_2(SiO_4)_3$, where A^{II} is a divalent cation and B^{III} is a trivalent cation. Garnets have a cubic unit cell that contains 8 formula units. The structure comprises 3 types of polyhedra: the A^{II} cation occupies a dodecahedral position (it is surrounded with eight O atoms), the B^{III} cation occupies an octahedral position (it is surrounded with six O atoms) and Si^{IV} is surrounded with four O atoms arranged into a tetrahedron.

The most common garnet mineral is almandine with the formula of $Fe_3Al_2(SiO_4)_3$. Its unit cell parameter is $a = 11.50$ Å.

5.1 Calculate the theoretical density of almandine.

The Bohemian garnet has the composition of $Mg_3Al_2(SiO_4)_3$. Pure compound is colourless and the colour of natural garnets comes from chromophores – transition metal cations that substitute the host material cations. The red colour of the Bohemian garnet comes from trace amounts of Cr^{III} ions in the octahedral sites and Fe^{II} ions in the dodecahedral sites.

5.2 Draw the splitting diagram for the $[Cr^{III}O_6]^{oct}$ d-orbitals and fill it with electrons.

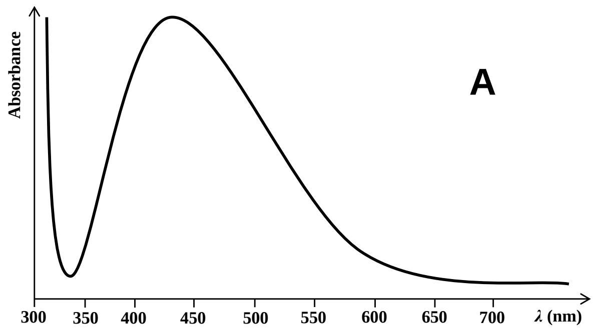
5.3 Identify the 1st transition row element(s) whose trivalent cation(s) M^{III} placed in an **octahedral** position is/are diamagnetic in the low-spin arrangement and paramagnetic in the high-spin arrangement.

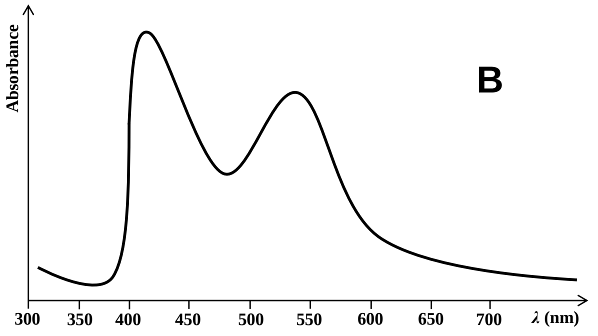
5.4 The figure below shows d-orbitals splitting in the dodecahedral crystal field. Fill in the electrons for the $[Fe^{II}O_8]^{dod}$ chromophore for both existing arrangements.

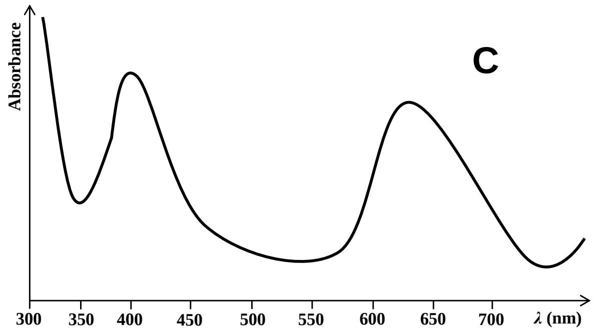
5.5 Derive the inequalities (e.g. $P < E_1 + E_2 + E_3$) for the pairing energy (P) magnitude Cr, Ni in relation to energies E_1, E_2 and E_3 for both arrangements.

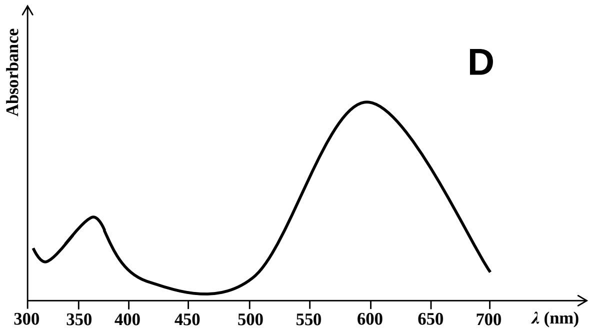
5.6 Assuming that $P > E_3$, identify the 1st transition row element(s) whose divalent cation M^{II} placed in dodecahedral position is diamagnetic in the low-spin arrangement and paramagnetic in the high-spin arrangement.

The figures below show simplified absorption spectra of four coloured minerals – blood-coloured Bohemian garnet, green uvarovite, blue sapphire and yellow-orange citrine.









5.7 Match the spectra with the minerals.

5.8 If illuminated with monochromatic blue-green light, how will the Bohemian garnet look?

☐ Red
☐ Yellow
☐ Blue
☐ Blue-green
☐ Yellow-orange
☐ Violet
☐ Black
☐ White

Andradite is another garnet mineral; its chemical composition is $Ca_3Fe_2(SiO_4)_3$. A double cation substitution – Ti^{IV} for Fe^{III} in the octahedral position and Fe^{III} for Si^{IV} in the tetrahedral position – gives rise to black schorlomite. Its chemical composition can be expressed as $Ca_3[Fe,Ti]_2^{oct}([Si,Fe]^{tet}O_4)_3$.

5.9 Calculate the percentage of Si^{IV} ions in a sample of schorlomite that must be substituted with Fe^{III}, if we know that 5% of Fe^{III} ions in octahedral position are substituted with Ti^{IV}.

The colour of the mineral is caused by two chromophores: $[Fe^{III}O_6]^{oct}$ and $[Fe^{III}O_4]^{tet}$. The central ions of both chromophores have equal number of unpaired electrons.

5.10 Draw the d-orbitals splitting diagrams for both chromophores and fill in the electrons.

Tetrahedral field causes a smaller splitting than the octahedral field ($\Delta_{tet} = \frac{4}{9}\Delta_{oct}$). Surprisingly for the Fe^{III} ion, the energy of the first d–d transition (although very weak) for the octahedral chromophore is smaller (11 000 cm^{-1}) than for the tetrahedral one (22 000 cm^{-1}).

5.11 Calculate the size of pairing energy (*P*) and the sizes of Δ_{oct} and Δ_{tet} splitting. Assume that the pairing energy is equal in both chromophores.

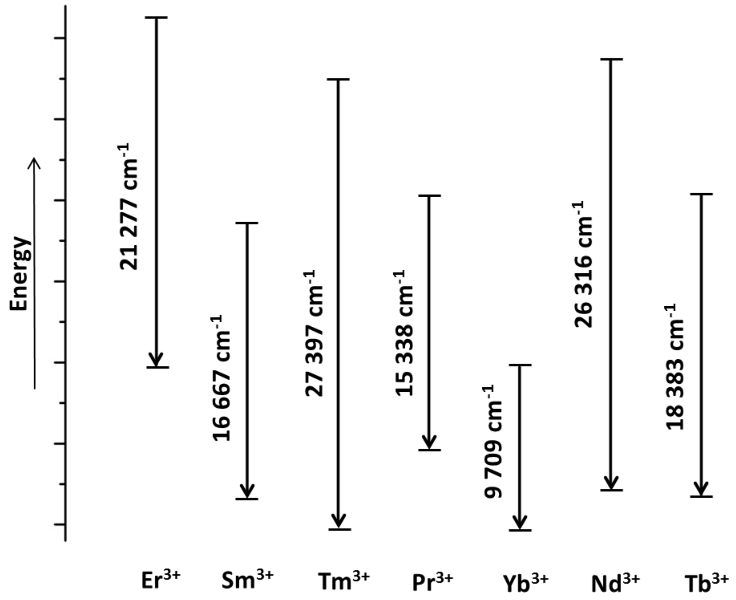
Synthetic garnet YAG (Yttrium Aluminium Garnet), used in optoelectronics, has the composition of $Y_3Al_5O_{12}$. Its structure is derived from the general garnet structure $A_3B_2(SiO_4)_3$ by placing the ions Y^{III} and Al^{III} to the A, B and Si positions.

5.12 Based on your knowledge of the relative ion radii, determine which cation occupies which position.

5.13 For the use in LED technology, YAG is doped with Ce^{III}. Determine the values of *x* and *y* in the formula of YAG in which 5% of yttrium atoms are substituted with cerium. (If you don’t get result, use *x* = 2.25 and y = 0.75.)

5.14 The Ce^{III}-doped YAG is prepared by annealing the mixture of Y_2O_3, Al_2O_3 and CeO_2 in H_2 atmosphere. Use the formula from 5.13, write down a balanced equation for this reaction with the smallest whole-number stoichiometric coefficients.

Doping the YAG structure with rare-earths ions enables the production of lasers with emission wavelengths ranging from the UV to the mid-IR region. In the scheme below, simplified f–f energy transitions of selected rare-earths ions are shown.



5.15 Which cation has a transition which corresponds to blue light emission.

☐ Er^{3+} ☐ Sm^{3+} ☐ Tm^{3+} ☐ Pr^{3+}

☐ Yb^{3+} ☐ Nd^{3+} ☐ Tb^{3+}

5.16 Calculate the emission wavelength of this light.

5.17 According to a legend, Noah used a stick with a garnet stone for illumination during his voyage. Assuming only the photoluminescence effect, determine the colour of the laser light emitted from his stick if the stone were the blood-coloured Bohemian garnet.

☐ Red ☐ Blue ☐ Yellow-orange ☐ Black

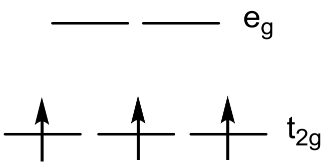
☐ Yellow ☐ Blue-green ☐ Violet ☐ White

SOLUTION

5.1 M(almandine) = 497.75 g mol^{-1}

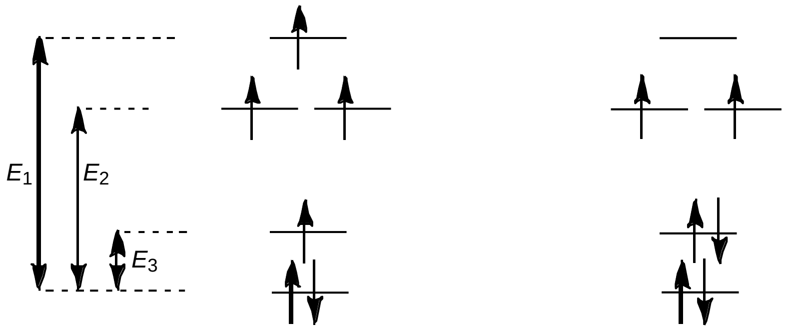
$\rho = m / V = (8 \times M) / (N_A \times a^3) = (8 \times 497.75) / [6.022 \times 10^{23} \times (11.50 \times 10^{-8})^3] =$
$= 4.35$ g cm^{-3}

5.2 Splitting diagram – configuration d^3:



5.3 Cobalt, Co

5.4 a) high-spin arrangement b) low-spin arrangement



5.5 a) high-spin arrangement: $P > E_1 - E_3$

b) low-spin arrangement: $P < E_1 - E_3$

5.6 Cr, Ni

5.7 Bohemian garnet: **B** Sapphire: **D**
Uvarovite: **C** Citrine: **A**

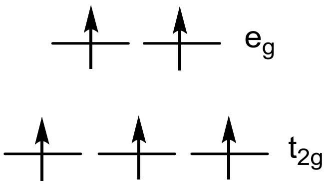
5.8 ☒ Black

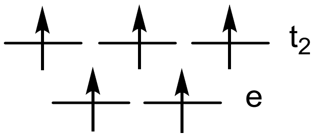
5.9 Both substitutions change the charge by 1 unit per ion. Taking total number of ions in formula into consideration we get:

$5\% \times 2 = p \times 3$

$p = 3.33\ \%$

5.10 $[Fe^{III}O_6]^{oct}$: $[Fe^{III}O_4]^{tet}$:





5.11 Because $\Delta_{oct} < P$ (high-spin configuration in tetrahedral as well as in octahedral field), the wavenumber corresponds to electron transition from the upper to the lower level in both cases and thus:

$11\ 000\ \text{cm}^{-1} = P - \Delta_{oct}$

$22\ 000\ \text{cm}^{-1} = P - \Delta_{tet} = P - \frac{4}{9}\Delta_{oct}$

By solving the system of these equations we get:

$P = 30\ 800\ \text{cm}^{-1}$

$\Delta_{oct} = 19\ 800\ \text{cm}^{-1}$

$\Delta_{tet} = 8\ 800\ \text{cm}^{-1}$

Alternative solution comes from the assumption (independent of the result of 5.10) of the low-spin arrangement in octahedral field and high-spin arrangement in tetrahedral field:

$11\ 000\ \text{cm}^{-1} = \Delta_{oct} - P$

$22\ 000\ \text{cm}^{-1} = P - \Delta_{tet} = P - \frac{4}{9}\Delta_{oct}$

By solving the system of these equations we get:

$P = 48\ 400\ \text{cm}^{-1}$

$\Delta_{oct} = 59\ 400\ \text{cm}^{-1}$

$\Delta_{tet} = 26\ 400\ \text{cm}^{-1}$

5.12 A: Y^{III} B: Al^{III} Si: Al^{III}

5.13 $Y_xCe_yAl_5O_{12}$ $x = 2.85$ $y = 0.15$

5.14 $57\ Y_2O_3 + 6\ CeO_2 + 100\ Al_2O_3 + 3\ H_2 \longrightarrow 40\ Y_{2.85}Ce_{0.15}Al_5O_{12} + 3\ H_2O$

(or $2\ Y_{57}Ce_3Al_{100}O_{240} + 3\ H_2O$)

for $x = 2.25$ and $y = 0.75$:

$9\ Y_2O_3 + 6\ CeO_2 + 20\ Al_2O_3 + 3\ H_2 \longrightarrow 8\ Y_{2.25}Ce_{0.75}Al_5O_{12} + 3\ H_2O$

(or $2\ Y_9Ce_3Al_{20}O_{48} + 3\ H_2O$)

5.15 ☒ Er^{3+}

5.16 $\lambda = \dfrac{1}{2\,127\,700}\ \text{m} = 4.70 \times 10^{-7}\ \text{m} = 470\ \text{nm}$

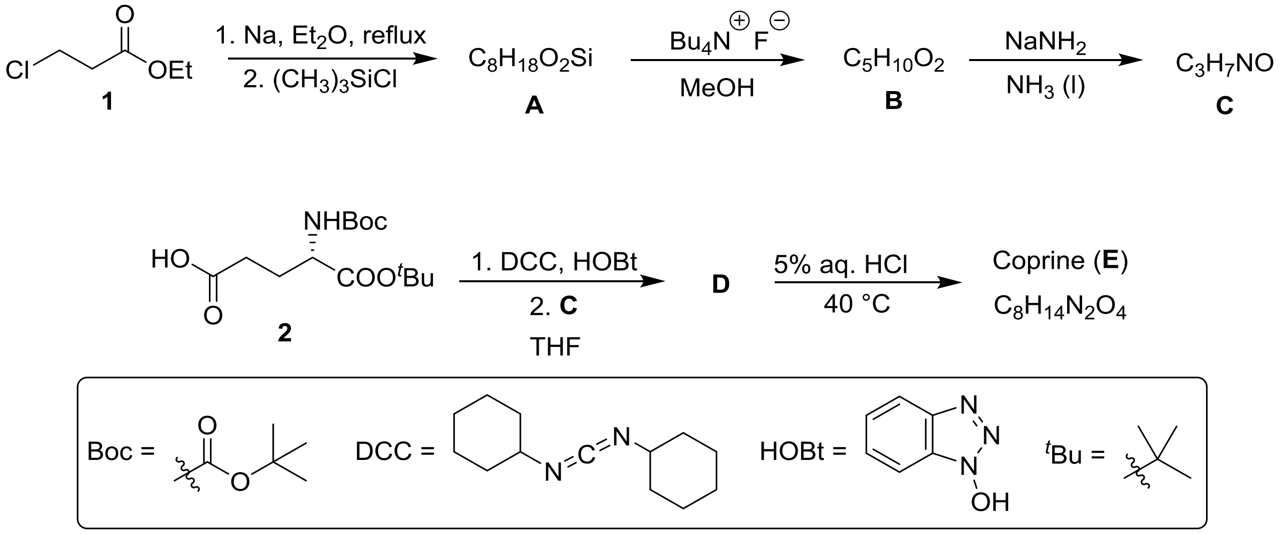
5.17 ☒ Blue-green

PROBLEM 6

Let's go mushrooming

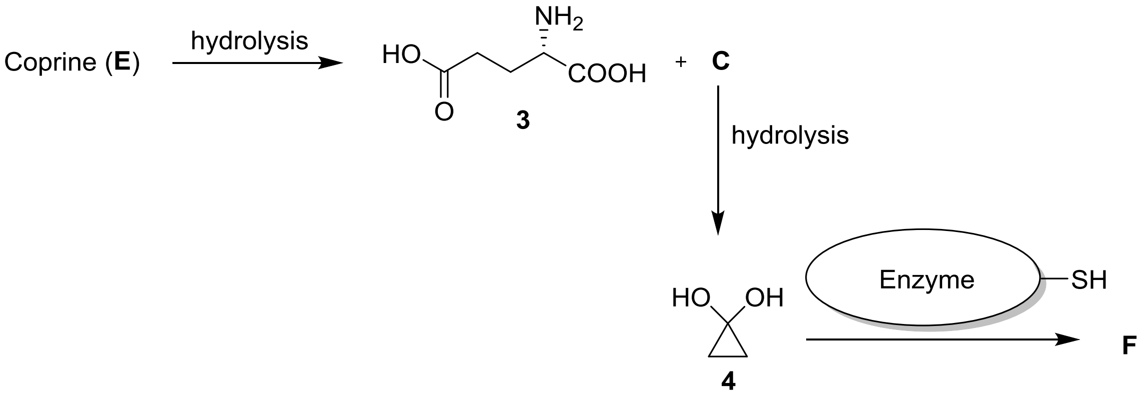
Mushrooming belongs to Czech and Slovak traditional pastimes. While some of our mushroom species are edible, some are inedible or even poisonous.

Inky cap (*Coprinopsis atramentaria*) is considered edible and delicious. It contains a natural compound called coprine (**E**), which can be easily synthesized from ethyl 3-chloropropanoate (**1**).



6.1 Draw the formulae of compounds **A**–**E** including stereochemistry when necessary. Hint: The first reaction affording compound **A** proceeds via an organometallic compound which then cyclizes.

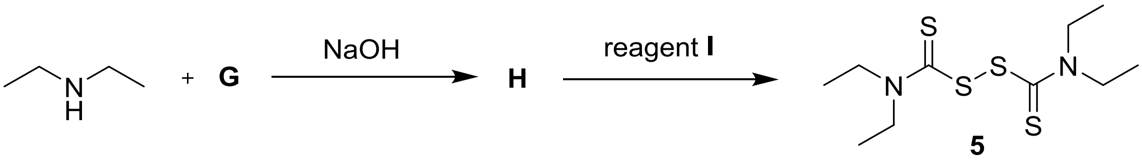
In the human body, coprine undergoes hydrolysis to L-glutamic acid (**3**) and compounds **C** and **4**, which are responsible for the coprine adverse side-effects. They inhibit the enzyme acetaldehyde dehydrogenase, which is involved in the metabolism of alcohol. When the enzyme is inhibited, acetaldehyde formed by alcohol dehydrogenase accumulates in the body, causing strong symptoms of hangover (so called antabuse effect). The active site of the enzyme contains a cysteine SH group, which is blocked either by compound **C** or **4**.



Enzyme = acetaldehyde dehydrogenase

6.2 Using the pictogram for acetaldehyde dehydrogenase above, draw the structure **F** of the enzyme inhibited by compound **4**.

The antabuse effect got its name after antabuse (**5**), the most known drug used in alcohol-addiction treatment. This drug can be synthesized according to the following scheme.



6.3 Draw the formulae of compounds **G** and **H**.

Hint: Compound ***H*** *contains five carbon atoms.*

6.4 Mark all possible reagents which could be used for **I** from the following list.

☐ *m*-chloroperbenzoic acid (mCPBA)

☐ Zn / CH_3COOH

☐ I_2

☐ K_2CO_3, H_2O

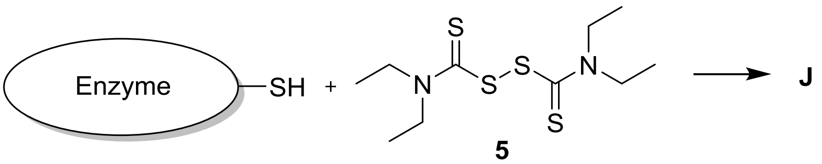
☐ diluted H_2O_2

☐ $NaBH_4$

☐ hot concentrated H_2SO_4

☐ $AlCl_3$

The way antabuse inhibits acetaldehyde dehydrogenase is similar to the effect of compounds **C** and **4**.

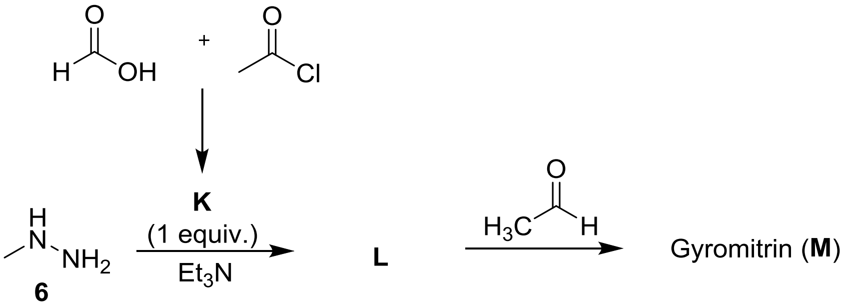


5

Enzyme = acetaldehyde dehydrogenase

6.5 Using the pictogram for acetaldehyde dehydrogenase above, draw the structure **J** of the enzyme inhibited by antabuse (**5**). *Hint: Three sulfur atoms should be in the structure.*

False morel (*Gyromitra esculenta*) is another interesting mushroom. Although it was considered edible in the past (*esculentus* means edible in Latin), there is clear evidence that this mushroom is poisonous due to the content of gyromitrin (**M**). This natural compound can be prepared from *N*-methylhydrazine (**6**):



6.6 Draw the formulae of compounds **K** – **M**.

In human body, gyromitrin (**M**) hydrolyzes and provides *N*-methylhydrazine (**6**), which is strongly hepatotoxic. Gyromitrin (**M**) hydrolysis occurs as soon as it enters the acidic environment in human stomach where both its amide and imine groups are hydrolyzed.

Let us focus on the hydrolysis of the amide moiety within the gyromitrin molecule. The vibrational wavenumber of the stretching mode of the relevant C−N bond amounts to 1 293.0 cm^{-1} and the potential energy surface does not significantly alter its shape with isotope substitution effect.

6.7 Calculate the highest possible hypothetical kinetic isotope effect at the temperature of human body, 37 °C, for the given hydrolysis reaction assuming that both relevant nitrogen and carbon atoms were simultaneously substituted, ^{14}N with the ^{15}N isotope and ^{12}C with the ^{13}C isotope. Consider that only the zero point vibrational energy affects the rate constants. Assume that the molar masses of all isotopes are integers. In all steps consider five significant digits.

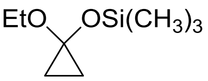
6.8 After making these isotopic changes, the rates of hydrolysis are not significantly different. Which of the following is the most likely the rate determining step?

- ☐ Nucleophilic attack of water on a protonated amidic moiety
- ☐ C−N bond cleavage
- ☐ Protonation of the gyromitrin molecule

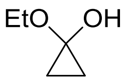
SOLUTION

6.1

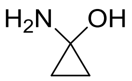
A



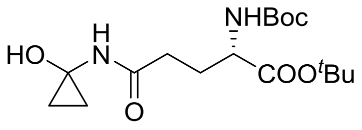
B



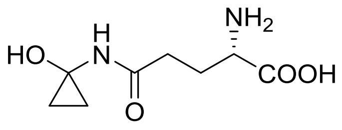
C



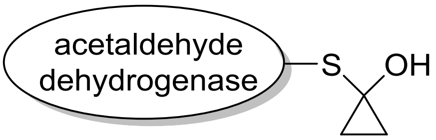
D



E



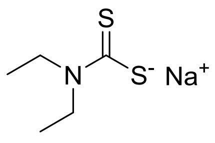
6.2 F



6.3

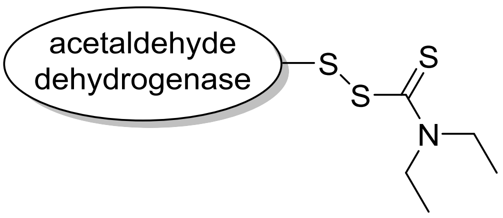
G: CS_2

H:



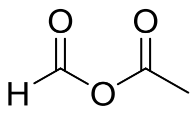
6.4 ☒ *m*-chloroperbenzoic acid (*m*CPBA); ☒ diluted H_2O_2; ☒ I_2.

6.5

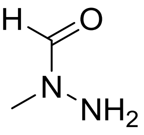


6.6

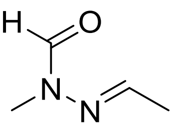
K:



L:



M:



6.7 C−N bond reduced mass:

$$\mu_{^{12}\text{C}}^{^{14}\text{N}} = \frac{14.000\ \text{g mol}^{-1} \times 12.000\ \text{g mol}^{-1}}{(14.000 + 12.000)\ \text{g mol}^{-1} \times 6.0221 \times 10^{23}\ \text{mol}^{-1}} = 1.0730 \times 10^{-26}\ \text{kg}$$

Alternatively, $(\mu_{^{12}\mathrm{C}}^{^{14}\mathrm{N}})' = 6.4615\ \mathrm{g\ mol^{-1}}$

$$\mu_{^{13}\mathrm{C}}^{^{15}\mathrm{N}} = \frac{15.000\ \mathrm{g\ mol^{-1}} \times 13.000\ \mathrm{g\ mol^{-1}}}{(15.000 + 13.000)\ \mathrm{g\ mol^{-1}} \times 6.0221 \times 10^{23}\ \mathrm{mol^{-1}}} = 1.1565 \times 10^{-26}\ \mathrm{kg}$$

Alternatively, $(\mu_{^{13}\mathrm{C}}^{^{15}\mathrm{N}})' = 6.9643\ \mathrm{g\ mol^{-1}}$

C−N bond force constant: $k = \left(2\pi\, c\, \tilde{\nu}_{^{12}\mathrm{C}}^{^{14}\mathrm{N}}\right)^2 \times \mu_{^{12}\mathrm{C}}^{^{14}\mathrm{N}} = 636.48\ \mathrm{kg\ s^{-2}}$

C−N substituted bond wavenumber:

$$\tilde{\nu}_{^{13}\mathrm{C}}^{^{15}\mathrm{N}} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu_{^{13}\mathrm{C}}^{^{15}\mathrm{N}}}} = 1\ 245.5\ \mathrm{cm^{-1}}$$

Hypothetical kinetic isotope effect:

$$\frac{k_{^{12}\mathrm{C}}^{^{14}\mathrm{N}}}{k_{^{13}\mathrm{C}}^{^{15}\mathrm{N}}} = \exp\left(\frac{hc}{2k_{\mathrm{B}}T}\left(\tilde{\nu}_{^{12}\mathrm{C}}^{^{14}\mathrm{N}} - \tilde{\nu}_{^{13}\mathrm{C}}^{^{15}\mathrm{N}}\right)\right) = 1.1166$$

Alternative to force constant and wavenumber one can derive formula for KIE as follows

$$\tilde{\nu}_{^{13}\mathrm{C}}^{^{15}\mathrm{N}} = \tilde{\nu}_{^{12}\mathrm{C}}^{^{14}\mathrm{N}}\sqrt{\frac{\mu_{^{12}\mathrm{C}}^{^{14}\mathrm{N}}}{\mu_{^{13}\mathrm{C}}^{^{15}\mathrm{N}}}} = 1\ 245.5\ \mathrm{cm^{-1}}$$

$$\mathrm{E}_{\tilde{\nu}_{^{12}\mathrm{C}}^{^{14}\mathrm{N}}} = \frac{hc\tilde{\nu}_{^{12}\mathrm{C}}^{^{14}\mathrm{N}}}{2} = 1.2851 \times 10^{-20}\ \mathrm{J}$$

$$\mathrm{E}_{\tilde{\nu}_{^{13}\mathrm{C}}^{^{15}\mathrm{N}}} = \frac{hc\tilde{\nu}_{^{13}\mathrm{C}}^{^{15}\mathrm{N}}}{2} = 1.2379 \times 10^{-20}\ \mathrm{J}$$

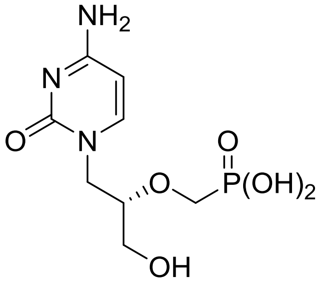
$$\frac{k_{^{12}\mathrm{C}}^{^{14}\mathrm{N}}}{k_{^{13}\mathrm{C}}^{^{15}\mathrm{N}}} = \exp\left(\frac{\mathrm{E}_{\tilde{\nu}_{^{12}\mathrm{C}}^{^{14}\mathrm{N}}} - \mathrm{E}_{\tilde{\nu}_{^{13}\mathrm{C}}^{^{15}\mathrm{N}}}}{k_{\mathrm{B}}T}\right) = 1.1166$$

6.8 ☒ Nucleophilic attack of water on a protonated amidic moiety.

PROBLEM 7

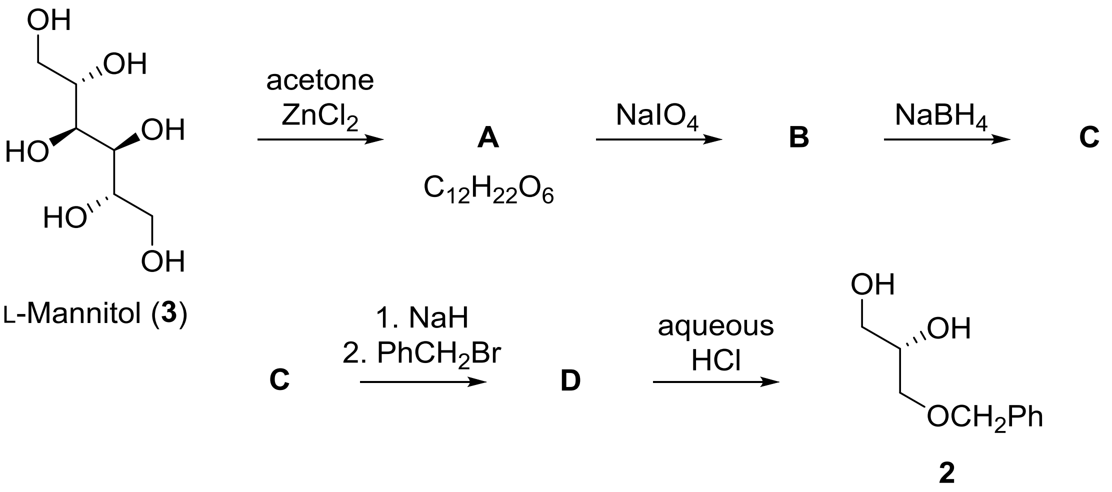
Cidofovir

Cidofovir (**1**), originally designed and prepared by the group of Professor Holy in former Czechoslovakia, is a nucleotide analogue with antiviral activity. It is used to treat viral infections, mostly in patients with AIDS.



Cidofovir (**1**)

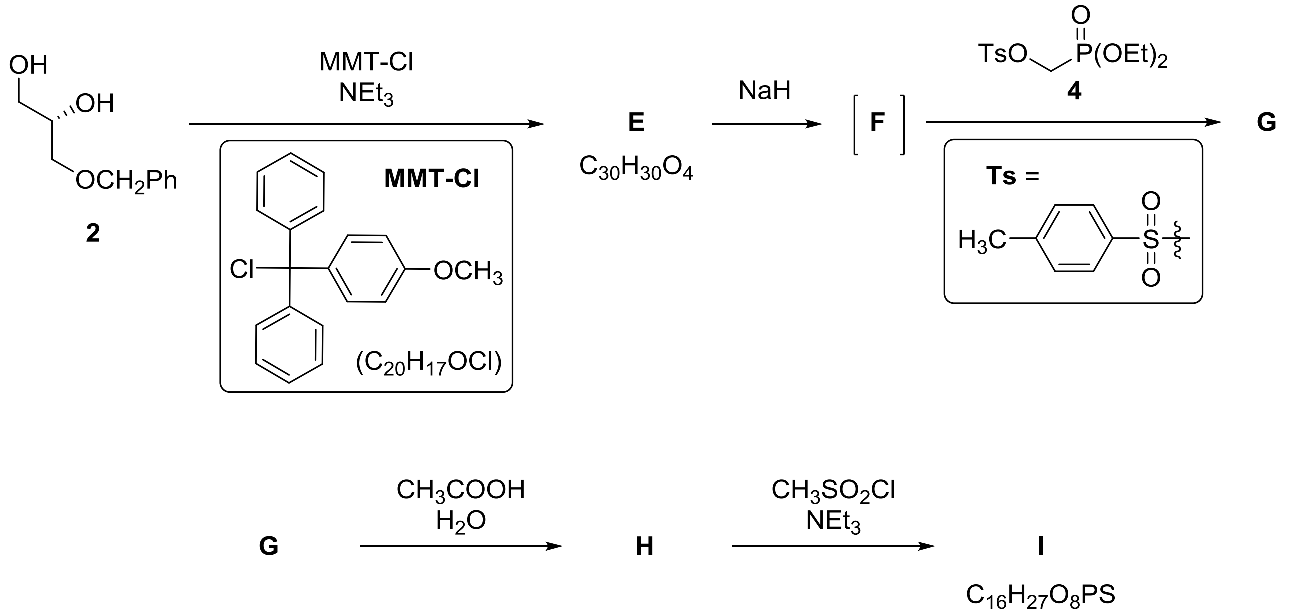
The key intermediate in the synthesis of cidofovir is optically pure diol **2**, which can be prepared from L-mannitol (**3**).



7.1 Draw the structures of compounds **A**–**D**, including stereochemistry. One molecule of **A** produces two molecules of **B**.

7.2 Draw the structural formulae of all alternative stereoisomers of compound **3** which could be used in the same reaction sequence to afford only the same product **2**.

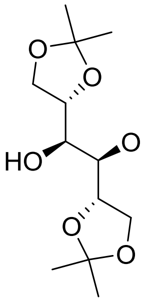
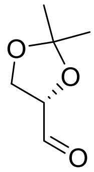
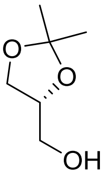
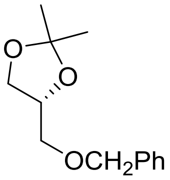
Diol **2** is further modified to provide compound **I**. The synthesis of phosphonate **4** used to convert compound **F** to **G** will be discussed later.



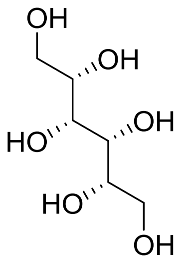
7.3 Draw the structures of compounds **E–I**, including stereochemistry. Use the abbreviation MMT for the (4-methoxyphenyl)diphenylmethyl group.

SOLUTION

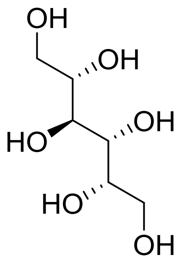
7.1

A $C_{12}H_{22}O_6$ 	**B** 
C 	**D** 

7.2

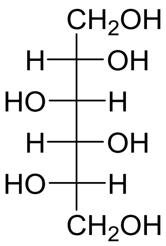


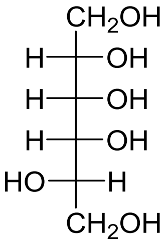
(2*S*,3*R*,4*R*,5*S*)



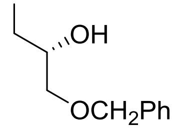
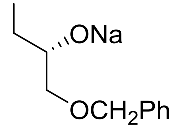
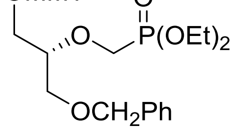
(2*S*,3*R*,4*S*,5*S*)

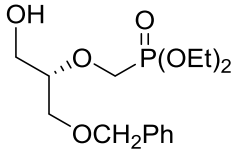
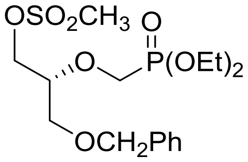
or in Fischer projection





7.3

E $C_{30}H_{30}O_4$ 	**F** 	**G** 

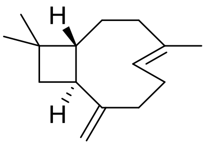
H	**I** $C_{16}H_{27}O_8PS$
	

PROBLEM 8

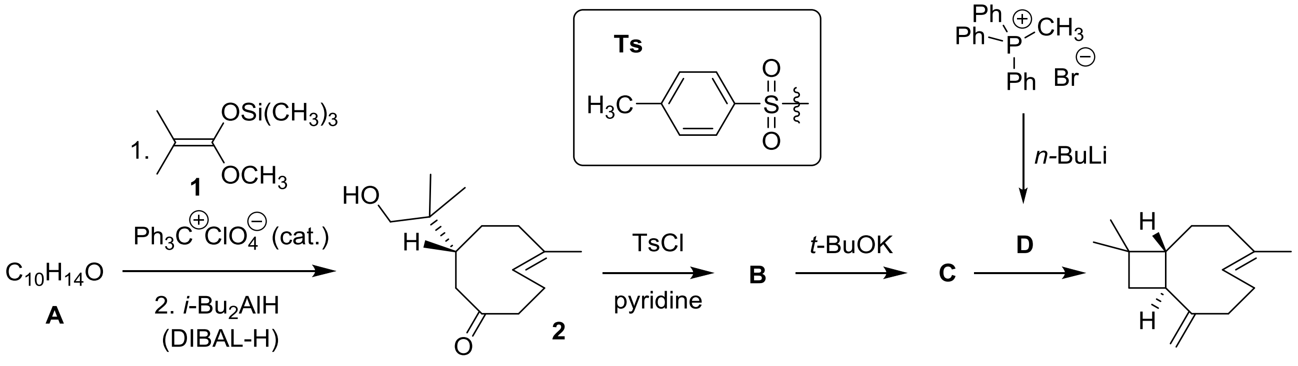
Caryophyllene

β-Caryophyllene (**3**) is a naturally occurring sesquiterpene present in clove tree and in some traditional Czech and Slovak plants, such as the hop plant or small-leaved linden.

The synthesis of β-caryophyllene starts from a single enantiomer of dienone **A**. The reaction of **A** with silyl ketene acetal **1**, followed by immediate reduction and aqueous work-up affords ketone **2**. This intermediate then undergoes reaction with tosyl chloride, providing **B**. Basic cyclization of this compound affords **C**. Finally, the reaction of **C** with ylide **D** provides β-caryophyllene.



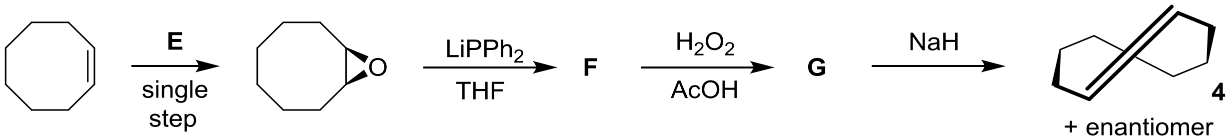
β-Caryophyllene (**3**)



β-Caryophyllene (**3**)

8.1 Draw the structures of compounds **A**–**D**, including the appropriate stereochemistry. *Hint: In transformation **A** → **2**, the silyl ketene acetal acts as a nucleophile.*

Due to the large ring size, both compounds **2** and **3** are stable, even though they contain a double bond in the *trans* configuration. *trans*-Cyclooctene (**4**) is the smallest ring that can accommodate a *trans* double bond. It can be prepared according to the following scheme:



4

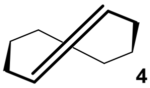
+ enantiomer

8.2 Draw the structures of reagent **E** and intermediates **F** and **G**, including the appropriate stereochemistry. For **F** and **G**, tick the box indicating the stereochemical outcome.

Mark the correct answer:

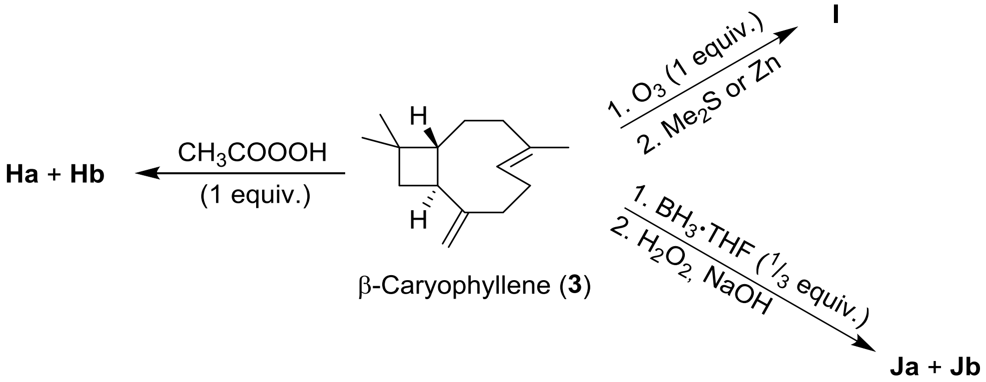
☐ achiral, ☐ single enantiomer, ☐ racemic mixture, ☐ mixture of diastereoisomers

8.3 Draw the structure of the enantiomer of cycloalkene **4**.



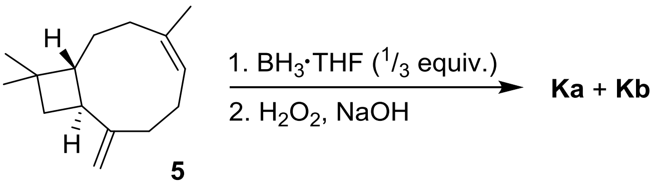
4

The two double bonds in β-caryophyllene display different reactivity: the double bond in the ring (endocyclic) is more reactive than the other one (exocyclic) due to the ring strain.



8.4 Draw the structures of compounds **Ha** + **Hb**, **I** and **Ja** + **Jb**, including the appropriate stereochemistry. *Hint: **Ha** + **Hb** and **Ja** + **Jb** are pairs of diastereomers.*

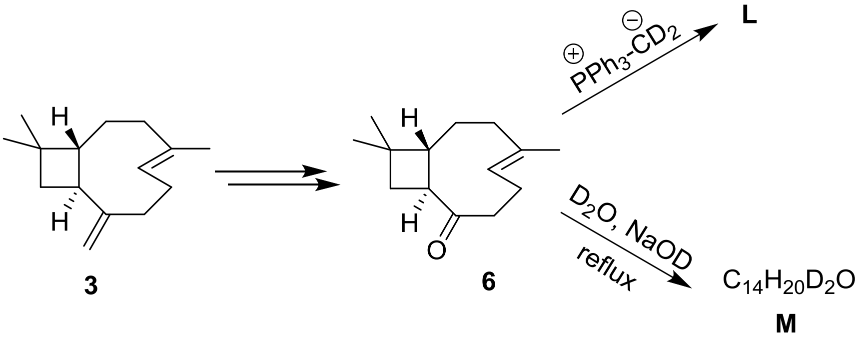
Interestingly, the reactivity of the double bonds is reversed when isocaryophyllene (**5**) is used instead of β-caryophyllene (**3**).



8.5 Draw the structures of compounds **Ka** and **Kb**.

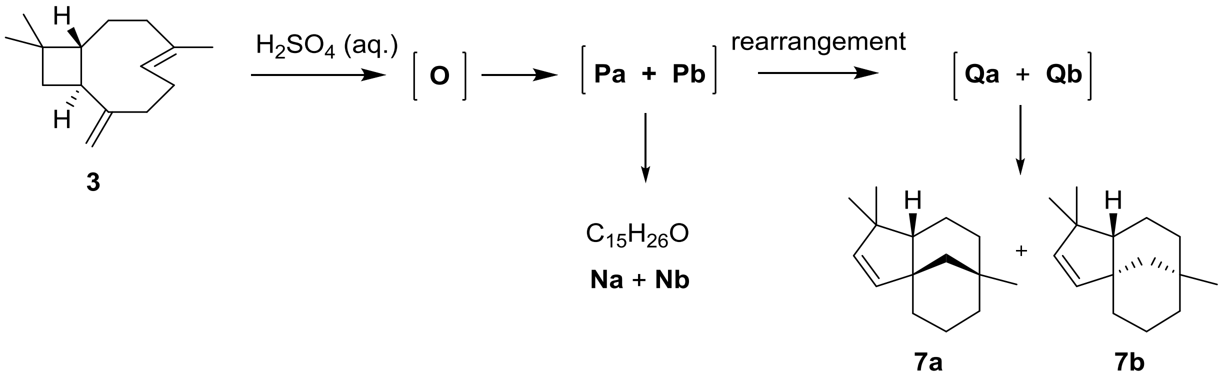
*Hint: **Ka** + **Kb** are a pair of diastereomers*.

Isotope-labelled compounds are invaluable tools for reaction mechanism investigation, structure determination, and mass or NMR spectroscopy studies. Let us have a look at the synthesis of some labelled analogues of β-caryophyllene.



8.6 Draw the structures of compounds **L** and **M**, including the appropriate stereochemistry.

β-Caryophyllene (**3**) undergoes acid-catalyzed cyclization, which leads to a complex mixture of products. Among them, the pair of diastereomers **Na** + **Nb** and the pair of diastereomers **7a** + **7b** are the most abundant. The reaction starts with protonation of the more reactive internal double bond affording cation **O**. This cyclizes without the cleavage of a carbon-carbon single bond to yield diastereomeric tricyclic cations **Pa** and **Pb**, which undergo hydration to give the target alcohols **Na** and **Nb**. Alternatively, the cations **Pa** and **Pb** rearrange with the cleavage of a carbon-carbon single bond to cations **Qa** and **Qb**, which deprotonate to compounds **7a** and **7b**.



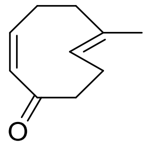
8.7 Draw the structures, including the appropriate stereochemistry, of the **three** intermediates **O**, **Pa**, **Qa** leading to the diastereomer **7a**, including the appropriate stereochemistry.

8.8 Draw the structures of diastereomers **Na** + **Nb**.

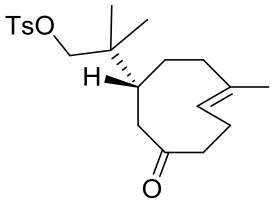
SOLUTION

8.1

A $C_{10}H_{14}O$



B



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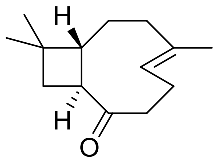

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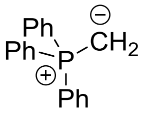

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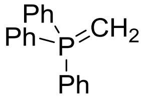
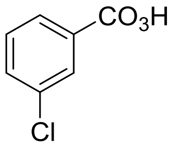


8.2

E



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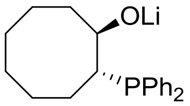
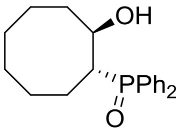


☒ racemic mixture

G



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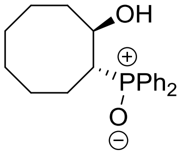
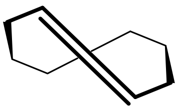


☒ racemic mixture

8.3



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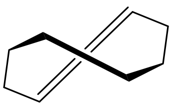
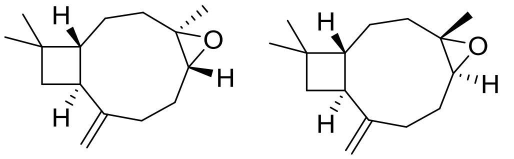


8.4 Ha + Hb



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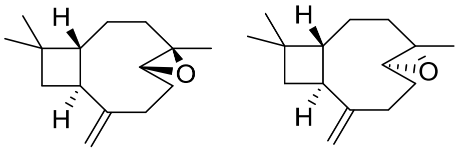

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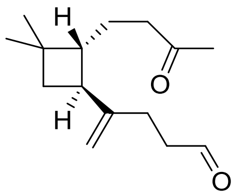
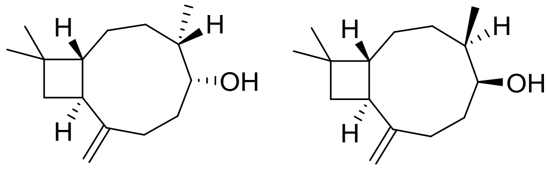


Ja + Jb



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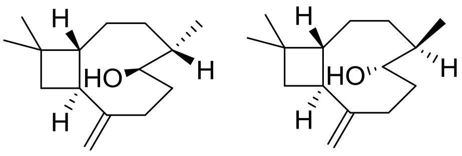
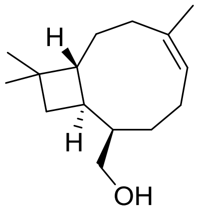
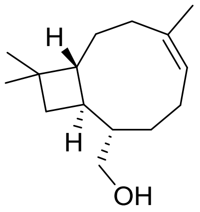
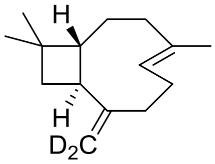
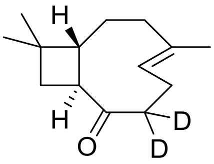
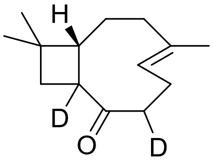


8.5 Ka + Kb



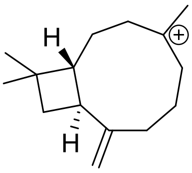


8.6

L 	**M** $C_{14}H_{20}D_2O$  *a half of points for the structure below:* 

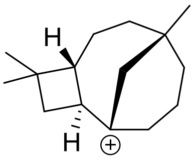
8.7

O



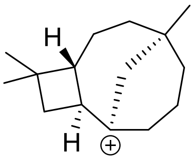
O

Pa



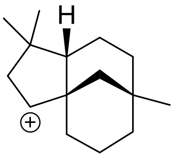
Pa

*2/3 points for structure **Pb***

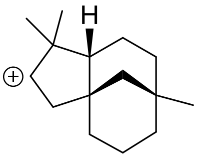


Pb

Qa

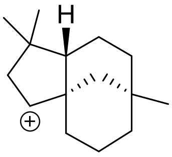


Qa



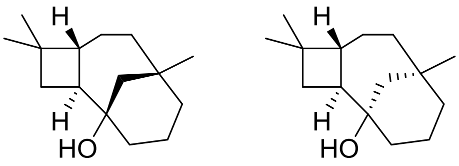
incorrect Qa'

*2/3 points for structure **Qb***



Qb

8.8 **Na + Nb** $C_{15}H_{26}O$



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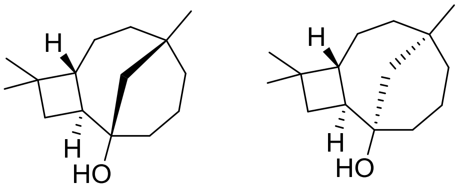


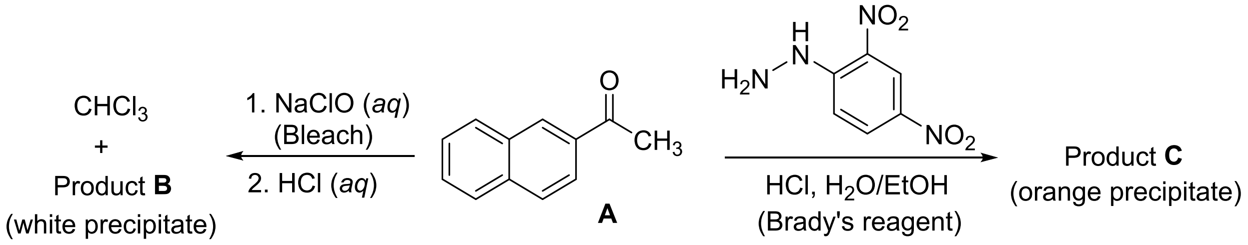
PRACTICAL PROBLEMS

PROBLEM 1P (Practical)

Haloform reaction with bleach

Chemical test reactions have been developed as a means of identifying functional groups in unknown compounds. In this task, you will explore two examples of chemical test reactions on a preparatory scale, starting from (2-naphthyl)ethanone (**A**, 2-acetonaphthone):

- The haloform reaction is a transformation typical for methyl ketones which react with basic aqueous hypohalite solution and provide a carboxylic acid (product **B**) and a haloform (trihalomethane).
- The reaction of Brady’s reagent (acidic solution of 2,4-dinitrophenylhydrazine) with the carbonyl group of an aldehyde or ketone results in the formation of an orange hydrazone precipitate (product **C**).



Task 1.1 Draw the structures of products **B** and **C**.

Notes:

- The total score will be based on the R_f values of compounds **A** and **B** calculated from the submitted TLC plate 1 and on the quality and quantity of the submitted products **B** and **C**.
- The quality of your products will be graded based on the TLC and melting points.
- The amount of the provided hypochlorite solution is not sufficient to convert all reactant **A** to product **B**. You will recover the residual reactant **A** by an acid-base extraction and isolate it after the reaction with Brady's reagent as hydrazone **C**. The grading is based on the combined yield of products **B** and **C**.

Chemicals

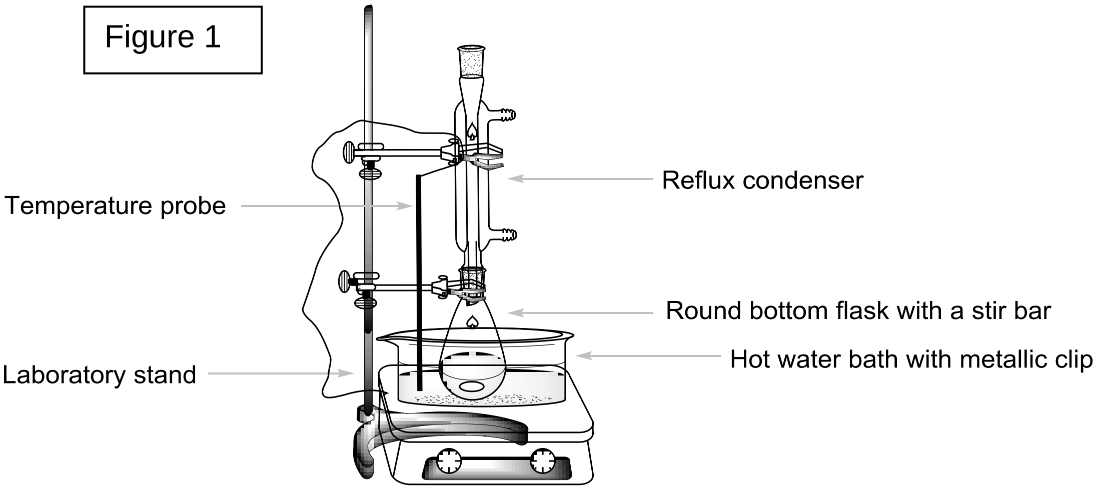
- Ethanol, 100 cm^3 in wash bottle,
- 2-Acetonaphthone, ca. 0.002 g in glass vial, standard for TLC; 0.500 g in glass vial,
- *2,4-Dinitrophenylhydrazine*, containing 33 % (w/w) of water, 0.300 g in glass vial,
- Bleach solution, containing 4.7 % of NaClO, 13.5 cm^3 in amber glass bottle,
- Ethyl acetate, 15 cm^3 in amber glass bottle,
- TLC Eluent for thin layer chromatography, hexane/ethyl acetate 4:1 (v/v), 5 cm^3 in amber glass bottle,
- 5% Na_2CO_3, aqueous solution, 20 cm^3 in plastic bottle,
- 20% HCl, aqueous solution, 15 cm^3 in plastic bottle.

Procedure

I. Haloform reaction

1. Turn on the stirrer and adjust the speed to 540 rpm. Immerse a temperature probe, resting the wire on the upper clamp into the bath almost to the bottom and set the temperature to 80 °C.
2. Transfer the 0.500 g of 2-acetonaphthone from the vial labelled **Reactant A** into a 50 cm^3 round bottom flask that contains a magnetic stir bar. Measure 3 cm^3 of ethanol (from the wash bottle) in a measuring cylinder and use it to transfer the remaining reactant **A** quantitatively into the round bottom flask using a glass Pasteur pipette.
3. Place the round bottom flask into the hot water bath. Attach an air reflux condenser (water connection is not needed) and secure it in the upper part by a loosely attached large clamp, as shown in Figure 1 (Setup for heating the reaction mixture in a water bath.) Let compound **A** dissolve with stirring.

Figure 1



4. When the bath temperature reaches 75 °C, slowly add all the NaClO solution (**Bleach**) to the reaction mixture through the top opening of the condenser using a small glass funnel. Heat the reaction mixture with stirring for 60 minutes between 75 and 80 °C.
5. Then turn off the heating of the hotplate stirrer. Loosen the upper clamp a bit and lift the reaction flask over the water bath. (*Caution!* Touch only the clamps, the flask is hot.) Allow the reaction mixture to cool down for 15 minutes.

II. Workup of the reaction mixture

1. Place a separatory funnel into a metal ring and place a 50 cm^3 Erlenmeyer flask without a ground joint under it. Using a glass funnel, pour the cooled reaction mixture into the separatory funnel. Remove the stir bar from the glass funnel with tweezers. Measure 5 cm^3 of ethyl acetate (EtOAc)

   and use it to rinse the reaction flask.. Add the washings into the separatory funnel using a glass Pasteur pipette.
2. Perform the extraction. Allow the layers to separate. Collect the aqueous layer into the 50 cm^3 Erlenmeyer flask without a ground joint. Using a small glass funnel, pour the organic layer through the top neck into the 25 cm^3 Erlenmeyer flask. Keep both phases!
3. Using a small funnel, pour the aqueous phase from the 50 cm^3 Erlenmeyer flask back to the separatory funnel. Measure another 5 cm^3 of ethyl acetate and repeat the extraction (step No. II.2). Combine the organic phases together in the 25 cm^3 Erlenmeyer flask. Keep both phases!
4. Prepare your TLC plate. Check it before use. Unused damaged plates will be replaced upon request without penalty. Use a pencil to draw the start line and mark the positions for spotting the samples. Write number **1** in a circle and your student code on the top of the TLC plate as shown in Figure 2. Dissolve the given sample of 2-acetonaphthone in a vial (**Standard A**) in ca. 2 cm^3 of ethanol (about 1 full glass Pasteur pipette). Mark three spot positions and label them **A**, **O1**, and **O2**. Spot 1 μl (one mark of the 5 μl capillary spotter) of standard **A** and the combined organic phase from step II.3 (**O1**). You will add spot **O2** later.
5. Extract the combined organic phases twice with 5 cm^3 of 5% Na_2CO_3 solution. Collect the aqueous phase into the same 50 cm^3 Erlenmeyer flask without a ground joint containing the aqueous phase from the first extraction.
6. Wash the organic phase in the funnel with 5 cm^3 of deionized water. Add the aqueous phase to the combined aqueous extracts. Pour the organic layer (**O2**) through the top

neck into a 50 cm^3 ground-joint Erlenmeyer flask. Spot 1 μl of the solution **O2** on your TLC plate prepared in step II.4 (Plate 1).

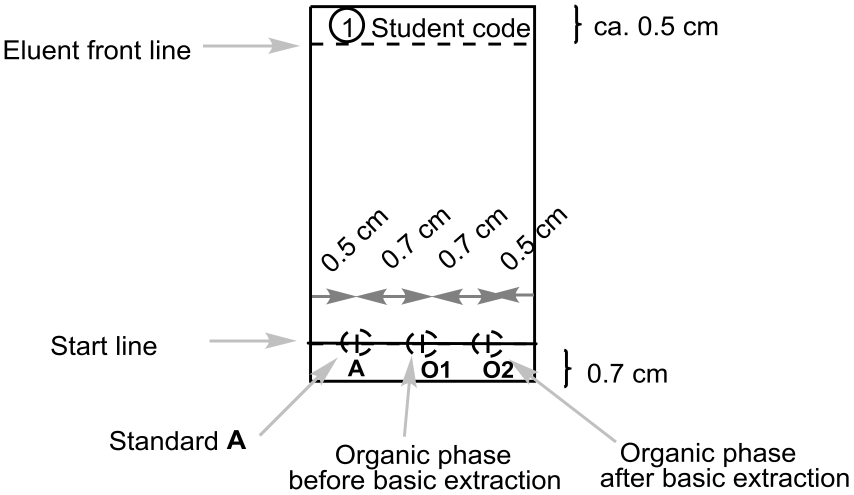


Figure 2. Instructions for the TLC plate preparation.

6. Wash the organic phase in the funnel with 5 cm^3 of deionized water. Add the aqueous phase to the combined aqueous extracts. Pour the organic layer (**O2**) through the top neck into a 50 cm^3 ground-joint Erlenmeyer flask. Spot 1 μl of the solution **O2** on your TLC plate prepared in step II.4 (Plate 1).
7. Perform a TLC analysis. Take a 50 cm^3 beaker and load it with ca. 2 cm^3 of the **TLC eluent**. Insert the TLC plate, cover the beaker with a Petri dish and let the eluent reach approximately 0.5 cm bellow the top edge of the plate. Using tweezers, take the TLC plate out, draw the eluent front line and let the plate air-dry. Place the TLC plate under the UV lamp in the hood. With a pencil, circle all the visualized spots and calculate the R_f values of reactant **A** and product **B**. Store your TLC plate in a plastic bag.

Note 1 Product **B** may tail on the TLC plate. Therefore, avoid excessive loading of the sample.

Note 2: In some cases, two additional spots of side products of a very low intensity may be seen in combined organic phase **O1** and **O2**. In this case, calculate the R_f value for the most intense spot(s).

Note 3: If the organic layer **O2** still contains both starting material **A** and product **B**, repeat the extraction with the Na_2CO_3 solution and water (steps No. II.5 and II.6). In this case, submit also another TLC plate after the repeated extraction (Plate 2), spotting only standard **A** and organic phase **O2**. Mark number **2** in a circle and your student code on the top of this TLC plate. Use a fresh batch of eluent to develop TLC Plate 2.**Task 1.2:**

a) Answer the following questions about your Plate(s).

- Based on the TLC analysis, your organic layer **O1** contains:

	YES	NO
Starting material **A**	☐	☐
Product **B**	☐	☐

- Based on the TLC analysis, your organic layer **O2** contains:

	YES	NO
Starting material **A**	☐	☐
Product **B**	☐	☐

b) From Plate 1, calculate the R_f values of standard **A** and product **B**. Provide the results rounded to 2 decimal places.

III. Reaction with Brady's reagent

Attention: Use gloves! Brady's reagent stains skin and all surfaces. Wash any spots immediately with ethanol! Change your gloves if necessary.

Preheat the water bath to 80 °C. Insert a magnetic stir bar into the 50 cm^3 ground-joint Erlenmeyer flask containing the organic phase **O2** from step II.6 and add 0.300 g of 2,4-*dinitrophenylhydrazine (***DNPH**). In a graduated cylinder, measure 10 cm^3 of ethanol. Using a glass Pasteur pipette, rinse the glass vial with 5 × 2 cm^3 of ethanol to transfer all of the **DNPH** into the Erlenmeyer flask. Place the Erlenmeyer flask into the hot water bath, attach a reflux condenser (similar setup as in Figure 1) rinsed with ethanol. Through the top opening of the condenser, add 3 cm^3 of 20% HCl using a funnel and stir the reaction mixture at 80 °C for 2 minutes. Fine orange crystals of product **C** start to form. Then turn off the heating of the hotplate stirrer. Lift the reaction flask above the water bath. (*Caution!* Touch only the clamps, the flask is hot.) Allow the reaction mixture to cool down for 15 min and then place it into a cold water bath (prepared by pouring cold tap water in a 150 cm^3 beaker).

IV. Isolation of the products

1. Check the pH of the combined aqueous phase from step No. II.6. Acidify it by carefully adding 20% HCl solution, stirring the mixture with a glass rod (ca. 2 cm^3 of the HCl solution should be required), to the final pH of 2 (check with pH indicator strips). A white precipitate of product **B** is formed.
2. Set up a vacuum filtration apparatus (Figure 3) using a glass fritted funnel with porosity **S2** (with white label) and secure it to a laboratory stand with a small clamp. Connect the suction flask to the vacuum source. Pour the suspension of product **B** (step No. IV.1) into the fritted funnel, let the solid set down, and then open the vacuum valve. *Caution*: notify the lab assistant before and after handling the valve! Wash the solid twice with 6 cm^3 of deionized water, until the pH of the dropping filtrate is about 6. Let air suck through the precipitate for 5 minutes to pre-dry the product. Disconnect the vacuum source. Use the spatula to transfer white product **B** to a glass vial labelled **Student code B** and leave it uncovered on the bench to dry. Discard the filtrate to the sink drain and wash the suction flask. *Note:* Be careful not to scratch the fritted glass into your product.

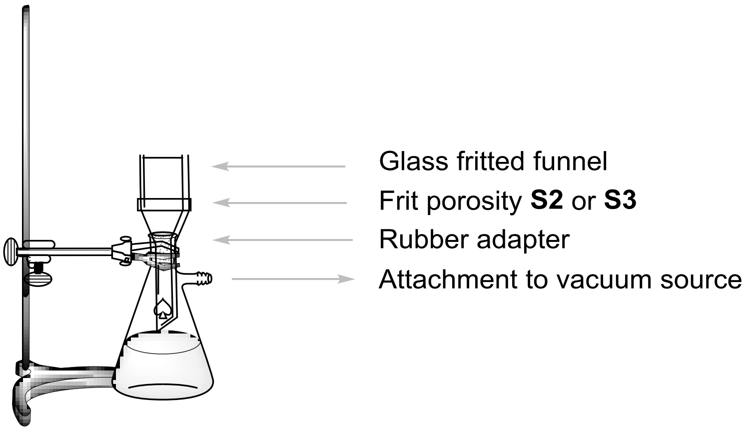


Figure 3. Setup for suction filtration.

3. Set up a vacuum filtration apparatus with a glass fritted funnel with porosity **S3** (with an orange label) similarly as in IV.2. Pour the suspension of product **C** (step No. III) into the fritted funnel, wait for a minute, and then open the vacuum valve. Do NOT stir or scratch the solid with the spatula while filtering and washing, otherwise the solid may go through the filter. Wash the precipitate three times with 5 cm^3 of ethanol (15 cm^3 in total) until neutral pH of the dropping filtrate is reached. Let air suck through the precipitate for 5 minutes. Disconnect the vacuum source. Use the spatula to transfer orange product **C** to a glass vial labelled **Student code C** and leave it uncovered on the bench to dry. Collect the filtrate into **Organic waste** bottle.

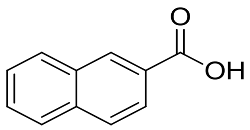
Note: If the product goes through the fritted funnel, filter the suspension once more. If the product still goes through, contact the lab assistant.

Your lab assistant will pick up following items:

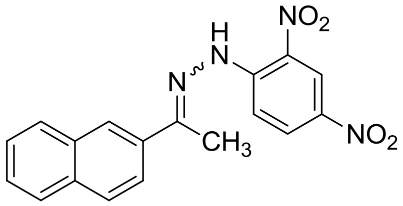
- Glass vials **B** and **C** with your products
- TLC plates in a zipped bag.

SOLUTION

Task 1.1:



Product **B**



Product **C**

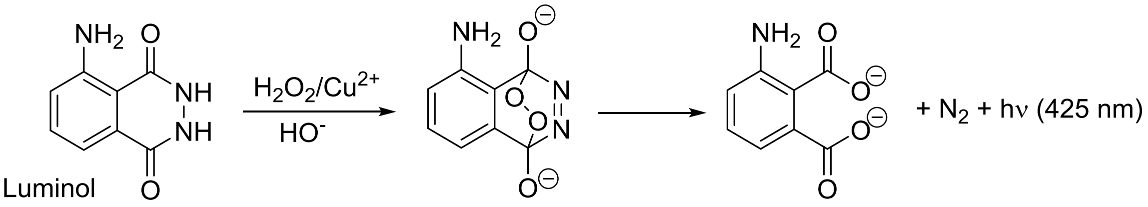
Notes:

- The total score will be based on the R_f values of compounds **A** and **B** calculated from the submitted TLC plate 1 and on the quality and quantity of the submitted products **B** and **C**.
- The quality of your products will be graded based on the TLC and melting points.
- The amount of the provided hypochlorite solution is not sufficient to convert all reactant **A** to product **B**. You will recover the residual reactant **A** by an acid-base extraction and isolate it after the reaction with Brady's reagent as hydrazone **C**. The grading is based on the combined yield of products **B** and **C**.

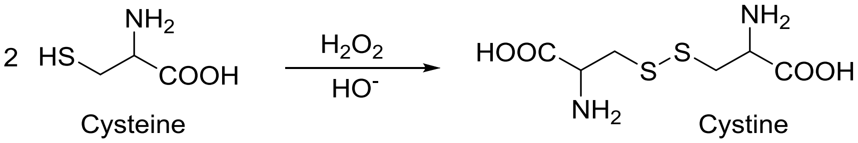
PROBLEM 2P (Practical)

A glowing clock reaction

Luminol is a well-known source of chemiluminescence. In the presence of a suitable redox catalyst, e.g. Cu^{2+}, it may react with oxidizing agents, most commonly H_2O_2, forming products in excited electronic states. These release the excess energy by the emission of blue light:



The procedure may be modified into a clock reaction, in which the light appears after a certain induction time. By adding cysteine, Cu(II) is reduced to Cu(I) and captured in a Cu(I)–cysteine complex that does not facilitate the luminol oxidation. However, the inhibition is only temporary. A cycle of reactions fuelled by H_2O_2 leads to the gradual oxidation of cysteine:



Eventually, all cysteine is consumed, Cu(I) is reoxidized to Cu(II), and its catalytic activity is restored. This is indicated by a flash of blue chemiluminescence. The time it takes for the flash to appear can be used to study the rates of the Cu-catalyzed cysteine oxidation.

Experiment

Chemicals

- Luminol (c = 8 mmol dm^{-3}) in an aqueous solution of NaOH (c = 0.4 mol dm^{-3}), 50 cm^3 in plastic bottle,
- 25 cm^3 of $CuSO_4$ aqueous solution (c = 2.00 mmol dm^{-3}) in a plastic bottle,
- 12 cm^3 of H_2O_2 aqueous solution (c = 2.00 mol dm^{-3}) in a small plastic bottle,
- 12 cm^3 cysteine hydrochloride aqueous solution (0.100 mol dm^{-3}) in a small plastic bottle
- Distilled w**ater**

Equipment

• Stopwatch	1
• Digital thermometer and card with its calibration constant	1
• Volumetric flask, 50 cm^3	1
• Bulb pipette, 5 cm^3 (bench, in pipette stand)	1
• Graduated pipette, 5 cm^3 (bench, in pipette stand)	3
• Graduated pipette, 1 cm^3 (bench, in pipette stand)	2
• Plastic bottle labelled **H_2O_2 dil.** for diluted stock solution of H_2O_2, 50 cm^3	1
• Plastic bottle labelled **Cys dil.** for diluted stock solution cysteine.HCl, 50 cm^3,	1
• Black plastic test tube, 15 cm^3	1
• Capless centrifuge tube, 1.5 cm^3	1
• Plastic beaker, 25 cm^3	1
• Erlenmeyer flask, 100 cm^3	1

Procedure

Caution: Always keep all your solutions and pipettes away from hotplates!

Reasonable temperature changes are not a problem, because your results will be marked based on the actual reaction temperatures that you report. You will not lose any points if your data is recorded at various temperatures. However, you must avoid excessive heat, e.g. placing the solutions or the pipettes near a hotplate.

Note: Report all the values with the requested number of significant figures or decimal places. Excessive rounding may make it impossible to distinguish a correct answer from an incorrect one.

General structure of the experiment

In Part I, you will dilute two stock solutions that are provided as concentrates. In Part II, you will measure the reaction times of the clock reaction for two different concentration sets, as defined in the table below:

	Volume in the black test tube			**In the centrifuge tube**	
	Water	**Luminol in NaOH**	**Cys dil.**	**Cu**	**H_2O_2 dil.**
Conc. set #1	3.00 cm^3	2.50 cm^3	3.30 cm^3	0.50 cm^3	0.70 cm^3
Conc. set #2	3.30 cm^3	2.50 cm^3	3.30 cm^3	0.50 cm^3	0.40 cm^3

It is recommended that before you start measuring the data to be graded, you should get familiar with the procedure in a trial run.

Because the reaction rate depends on temperature, you must record the actual temperatures in all replicates. The temperatures in the reaction mixtures should be measured IMMEDIATELY AFTER you have recorded the reaction time required to produce the blue flash.

In data evaluation, each temperature recorded from the thermometer's display must be corrected by summing it with the thermometer's calibration constant. This constant is printed on a piece of paper in the basket for Problem 2.

Then, each reaction time $t(x\ °C)$ observed at x °C (corrected) must be converted to the time $t(25\ °C)$ that would be observed at 25 °C. This normalization of reaction times to 25 °C is a simple multiplication of $t(x\ °C)$ with a normalization coefficient $n_{x\rightarrow 25}$:

$$t(25\ °C) = n_{x\rightarrow 25}\ t(x\ °C)$$

The values of the normalization coefficients $n_{x\rightarrow 25}$ corresponding to various temperatures, are listed in Table 2 at the end of this task.

I. Dilution of the concentrated stock solutions

Solutions of H_2O_2 (2.00 mol dm^{-3}) and cysteine (0.100 mol dm^{-3}) are provided as concentrates, labelled H_2O_2 conc. and Cys conc. Using the 5 cm^3 bulb pipette and the 50 cm^3 volumetric flask, dilute 5.00 cm^3 of each to 50.00 cm^3 with deionized water and store the diluted solution in the bottles labelled H_2O_2 dil. and Cys dil.

For measuring the solution volumes in the following steps, assign one graduated pipette for each of the bottles. The 5 cm^3 pipettes are for Luminol in NaOH, Cys dil., and water. The 1 cm^3 pipettes are for Cu (2.00 mmol dm^{-3}) and H_2O_2 dil.

II. The clock reaction procedure

Note: Read the entire Section II carefully before starting the experiment.

1. Place the black test tube inside the Erlenmeyer flask serving as a stand. Using the assigned pipettes, charge the test tube with the prescribed volumes of **Water**, **Luminol** in NaOH and Cys dil. solution.
2. Place the small centrifuge tube inside the small plastic beaker and charge it with the prescribed volumes of **Cu** solution and **H_2O_2 dil.** solution.

3. Without delay, insert the small centrifuge tube inside the black test tube – gently, without mixing the two solutions!
4. Close the test tube with its screw-on cap. Make sure that the tube is closed tightly, because you will be shaking it. *Caution*: **Do not force the cap beyond its end-point**, because the tube will start leaking. If this happens, you must ask for a replacement immediately (penalty rules apply).
5. Have the stopwatch ready in your hand, in timing mode. The moment you begin shaking the test tube, start timing. You must shake vigorously during the initial 10 seconds, so that the two solutions mix perfectly. It is crucial that you do not cut down the shaking time.
6. Return the test tube into the Erlenmeyer flask, open the lid and watch the solution inside closely. It may help to shield away the daylight with your hand. Eventually, you will see a flash of blue light through the whole solution. At that moment, stop timing.
7. Immediately, insert the metal probe of the digital thermometer into the black test tube. Wait for the reading to stabilize (typically 10–30 s) and record the reaction time and the reaction temperature.
8. Using tweezers, remove the small centrifuge tube from the black test tube. After each experiment, empty and wash both tubes and dry them with paper wipes.

Measured data and their evaluation

Task 2.1

In the following table, record your experimental results for concentration set #1. To the displayed temperature add the thermometer's calibration constant. Look up the value of the normalization coefficient $n_{x\rightarrow 25}$ for each temperature in Table 2 and calculate the reaction times normalized to 25 °C. In an unlikely case that your temperatures are not listed in Table 2, get the value of $n_{x\rightarrow 25}$ from the lab assistant.

Note: Since the tolerance for correct values in titration is ± 0.1 cm^3, the tolerance for correct values of the normalized times in the concentration set #1 is ± 2.3 s.

(Use as many replicates as you consider necessary, you do not need to fill in all the rows. Points will be awarded for the accepted value only.)

Table 2.1:

	Replicate	Reaction time [s] (1 decimal place)	Displayed temperature [°C] (1 decimal place)	Corrected temperature [°C] (1 decimal place)	Reaction time normalized to 25 °C [s] (3 significant figures)
Conc. set #1	1				
	2				
	3				
	Accepted value of the normalized reaction time for concentration set #1				

Task 2.2

In the following table, record your experimental results, the corrected temperature and calculate the reaction times normalized to 25 °C for concentration set #2.

Note: Just as the tolerance for correct values in titration is ± 0.1 cm^3, the tolerance for the correct values of the normalized times in the concentration set #2 is ± 3.0 s.

(Use as many replicates as you consider necessary; you do not need to fill in all the rows. Points will be awarded for the accepted value only.)

Table 2.2:

	Replicate	Reaction time [s] (1 decimal place)	Displayed temperature [°C] (1 decimal place)	Corrected temperature [°C] (1 decimal place)	Reaction time normalized to 25 °C [s] (3 significant figures)
Conc. set #2	1				
	2				
	3				
	Accepted value of the normalized reaction time for concentration set #2				

Task 2.3

Based on the procedure and on the concentrations of the stock solutions (specified in the list of chemicals and in Part I. of the Procedure), calculate the initial concentrations of cysteine, copper and H_2O_2 in both concentration sets.

Express the accepted reaction times (t_1 and t_2) from Tasks 2.1 and 2.2 in minutes and calculate the corresponding reaction rates (v_1 and v_2), expressed as the rates of the consumption of the cysteine concentration, in mmol dm^{-3} min^{-1}. You can assume that the rate of cysteine consumption during the reaction is constant.

If you cannot find the reaction rates, use in further calculations the values 11.50 and 5.500 for conc. set #1 and set #2, respectively.

Table 2.3

	Initial concentrations [mmol dm^{-3}] (3 significant figures)			Accepted reaction time [min] (4 significant figures)	Reaction rate [mmol dm^{-3} min^{-1}] (4 significant figures)
	Cysteine	Copper [Cu]	H_2O_2		
Conc. set #1					
Conc. set #2					

Task 2.4

Assuming the rate equation can be expressed as

$$v = k\,[H_2O_2]^p$$

use your experimental data to calculate the partial reaction order p with respect to H_2O_2. Write down your answer with 2 decimal places and show your calculation.

An expression of the rate law of cysteine consumption that is closer to reality is more complicated and takes the following form:

$$v = k_1\,[H_2O_2][Cu] + k_2[Cu]$$

Task 2.5

Using the data from Task 2.3, evaluate the dependence of v on $[H_2O_2]$ as a linear function to find the slope and the intercept. Write down both answers with

4 significant figures. If you cannot find constants a and b, use the value 11.50 for both a and b in further calculations.

Task 2.6

Use the numeric values from Task 2.5 to evaluate the rate constants k_1 and k_2. Write down their values with 3 significant figures.

Table 2. Normalization coefficients $n_{x \rightarrow 25}$ for converting reaction times measured at various temperatures to times representing the reactions at 25.0 °C.
(See the next page.)

Temp. °C	Set #1	Set #2
22.0	0.8017	0.8221
22.1	0.8076	0.8274
22.2	0.8135	0.8328
22.3	0.8195	0.8382
22.4	0.8255	0.8437
22.5	0.8316	0.8492
22.6	0.8377	0.8547
22.7	0.8438	0.8603
22.8	0.8500	0.8659
22.9	0.8563	0.8715
23.0	0.8626	0.8772
23.1	0.8690	0.8829
23.2	0.8754	0.8887
23.3	0.8818	0.8945
23.4	0.8884	0.9004
23.5	0.8949	0.9063
23.6	0.9015	0.9122
23.7	0.9082	0.9182
23.8	0.9149	0.9242
23.9	0.9217	0.9303
24.0	0.9285	0.9364
24.1	0.9354	0.9425
24.2	0.9424	0.9487
24.3	0.9494	0.9550
24.4	0.9564	0.9613
24.5	0.9636	0.9676
24.6	0.9707	0.9740
24.7	0.9780	0.9804
24.8	0.9852	0.9869
24.9	0.9926	0.9934
25.0	1.0000	1.0000
25.1	1.0075	1.0066
25.2	1.0150	1.0133
25.3	1.0226	1.0200
25.4	1.0302	1.0268
25.5	1.0379	1.0336
25.6	1.0457	1.0404

Temp. °C	Set #1	Set #2
25.7	1.0536	1.0474
25.8	1.0614	1.0543
25.9	1.0694	1.0613
26.0	1.0774	1.0684
26.1	1.0855	1.0755
26.2	1.0937	1.0827
26.3	1.1019	1.0899
26.4	1.1102	1.0972
26.5	1.1186	1.1045
26.6	1.1270	1.1119
26.7	1.1355	1.1194
26.8	1.1441	1.1268
26.9	1.1527	1.1344
27.0	1.1614	1.1420
27.1	1.1702	1.1497
27.2	1.1790	1.1574
27.3	1.1879	1.1651
27.4	1.1969	1.1730
27.5	1.2060	1.1809
27.6	1.2151	1.1888
27.7	1.2243	1.1968
27.8	1.2336	1.2049
27.9	1.2430	1.2130
28.0	1.2524	1.2212
28.1	1.2619	1.2294
28.2	1.2715	1.2377
28.3	1.2812	1.2461
28.4	1.2909	1.2545
28.5	1.3008	1.2630
28.6	1.3107	1.2716
28.7	1.3207	1.2802
28.8	1.3307	1.2889
28.9	1.3409	1.2976
29.0	1.3511	1.3064
29.1	1.3615	1.3153
29.2	1.3719	1.3243
29.3	1.3823	1.3333

Temp. °C	Set #1	Set #2
29.4	1.3929	1.3424
29.5	1.4036	1.3515
29.6	1.4143	1.3607
29.7	1.4252	1.3700
29.8	1.4361	1.3793
29.9	1.4471	1.3888
30.0	1.4582	1.3983
30.1	1.4694	1.4078
30.2	1.4807	1.4175
30.3	1.4921	1.4272
30.4	1.5035	1.4369
30.5	1.5151	1.4468
30.6	1.5267	1.4567
30.7	1.5385	1.4667
30.8	1.5503	1.4768
30.9	1.5623	1.4869
31.0	1.5743	1.4972
31.1	1.5865	1.5075
31.2	1.5987	1.5179
31.3	1.6111	1.5283
31.4	1.6235	1.5388
31.5	1.6360	1.5495
31.6	1.6487	1.5602
31.7	1.6614	1.5709
31.8	1.6743	1.5818
31.9	1.6872	1.5927
32.0	1.7003	1.6038
32.1	1.7135	1.6149
32.2	1.7268	1.6260
32.3	1.7402	1.6373
32.4	1.7536	1.6487
32.5	1.7673	1.6601
32.6	1.7810	1.6716
32.7	1.7948	1.6833
32.8	1.8087	1.6950
32.9	1.8228	1.7068
33.0	1.8370	1.7186

SOLUTION

2.1

	Replicate	Reaction time [s] (1 decimal place)	Displayed temperature [°C] (1 decimal place)	Corrected temperature [°C] (1 decimal place)	Reaction time normalized to 25 °C [s] (3 significant figures)
Conc. set #1	1	57.1	27.5	27.4	68.3
	2	56.0	27.7	27.6	68.0
	3	55.7	27.8	27.7	68.2
	Accepted value of the normalized reaction time for concentration set #1				68.2

2.2

	Replicate	Reaction time [s] (1 decimal place)	Displayed temperature [°C] (1 decimal place)	Corrected temperature [°C] (1 decimal place)	Reaction time normalized to 25 °C [s] (3 significant figures)
Conc. set #2	1	71.9	27.9	27.8	86.6
	2	70.6	27.9	27.8	85.1
	3	72.5	27.8	27.7	86.8
	Accepted value of the normalized reaction time for concentration set #2				86.2

2.3

	Initial concentrations [mmol dm^{-3}] (3 significant figures)			Accepted reaction time [min] (4 significant figures)	Reaction rate [mmol dm^{-3} min^{-1}] (4 significant figures)
	Cysteine	Copper [Cu]	H_2O_2		
Conc. set #1	3.30	0.100	14.0	1.137	2.902
Conc. set #2			8.00	1.437	2.296

2.4 Answer: $p = 0.42$

Calculation:

$$2.902 \text{ mmol dm}^{-3} \text{ min}^{-1} = k\left(14.0 \text{ mmol dm}^{-3}\right)^{p}$$

$$2.296 \text{ mmol dm}^{-3} \text{ min}^{-1} = k\left(8.00 \text{ mmol dm}^{-3}\right)^{p}$$

$$\frac{2.902}{2.296} = \left(\frac{14.0}{8.00}\right)^{p}$$

$$p = \frac{\log 1.264}{\log 1.75}$$

2.5 Answers (do not include the calculation, but include units):

$v = a[H_2O_2] + b$ $a = 0.1010 \text{ min}^{-1}$ $b = 1.488 \text{ mmol dm}^{-3} \text{ min}^{-1}$

2.6 Answers (including units):

$k_1 = 1.01 \text{ min}^{-1} \text{ mmol}^{-1} \text{ dm}^3$ $k_2 = 14.9 \text{ min}^{-1}$

Calculations:

$k_1 [Cu] = a \Rightarrow k_1 = a / [Cu] = 0.1010 \text{ min}^{-1} / (0.100 \text{ mmol dm}^{-3})$

$k_2 [Cu] = b \Rightarrow k_2 = b / [Cu] = 1.488 \text{ mmol dm}^{-3} \text{ min}^{-1} / (0.100 \text{ mmol dm}^{-3})$

PROBLEM 3P (Practical)

Mineral water identification

Many mineral and thermal water springs are registered in Slovakia. Mineral waters with a balanced composition and natural or modified carbon dioxide content are sold for daily consumption. These waters do not contain nitrites, nitrates, phosphates, fluorides and sulfides and are also free of iron and manganese.

The mass concentration of the most important ions is reported on the packaging. Your task is to identify the trade brand (from Table P3.1) of your mineral water sample.

Note: CO_2 has been removed from the sample.

Table P 3.1. Mass concentrations of ions in selected Slovak mineral waters. (As reported by the supplier.)

No.	Trade brand	Mass concentration of ion, mg dm^{-3}						
		Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}
1	Kláštorná	290	74	71	16	15	89	1 341
2	Budišská	200	50	445	50	25	433	1 535
3	Baldovská	378	94	90	0	78	215	1 557
4	Santovka	215	67	380	45	177	250	1 462
5	Slatina	100	45	166	40	104	168	653
6	Fatra	45	48	550	16	36	111	1 693
7	Ľubovnianka	152	173	174	5	10	20	1 739
8	Gemerka	376	115	85	0	30	257	1 532
9	Salvator	473	161	214	30	116	124	2 585
10	Brusnianka	305	101	187	35	59	774	884
11	Maxia	436	136	107	18	37	379	1 715

Notes:

- Use the prescribed symbols in the notations of calculations.
- You are provided with a swollen cation exchange resin (Catex) in its H^+ form. Use a thick stem Pasteur pipette for transferring it. You can add more deionized water to the resin if necessary (it should not dry out).
- Concentrations of the standard solutions:
  $c(NaOH) = 0.2660 \text{ mol dm}^{-3}$ $c(EDTA) = 5.965 \times 10^{-3} \text{ mol dm}^{-3}$

Laboratory stand (bench) with white sheet of paper and burette clamp

Equipment and chemical glassware

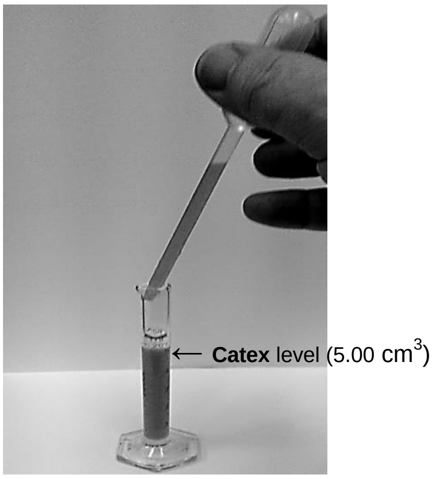
• Burette, 25 cm^3	1
• Bulb pipette, 50 cm^3 (bench, in pipette stand)	1
• Bulb pipette, 10 cm^3 (bench, in pipette stand)	1
• Glass funnel	1
• Measuring cylinder, 5 cm^3	1
• Titration flask (flat bottom flask), 250 cm^3	2
• Erlenmeyer flask, 250 cm^3	1
• Fritted glass filter funnel, porosity **S1** (blue label)	1
• Glass beaker, 100 cm^3	2
• Glass beaker, 250 cm^3	1
• Plastic Pasteur pipette, narrow stem, nongraduated	2
• Plastic Pasteur pipette, thick stem, graduated	1
• Zipped bag with 5 pH indicator strips and 1 pH scale	1
• Zipped bag with 5 absorbing paper strips	1

Waste catex plastic bottle (bench)	1

Experiment

Procedure

1a. Measure 5.00 cm^3 of the catex into the graduated cylinder (volume *V1*). Then using deionized water transfer the catex quantitatively into a titration flask. Add an appropriate amount of deionized water so that the suspension can be swirled well and the colour of the solution over the catex can be observed.



1b. Add 3–4 drops of the bromothymol blue indicator (**BTB**) and about 1 g (half a spoon) of solid NaCl. When NaCl dissolves, titrate all the suspension with the standard sodium hydroxide solution (volume *V2*) from yellow to blue. Close to the equivalence point, titrate slowly and swirl well so that any analyte inside the catex skeleton may diffuse into the solution. Repeat the experiment as necessary.

1c. After the titration, decant and discard most of the aqueous solution in the titration flask above the catex and transfer the suspension to the **Waste catex** container.

P 3.1 Write down all the chemical reactions which occur in Step 1. Use R–H as a formula for the catex in a H^+ form and HInd for the indicator.

P 3.2 Enter the experimental and accepted values from Step 1 into the table.
(You do not need to fill in all the rows.)

Analysis No.	**Catex volume** V_1 **[cm^3]**	**NaOH consumption** V_2 **[cm^3]**
1	5.00	
2		
3		
Accepted value V_2 (4 significant figures)		

P 3.3 Using the accepted value of $V2$, calculate the ion exchange volume capacity $Q_V(H^+)$ in mmol cm^{-3}.
If you cannot find the $\mathbf{Q_V(H^+)}$ value, use 1.40 mmol cm^{-3} for further calculations.

2a. Using a graduated cylinder, measure 5.00 cm^3 of the swollen catex (volume V_3). Transfer the measured catex quantitatively into the 250 cm^3 beaker. Using a pipette, add 50.00 cm^3 of your sample (volume $V4$). Swirl the mixture occasionally for about 5 minutes. Use the Erlenmeyer flask as a stand for the funnel and to collect the filtrate. Then filter the catex through a fritted funnel (porosity **S1**) and wash it with deionized water to a neutral pH (check with pH paper). Discard the filtrate.

2b. Using deionized water, transfer the catex quantitatively from the funnel into a titration flask and discard the filtrate.

2c. Add 3 – 4 drops of bromothymol blue indicator and about 1 g (half a spoon) of solid NaCl and titrate the suspension with the standard sodium hydroxide solution (volume $V5$) from yellow to blue. Repeat the experiment as necessary.

2d. After the titration, decant and discard most of the aqueous solution in the titration flask above the catex and transfer the suspension to the **Waste catex** container.

P 3.4 Write down the equations for the ion exchange reactions. Monovalent and divalent ions should be abbreviated M^+ and M^{2+}, respectively.

P 3.5 Enter the experimental and accepted values from Step 2 into the table.

(You do not need to fill in all the rows.)

Analysis No.	**Catex volume *V*₃ [cm³]**	**Sample volume *V*₄ [cm³]**	**NaOH consumption *V*₅ [cm³]**
1	5.00	50.00	
2			
3			
Accepted value ***V*₅** (4 significant figures)			

P 3.6 Consider that all the ions in your solution are M^+ ions. For the accepted value of V_5, calculate the total amount of cations (as M^+ molar concentration) in 1 dm^3 of mineral water. Show the calculation of the total equivalent concentration of cations, $c^*(M^+)$ in mmol dm^{-3}.

If you cannot find the $\boldsymbol{c^*(M^+)}$ value, use 35.00 mmol dm^{-3} for further procedure.

In the next step, you are going to perform complexometric analysis to determine the concentration of Ca^{2+} and Mg^{2+} together (hereinafter written as M^{2+}).

3. Pipette 10.00 cm^3 (V_6) of the sample into the titration flask and add ca. 25 cm^3 of deionized water. Adjust pH by adding 3 cm^3 of the buffer solution. Add some Eriochrome black T indicator (**EBT**, on the tip of the spatula) and titrate with the standard EDTA solution from wine red to blue (V_7).

P 3.7 Enter the experimental and accepted values from Step 3 into the table.

(You do not need to fill in all the rows)

Analysis No.	**Sample volume *V6* [cm³]**	**EDTA consumption, *V7* [cm³]**
1	10.00	e.g. 14.20
2		e.g. 14.25

3		e.g. 14.25
Accepted value V_7 (4 significant figures)		**e.g. 14.25**

P 3.8 For the accepted volume of V_7, calculate the molar concentration of M^{2+} cations in mineral water, $c(M^{2+})$ in mmol dm^{-3}.

If you cannot find the $c(M^{2+})$ value, use 15.00 mmol dm^{-3} for further solution.

4. Use Table P3.2 in next identification procedure.

P 3.9 In Table P3.2, write down experimentally found values from tasks P3.6 and P3.8 and tick (✓) all the lines with approximate match (±10%) of the found parameter $c(M^{2+})$ and $c^*(M^+)$ with the data from the label.

Table P 3.2

Mineral water		**Supplier data**			**Match with the experiment**	
No.	**Trade brand**	**$c(M^{2+})$ [mmol dm^{-3}]**	**$c(M^+)$ [mmol dm^{-3}]**	**Total equivalent concentration of cations $c^*(M^+)$ [mmol dm^{-3}]**	**Conformity for $c(M^{2+})$**	**Conformity for $c^*(M^+)$**
Your experimental values			XXX		XXX	XXX
1	Kláštorná	10.30	3.50	24.1		
2	Budišská	7.06	20.63	34.7		
3	Baldovská	13.32	3.91	30.5		
4	Santovka	8.13	17.67	33.9		
5	Slatina	4.35	8.25	16.9		
6	Fatra	3.11	24.32	30.5		
7	Ľubovnianka	10.92	7.70	29.5		
8	Gemerka	14.13	3.70	32.0		
9	Salvator	18.46	10.07	47.0		
10	Brusnianka	11.79	9.03	32.6		
11	Maxia	16.50	5.11	38.1		

P 3.10 Based on your results, decide which mineral water is in your sample.

SOLUTION

P 3.1 Ion exchange

$R–H + NaCl \leftrightarrows R–Na + HCl$

Neutralization

$HCl + NaOH \leftrightarrows NaCl + H_2O$

Indication

$HInd + OH^- \leftrightarrows Ind^- + H_2O$

P 3.2 Enter the experimental and accepted values from Step 1 into the table.

Analysis No.	**Catex volume V_1 [cm^3]**	**NaOH consumption V_2 [cm^3]**
1	5.00	e.g. 19.00
2		e.g. 19.50
3		e.g. 19.70
Accepted value V_2 (4 significant figures)		e.g. 19.40

P 3.3 Calculation:

$$Q_v(H^+) = \frac{V2 \times c(\text{NaOH})}{V1} = \frac{19.40\ \text{cm}^3 \times 0.2660\ \text{mol dm}^{-3}}{5.0\ \text{cm}^3} = 1.032\ \text{mmol cm}^{-3}$$

P 3.4 Ion exchange from the sample:

$R–H + M^+ \leftrightarrows R–M + H^+$

$2\ R–H + M^{2+} \leftrightarrows R_2–M + 2\ H^+$

P 3.5

Analysis No.	**Catex volume V_3 [cm^3]**	**Sample volume V_4 [cm^3]**	**NaOH consumption V_5 [cm^3]**
1	5.00	50.00	e.g. 13.00
2			e.g. 13.20
3			e.g. 13.10
Accepted value V_5 4 significant figures			e.g. 13.10

P 3.6 Calculation:

$$c^*(\text{M}^+) = \frac{V3 \times Q_v(\text{H}^+)_{\text{ionex}} - V5 \times c(\text{NaOH})}{V4}$$

$$c^*(\text{M}^+) = \frac{5.00\ \text{cm}^3 \times 1.032\ \text{mol dm}^{-3} - 13.10\ \text{cm}^3 \times 0.2660\ \text{mol dm}^{-3}}{50.00\ \text{cm}^3}$$

$$c^*\left(\text{M}^+\right) = 33.51\ \text{mmol dm}^{-3}$$

P 3.7

Analysis No.	Sample volume V_6 [cm^3]	EDTA consumption, V_7 [cm^3]
1	10.00	e.g. 14.20
2		e.g. 14.25
3		e.g. 14.25
Accepted value V_7 (4 significant figures)		e.g. 14.25

P 3.8 Calculation:

$$c\left(\text{M}^{2+}\right) = \frac{V7 \times c(\text{EDTA})}{V6}$$

$$c\left(\text{M}^{2+}\right) = \frac{14.25\ \text{cm}^3 \times 5.965\ \text{mmol dm}^{-3}}{10.00\ \text{cm}^3} = 8.500\ \text{mmol dm}^{-3}$$

Table P 3.2

Mineral water		**Supplier data**			**Match with the experiment**	
No.	**Trade brand**	c(M^{2+}) [mmol dm^{-3}]	c(M$^+$) [mmol dm^{-3}]	**Total equivalent concentration of cations c*(M$^+$) [mmol dm^{-3}]**	**Conformity for c(M^{2+})**	**Conformity for c*(M$^+$)**
Your experimental values		**8.50**	XXX	**33.51**	XXX	XXX
1	Kláštorná	10.30	3.50	24.1		
2	Budišská	7.06	20.63	34.7		✓

Table continued:

3	Baldovská	13.32	3.91	30.5		✓
4	Santovka	8.13	17.67	33.9	✓	✓
5	Slatina	4.35	8.25	16.9		
6	Fatra	3.11	24.32	30.5		✓
7	Ľubovnianka	10.92	7.70	29.5		
8	Gemerka	14.13	3.70	32.0		✓
9	Salvator	18.46	10.07	47.0		
10	Brusnianka	11.79	9.03	32.6		✓
11	Maxia	16.50	5.11	38.1		

P 3.10 Mineral water No 4 – Santovka.

Physical constants and equations

Avogadro's constant:	$N_A = 6.022 \times 10^{23}$ mol^{-1}
Universal gas constant:	$R = 8.314$ J K^{-1} mol^{-1}
Speed of light:	$c = 2.998 \times 10^{8}$ m s^{-1}
Planck's constant:	$h = 6.626 \times 10^{-34}$ J s
Faraday constant:	$F = 9.6485 \times 10^{4}$ C mol^{-1}
Standard pressure:	$p = 1$ bar $= 10^{5}$ Pa
Normal (atmospheric) pressure:	$p_{atm} = 1.01325 \times 10^{5}$ Pa
Zero of the Celsius scale:	273.15 K
Mass of electron:	$m_e = 9.109 \times 10^{-31}$ kg
Unified atomic mass unit:	$u = 1.6605 \times 10^{-27}$ kg
Ångström:	1 Å = 10^{-10} m
Electronvolt:	1 eV = 1.602×10^{-19} J
Watt:	1 W = 1 J s^{-1}

Ideal gas equation:	$pV = nRT$
The first law of thermodynamics:	$\Delta U = q + W$
Power input for electrical device:	$P = U I$ where U is voltage and I electric current
Enthalpy:	$H = U + pV$
Gibbs free energy:	$G = H - TS$ $\Delta G^{o} = -RT \ln K = -zFE^{o}_{cell}$ $\Delta G = \Delta G^{o} + RT \ln Q$
Reaction quotient Q for a reaction a A + b B $\rightleftharpoons$ c C + d D:	$Q = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$
Entropy change:	$\Delta S = \dfrac{q_{rev}}{T}$ where q_{rev} is heat for the reversible process
Heat change for temperature-independent c_m:	$\Delta q = nc_m\Delta T$ where c_m is molar heat capacity
Van 't Hoff equation:	$\dfrac{d \ln K}{dT} = \dfrac{\Delta_r H_m}{RT^2} \quad \Rightarrow \quad \ln\left(\dfrac{K_2}{K_1}\right) = -\dfrac{\Delta_r H_m}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$

Henderson–Hasselbalch equation: $\text{pH} = \text{p}K_a + \log\frac{[\text{A}^-]}{[\text{HA}]}$

Nernst–Peterson equation: $E = E^o - \frac{RT}{zF}\ln Q$

Energy of a photon: $E = \frac{hc}{\lambda}$

Relation between E in eV and in J: $E/\text{eV} = \frac{E/\text{J}}{q_e/\text{C}}$

Lambert–Beer law: $A = \log\frac{I_0}{I} = \varepsilon lc$

Wavenumber: $\tilde{v} = \frac{v}{c} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

Reduced mass μ for a molecule AX: $\mu = \frac{m_A\, m_X}{m_A + m_X}$

Energy of harmonic oscillator: $E_n = hv\,(n + \frac{1}{2})$

Arrhenius equation: $k = A\,\text{e}^{-\frac{E_a}{RT}}$

Rate laws in integrated form:

Zero order: $[\text{A}] = [\text{A}]_0 - kt$

First order: $\ln[\text{A}] = \ln[\text{A}]_0 - kt$

Second order: $\frac{1}{[\text{A}]} = \frac{1}{[\text{A}]_0} + kt$