IChO
International Chemistry Olympiad

THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS

Volume 3

41st – 45th IChO
2009 – 2013

Edited by Anton Sirota

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THE COMPETITION PROBLEMS FROM THE INTERNATIONAL CHEMISTRY OLYMPIADS,
Volume 3
41st – 45th IChO (2009 – 2013)

Editor: Anton Sirota

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Preface

This publication contains 39 theoretical and 14 practical competition problems from the 41st – 45th International Chemistry Olympiads (IChO) organized in the years 2009 – 2013. It has been published by the IChO International Information Centre in Bratislava (Slovakia) as a continuation of the preceding Volumes 1 and 2 published on the occasion of the 40th anniversary of the IChO with the titles:

- The competition problems from the International Chemistry Olympiads, Volume 1, 1st – 20th IChO, 1968 – 1988 (IUVENTA, Bratislava, 2008).
- The competition problems from the International Chemistry Olympiads, Volume 2, 21st – 40th IChO, 1989 – 2008 (IUVENTA, Bratislava, 2009).

Not less than 318 theoretical and 110 practical problems were set in the IChO during the forty-five 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 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 the tasks of 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 41st – 45th 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 forty-five 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 2014

Anton Sirota, editor

41st

IChO

International Chemistry Olympiad

6 theoretical problems
3 practical problems

THE FORTY-FIRST
INTERNATIONAL CHEMISTRY OLYMPIAD
18–27 JULY 2009, CAMBRIDGE, UNITED KINGDOM

THEORETICAL PROBLEMS

PROBLEM 1

Estimating the Avogadro constant

Many different methods have been used to determine the Avogadro constant. Three different methods are given below.

Method A – from X-ray diffraction data (modern)

The unit cell is the smallest repeating unit in a crystal structure. The unit cell of a gold crystal is found by X-ray diffraction to have the face-centred cubic unit structure (i.e. where the centre of an atom is located at each corner of a cube and in the middle of each face). The side of the unit cell is found to be 0.408 nm.

1.1 Sketch the unit cell and calculate how many Au atoms the cell contains.

1.2 The density of Au is $1.93 \cdot 10^4$ kg m^{-3}. Calculate the volume and mass of the cubic unit cell.

1.3 Hence calculate the mass of a gold atom and the Avogadro constant, given that the relative atomic mass of Au is 196.97.

Method B – from radioactive decay (Rutherford, 1911)

The radioactive decay series of ^{226}Ra is as follows:

$$^{226}\text{Ra} \xrightarrow{t} {}^{222}\text{Rn} \xrightarrow{3.825\text{ d}} {}^{218}\text{Po} \xrightarrow{3.10\text{ m}} {}^{214}\text{Pb} \xrightarrow{26.8\text{ m}} {}^{214}\text{Bi} \xrightarrow{19.9\text{ m}}$$

$$^{214}\text{Po} \xrightarrow{164.3\ \mu\text{s}} {}^{210}\text{Pb} \xrightarrow{22.3\text{ y}} {}^{210}\text{Bi} \xrightarrow{5.013\text{ d}} {}^{210}\text{Po} \xrightarrow{138.4\text{ d}} {}^{206}\text{Pb}$$

The times indicated are half-lives, the units are y = years, d = days, m = minutes. The first decay, marked *t* above, has a much longer half-life than the others.

1.4 In the table below, identify which transformations are α-decays and which are β-decays.

	α-decay	β-decay
$^{226}Ra \longrightarrow {}^{222}Rn$		
$^{222}Rn \longrightarrow {}^{218}Po$		
$^{218}Po \longrightarrow {}^{214}Pb$		
$^{214}Pb \longrightarrow {}^{214}Bi$		
$^{214}Bi \longrightarrow {}^{214}Po$		
$^{214}Po \longrightarrow {}^{210}Pb$		
$^{210}Pb \longrightarrow {}^{210}Bi$		
$^{210}Bi \longrightarrow {}^{210}Po$		
$^{210}Po \longrightarrow {}^{206}Pb$		

1.5 A sample containing 192 mg of ^{226}Ra was purified and allowed to stand for 40 days. Identify the first isotope in the series (excluding Ra) that has not reached a steady state.

1.6 The total rate of α-decay from the sample was then determined by scintillation to be 27.7 GBq (where 1 Bq = 1 count s^{-1}). The sample was then sealed for 163 days. Calculate the number of α particles produced.

1.7 At the end of the 163 days the sample was found to contain 10.4 mm^3 of He, measured at 101325 Pa and 273 K. Calculate the Avogadro constant from these data.

1.8 Given that thee relative isotopic mass of ^{226}Ra measured by mass spectrometry is 226.25, use the textbook value of the Avogadro constant ($6.022 \cdot 10^{23}$ mol^{-1}) to calculate the number of ^{226}Ra atoms in the original sample, n_{Ra}, the decay rate constant, λ, and the half-life, t, of ^{226}Ra (in years). You need only consider the decays up to but not including the isotope identified in 1.5.

Method C – dispersion of particles (Perrin, 1909)

One of the first accurate determinations of the Avogadro constant was carried out by studying the vertical distribution under gravity of colloidal particles suspended in water. In one such experiment, particles with radius $2.12 \cdot 10^{-7}$ m and density $1.206 \cdot 10^{3}$ kg m^{-3} were suspended in a tube of water at 15 °C. After allowing sufficient time to equilibrate, the mean numbers of particles per unit volume observed at four heights from the bottom of the tube were:

height / 10^{-6} m	5	35	65	95
mean number per unit volume	4.00	1.88	0.90	0.48

1.9 Assuming the particles to be spherical, calculate:

i) the mass, m, of a particle;

ii) the mass, m_{H_2O}, of the water it displaces;

iii) the effective mass, m^*, of the particle in water accounting for buoyancy (i.e. taking account of the upthrust due to the displaced volume of water).

Take the density of water to be 999 kg m^{-3}.

At equilibrium, the number of particles per unit volume at different heights may be modelled according to a Boltzmann distribution:

$$\frac{n_h}{n_{h_0}} = \exp\left[-\frac{E_h - E_{h_0}}{RT}\right]$$

where

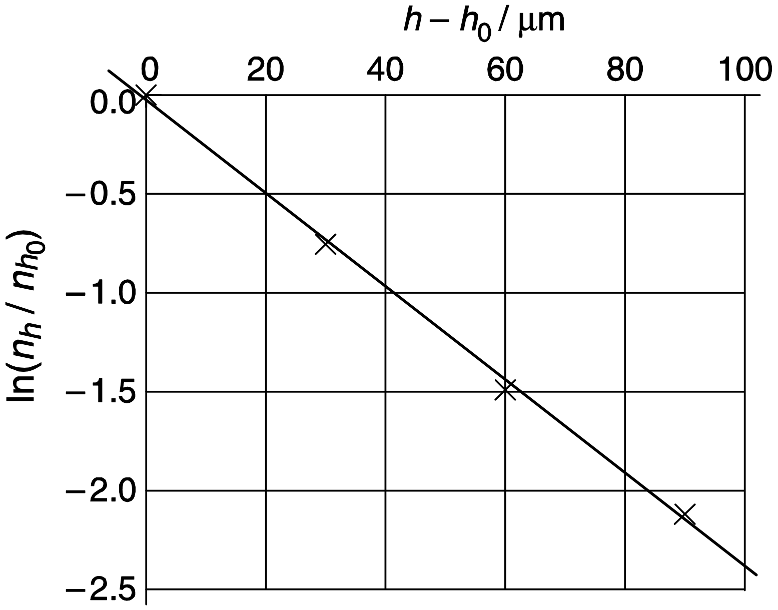
n_h is the number of particles per unit volume at height h,

n_{h0} is the number of particles per unit volume at the reference height h_0,

E_h is the gravitational potential energy per mole of particles at height h relative to the particles at the bottom of the tube,

R is the gas constant, 8.3145 J K^{-1} mol^{-1}.

A graph of $\ln(n_h / n_{h0})$ against $(h - h_0)$, based on the data in the table above, is shown below. The reference height is taken to be 5 μm from the bottom of the tube.

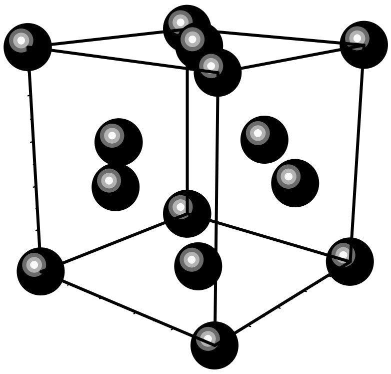


1.10 Derive an expression for the gradient (slope) of the graph.

1.11 Determine the Avogadro constant from these data.

SOLUTION

1.1 Unit cell:



Number of Au atoms in the unit cell:

8 × 1/8 from each corner = 1

6 × ½ from each face = 3

Total = 4 atoms

1.2 Volume:

V = (0.408 nm)^3 = 6.79 ·10^{-29} m^3

Mass:

$m = \rho V$ = 1.93 ·10^4 kg m^{-3} × 6.79 ·10^{-29} m^3 = 1.31 ·10^{-24} kg

1.3 Mass of Au atom:

$$m = \frac{1.31 \cdot 10^{-24}\ \text{kg}}{4} = 3.28 \cdot 10^{-25}\ \text{kg}$$

Avogadro constant:

$$N_A = \frac{196.97\ \text{g mol}^{-1}}{3.28 \cdot 10^{-22}\ \text{g}} = 6.01 \cdot 10^{23}\ \text{mol}^{-1}$$

1.4

	α-decay	β-decay
$^{226}\text{Ra} \longrightarrow {}^{222}\text{Rn}$	✓	
$^{222}\text{Rn} \longrightarrow {}^{218}\text{Po}$	✓	
$^{218}\text{Po} \longrightarrow {}^{214}\text{Pb}$	✓	
$^{214}\text{Pb} \longrightarrow {}^{214}\text{Bi}$		✓
$^{214}\text{Bi} \longrightarrow {}^{214}\text{Po}$		✓
$^{214}\text{Po} \longrightarrow {}^{210}\text{Pb}$	✓	
$^{210}\text{Pb} \longrightarrow {}^{210}\text{Bi}$		✓
$^{210}\text{Bi} \longrightarrow {}^{210}\text{Po}$		✓
$^{210}\text{Po} \longrightarrow {}^{206}\text{Pb}$	✓	

1.5 Answer: ^{210}Pb

1.6 $2.77 \cdot 10^{10}\ \text{s}^{-1} \times 163 \times 24 \times 60 \times 60\ \text{s} = 3.90 \cdot 10^{17}$

1.7 Answer:

$$n = \frac{pV}{RT} = 4.64 \cdot 10^{-7}\ \text{mol}$$

$$N_A = \frac{3.90 \cdot 10^{17}}{4.64 \cdot 10^{-7}\ \text{mol}} = 8.4 \cdot 10^{23}\ \text{mol}^{-1}$$

1.8 $$n_{\text{Ra}} = \frac{0.192\ \text{g} \times 6.022 \cdot 10^{23}\ \text{mol}^{-1}}{226.25\ \text{g mol}^{-1}} = 5.11 \cdot 10^{20}\ \text{atoms}$$

$$\lambda = \frac{2.77 \cdot 10^{10}\ \text{s}^{-1}}{5.11 \cdot 10^{20} \times 4} = 1.36 \cdot 10^{-11}\ \text{s}^{-1}$$

(only ¼ of the decays are from ^{226}Ra)

$$t = \frac{\ln 2}{\lambda} = 5.12 \cdot 10^{10}\ \text{s} = 1620\ \text{years}$$

1.9 $V = 3.99 \cdot 10^{-20}$ m^3

$m = 4.81 \cdot 10^{-17}$ kg

$m_{H_2O} = 3.99 \cdot 10^{-17}$ kg

$m^* = 8.3 \cdot 10^{-18}$ kg

1.10 gradient = $\dfrac{-m^* N_A\, g}{R\,T}$

1.11 Acceptable range of slopes is 0.0235 ± 0.002 μm

Hence $N_A = (6.9 \pm 0.8) \cdot 10^{23}$ mol^{-1} (error range needs widening here).

PROBLEM 2

Interstellar production of H_2

If two atoms collide in interstellar space the energy of the resulting molecule is so great that it rapidly dissociates. Hydrogen atoms only react to give stable H_2 molecules on the surface of dust particles. The dust particles absorb most of the excess energy and the newly formed H_2 rapidly desorbs. This question examines two kinetic models for H_2 formation on the surface of a dust particle.

In both models, the rate constant for adsorption of H atoms onto the surface of dust particles is $k_a = 1.4 \cdot 10^{-5}$ cm^3 s^{-1}. The typical number density of H atoms (number of H atoms per unit volume) in interstellar space is [H] = 10 cm^{-3}.

[Note: In the following, you may treat numbers of surface-adsorbed atoms and number densities of gas-phase atoms in the same way as you would normally use concentrations in the rate equations. As a result, the units of the rate constants may be unfamiliar to you. Reaction rates have units of numbers of atoms or molecules per unit time.]

2.1 Calculate the rate at which H atoms adsorb onto a dust particle. You may assume that this rate is constant throughout.

Desorption of H atoms is first order with respect to the number of adsorbed atoms. The rate constant for the desorption step is $k_d = 1.9 \cdot 10^{-3}$ s^{-1}.

2.2 Assuming that only adsorption and desorption take place, calculate the steady-state number, N, of H atoms on the surface of a dust particle.

The H atoms are mobile on the surface. When they meet they react to form H_2, which then desorbs. The two kinetic models under consideration differ in the way the reaction is modelled, but share the same rate constants k_a, k_d, and k_r, for adsorption, desorption, and bimolecular reaction, as given below.

$k_a = 1.4 \cdot 10^{-5}$ cm^3 s^{-1}

$k_d = 1.9 \cdot 10^{-3}$ s^{-1}

$k_r = 5.1 \cdot 10^{4}$ s^{-1}

Model A

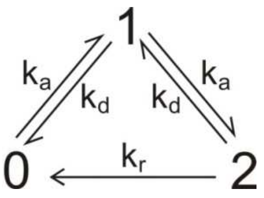
Reaction to form H_2 is assumed to be second order. On a dust particle the rate of removal of H atoms by reaction is $k_r N^2$.

2.3 Write down an equation for the rate of change of N, including adsorption, desorption and reaction. Assuming steady state conditions, determine the value of N.

2.4 Calculate the rate of production of H_2 per dust particle in this model.

Model B

Model B attempts to analyse the probability that the dust particles carry 0, 1 or 2 H atoms. The three states are linked by the following reaction scheme. The assumption is made that no more than 2 atoms may be adsorbed simultaneously.



x_0, x_1 and x_2 are the fractions of dust particles existing in state 0, 1 or 2, respectively. These fractions may be treated in the same way as concentrations in the following kinetic analysis. For a system in state m with fraction x_m, the rates of the three possible processes are

Adsorption ($m \rightarrow m + 1$) : rate = $k_a [H] x_m$

Desorption ($m \rightarrow m - 1$) : rate = $k_d m x_m$

Reaction ($m \rightarrow m - 2$) : rate = $\frac{1}{2} k_r m(m-1) x_m$

2.5 Write down equations for the rates of change, dx_m / dt, of the fractions x_0, x_1 and x_2.

2.6 Assuming steady-state conditions, use the above rate equations to find expressions for the ratios x_2/x_1 and x_1/x_0, and evaluate these ratios.

2.7 Evaluate the steady state fractions x_0, x_1 and x_2.
[If you were unable to determine the ratios in 2.6, use $x_2/x_1 = a$ and $x_1/x_0 = b$ and give the result algebraically.]

2.8 Evaluate the rate of production of H_2 per dust particle in this model.

2.9 It is currently not possible to measure the rate of this reaction experimentally, but the most recent computer simulations of the rate give a value of $9.4 \cdot 10^{-6}$ s^{-1}. Which of the following statements apply to each model under these conditions? Mark any box you consider to be appropriate.

Statement	**Model A**	**Model B**	**Neither model**
The rate determining step is adsorption of H atoms.			
The rate-determining step is desorption of H_2 molecules.			
The rate determining step is the bimolecular reaction of H atoms on the surface.			
The rate determining step is adsorption of the second H atom.			
The implicit assumption that reaction can take place regardless of the number of atoms adsorbed leads to substantial error (at least a factor of two).			
Limiting the number of atoms adsorbed on the particle to 2 leads to substantial error (at least a factor of two).			

SOLUTION

2.1 Answer: $1.4 \cdot 10^{-4}\ s^{-1}$

2.2 Answer: $1.4 \cdot 10^{-4}\ s^{-1} = 1.9 \cdot 10^{-3}\ s^{-1}\ N \ \Rightarrow\ N = 7.4 \cdot 10^{-2}$

2.3 $$\frac{dN}{dt} = 0 = k_a[H] - k_d N - k_r N^2$$

$$N = \frac{-k_d + \sqrt{k_d^2 + 4\,k_r k_a[H]}}{2\,k_r}$$

$$N = 5.2 \cdot 10^{-5}$$

2.4 Answer: $\frac{1}{2} k_r\, N^2 = 7.0 \cdot 10^{-5}\ s^{-1}$

2.5

$$\frac{dP_0}{dt} = -k_a[H]P_0 + k_d P_1 + k_r P_2$$

$$\frac{dP_1}{dt} = k_a[H]P_0 - (k_a[H] + k_d)P_1 + 2\,k_d P_2$$

$$\frac{dP_2}{dt} = k_a[H]P_1 - (2\,k_d + k_r)P_2$$

(remember P is changed to x)

2.6

$$\frac{P_2}{P_1} = \frac{k_a[H]}{(2\,k_d + k_r)} \approx \frac{k_a[H]}{k_r} = 2.7 \cdot 10^{-9}$$

$$\frac{P_1}{P_0} = \frac{k_a[H]\,(2\,k_d + k_r)}{k_d\,(2\,k_d + k_r) + k_r k_a[H]} \approx \frac{k_a[H]}{k_d + k_a[H]} = 6.9 \cdot 10^{-2}$$

2.7

$P_0 = 0.94,$

$P_1 = 0.064,$

$P_2 = 1.8 \cdot 10^{-10}$

2.8 $k_r\, x_2 = 9.0 \cdot 10^{-6}\ s^{-1}$

2.9

Statement	**Model A**	**Model B**	**Neither model**
The rate determining step is adsorption of H atoms.	✓	(✓)	
The rate-determining step is desorption of H_2 molecules.			✓
The rate determining step is the bimolecular reaction of H atoms on the surface.			✓
The rate determining step is adsorption of the second H atom.		✓	
The implicit assumption that reaction can take place regardless of the number of atoms adsorbed leads to substantial error (at least a factor of two).	✓		
Limiting the number of atoms adsorbed on the particle to 2 leads to substantial error (at least a factor of two).			✓

PROBLEM 3

Protein Folding

The unfolding reaction for many small proteins can be represented by the equilibrium:

$$\text{Folded} \rightleftharpoons \text{Unfolded}$$

You may assume that the protein folding reaction takes place in a single step. The position of this equilibrium changes with temperature; the melting temperature T_m is defined as the temperature at which half of the molecules are unfolded and half are folded.

The intensity of the fluorescence signal at a wavelength of 356 nm of a 1.0 μM (M = mol dm^{-3}) sample of the protein Chymotrypsin Inhibitor 2 (CI2) was measured as a function of temperature over the range 58 to 66 °C:

Temperature / °C	58	60	62	64	66
Fluorescence intensity (arbitrary units)	27	30	34	37	40

A 1.0 μM sample in which all of the protein molecules are folded gives a fluorescence signal of 21 units at 356 nm. A 1.0 μM sample in which all of the protein molecules are unfolded gives a fluorescence signal of 43 units.

3.1 Assuming that the fluorescence intensity from each species is directly proportional to its concentration, calculate the fraction, x, of unfolded molecules present at each temperature.

3.2 Give an expression for the equilibrium constant, K, in terms of x, and hence calculate the value of K at each temperature.

3.3 Estimate the value of T_m for this protein (to the nearest 1 °C).

Assuming that the values of ΔH^o and ΔS^o for the protein unfolding reaction are constant with temperature then:

$$\ln K = -\frac{\Delta H^o}{RT} + C$$

where C is a constant.

3.4 Plot a suitable graph and hence determine the values of ΔH^o and ΔS^o for the protein unfolding reaction.

[If you have been unable to calculate values for ΔH^o and ΔS^o, you should use the following incorrect values for the subsequent parts of the problem:
ΔH^o = 130 kJ mol^{-1}; ΔS^o = 250 J K^{-1} mol^{-1}.]

3.5 Calculate the equilibrium constant for the unfolding reaction at 25 °C.
[If you have been unable to calculate a value for K, you should use the following incorrect value for the subsequent parts of the problem: $K = 3.6 \cdot 10^{-6}$]

The first order rate constant for the CI2 protein folding reaction can be determined by following the fluorescence intensity when a sample of unfolded protein is allowed to refold (typically the pH of the solution is changed). The concentration of protein when a 1.0 µM sample of unfolded CI2 was allowed to refold was measured at a temperature of 25 °C:

time / ms	0	10	20	30	40
concentration / µM	1	0.64	0.36	0.23	0.14

3.6 Plot a suitable graph and hence determine the value of the rate constant for the protein folding reaction, k_f, at 25 °C.
[If you have been unable to calculate the value for k_f, you should use the following incorrect value for the subsequent parts of the question: k_f = 60 s^{-1}.]

3.7 Determine the value of the rate constant for the protein *unfolding* reaction, k_u, at 25 °C.

3.8 At 20 °C the rate constant for the protein folding reaction is 33 s^{-1}. Calculate the activation energy for the protein folding reaction.

SOLUTION

3.1

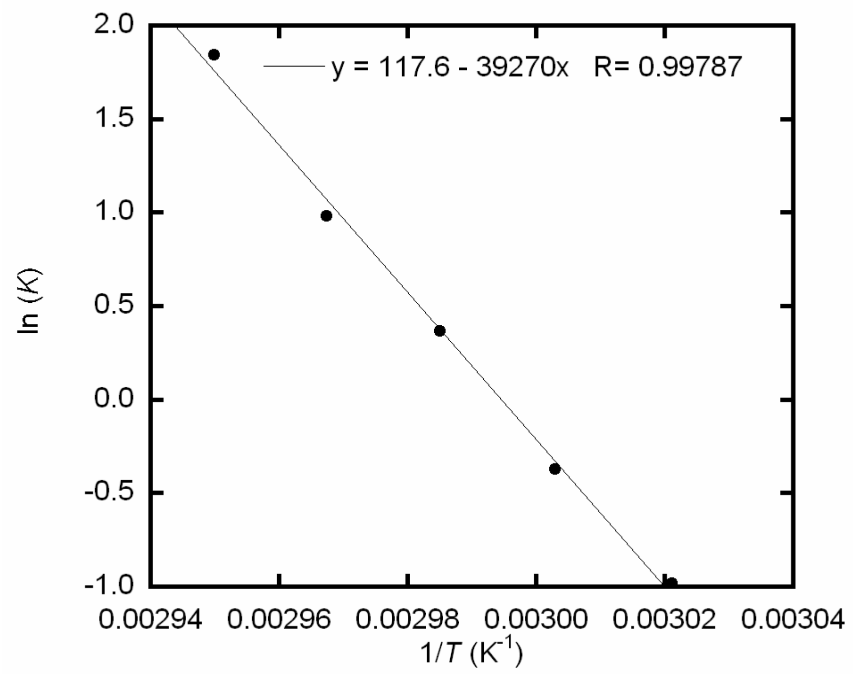
Temp / ℃	58	60	62	64	66
x	0.27	0.41	0.59	0.73	0.86

3.2

Temp / ℃	58	60	62	64	66
K	0.38	0.69	1.4	2.7	6.3

3.3 Answer: T_m = 61 ℃

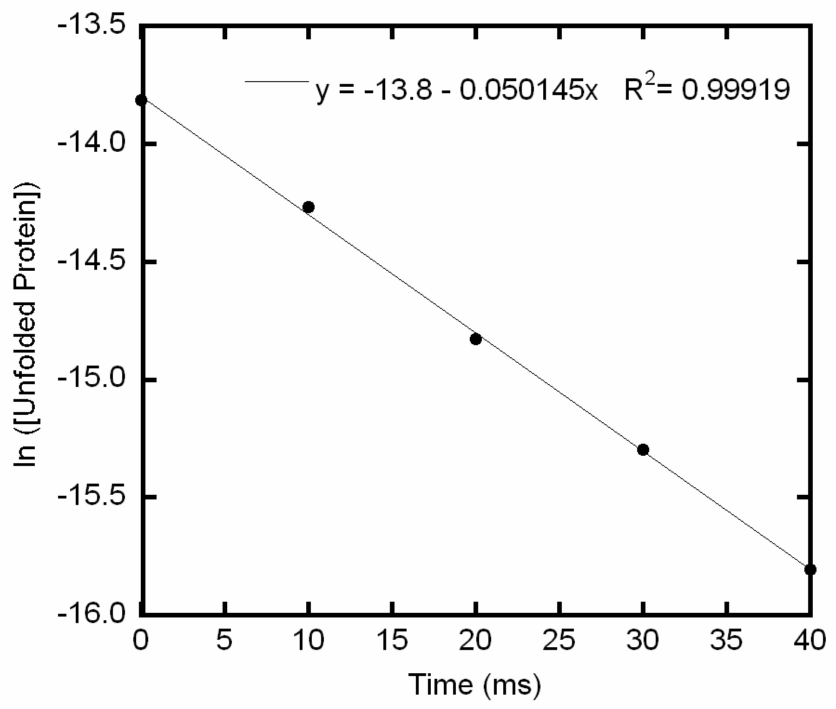
3.4



Answers: ΔH^o = 330 kJ mol^{-1} ; ΔS^o = 980 J mol^{-1} K^{-1}

3.5 ΔH^o = 330000 J mol^{-1} and ΔS^o= 980 J mol^{-1} K^{-1} then ΔG^o = 35000 J mol^{-1} at 25 ^{o}C, hence $K = 6.9 \cdot 10^{-7}$.

3.6



Answer: Rate constant for the protein folding reaction, $k_f = 50\ s^{-1}$.

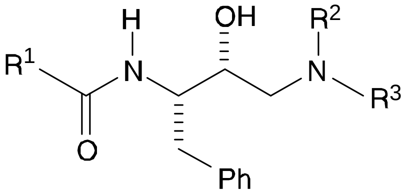
3.7 Answer: Rate constant for the protein *unfolding* reaction, $k_u = 3.5 \cdot 10^{-5}\ s^{-1}$.

3.8 Answer: Activation energy = 61 kJ mol^{-1}.

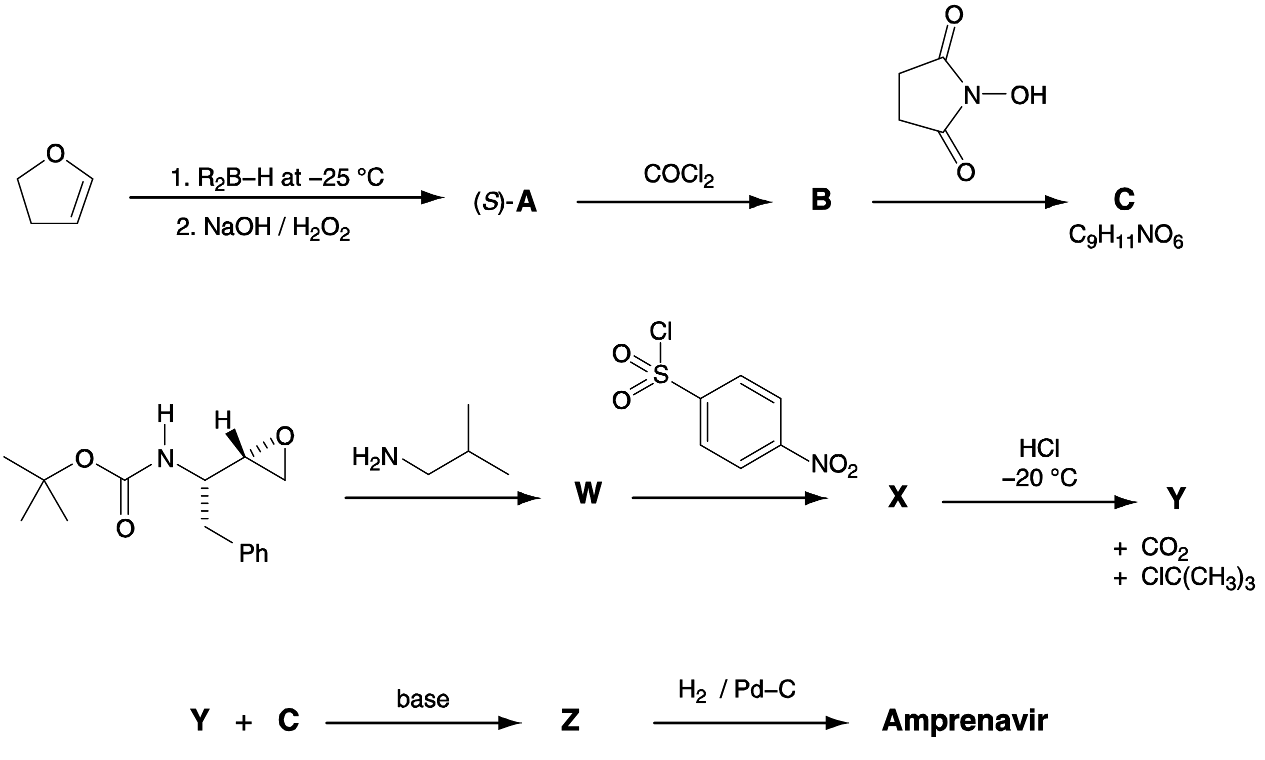
PROBLEM 4

Synthesis of Amprenavir

One class of anti-HIV drugs, known as *protease inhibitors*, works by blocking the active site of one of the enzymes used in assembly of the viruses within the host cell. Two successful drugs, *saquinavir* and *amprenavir*, contain the structural unit shown below which mimics the transition state within the enzyme. In the structure, R^1, R^2 and R^3 may represent any atom or group other than hydrogen.



Amprenavir may be synthesised as shown in the convergent scheme below.



The reagent R_2B-H used in the first step is chiral.

Product **A** is formed as the (*S*)-enantiomer.

Three of the signals in the ^{1}H NMR spectrum of Amprenavir disappear on shaking with D_2O: δ 4.2 (2H), δ 4.9 (1H) and δ 5.1 (1H).

4.1 Suggest structures for:

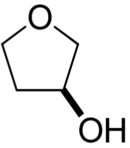
a) the intermediates **A**, **B**, **C**, **W**, **X**, **Y** and **Z**,

b) *Amprenavir*.

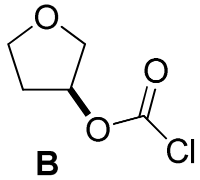
Your answers should clearly show the stereochemistry at each centre.

SOLUTION

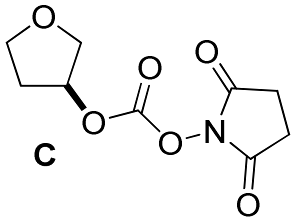
4.1



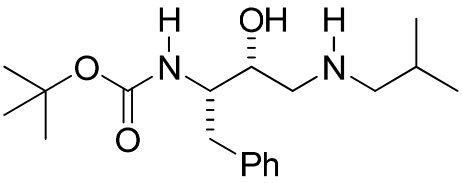
A



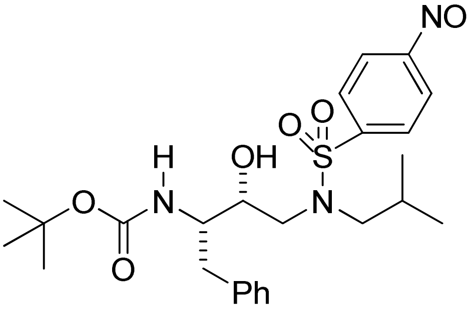
B



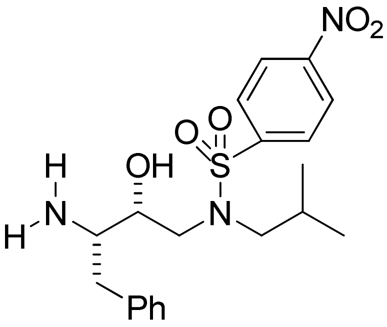
C



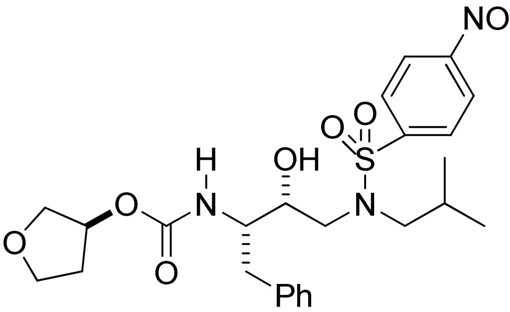
W



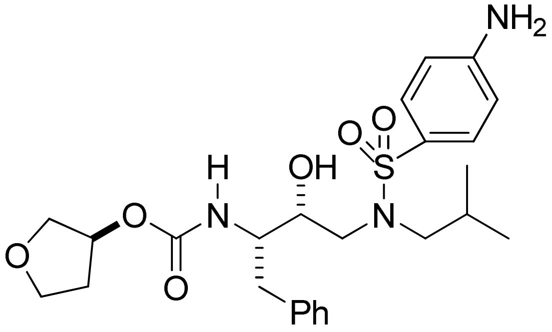
X



Y



Z

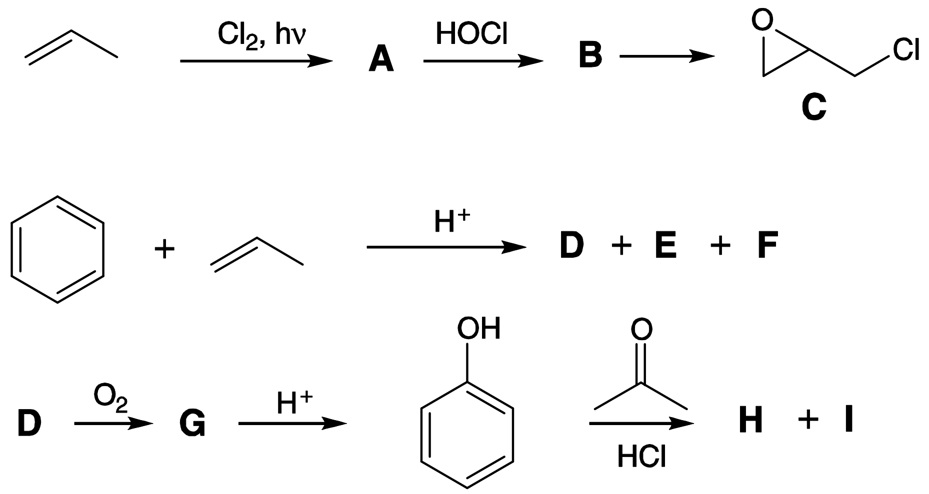


Amprenavir

PROBLEM 5

Epoxy resins

The synthesis of epoxy resins is a multi-billion dollar industry worldwide. Epoxy resins are high performance adhesives synthesised from the reaction of a bis-epoxide with a diamine. The bis-epoxide is made from **H** and epichlorohydrin, **C**. Compounds **C** and **H** can be synthesised according to the schemes below.



The synthesis of epichlorohydrin **C** begins with the reaction of propene with chlorine in the presence of light.

5.1 Draw the structures of **A** and **B**.

5.2 Give the formula of a suitable reagent for the conversion of **B** into epichlorohydrin **C**.

The synthesis of **H** commences with the reaction of benzene with propene in the presence of an acid catalyst which gives **D** as the major product and **E** and **F** as minor products.

5.3 Draw the structures of **D**, **E**, and **F** from the following data:

D: Elemental composition: C 89.94 %, H 10.06 %; 6 signals in the ^{13}C NMR spectrum.

E: Elemental composition: C 88.82 %, H 11.18 %; 4 signals in the ^{13}C NMR spectrum.

F: Elemental composition: C 88.82 %, H 11.18 %; 5 signals in the ^{13}C NMR spectrum.

Bubbling oxygen through a hot solution of **D** gives **G** which on exposure to acid gives phenol (hydroxybenzene) and acetone (propanone). **G** turns starch iodide paper from white to dark blue. **G** has 6 signals in the ^{13}C NMR spectrum and the following signals in the ^{1}H NMR spectrum: δ 7.78 (1H, s), 7.45 – 7.22 (5H, m), 1.56 (6H, s); addition of D_2O results in the disappearance of the signal at δ = 7.78.

5.4 Draw the structure of **G**.

Exposure of phenol and acetone to hydrochloric acid gives compound **H**. The ^{13}C NMR spectrum for **H** is shown in Fig. 1. The ^{1}H NMR spectrum is shown in Fig. 2 together with a four-fold expansion of the region 6.5 – 7.1 ppm. The ^{1}H NMR spectrum after the addition of a drop of D_2O, is shown in Fig. 3. Peaks due to the solvent are marked with an asterisk (*).

Fig. 1

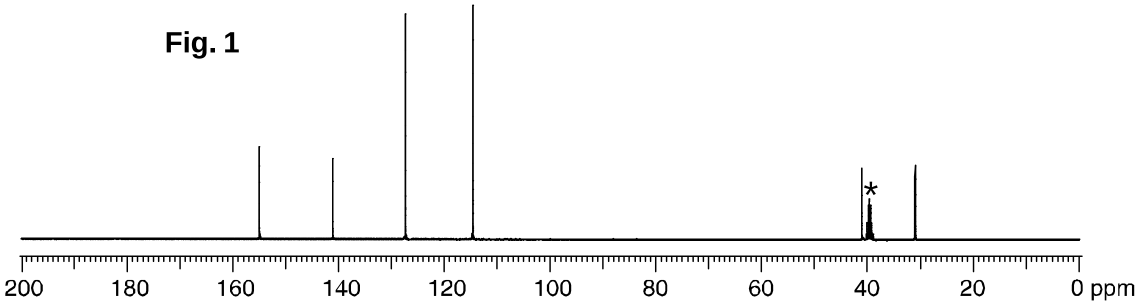


Fig. 2

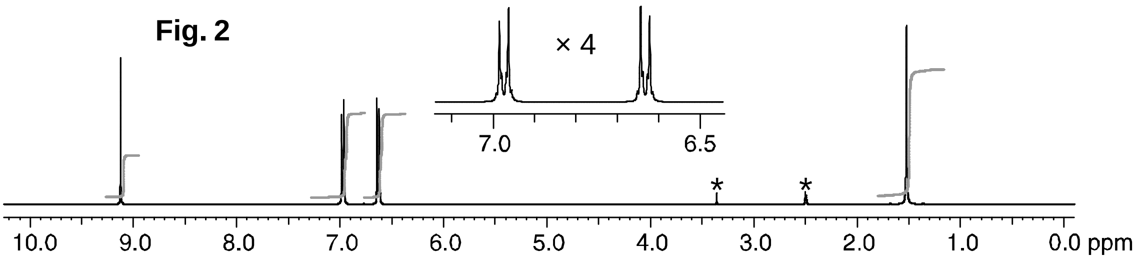
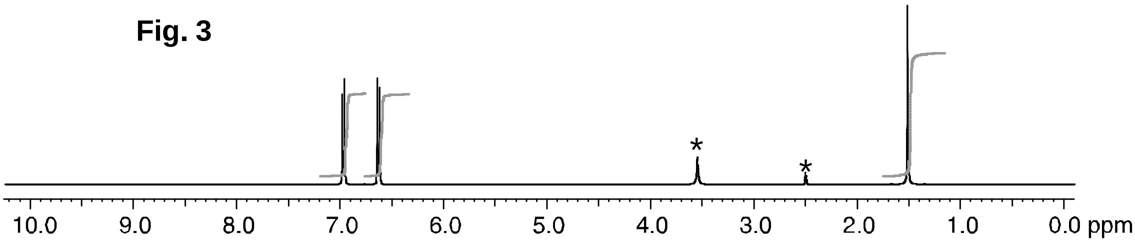


Fig. 3



5.5 Draw the structure of **H**.

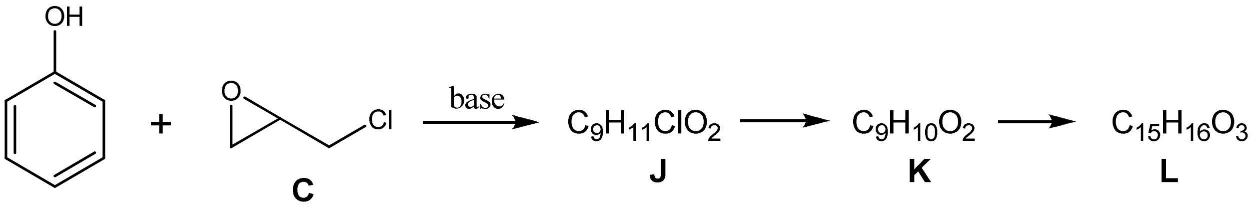
5.6 Draw one resonance structure of phenol which explains the regioselective formation of **H**.

A second compound, **I**, is also formed in the reaction of phenol with acetone. The ^{13}C NMR spectrum of **I** has 12 signals. The ^{1}H NMR spectrum has the following signals:

δ 7.50 – 6.51 (8H, m), 5.19 (1H, s), 4.45 (1H, s), 1.67 (6H, s); addition of D_2O results in the disappearance of the signals at δ = 5.19 and 4.45

5.7 Draw a structure for **I**.

Excess phenol reacts with epichlorohydrin **C** in the presence of base to give compound **L** which has 6 signals in its ^{13}C NMR spectrum. If the reaction is stopped before completion compounds **J** and **K** can also be isolated. Compound **L** is formed from compound **K** and compound **K** is formed from compound **J**.



5.8 Draw the structures of **J**, **K** and **L**.

Treatment of **H** with a large excess of epichlorohydrin **C** and base gives a monomeric bis-epoxide **M**. **M** contains no chlorine atoms or OH groups.

5.9 Draw the structure of **M**.

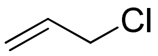
Treatment of **H** with a small excess of epichlorohydrin and base gives **N**. **N** has the form: endgroup 1-[repeat unit]$_n$-endgroup 2 where *n* is approximately 10 – 15. **N** does not contain chlorine atoms and contains one OH group per repeat unit.

5.10 Draw the structure of **N** in the form indicated above:
(endgroup 1-[repeat unit]$_n$-endgroup 2).

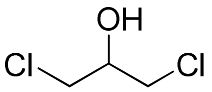
5.11 Draw the repeat unit of the polymeric epoxy resin **O** formed from the reaction of the bis-epoxide **M** with ethane-1,2-diamine.

SOLUTION

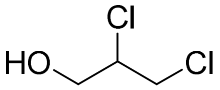
5.1



A



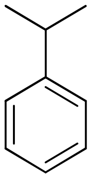
and / or



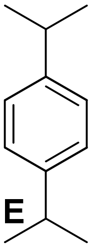
B

5.2 NaOH, or the formula of another suitable base.

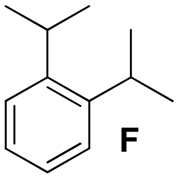
5.3



D



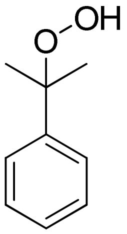
E



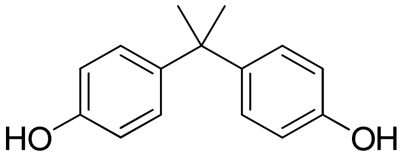
F

5.4

G

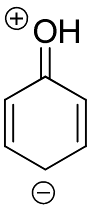


5.5

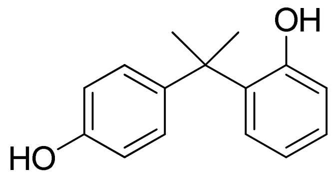


H

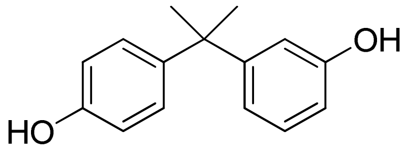
5.6



5.7

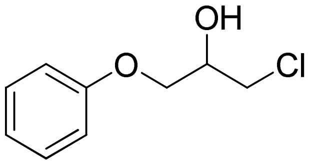


I

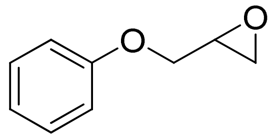


also fits the data

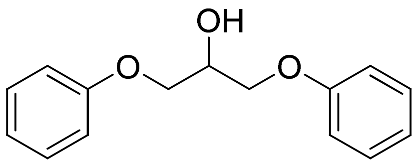
5.8



J

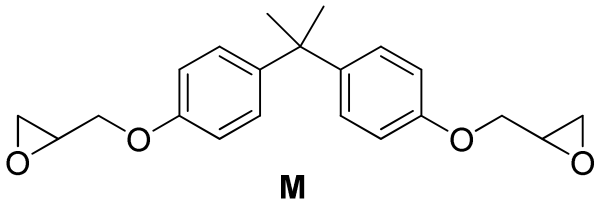


K



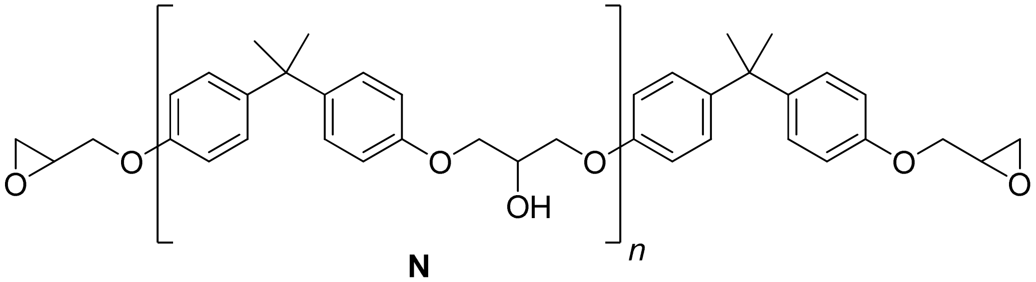
L

5.9



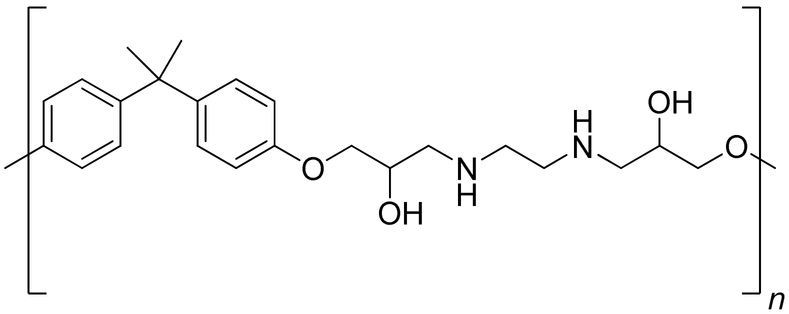
M

5.10



N

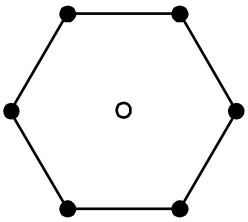
5.11



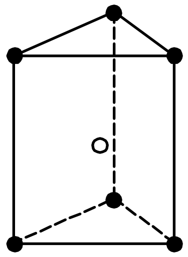
PROBLEM 6

Transition metal complexes

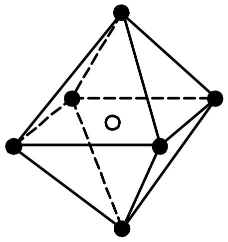
Alfred Werner used the technique of 'isomer counting' to deduce the structure of metal complexes with coordination number six. Three of the shapes he considered are shown below.



X



Y



Z

In each structure, the empty circle shows the location of the central metal atom and the filled circles show the location of the ligands. Structure **X** is hexagonal planar, structure **Y** is trigonal prismatic and structure **Z** is octahedral.

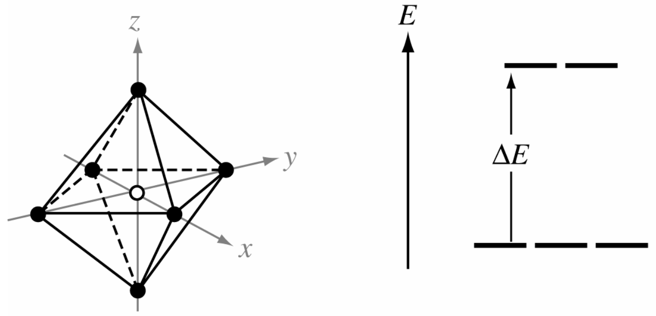
For each of the three shapes, there is just one structure when all of the ligands are the same, i.e. when the complex has the general formula MA_6 where A is the ligand. However, when achiral ligands A are substituted by one or more achiral ligands, it may be possible for each structure to form geometrical isomers. It might also be possible for one or more of the geometrical isomers to be optically active and exist as pairs of enantiomers.

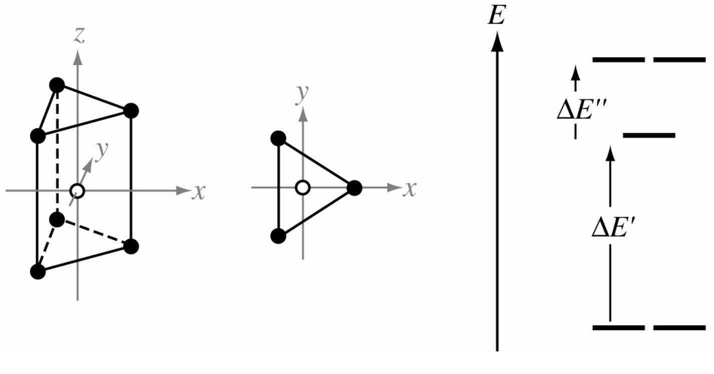
6.1 Fill in the table below to indicate how many geometrical isomers may be formed for each structure **X**, **Y**, and **Z** as the monodentate ligands A are substituted by mono-dentate ligands B or by symmetrical bidentate ligands, denoted C–C. Bidentate ligand C–C can only link between two atoms on adjacent positions, i.e. those positions connected by a line in the structures **X**, **Y**, and **Z**.

In each case write the number of geometrical isomers in the space provided. If one of the isomers exists as a pair of enantiomers, include an asterisk, *****, in the box. If two exist as two pairs of enantiomers, include two asterisks and so on. For example, if you think there are five geometrical isomers of a particular structure, three of which exist as pairs of enantiomers, write 5 *******

	Number of predicted geometrical isomers		
	Hexagonal planar **X**	Trigonal Prismatic **Y**	Octahedral **Z**
MA_6	1	1	1
MA_5B			
MA_4B_2			
MA_3B_3			
MA_4(C-C)			
$MA_2(C\text{-}C)_2$			
M$(C\text{-}C)_3$			

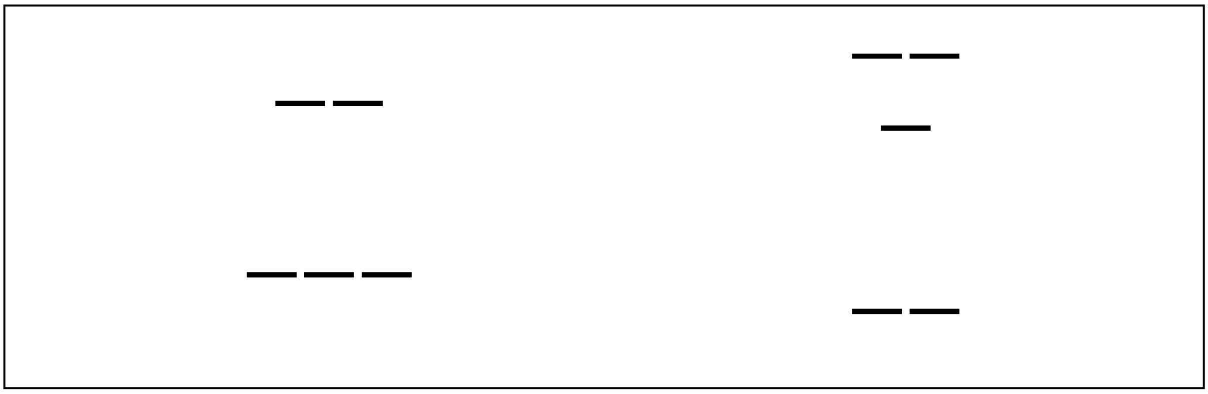
There are no known complexes that adopt the hexagonal planar geometry **X**, but structures are known for both the trigonal prismatic geometry **Y** and the octahedral geometry **Z**. In these complexes, the orbitals derived from the metal d orbitals have different energies depending on the geometry of the complex. The splitting patterns for the trigonal prismatic geometry and for the octahedral geometry are shown below.





The separations in energy, ΔE, $\Delta E'$ and $\Delta E''$ depend on the particular complex.

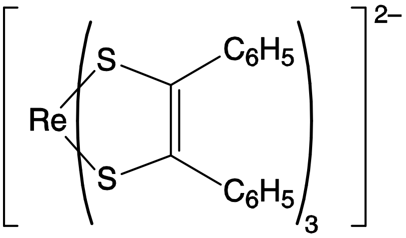
6.2 For each of the splitting patterns shown below label which d orbitals are which.



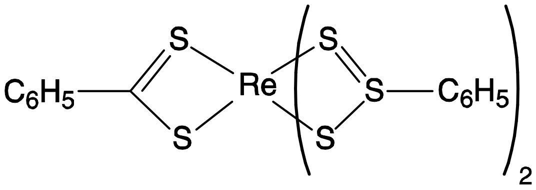
The two complexes $[Mn(H_2O)_6]^{2+}$ and $[Mn(CN)_6]^{2-}$ are both octahedral. One has a magnetic moment of 5.9 BM, the other has a magnetic moment of 3.8 BM but you must decide which is which.

6.3 On the diagram below, draw the electronic arrangements for each of the complexes.

The magnetic moments of complexes **A** and **B** shown below have been measured and found to be 1.9 and 2.7 BM but you must decide which is which.



A



B

6.4 Draw the orbital splitting diagrams for the two complexes, including the arrangements of the electrons.

Octahedral complexes are far more common than trigonal prismatic. Werner isolated five compounds **C** – **G** containing Co(III), Cl, and NH_3 only, each of which contained one octahedral complex. (There is actually a sixth compound but Werner could not isolate it.) Werner's five compounds had the molar conductivities shown below. The conductivities are extrapolated to infinite dilution and are expressed in arbitrary units. Compound **G** does not react with aqueous $AgNO_3$; compounds **C**, **D**, and **E** react with different stoichiometric ratios of aqueous $AgNO_3$; **E** and **F** react with the same stoichiometric ratio of aqueous $AgNO_3$.

	C	**D**	**E**	**F**	**G**
molar conductivity	510	372	249	249	~0

6.5 As far as you are able, suggest a structure for each of the compounds **C** – **G**.

Werner was also the first person to separate the enantiomers of an octahedral compound, **H**, which contained no carbon atoms. The compound, **H**, is composed of only cobalt, ammonia, chloride and an oxygen species which could be either H_2O, or HO^- or O^{2-}. The compound contains octahedrally coordinated cobalt ions. All of the chloride is easily removed from the compound by titration with aqueous silver nitrate. A 0.2872 g sample of **H** (containing no water of crystallization) required 22.8 cm^3 of a silver nitrate solution (c = 0.100 mol dm^{-3}) to exchange all of the chloride.

6.6 Calculate the percentage, by mass, of chloride in **H**.

H is stable to acids, but is hydrolysed in alkali. A 0.7934 g sample of **H** (containing no water of crystallization) was heated with excess aqueous sodium hydroxide. Cobalt(III) oxide was formed and ammonia gas given off. The ammonia produced was distilled off and absorbed into 50.0 cm^3 of aqueous HCl (c_{HCl} = 0.500 mol dm^{-3}). The residual HCl required 24.8 cm^3 of aqueous KOH solution (c_{KOH} = 0.500 mol dm^{-3}) to be neutralized.

The remaining suspension of cobalt(III) oxide was allowed to cool, approximately 1 g of potassium iodide was added, and then the mixture was acidified with aqueous HCl. The liberated iodine was then titrated with aqueous solution of sodium thiosulfate (c = 0.200 mol dm^{-3}) and required 21.0 cm^3 for complete reaction.

6.7 Calculate the percentage, by mass, of ammonia in **H**.

6.8 Give the equation for the reaction of cobalt(III) oxide with potassium iodide in aqueous acid.

6.9 Calculate the percentage, by mass, of cobalt in **H**.

6.10 Calculate the identity of the oxygen species contained in **H**. Show your working.

6.11 Give the empirical formula of **H**.

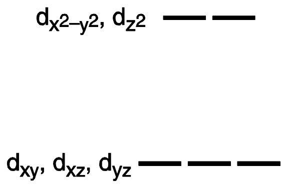
6.12 Suggest a structure for the chiral compound **H**.

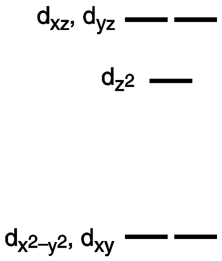
SOLUTION

6.1

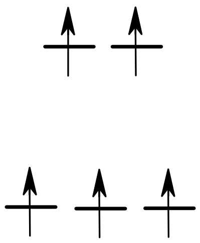
	Number of predicted geometrical isomers		
	Hexagonal planar **X**	Trigonal Prismatic **Y**	Octahedral **Z**
MA_6	1	1	1
MA_5B	1	1	1
MA_4B_2	3	3*	2
MA_3B_3	3	3*	2
MA_4(C-C)	1	2	1
MA_2(C-C)$_2$	2	4*	2*
M(C-C)$_3$	1	2	1*

6.2

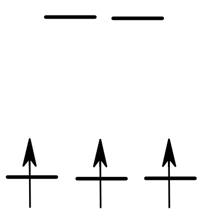




6.3

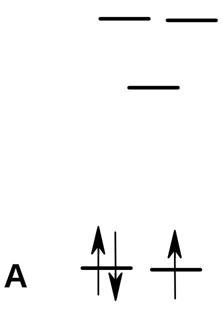


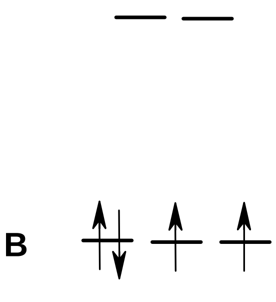
[Mn(H$_2$O)$_6$]$^{2+}$



[Mn(CN)$_6$]$^{2-}$

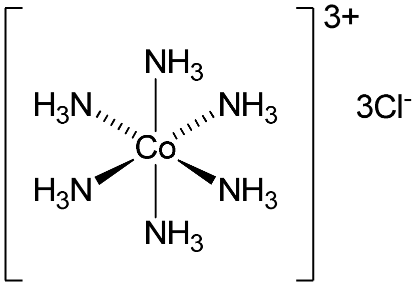
6.4



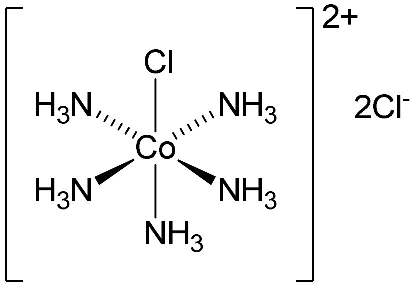


6.5

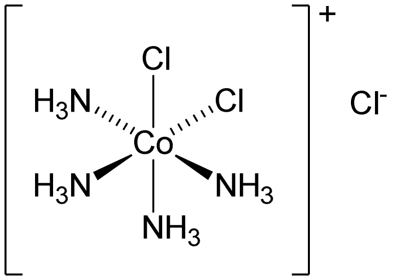
C



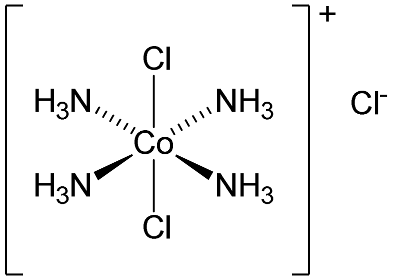
D



E

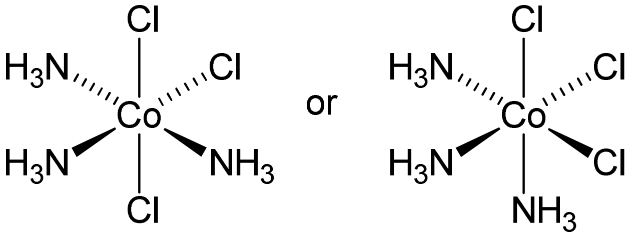


F



E and F could be either way round

G



6.6 $n(Ag^+) = 0.100 \text{ mol dm}^{-3} \times 0.0228 \text{ dm}^3 = 2.28 \cdot 10^{-3} \text{ mol}$

$n(Cl^-) = 2.28 \cdot 10^{-3} \text{ mol}$

$m(Cl) = 8.083 \cdot 10^{-2} \text{ g}$

$$\% \text{ Cl} = \frac{8.083 \cdot 10^{-2} \text{ g}}{0.2872 \text{ g}} \times 100 = 28.1$$

6.7 $n(KOH) = 0.0124 \text{ mol}$

$n(HCl)$ neutralised by ammonia = 0.025 mol – 0.0124 mol = 0.0126 mol

$m(NH_3) = 17.034 \text{ g mol}^{-1} \times 0.0126 \text{ mol} = 0.2146 \text{ g}$

$$\% \ NH_3 = \frac{0.2146 \text{ g}}{0.7934 \text{ g}} \times 100 = 27.1 \%$$

6.8 $Co_2O_3 + 2 \ KI + 6 \ HCl \rightarrow 2 \ CoCl_2 + I_2 + 3 \ H_2O + 2 \ KCl$

6.9 $2 \ Na_2S_2O_3 + I_2 \rightarrow 2 \ NaI + Na_2S_4O_6$

$n(Na_2S_2O_3) = 0.200 \text{ mol dm}^{-3} \times 0.021 \text{ dm}^3 = 4.20 \cdot 10^{-3} \text{ mol}$

$n(I_2) = 2.10 \cdot 10^{-3} \text{ mol}$

$n(Co^{2+}) = 4.20 \cdot 10^{-3} \text{ mol}$

$m(Co) = 4.20 \cdot 10^{-3} \text{ mol} \times 58.93 \text{ g mol}^{-1} = 0.2475 \text{ g}$

$$\% \text{ Co by mass} = \frac{0.2475 \text{ g}}{0.7934 \text{ g}} \times 100 = 31.2$$

6.10 Assuming 100 g of complex, there is 13.6 g unaccounted. for molar ratio of

$$n(Co) : n(NH_3) : n(Cl) = \frac{31.2}{58.93} : \frac{27.1}{17.034} : \frac{28.1}{35.453} = 0.529 : 1.591 : 0.7926 = 2 : 6 : 3.$$

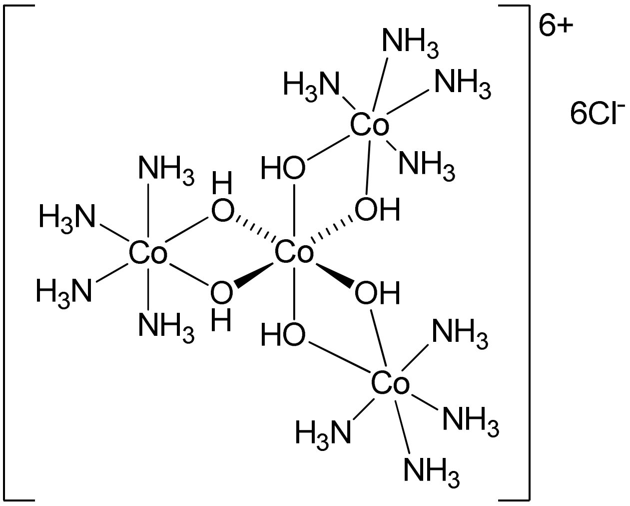
Missing species is either O^{2-}, OH^- or H_2O with similar molar mass ≈ 17 g mol^{-1}.

Molar fraction of missing oxygen species ≈ 13.6 / 17 = 0.8 i.e. the same as the Cl.

Considering charge balance, 2(+3) + 6(0) + 3(–1) = +3, it is needed –3 to balance i.e. the missing species must be OH^-.

6.11 Empirical formula of H: $Co_2 \ N_6 \ H_{21} \ O_3 \ Cl_3$

6.12 Structure must fit the empirical formula worked out above, contain only octahedral cobalt, and be chiral. Some marks deducted if chloride is directly coordinated to cobalt, or if any single ammonia molecule is coordinated to more than one cobalt atom.

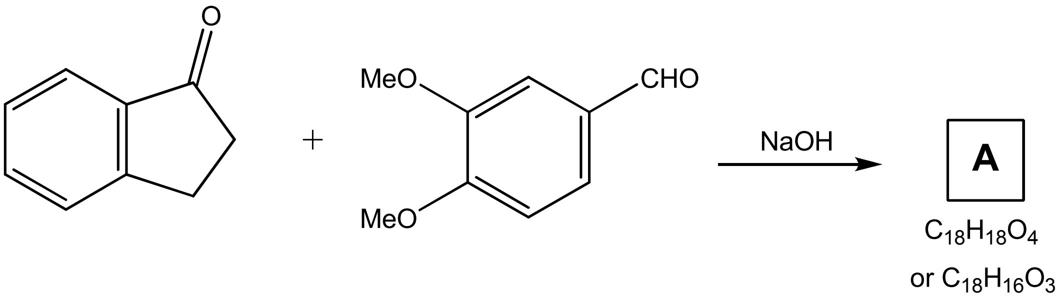


PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

An Environmentally Friendly Aldol Condensation

In attempts to become more environmentally friendly, increasing attention is being paid to minimising the large amounts of solvents used in chemical reactions. In the following experiment, an aldol condensation reaction is carried out in the absence of solvent.



Chemicals

- 3,4-dimethoxybenzaldehyde, 0.50 g pre-weighed in vial,
- 1-indanone, 0.40 g pre-weighed in vial,
- NaOH, 0.10 g pre-weighed in vial,
- HCl, aqueous solution, c = 3.0 mol dm^{-3}, 10 cm^3 in a bottle,
- Diethyl ether : Heptane (1:1), 25 cm^3 in a bottle,
- Ethyl ethanoate, 1 cm^3 in a small vial,
- Sample of 1-indanone dissolved in ethyl ethanoate, 1.0 cm^3 in small vial,
- Sample of 3,4-dimethoxybenzaldehyde dissolved in ethyl ethanoate, 1.0 cm^3 in small vial,
- Ethyl alcohol (9:1 mixture with H_2O): 100 cm^3 in a bottle.

Procedure

(a) Add 3,4-dimethoxybenzaldehyde (DMBA 0.50 g, 3.0 mmol) and 1-indanone (0.40 g, 3.0 mmol) to a 25 cm^3 beaker. Use a metal spatula to scrape and crush the two solids together until they become a clear oil.

(b) Add NaOH (0.1 g, 2.5 mmol) to the reaction mixture, crush any lumps formed and continue scraping and crushing until the mixture becomes solid.

(c) Allow the mixture to stand for 20 minutes. Then add 4 cm^3 of aqueous HCl solution (c = 3 mol dm^{-3}) and scrape around the beaker so as to dislodge all product from the walls. Use a flat-ended glass rod to crush any lumps present.

1.1 Measure and record the pH of the solution.

(d) Isolate the crude product using vacuum filtration through a Hirsch funnel. Rinse out the beaker with 2 cm^3 of aqueous HCl solution (c = 3 mol dm^{-3}) and pour over the crude product in Hirsch funnel to wash, continuing to pull air through the solid for 10 minutes to facilitate drying.

1.2 Report the mass of the crude product (which may still be a little wet), using the vial labelled 'CPA' as a container.

(e) Take a TLC to assess whether the reaction is complete, using Et_2O : heptane (1 : 1) as the eluant. Solutions of both starting materials in ethyl ethanoate are provided. The crude product is soluble in ethyl ethanoate.

[Note: Three TLC plates are provided. You may use them all, but you must only submit *one* in your labelled Ziploc bag. This should be the plate that you draw in your answer booklet.]

1.3 Using UV light to visualize, draw around the spots on the plate in pencil to show where they are, copy your plate onto the answer sheet, and place your plate in the Ziploc bag labelled with your student code.

Determine and record the relevant R_F values.

(f) Using a 100 cm^3 conical flask with a stir bar in the bottom, recrystallize the product from a mixture of EtOH : H_2O (9 : 1). (N.B. A hot filtration, using the glass funnel provided, is required as part of this process to remove small amounts of insoluble impurities.) Any lumps may be crushed using the flat-ended glass rod. Allow the conical flask containing the filtered solution to cool to room temperature and then cool in an ice bath (use the polystyrene tray to make the ice bath in) for one hour before filtration through a Büchner funnel to collect your product. Suck air through for 10 minutes to dry the product. Place your product in the vial marked with your code and labelled 'RPA'.

1.4 Report the mass of the purified product.

Product **A** could have one of the two formulae: $C_{18}H_{18}O_4$ or $C_{18}H_{16}O_3$.

1.5 Draw the structure of every geometrical and/or stereoisomer with formula:

i) $C_{18}H_{18}O_4$,

ii) $C_{18}H_{16}O_3$

that could be formed in this reaction. Indicate how many peaks you would expect in total in the ^{13}C NMR spectrum of each.

1.6 The ^{13}C NMR spectrum for **A** is shown in the practical instructions. Peaks due to the solvent, $CDCl_3$, are marked with an asterisk. With the aid of the spectrum, decide which is the correct formula for **A**. Mark on the answer sheet one of the two boxes below to indicate which you have chosen:

$C_{18}H_{18}O_4$: ☐ $C_{18}H_{16}O_3$: ☐

1.7 Report the mass and calculate the percentage yield of the purified product, based on the formula you gave for its structure.

SOLUTION

1.1 Values of pH = 1 – 2 are accepted.

1.2 Because the sample is not completely dry, often this mass is above 100 % of that expected. Usual range is 800 – 1000 mg (94 – 117 %). Zero points for any less than 400 mg (product has been lost).

1.3 Evaluation:

Maximum points if both standards plus crude product are present and no starting materials remain and student has co-spotted crude product with one or both starting materials and solvent front is marked and plate is not over- or under-loaded.

Minus points if:

- plate has no co-spots,
- substantial amount of either or both starting materials remain,
- over- or under-loading occurs which does not interfere with evaluation,
- over- or under-loading occurs and does interfere with evaluation,
- over- or under-loading occurs and prevents evaluation,
- any sample is missing.

The relevant R_F values:

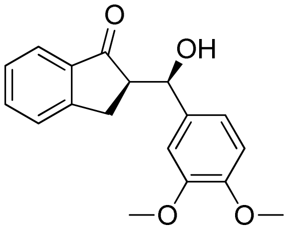
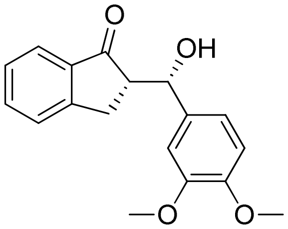
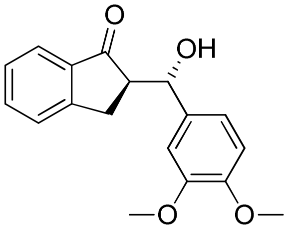
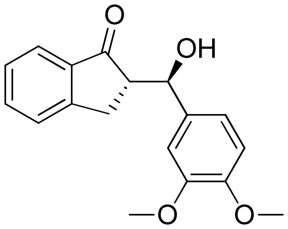
Chemical	R_F
3,4-DMBA	0.16 – 0.25
1-Indanone	0.34 – 0.43
CPA	0.11 – 0.20

Maximum points if both starting materials and reaction product are present with R_f values which fall within those given.

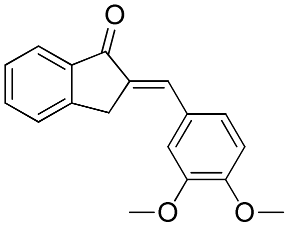
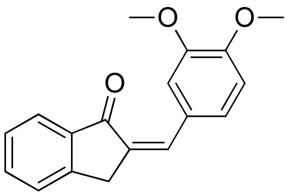
Minus points if:

- R_F values are missing for one or more chemicals,
- both starting materials and reaction product are present with R_F values which fall outside those given due to the plate running too long or the student having marked the solvent front incorrectly,
- both starting materials and reaction product are present with R_F values which fall outside those given, due to an inability to calculate R_F values.

1.4 For $C_{18}H_{18}O_4$:

Structure	Number of ^{13}C NMR signals expected:
	18
	18
	18
	18

For $C_{18}H_{16}O_3$:

Structure	Number of ^{13}C NMR signals expected:
	18
	18

1.5 $C_{18}H_{16}O_3$: ☑

1.6 Mass: 0.5 g (example mass of product)

Calculation:

For formula $\mathbf{C_{18}H_{18}O_4}$: Molar mass = 298.324 g mol^{-1}

Expect: 0.3 mmol maximum = 0.895 g

$$\frac{0.5\ \text{g}}{0.895\ \text{g}} \times 100 = 56\ \%$$

For formula $\mathbf{C_{18}H_{16}O_3}$: Molar mass = 280.308 g mol^{-1}

Expect: 0.3 mmol maximum = 0.841 g

$$\frac{0.5\ \text{g}}{0.841\ \text{g}} \times 100 = 59.5\ \%$$

YIELD:

The samples were also weighed by the organizer, before and after drying for one hour in a vacuum desiccator. Sample purity was then checked by ^{1}H and ^{13}C NMR. The evaluations of the results were adapted to the results obtained by the above measurements.

PROBLEM 2 (Practical)

Analysis of a Copper(II) Complex

You are provided with a sample of an inorganic copper(II) complex, the anion of which is made from copper, chlorine, and oxygen. The counter ion is the tetramethyl ammonium cation. There is no water of crystallisation. You are required to determine proportions of copper ions and chloride ions by titration and hence determine the composition of the complex.

Chemicals

- Inorganic complex: three samples of approximately 0.1 g, accurately pre-weighed in vials labelled 'Sample 1', 'Sample 2', 'Sample 3'.
- Inorganic complex: three samples of approximately 0.2 g, accurately pre-weighed in vials labelled 'Sample 4', 'Sample 5' and 'Sample 6'.
- pH 10 ammonia buffer, 10 cm^3.
- Murexide indicator, solution in H_2O, 10 cm^3.
- EDTA disodium salt, aqueous solution, c = 0.0200 mol dm^{-3}, 150 cm^3.
- Ethanoic acid, 10 cm^3.
- 2,7-Dichlorofluorescein indicator, solution in 7 : 3 EtOH : H_2O), 10 cm^3.
- Dextrin, 2 % solution in H_2O, 25 cm^3.
- Silver nitrate, aqueous solution, c = 0.1000 mol dm^{-3}, 150 cm^3.

Procedure

Titration to determine the proportion of copper ions

(a) You are provided with three accurately pre-weighed samples of copper complex, each of approximately 0.1 g. These are labelled "Sample 1", "Sample 2", "Sample 3", together with the exact mass of the copper complex. Take the first of these, note down the mass of the sample and quantitatively transfer the contents to a 250 cm^3 conical flask using approximately 25 cm^3 of water.

(b) Add pH 10 ammonia buffer solution until the precipitate which forms initially just redissolves (about 10 drops).

(c) Add 10 drops of the murexide indicator.

(d) Titrate with the 0.0200 mol dm^{-3} EDTA solution until the solution turns violet and the colour persists for at least 15 seconds. Record the volume of solution used in the titration.

(e) Repeat if necessary with samples 2 and 3.

Note: You will be marked only on a single value you report in the answer booklet. This may either be an average value, or a single value you feel most confident in.

2.1 Calculate the volume of EDTA solution needed to react completely with 0.100 g of complex.

2.2 Give an equation for the titration reaction.

2.3 Calculate the percentage by mass of copper in the sample.

You will need to wash out your burette before you start the titration for the determination of chloride ions. Any remaining EDTA solution may be disposed of into the waste containers labelled 'EDTA'.

Titration to determine the proportion of chloride ions present

(f) You are provided with three accurately pre-weighed samples of copper complex each of approximately 0.2 g. These are labelled "Sample 4", "Sample 5", "Sample 6", together with the exact mass of the copper complex. Take the first of these, note down the mass of the sample and quantitatively transfer the contents to a 250 cm^3 conical flask using approximately 25 cm^3 of water.

(g) Add 5 drops of ethanoic acid, followed by 10 drops of dichlorofluorescein indicator and 5 cm^3 dextrin (2 % suspension in water). Shake the bottle well before adding the dextrin suspension.

(h) Titrate with the 0.1000 mol dm^{-3} silver nitrate solution, swirling constantly until the white suspension turns pink and the colour does not disappear after swirling.

(i) Repeat if necessary.

Note: You will be marked only on a single value you report in the answer booklet. This may either be an average value, or the value you feel most confident in.

2.4 Calculate the volume of silver nitrate solution needed to react completely with 0.200 g of complex.

2.5 Give an equation for the titration reaction.

2.6 Calculate the percentage by mass of chloride ions in the sample.

The percentage of carbon, hydrogen and nitrogen in the complex was determined by combustion analysis and found to be as follows:

Carbon: 20.87 %; Hydrogen: 5.17 %; Nitrogen: 5.96 %.

2.7 Mark in the answer booklet, which element in the complex has the greatest percentage error in the determination of its proportion.

Cu Cl O C H N

2.8 Determine the formula of the copper complex. Show your working.

SOLUTION

2.1 Full marks if answer is $V_{corr.}$ ± 0.1 cm^3. Zero marks if answer is less than ($V_{corr.}$ – 0.5 cm^3) or greater than ($V_{corr.}$ + 0.5 cm^3), linear point scale is applied in between.

2.2 $Cu^{2+} + EDTA^{4-} \rightarrow [Cu(EDTA)]^{2-}$

2.3 $n(\text{EDTA}) = 0.0200 \text{ mol dm}^{-3} \times V(\text{EDTA}) \text{ (in dm}^3) = (0.0200 \text{ mol dm}^{-3} \times V) \text{ mol}$

$n(\text{Cu}^{2+}) = (0.0200 \text{ mol dm}^{-3} \times V) \text{ mol}$

$m(\text{Cu}) = M(\text{Cu}) \times n(\text{Cu}) = 63.55 \text{ g mol}^{-1} \times (0.0200 \text{ mol dm}^{-3} \times V) \text{ mol}$

$$\% \text{ Cu} = \frac{m(\text{Cu})}{m(\text{sample})} \times 100$$

2.4 Full marks if answer is $V_{corr.}$ ± 0.1 cm^3.

Zero marks if answer is less than ($V_{corr.}$ – 0.5 cm^3) or greater than ($V_{corr.}$ + 0.5 cm^3), linear point scale is applied in between.

2.5 $Ag^+ + Cl^- \rightarrow AgCl$

2.6 $n(\text{Ag}^+) = 0.100 \text{ mol dm}^{-3} \times V(\text{Ag}^+) \text{ (in dm}^3) = (0.100 \text{ mol dm}^{-3} \times V) \text{ mol}$

$n(\text{Cl}^-) = (0.100 \text{ mol dm}^{-3} \times V) \text{ mol}$

$m(\text{Cl}) = M(\text{Cl}) \times n(\text{Cl}) = 35.45 \text{ g mol}^{-1} \times (0.100 \text{ mol dm}^{-3} \times V) \text{ mol}$

$$\% \text{ Cl} = \frac{m(\text{Cl})}{m(\text{sample})} \times 100$$

2.7 If the percentage of oxygen is calculated by subtracting all the others from 100, it has all the errors from the determination of the other elements combined. In practice this leads to a large error which affects the subsequent calculation of the formula unless this point is appreciated.

Cu Cl [✓ O] C H N

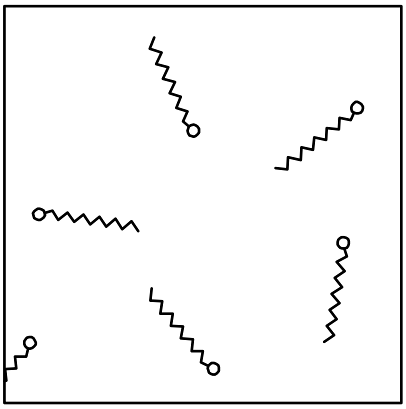
2.8 Full marks if the formula is correctly calculated from the student data and the large error in oxygen is taken into account (either by using one of the proportions of the other elements to determine the elemental ratios, or by a consideration of charge balance).

PROBLEM 3 (Practical)

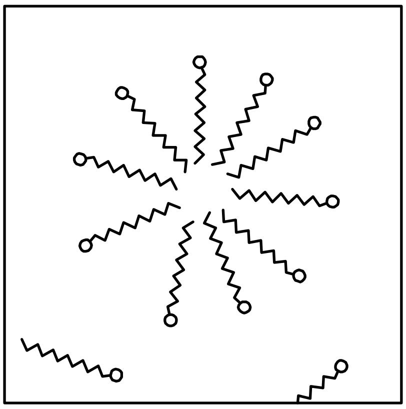
The Critical Micelle Concentration of a Surfactant

Surfactants are used extensively in many everyday cleaning products, such as shampoos or detergents for washing clothes. One such surfactant is SDS, sodium *n*-dodecyl sulfate, $CH_3(CH_2)_{11}OSO_3Na$ (Relative Molecular Mass: 288.37).

Very dilute aqueous solutions consist of solvated individual molecules of SDS. However, if the concentration is gradually increased beyond a specific concentration, the concentration of monomeric SDS does not change, but instead the surfactant begins to form clusters known as *micelles*. It is these micelles that assist in the removal of grease and dirt. The concentration at which the micelles form is called the *critical micelle concentration*. This process is shown schematically in the figure below.



low SDS concentration
free monomer only



high SDS concentration
micelles and some free monomer

In this experiment, you will determine the critical micelle concentration of SDS by measuring the conductivity of different concentrations of SDS.

Chemicals

- Sodium dodecyl sulphate, (99%), approximately 4.3 g, accurately pre-weighed in vial labelled 'SDS'.
- Conductivity solution 'HI 70031', 20 cm^3 in pouch.

Procedure

(a) You are provided with approximately 4.3 g SDS, accurately pre-weighed in a vial, a 250 cm^3 volumetric flask, a 50 cm^3 burette, 50 cm^3 bulb pipette, a conductivity meter, conductivity solution (used only for calibration), and a tall plastic vessel.

(b) You need to measure the conductivity (σ, in μS cm^{-1}) of various concentrations of aqueous SDS (c, up to 30 mmol dm^{-3}). [Note: You may assume that all volumes are additive.]

3.1 Give the concentration of your stock SDS solution.

3.2 Use the table given in the answer booklet to record your results and plot a suitable graph to determine the critical micelle concentration (CMC) on the paper provided.

3.3 State the concentration at which micelles begin to form (the critical micelle concentration).

Notes

1) Solutions of SDS readily form bubbles if shaken.

2) The conductivity meter needs at least 50 cm^3 of solution to be inside the plastic vessel in order to work correctly.

3) To calibrate the conductivity meter:
   - Switch the meter on by pressing the ON/OFF button once.
   - Press and hold the ON/OFF button again, this time for about 3 seconds, until you see the letters 'CAL' on the screen, indicating that the calibration mode has been entered. Let go of the ON/OFF button and '1413' will start blinking on the display. To calibrate, carry out the next step immediately, before the meter has reverted back to reading '0' on the screen (meaning you have exited the calibration mode)
   - Immerse the probe in the pouch containing the 'HI 70031' calibration solution, without exceeding the maximum immersion level.
   - Stir gently and wait for about 20 seconds to confirm the reading.
   - Once the display stops blinking, the meter is calibrated and ready for use.
   - Rinse the meter with distilled water and dry before making measurements.

4) To record the reading:
   - Switch the meter on by pressing the ON/OFF button.
   - Immerse the probe in the sample without exceeding the maximum immersion level and being above the minimum immersion level.

- Stir gently and wait for the reading to stabilize. The meter automatically compensates for temperature variations.
- The conductivity value of the sample will be shown on the LCD.

SOLUTION

3.1 Correct concentration with correct units is expected - full points.

Correct concentration but with missing or incorrect units - 1/2 points.

Note:

The evaluation of the graphs, constructed by competitors in this practical problem, differs from that used for grading especially titration results in the other practical problems. That is the reason why the evaluation in this particular case is given here more in detail.

3.2 Number and spread of data points

The graph should show two distinct gradients and the point at which the gradients change is the critical micelle concentration (CMC). The region where the concentrations are lower than the point at which the gradients change is referred to as “Region 1”; “Region 2” refers to the region where the concentrations are higher than this point. The gradient change will be taken from the data presented. If no gradient change is obvious the literature value of 8.3 mmol dm^{-3} will be used to distinguish between the two Sections.

Maximum marks are allotted if:

a) in Region 1 at least three points are distributed with a spacing of approx CMC/(n+1) mmol (where n is the number of points).

b) in Region 2 at least three points are distributed through a range of at least 10 mmol with a spacing of approx c/(n+1) mmol (where n is the number of points and c the concentration range and $c \geq$ 10 mmol dm^{-3}).

Indicating gradients

Straight lines plotted through experimental points with different gradients and extended to identify crossing points are expected.

Alternative graphs with marks allotted are shown below.

Accuracy of data

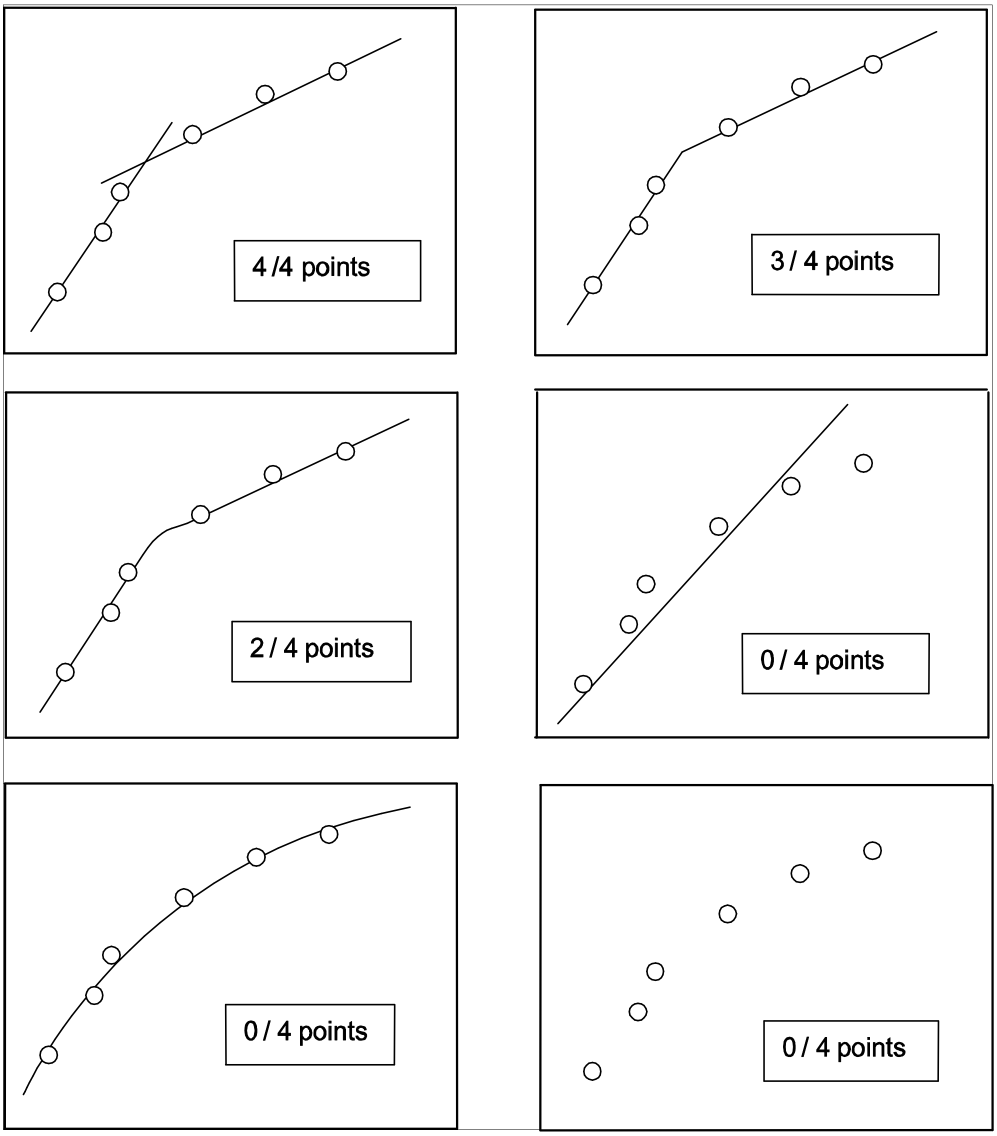
A transparent overlay will be used to judge the accuracy of the experimental measurements as plotted on the graph. If a systematic error in calculation can be determined from the table of data the graph will be re-plotted by the organisers for the purposes of this part of the marking.

The overlay has a number of bands marked and the marking scheme has been devised to reward careful experimental technique. There is one set of bands for Region 1 and another for Region 2. The bands are numbered from the innermost (band 1) to the outermost (band 5) (see Fig. 3.1).

The maximum number of points for each band is shown in the following table:

Band	1	2	3	4	5	Outside 5
Maximum number of points	10	8	6	4	2	0

Alternative graphs with marks allotted

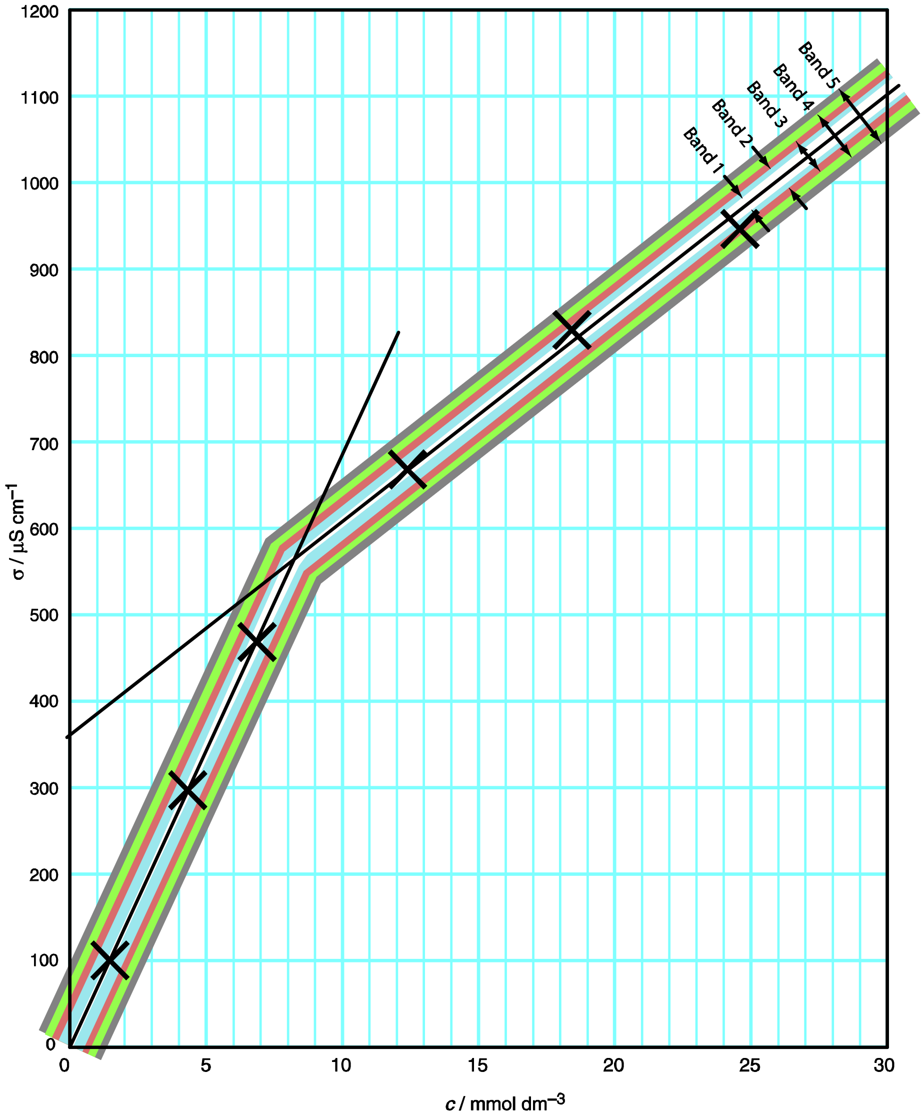


Points will be awarded as follows:

If there are three or more points in a Region and 50 % are in band *m* (where *m* is the number of the band) with none falling in band *m*+2 or beyond, the full marks for band *m* are awarded.

If *n*, the number of points in the Region, is less than 3, only (*n*/3) of the relevant band marks will be given (and rounded up to the nearest half-integer when necessary).

Fig. 3.1. Examples



In Region 1 all of the datapoints lie in Band 1 (cross hatched) so 10 points scored for that Region.

In section 2 one of the three datapoints lies in Band 1 (not 50%) but two lie in band 2. The remaining point does not lie in Band 4 (*m*+2) so full 8 points are scored.

3.3 Correct concentration as read from graph with correct units is expected.

42th

International Chemistry Olympiad

9 theoretical problems
3 practical problems

THE FORTY-SECOND
INTERNATIONAL CHEMISTRY OLYMPIAD
19–28 JULY 2010, TOKYO, JAPAN

THEORETICAL PROBLEMS

PROBLEM 1

In 1894, Lord Rayleigh reported that the mass of chemically prepared nitrogen was different from that of nitrogen extracted from the atmosphere, as shown in Tables 1 and 2. Later, this difference was attributed to the presence of argon in *atmospheric nitrogen*. The masses of gases were measured by using a glass vessel with a known volume under atmospheric pressure ($1.013 \cdot 10^5$ Pa).

Table 1. Mass of *Chemical Nitrogen* in the Vessel

From nitric oxide	2.3001 g
From nitrous oxide	2.2990 g
From ammonium nitrite purified at a red heat	2.2987 g
From urea	2.2985 g
From ammonium nitrite purified in the cold	2.2987 g
Mean	**2.2990 g**

Table 2. Mass of *Atmospheric Nitrogen* in the Vessel

O_2 was removed by hot copper (1892)	2.3103 g
O_2 was removed by hot iron (1893)	2.3100 g
O_2 was removed by ferrous hydrate (1894)	2.3102 g
Mean	**2.3102 g**

1.1 Calculate the volume V [m^3] of the vessel used by Rayleigh from the mean mass of *chemical nitrogen*, which must have been pure nitrogen. Assume that the measurements were carried out at a temperature of 15.0 °C.

1.2 Estimate the mole fraction x of argon in Rayleigh's *atmospheric nitrogen*, by assuming that argon and nitrogen were the only constituents. Use the mean masses of the *atmospheric* and *chemical nitrogen* for the calculation.

Ramsay and Clève discovered helium in cleveite (a mineral consisting of uranium oxide and oxides of lead, thorium, and rare earths; an impure variety of uraninite) independently and virtually simultaneously in 1895. The gas extracted from the rock showed a unique spectroscopic line at around 588 nm (indicated by D_3 in Figure 1), which was first observed in the spectrum of solar prominence during a total eclipse in 1868, near the well-known D_1 and D_2 lines of sodium.

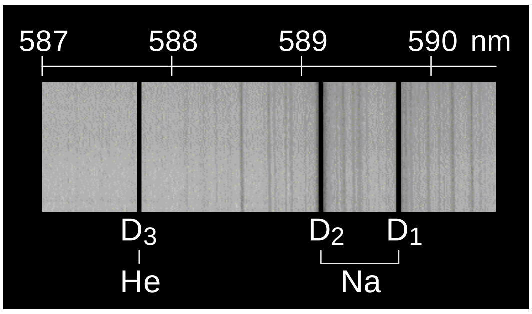


Figure 1. Spectral lines around 588 nm

1.3 Calculate the energy E [J] of a photon with the wavelength of the D_3 line of helium shown in Figure 1.

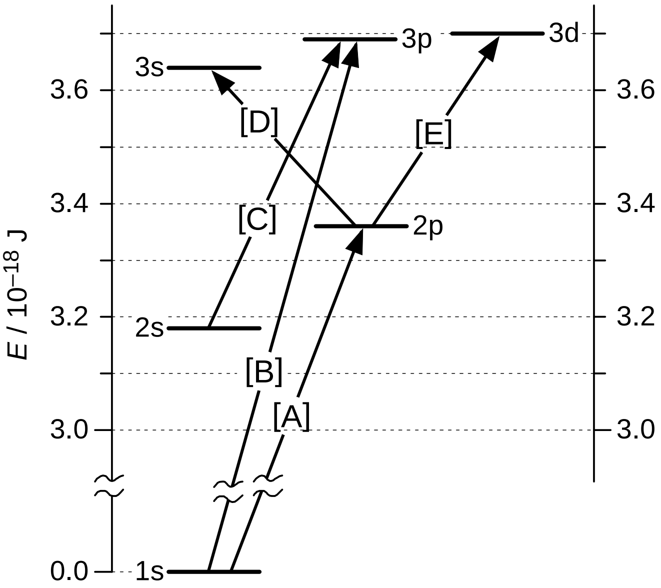


Figure 2.
Energy diagram of atomic orbitals of helium when an electron resides in the 1s orbital.

Figure 2 shows an energy diagram of the atomic orbitals of helium. The arrows indicate the "allowed" transitions according to the spectroscopic principle.

1.4 Identify the transition relevant to the D_3 line of helium among the transitions [A] to [E] indicated in Figure 2. Mark one of the following:

☐ [A] ☐ [B] ☐ [C] ☐ [D] ☐ [E]

1.5 Which equation explains the occurrence of helium in cleveite among [A] to [D] below? Mark one.

☐ [A] $^{238}U \rightarrow {}^{234}Th + \alpha$

☐ [B] $UHe_2 \rightarrow U + 2\ He$

☐ [C] $^{240}U \rightarrow {}^{240}Np + \beta^-$

☐ [D] $^{235}U + n \rightarrow {}^{95}Y + {}^{139}I + 2\ n$

Argon is also found in minerals such as *malacon*.

1.6 Which equation explains the occurrence of argon in rocks among [A] to [D] below? Mark one.

☐ [A] $ArF_2 \rightarrow Ar + F_2$

☐ [B] $ArXe \rightarrow Ar + Xe$

☐ [C] $^{40}K \rightarrow {}^{40}Ar + \varepsilon/\beta^+$ (electron capture / positron emission)

☐ [D] $^{126}I \rightarrow {}^{126}Ar + \beta^-$

One of the strongest evidences for the monoatomicity of argon and helium is the ratio of the heat capacity under constant pressure to that at constant volume, $\gamma = C_p / C_V$, which is exactly 5/3 (1.67 ± 0.01) for a monoatomic gas. The ratio was derived from the measurement of speed of sound v_s by using the following equation, where f and λ are the frequency and wavelength of the sound, and R, T, and M denote the molar gas constant, absolute temperature, and molar mass, respectively.

$$v_s = f\lambda = \sqrt{\frac{\gamma RT}{M}}$$

For an unknown gas sample, the wavelength of the sound was measured to be λ = 0.116 m at a frequency of f = 3520 Hz (Hz = s^{-1}) and temperature of 15.0 °C and under atmospheric pressure (1.013 ·10^5 Pa). The density ρ of the gas for these conditions was measured to be 0.850 ± 0.005 kg m^{-3}.

1.7 Calculate the molar mass M [kg mol^{-1}] of this gas.

1.8 Calculate the heat capacity ratio γ for this gas sample.

1.9 Which is this gas? Choose and mark among [A] to [D] .

☐ [A] HCl

☐ [B] HF

☐ [C] Ne

☐ [D] Ar

SOLUTION

1.1 The amount of the pure nitrogen (*chemical nitrogen*), M = 28.02 g mol^{-1}, is

$$n(N_2) = \frac{m(N_2)}{M(N_2)} = \frac{2.2990\ \text{g}}{28.02\ \text{g mol}^{-1}} = 8.205 \cdot 10^{-2}\ \text{mol}$$

$$V(N_2) = \frac{nRT}{p} = \frac{8.205 \cdot 10^{-2} \times 8.314 \times 288.15}{1.013 \cdot 10^{5}} = 1.940 \cdot 10^{-3}\ \text{m}^3$$

1.2 The equation for the ratio of the mass of *atmospheric nitrogen* to the mass of *chemical nitrogen* is

$$\frac{28.02\,(1-x) + 39.95\,x}{28.02} = \frac{2.3102}{2.2990}$$

Transformation gives

$$x = \frac{\dfrac{2.3102 - 2.2990}{2.2990}}{39.95 - 28.02} \times 28.02 = 1.14 \cdot 10^{-2}\ (\text{or } 1.14\ \%)$$

1.3 According to Figure 1, the wavelength of the D_3 line is approximately 587.7 nm.

The corresponding photon energy is

$$E = \frac{hc}{\lambda} = \frac{6.626 \cdot 10^{-34} \times 2.998 \cdot 10^{8}}{587.7 \cdot 10^{9}} = 3.380 \cdot 10^{-19}\ \text{J}$$

1.4 The correct answer is [E].

The energy 3.380 · 10^{-19} J matches with the energy of the transition between 2p and 3d orbitals.

1.5 Considering that the α particle is the nucleus of helium, α decay [A] is the relevant source of helium in such rocks. No compounds of He such as UHe_2 in [B] is known to be stable at ambient temperature. [C] is a radioactive decay of ^{240}U in the thorium series. [D] is a nuclear fission reaction of ^{235}U occurring in nuclear reactors. Thus, the correct answer is [A].

1.6 [C] is a well known radioactive decay reaction occurring with a half life of the order of the earth age. No stable compound of Ar, such as ArF_2 or ArXe, can be expected. Products of [D] should be $^{126}Xe + \beta^-$. The correct answer is [C].

1.7 The density ρ is given by $\rho = \frac{nM}{V}$

By combining with the ideal gas law gives:

$$M = \frac{\rho RT}{p} = \frac{0.850 \times 8.314 \times 288.15}{1.013 \cdot 10^5} = 2.01 \cdot 10^{-2}\ \text{kg mol}^{-1} \quad (20.1\ \text{g mol}^{-1})$$

1.8 From the equation for the sonic velocity, $f\lambda = \sqrt{\frac{\gamma RT}{M}}$,

$$\gamma = \frac{M}{RT}(f\lambda)^2 = \frac{2.01 \cdot 10^{-2}}{8.314 \times 288.15}(3520 \times 0.116)^2 = 1.40$$

(or using $\frac{M}{RT} = \frac{\rho}{p}$, $\gamma = \frac{\rho}{p}(f\lambda)^2 = \frac{0.850}{1.013 \cdot 10^5}(3520 \times 0.116)^2 = 1.40$)

1.9 From M = 20.1 g mol^{-1}, this gas must be HF or Ne.

From γ = 1.4 ($\neq 5/3 \approx 1.67$), this is NOT a monoatomic gas. Thus, the gas must be HF. The correct answer is [B].

Note: It is not possible to distinguish between HF (M = 20.01 g mol^{-1}) and Ne (M = 20.18 g mol^{-1}) from the molar mass only which is 20.10 ± 0.12 g mol^{-1} by taking into account uncertainty of γ (± 0.005/0.850 = ± 0.6 %). However, the precision of γ = 1.40 is enough to exclude the possibility of monoatomic gas ($\gamma = 5/3 \approx 1.67$).

PROBLEM 2

Crystal structure of alkali metal halide

In crystals of ionic compounds, cations are generally arranged in the interstices of the closest packed lattice of anions. The structure of an ionic crystal such as sodium chloride becomes stable when the cations are in contact with the nearest anions.

2.1 In the crystal of sodium chloride, both Na^+ and $Cl^–$ ions form a face-centred cubic lattice. Give the numbers of Na^+ and $Cl^–$ ions in a unit cell and the coordination numbers of Na^+ and $Cl^–$ ions in sodium chloride crystal.

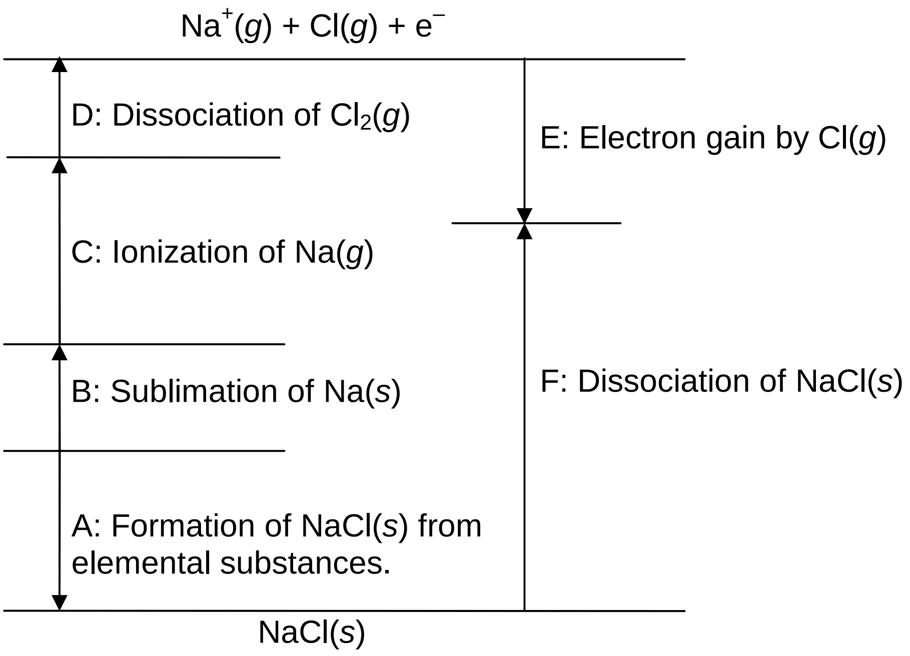
2.2 The ionic radii of Na^+ and $Cl^–$ ions in the crystal of sodium chloride are 0.102 nm and 0.181 nm, respectively.

Calculate the density [kg m^{-3}] of the sodium chloride crystal.

Born-Haber cycle and lattice enthalpy

In ionic inorganic compounds such as sodium chloride, the heat of lattice formation from gaseous ions is very high, and the contribution of the change in entropy is small. Therefore, the lattice formation enthalpy is estimated from enthalpy data by using a Born-Haber cycle.

2.3 The figure below shows the Born-Haber cycle of NaCl. The labels "*g*" and "*s*" represent "gas" and "solid" states, respectively. Show chemical equations in the A and F steps.



2.4 Calculate the enthalpy of the lattice formation of NaCl [kJ mol^{-1}] by using the following enthalpy data of the respective steps in the above Born-Haber cycle.

Formation of NaCl(*s*)	Sublimation of Na(*s*)	Ionization of Na(*g*)	Dissociation of Cl_2(*g*)	Electron gain by Cl(*g*)
–411 kJ mol^{-1}	109 kJ mol^{-1}	496 kJ mol^{-1}	242 kJ mol^{-1}	–349 kJ mol^{-1}

Synthesis of sodium carbonate by the ammonia-soda process (Solvay process)

Sodium carbonate (anhydrous soda ash) is a raw material in the manufacture of glass, medicaments, alkaline detergents, etc.

2.5 The total chemical reaction in the ammonia-soda process is represented as follows:

$2\ NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$

This reaction between sodium chloride and calcium carbonate does not proceed directly. The process comprises the following five reactions involving ammonia:

$CaCO_3 \xrightarrow{\Delta} [\ A\ ] + [\ B\ ]$

$NaCl + NH_3 + [\ B\ ] + H_2O \rightarrow [\ C\ ] + [\ D\ ]$

$2\ [\ C\ ] \xrightarrow{\Delta} Na_2CO_3 + H_2O + [\ B\ ]$

$[\ A\ ] + H_2O \rightarrow [\ E\ ]$

$[\ E\ ] + 2\ [\ D\ ] \rightarrow CaCl_2 + 2\ H_2O + 2\ NH_3$

where Δ represents applying heat treatment. Insert the chemical formulas of the appropriate compounds instead of [A] – [E] in the above reactions.

SOLUTION

2.1

Number of ions	$Na^+ = 4$	$Cl^- = 4$
Coordination number of ions	$Na^+ = 6$	$Cl^- = 6$

2.2 Length of lattice *l*: $l = 0.102 \times 2 + 0.181 \times 2 = 0.566$ nm

Density ρ :

$$\rho = \frac{(22.99 + 35.45) \times 4}{(0.566 \cdot 10^{-9})^3 \times 6.022 \cdot 10^{23}} = 2.1408 \cdot 10^6 \text{ g m}^{-3} = 2.14 \cdot 10^3 \text{ kg m}^{-3}$$

2.3 **A**: $Na(s) + \frac{1}{2} Cl_2(g) \rightarrow NaCl(s)$

F: $NaCl(s) \rightarrow Na(g) + Cl^-(g)$

2.4 Enthalpy conservation condition: – **A** + **B** + **C** + **D**/2 = **F** – **E**

From the above equation: – (–411) + 109 + 496 + (242 / 2) = F + 349

Thus: F = 788

Lattice formation enthalpy of NaCl is –**F**, thus –788 kJ mol^{-1}.

2.5 **A**: CaO

B: CO_2

C: $NaHCO_3$

D: NH_4Cl

E: $Ca(OH)_2$

PROBLEM 3

The chemical oxygen demand (COD) refers to the amount of oxidizable substance, such as organic compounds, in a sample solution, and it is used as an indication of water quality in seas, lakes, and marshes. For example, the COD of service water is kept below 1 mg dm^{-3}. The COD (mg dm^{-3}) is represented by mass of O_2 (mg) which accepts the same amount of electrons which would be accepted by the strong oxidizing agent when 1 dm^3 of a sample solution is treated with it. An example of the operation is presented below.

Analytical Operation

A sample solution with a volume of 1.00 dm^3 was acidified with a sufficient amount of sulphuric acid, and chloride ions were removed by the addition of silver nitrate solution. A volume of $1.00 \cdot 10^{-1}$ dm^3 of potassium permanganate solution ($c = 5.00 \cdot 10^{-3}$ mol dm^{-3}) was added to the sample solution, and the mixture was heated for 30 min. Further, a volume of $1.00 \cdot 10^{-1}$ dm^3 of disodium oxalate ($Na_2C_2O_4$ or NaOOC–COONa) standard solution ($c = 1.\ 25 \cdot 10^{-2}$ mol dm^{-3}) was added, and the mixture was stirred well. Oxalate ions that remained unreacted were titrated with potassium permanganate solution ($c = 5.00 \cdot 10^{-3}$ mol dm^{-3}). A volume of $3.00 \cdot 10^{-2}$ dm^3 of the solution was used for the titration.

3.1 Give the equation of the redox reaction of potassium permanganate and disodium oxalate.

3.2 Calculate the mass of O_2 (in mg) that will oxidize the same number of moles of oxidizable substance as $1.00 \cdot 10^{-3}$ dm^3 of potassium permanganate solution with a concentration of $5.00 \cdot 10^{-3}$ mol dm^{-3} does.

3.3 From the following choices, select the most appropriate reason for the removal of chloride ions:

[A] Some of the chloride ions react with potassium permanganate, resulting in an error in COD.

[B] Some of the chloride ions react with disodium oxalate, resulting in an error in COD.

[C] Some of the chloride ions react with organic compounds in the sample solution, resulting in an error in COD.

[D] A colour is developed during titration, resulting in an error in COD.

3.4 Calculate the COD (mg dm^{-3}) of the sample solution described in the analytical operation above.

SOLUTION

3.1 $2\ KMnO_4 + 5\ Na_2C_2O_4 + 8\ H_2SO_4 \rightarrow 2\ MnSO_4 + 5\ Na_2SO_4 + K_2SO_4 + 10\ CO_2 + 8\ H_2O$

or

$2\ KMnO_4 + 5\ H_2C_2O_4 + 3\ H_2SO_4 \rightarrow 2\ MnSO_4 + K_2SO_4 + 10\ CO_2 + 8\ H_2O$

or

$2\ MnO_4^- + 5\ C_2O_4^{2-} + 16\ H^+ \rightarrow 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O$

3.2 The reactions of potassium permanganate and O_2 are as follows:

$MnO_4^- + 8\ H^+ + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$

$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O$

$n(MnO_4^-) = 1.00 \cdot 10^{-3}\ dm^3 \times 5.00 \cdot 10^{-3}\ mol\ dm^{-3} = 5.00 \cdot 10^{-6}\ mol$

$n(O_2) = 5.00 \cdot 10^{-6}\ mol \times 5/4 = 6.25 \cdot 10^{-6}\ mol$

$m(O_2) = 6.25 \cdot 10^{-6}\ mol \times 32\ g\ mol^{-1} = 2.00 \cdot 10^{-4}\ g = 2.00 \cdot 10^{-1}\ mg$

3.3 The correct answer is [A].

3.4 The amounts of electrons used for reduction or oxidation are equal. Then:

$5 \times 5.00 \cdot 10^{-3}\ mol\ dm^{-3} \times (1.00 \cdot 10^{-1} + A)\ dm^3 =$

$= 2 \times 1.25 \cdot 10^{-2}\ mol\ dm^{-3} \times 1.00 \cdot 10^{-1}\ dm^3 + X \qquad (1)$

where A (cm^3) is an amount of potassium permanganate used for the final titration, and X (mol) is the amount of electrons for the oxidizable substance.

Equation (1) gives $X = 2.50 \cdot 10^{-2} \times A$.

When $A = 3.00 \cdot 10^{-2}\ dm^3$, $X = 7.50 \cdot 10^{-4}$ mol.

Hence, $COD = (32/4)\ g\ mol^{-1} \times 7.50 \cdot 10^{-4}\ mol \times 10^3\ (mg/g) \times 1/1\ (dm^{-3}) =$

$= 6.00\ mg\ dm^{-3}$

or

The amount of potassium permanganate consumed by the oxidizable substance, B (cm^3), is

$5 \times 5.00 \cdot 10^{-3} \times (1.00 \cdot 10^{-1} + A - B) = 2 \times 1.25 \cdot 10^{-2} \times 1.00 \cdot 10^{-1}$

At $A = 3.00 \cdot 10^{-2}\ dm^3$ B equals to $3.00 \cdot 10^{-2}\ dm^3$.

From the solution to question 3.2 above

$$\text{COD} = \frac{2.00 \cdot 10^{-1}}{1.00 \cdot 10^{-3}} \; (\text{mg dm}^{-3}) \times 3.00 \cdot 10^{-2} \; (\text{dm}^{3}) \times 1/1 \; (\text{dm}^{-3}) = 6.00 \text{ mg dm}^{-3}$$

PROBLEM 4

The rechargeable lithium ion battery has been developed in Japan.

The standard electromotive force of the battery is 3.70 V. Assume that the half-reaction at the cathode is

$$CoO_2 + Li^+ + e^- \rightarrow LiCoO_2,$$

and the half-reaction at the anode is

$$LiC_6 \rightarrow 6\ C + Li^+ + e^-.$$

4.1 Write the total reaction equation of the battery and calculate the value of the standard Gibbs energy of the reaction [kJ mol^{-1}].

The battery cell is constructed using $LiCoO_2$ and graphite (C) as the electrode materials.

4.2 Calculate the mass of the anode in the completely charged state and that in completely discharged state if 10.00 g of $LiCoO_2$ and 10.00 g of graphite (C) are present initially.

4.3 Calculate the maximum energy generated per mass of the lithium ion battery cell [kJ kg^{-1}]. Assume that the correct ratio for complete reaction between the cathode and anode materials is used and the sum of the mass of electrodes is 50.0 % of the total mass of the battery cell. In comparison, the energy density of lead-acid batteries used for vehicles is about 200 kJ kg^{-1}.

Because an aqueous solution cannot be used as an electrolyte, an organic solution is used in the lithium ion battery cell.

4.4 Give the chemical formula of the gas generated if water is present in the electrolyte.

SOLUTION

4.1 Total reaction equation:

$CoO_2 + LiC_6 \rightarrow LiCoO_2 + 6\,C$

The standard Gibbs energy of the reaction:

$\Delta G^o = -nFE^o = -1 \times 96485\ \text{C mol}^{-1} \times 3.70\ \text{V} = -357\ \text{kJ mol}^{-1}$

4.2 In the completely charged state: 10.71 g

$$n(LiCoO_2) = \frac{10.00\ \text{g}}{97.87\ \text{g mol}^{-1}} = 0.1022\ \text{mol}$$

$$n(C) = \frac{10.00\ \text{g}}{12.01\ \text{g mol}^{-1}} = 0.8326\ \text{mol},$$ which is larger than 0.1022 mol × 6 = 0.6132 mol

Thus, the mass in the completely charged state of the anode is

$10.00 + (0.1022 \times 6.94) = 10.71$ g

In the completely discharged state: 10.00 g

4.3 The mass of 1 mol $LiCoO_2$ is 97.87 g

The mass of 6 mol C is 12.01 g × 6 = 72.06 g

The total mass of the electrode is (97.87 + 72.06) g = 169.93 g

The mass of the cell is 169.93 / 0.500 = 340 g

The maximum energy generated is 357 kJ

Thus, the maximum energy per unit mass of the cell is 1050 kJ kg^{-1}

4.4 H_2 or H_2 and O_2

PROBLEM 5

When an atom X absorbs radiation with a photon energy greater than the ionization energy of the atom, the atom is ionized to generate an ion X^+ and the electron (called a photoelectron) is ejected at the same time. In this event, the energy is conserved as shown in Figure 1, that is,

Photon energy ($h\nu$) = ionization energy (IE) of X + kinetic energy of photoelectron.

When a molecule, for example, H_2, absorbs short-wavelength light, the photoelectron is ejected and an H_2^+ ion with a variety of vibrational states is produced. A photoelectron spectrum is a plot of the number of photoelectrons as a function of the kinetic energy of the photoelectrons. Figure 2 shows a typical photoelectron spectrum when H_2 in the lowest vibrational level is irradiated by monochromatic light of 21.2 eV. No photoelectrons are detected above 6.0 eV. (eV is a unit of energy and 1.0 eV is equal to $1.6 \cdot 10^{-19}$ J.)

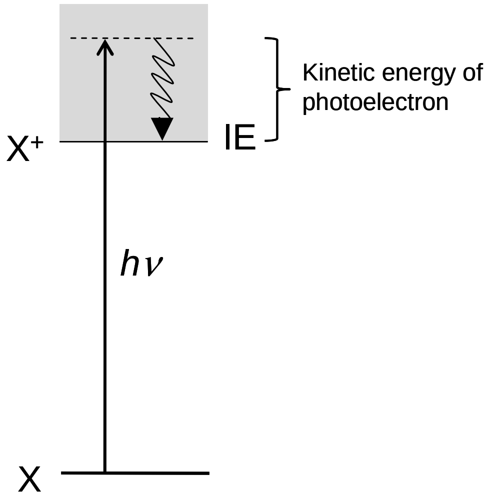


Figure 1.
Schematic diagram of
photoelectron spectroscopy.

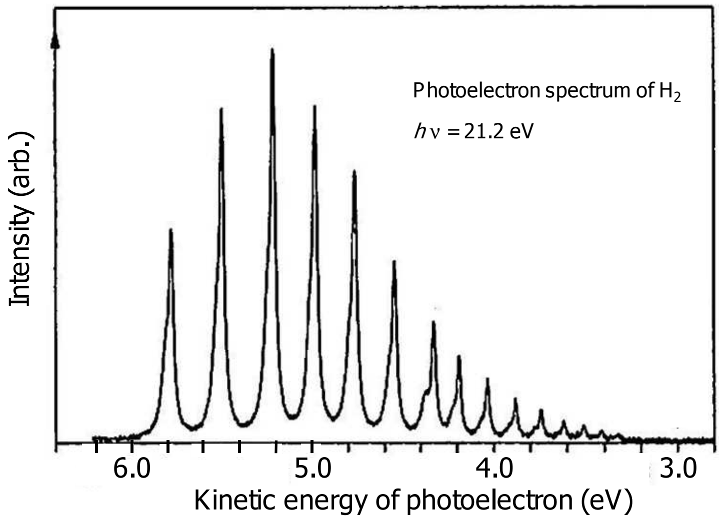


Figure 2.
Photoelectron spectrum of H_2.
The energy of the incident light is 21.2 eV.

5.1 a) Determine the energy difference ΔE_{A1} (eV) between H_2 (v = 0) and H_2^+ (v_{ion} = 0) to the first decimal place. v and v_{ion} denote the vibrational quantum numbers of H_2 and H_2^+, respectively.

b) Determine the energy difference ΔE_{A2} (eV) between H_2^+ (v_{ion} = 0) and H_2^+ (v_{ion} = 3) to the first decimal place.

The electronic energy levels E_n^H of a hydrogen atom are given by the equation

$$E_n^H = -\frac{Ry}{n^2} \qquad (n = 1, 2, 3\cdots)$$

Here n is a principal quantum number, and Ry is a constant with dimensions of energy. The energy from n = 1 to n = 2 of the hydrogen atom is 10.2 eV.

5.2 Calculate the ionization energy E_B (eV) of the hydrogen atom to the first decimal place.

The energy threshold for the generation of two electronically excited hydrogen atoms H* (n = 2) from H_2 (v = 0) has been derived to be 24.9 eV by an experiment.

5.3 Determine the bond energy E_C (eV) of H_2 to the first decimal place.

5.4 Considering an energy cycle, determine the bond energy E_D (eV) of H_2^+ to the first decimal place. If you were unable to determine the values for E_B and E_C, then use 15.0 eV and 5.0 eV for E_B and E_C, respectively.

5.5 Calculate the threshold energy E_E (eV) of the following dissociative ionization reaction to the first decimal place:

$$H_2 \rightarrow H^*(n = 2) + H^+ + e^- .$$

If you were unable to determine the values for E_B and E_C, then use 15.0 eV and 5.0 eV for E_B and E_C, respectively.

When H_2 absorbs monochromatic light of 21.2 eV, the following dissociation process occurs at the same time.

$$H_2 \xrightarrow{21.2\ \text{eV}} H(n = 1) + H(n = 1)$$

Two hydrogen atoms move in opposite directions with the same speed.

5.6 Calculate the speed u (m s^{-1}) of the hydrogen atoms generated in the above reaction. H_2 is assumed to be at rest. If you were unable to determine the value for E_C, then use 5.0 eV for E_C.

SOLUTION

5.1 a) The spectral peak at 5.8 eV in Fig. 2 corresponds to the electron with the highest kinetic energy, which is generated by the reaction

$H_2(v = 0) \rightarrow H_2^+(v_{ion} = 0) + e$.

Accordingly,

$\Delta E_{A1} = 21.2\text{ eV} - 5.8\text{ eV} = 15.4\text{ eV}$

b) One can estimate from Fig. 2 that the energy difference ΔE_{A2} between $H_2^+(v_{ion} = 0)$ and $H_2^+(v_{ion} = 3)$ is approximately 0.8 eV.

The answers are as follows: $\Delta E_{A1} = 15.4$ eV

$\Delta E_{A2} = 0.8$ eV.

5.2 The ionization energy corresponds to n = ∞. Accordingly,

$\Delta E_{n=2 \leftarrow n=1} = ¾\, Ry$

$\Delta E_{n=\infty \leftarrow n=1} = Ry$

Thus, the energy required for the ionization is 4/3 times larger than the transition energy of the Lyman α-line.

$$E_B = 10.2\text{ eV} \times \frac{4}{3} = 13.6\text{ eV}$$

5.3 24.9 eV = binding energy of a hydrogen molecule + 10.2 eV + 10.2 eV.

Thus, the binding energy of a hydrogen molecule $E_C = 4.5$ eV.

5.4 From Fig. 3 below

$E_D = E_B + E_C - \Delta E_{A1} = 13.6 + 4.5 - 15.4 = 2.7$ eV

5.5

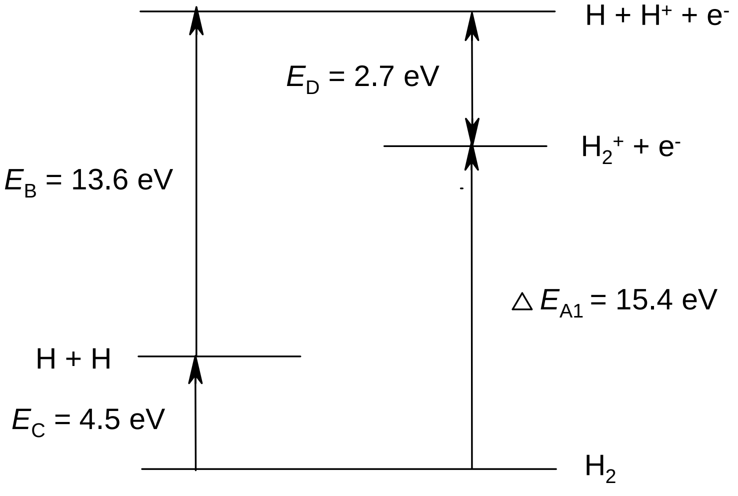


Figure 3

From Figure 3 above, the threshold energy E_E for the dissociative ionization reaction

$H_2 \rightarrow H^*(n=2) + H^+ + e^-$ is $E_B + E_C$ + 10.2 eV = 13.6 + 4.5 + 10.2 = 28.3 eV.

E_E = 28.3 eV

5.6 The excess energy is 16.7 eV (= 21.2 eV – 4.5 eV). Because two hydrogen atoms are generated upon photodissociation, half of this excess energy is released as translational energy of the hydrogen atoms.

$$\frac{1}{2} mu^2 = 8.35 \text{ eV} = 1.34 \cdot 10^{-18} \text{ J}$$

$$m = \frac{1.008 \cdot 10^{-3} \text{ kg mol}^{-1}}{6.022 \cdot 10^{23} \text{ mol}^{-1}} = 1.67 \cdot 10^{-27} \text{ kg}$$

Then,

$u^2 = 1.6 \cdot 10^9 \text{ m}^2 \text{ s}^{-2}$

$u \approx 4.0 \cdot 10^4 \text{ m s}^{-1}$

PROBLEM 6

Read the description of four kinds of isomeric organic compounds **A**, **B**, **C**, and **D**. All of them have the formula $C_8H_{10}O$ and contain a benzene ring. Answer the questions that follow. If there are stereoisomers, give also their structural formulas.

- At room temperature, a piece of sodium metal was added (procedure 1) to **A**, **B**, and **C** in test tubes. The evolution of hydrogen gas was observed only in the case of **C**.
- When an iron(III) chloride aqueous solution was added to **C** and **D**, no coloration was observed in **C**, whereas **D** was coloured.
- **A** was oxidized when aqueous potassium permanganate was added to it and the mixture was heated. The acidification of the heated mixture and its isolation (procedure 2) afforded benzoic acid.
- Let's imagine that a hydrogen atom in the benzene ring is replaced by a chlorine atom (procedure 3). It is possible to obtain in this way four kinds of monochlorinated structural isomers from **B**, while only two kinds of such isomers can be obtained from **D**.
- Hydrogenation of the benzene ring in **C** and **D** using a catalyst gave saturated alcohol(s). It was found that the saturated alcohol(s) obtained from **C** has no stereogenic carbons while those obtained from **D** has stereogenic carbon(s).

6.1 Among all the isomeric organic compounds with a formula of $C_8H_{10}O$ and having a benzene ring, give the structural formulas of all the isomers that do NOT yield hydrogen gas in the underlined procedure 1, in which a piece of sodium is added:
i) to the neat samples in the case of the liquid samples,
ii) to the concentrated solution of the samples in an aprotic solvent in the case of the solid samples.

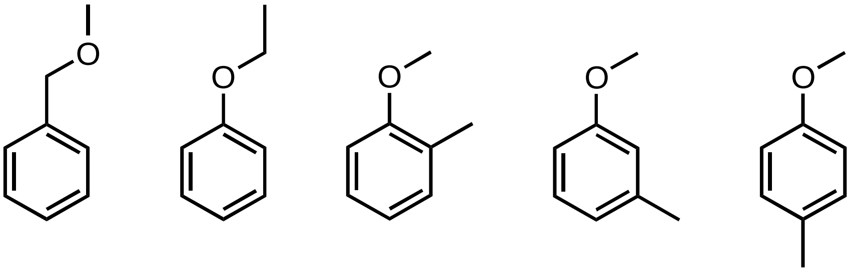
6.2 Among all the isomeric organic compounds with a formula of $C_8H_{10}O$ having a benzene ring, give the structural formulas of all the isomers that yield benzoic acid in the underlined procedure 2.

6.3 Among all the isomeric organic compounds with a formula of $C_8H_{10}O$ having a benzene ring, give the structural formulas of all the isomers that could yield four different monochlorinated structural isomers when the underlined procedure 3 is performed.

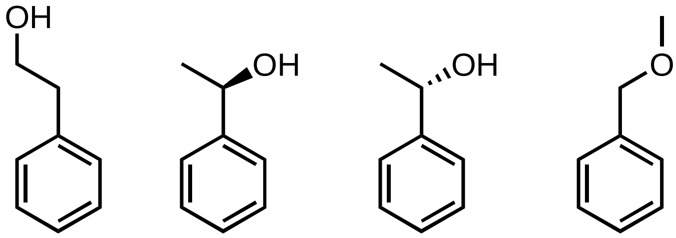
6.4 Give the structural formulas of **A**, **B**, **C**, and **D**. When several isomers can be considered, give the structural formulas of all of them.

SOLUTION

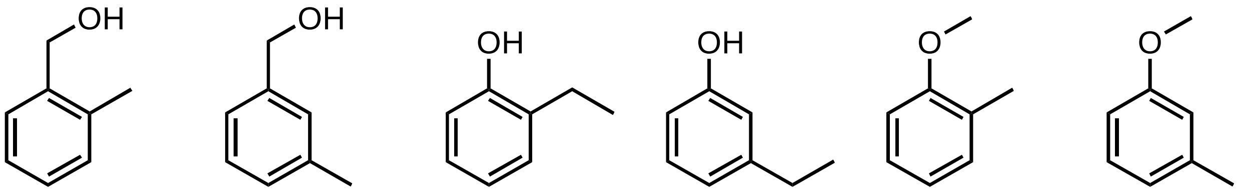
6.1



6.2

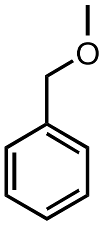


6.3

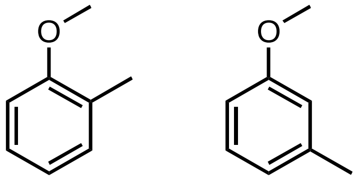


6.4

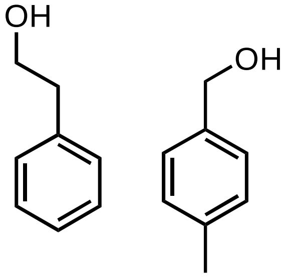
A



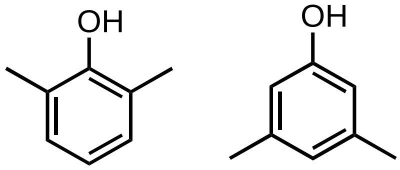
B



C

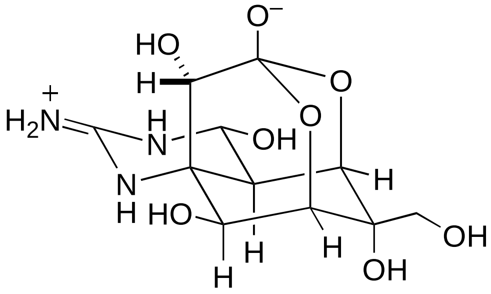


D



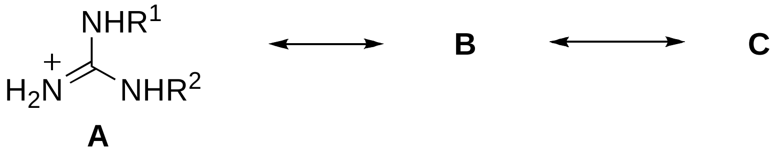
PROBLEM 7

Certain varieties of puffer fish, *Fugu* in Japanese, are highly prized as foods in Japan. Since the viscera (especially ovaries and livers) of the fish contain a potent toxin (tetrodotoxin), food poisoning often results from its ingestion. Studies on tetrodotoxin (**1**) have been performed from the beginning of the 20th century. Its chemical structure was elucidated in 1964.



tetrodotoxin (**1**)

The guanidine group in tetrodotoxin exhibits strong basicity. The guanidinium ion resulting from protonation on the guanidine group is stabilized by the existence of the following resonance.

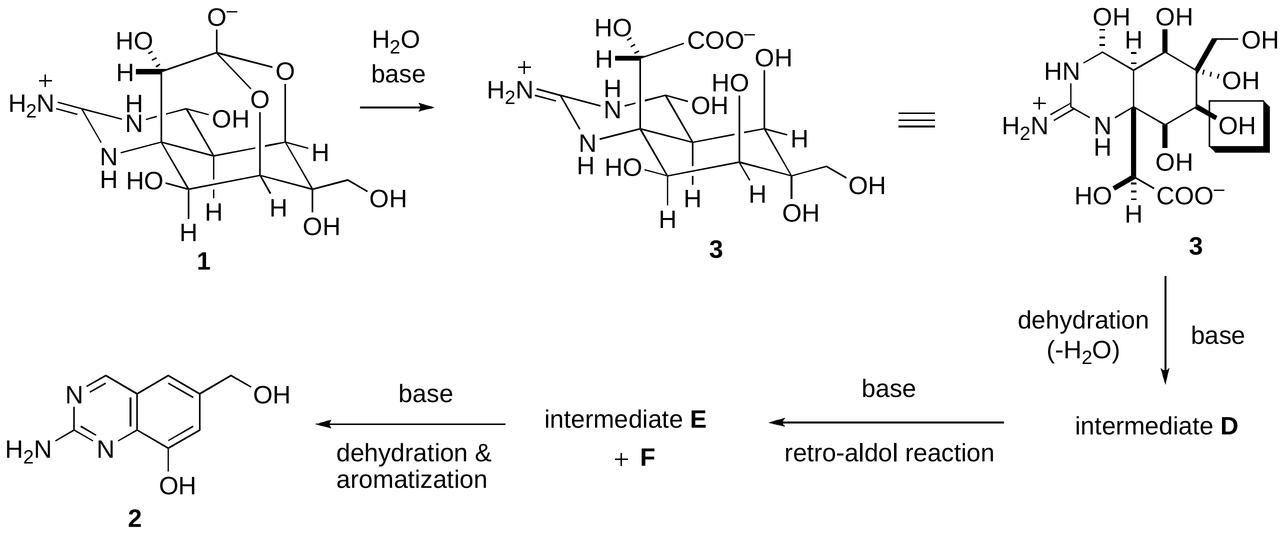


7.1 Draw two resonance structures **B** and **C**.

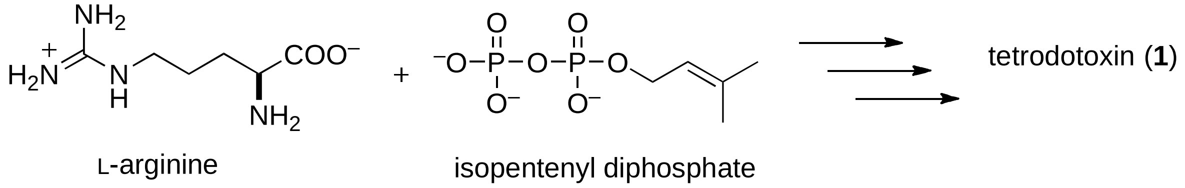
Many derivatization reactions were performed in structure studies of tetrodotoxin. Treatment of tetrodotoxin (**1**) (see reaction scheme 1) with ethanolic potassium hydroxide upon heating afforded quinazoline derivative **2**, which provided an insight into the nature of the fundamental skeleton of tetrodotoxin. The reaction mechanism can be described as follows. First, tetrodotoxin is hydrolyzed into carboxylate **3**. Then the hydroxyl group highlighted with a frame is eliminated by the base to give intermediate **D**. A retro-aldol reaction of **D** cleaves a carbon-carbon bond to provide intermediates **E** and **F**. Finally, dehydration and aromatization from **E** produce quinazoline derivative **2**.

7.2 Draw structures of the postulated intermediates **D**, **E**, and **F**.

Reaction scheme 1

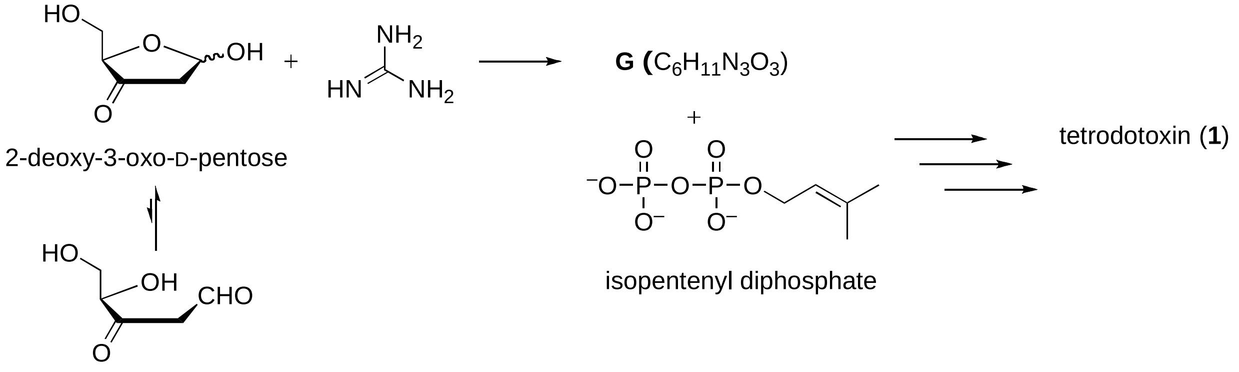


Although biosynthesis of tetrodotoxin still remains to be clarified, it is proposed that tetrodotoxin may be biologically synthesized from L-arginine and isopentenyl diphosphate.



7.3 Among the carbon atoms included in tetrodotoxin, circle all those that are expected to be of L-arginine origin.

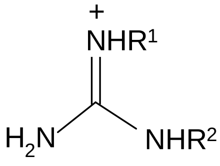
In the 1990s, an alternative biosynthetic pathway of tetrodotoxin was proposed. Condensation between 2-deoxy-3-oxo-D-pentose and guanidine provides intermediate **G** with cyclic guanidine moiety (molecular formula $C_6H_{11}N_3O_3$). Tetrodotoxin may be biologically synthesized from intermediate **G** and isopentenyl diphosphate.



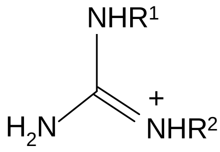
7.4 Draw a structure of the postulated intermediate **G** showing the stereochemistry.

SOLUTION

7.1

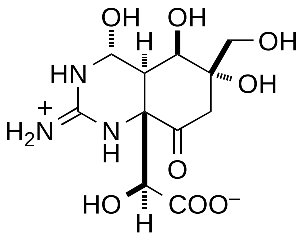


B

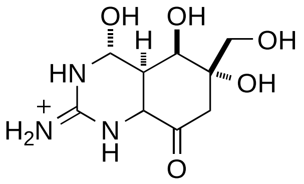


C

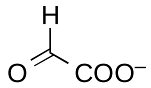
7.2



D

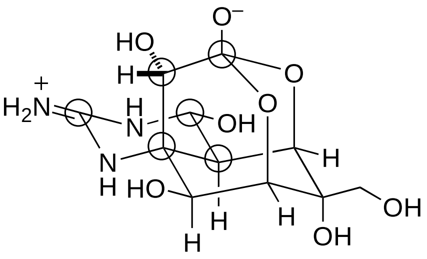


E

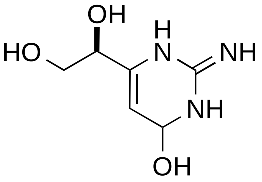


F

7.3

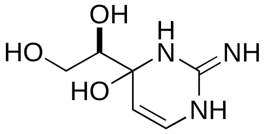


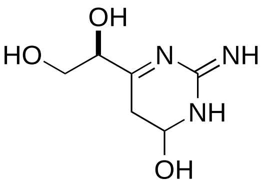
7.4

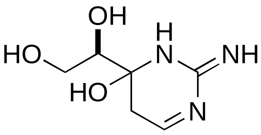


G

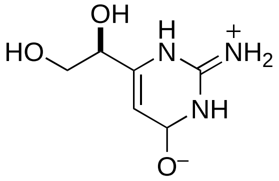
Acceptable:







Each zwitterionic structure (and protonated structure) like below is acceptable.



Tautomers concerning guanidine moiety are all acceptable.

PROBLEM 8

The esterification reaction between bi-functional molecules gives one of the typical linear chain polymers, as shown in equation (1), by polycondensation (often called "condensation polymerization"). The control of polymerization conditions and procedures determines the length of polymer strands, i. e. *the average degree of polymerization,* ***X*** (note that $\boldsymbol{X} = 2\boldsymbol{n}$ in the present instance). Because ***X*** (and also ***n***) is an averaged number, it is not always an integer but a value with decimal figures.

$$n\ \mathrm{HOOC\text{-}R^1\text{-}COOH} + n\ \mathrm{HO\text{-}R^2\text{-}OH} \rightarrow \mathrm{HO\text{-}[COR^1CO\text{-}OR^2O]}_n\mathrm{\text{-}H} + (2n - 1)\ \mathrm{H_2O} \qquad (1)$$

X can be estimated from the consumption of functional groups (here, -COOH and -OH). Let us define the degree of reaction, ***p***, as $\boldsymbol{p} = (N_0 - N) / N_0$ (≤ 1), where N_0 and N denote the total numbers of functional groups before and after the polymerization, respectively. For each functional group of the dicarboxylic acid molecules (**A**) and diol molecules (**B**), we add the suffixes of "A" or "B" such as N_{A0}, N_{B0}, N_A or N_B, respectively, i. e. $N_0 = N_{A0} + N_{B0}$ and $N = N_A + N_B$. When the initial feed is unbalanced such as $N_{A0} \leq N_{B0}$, ***X*** is expressed by $\boldsymbol{p}_A$ and ***r*** as shown in equation 2, where $\boldsymbol{r} = N_{A0} / N_{B0}$ (≤ 1) and $\boldsymbol{p}_A = (N_{A0} - N_A) / N_{A0}$. If $\boldsymbol{r} = 1$, $\boldsymbol{p}_A$ is identical to ***p*** and equation 2 becomes the same to the Carothers equation.

$$X = \frac{1 + r}{1 + r - 2\,p_A r} \qquad (2)$$

Some nylon-6,6 sample was prepared by polycondensation between an e*quimolar* mixture of adipic acid (hexanedioic acid) and hexamethylenediamine (hexane-1,6-diamine).

8.1 Show the chemical structure of this nylon-6,6 sample.
[Caution: What are the end groups when polycondensation was started from the *equimolar* mixture?]

8.2 When an average molar weight, ***M***, of this nylon-6,6 sample is 5507.25 (g mol^{-1}), calculate its ***X*** value to *the second decimal place*.

8.3 Give the ***p*** value to *the fifth decimal place* that is necessary to prepare the above nylon-6,6 sample. If you get no numerical answer in **8.2** use the value 52.50 instead.

The low-molecular-weight polyester (oligoester) is prepared from the mixture of 36.54 g of adipic acid (hexanedioic acid) and an unknown amount [***W*** (g)] of butane-1,4-diol (Bdiol). Under the condition of $\boldsymbol{p}_A \rightarrow 1$, the oligoester with ***X*** = 11.00 carrying Bdiol units in both chain ends, is obtained.

8.4 Show the *precise* chemical structure of this oligoester of ***X*** = 11.00.

8.5 Calculate the unknown amount, ***W*** (g), to the first decimal place.

SOLUTION

8.1 $HO–[CO(CH_2)_4CO–NH(CH_2)_6NH]_n–H$ or equivalent structures.

8.2 The unit molecular weight, M_u, is calculated as follows:

$$M_u = \frac{12.01 \times 12 + 1.01 \times 22 + 14.01 \times 2 + 16.00 \times 2}{2} = \frac{226.36}{2} = 113.18$$

$$X = \frac{5507.25 - 18.02}{M_u} = \frac{5507.25 - 18.02}{113.18} = 48.50$$

or

$$X = 2\,n = 2 \times \frac{5507.25 - 18.02}{226.36} = 48.50$$

8.3 From equation 2 at r = 1 (Carothers eq.):

$$X = 48.50 = \frac{1}{1 - p}$$

$p = 0.97938$

($p = 0.98095$ when $\boldsymbol{X} = 52.50$ was used instead of $X = 48.50$.)

8.4 $[HO(CH_2)_4O]_{1.000}–[CO(CH_2)_4CO–O(CH_2)_4O]_{5.000}–H$ or

$HO(CH_2)_4O–[CO(CH_2)_4CO–O(CH_2)_4O]_{5.000}–H$ is accurate

However,

$HO(CH_2)_4O–[CO(CH_2)_4CO–O(CH_2)_4O]_5–H$ is acceptable.

8.5 M(adipic acid) = 146.16 g mol^{-1}; M(Bdiol) = 90.14 g mol^{-1}

Answer 1:

Since $X = 11.00$, the oligoester contains 5.00 units of adipate and 6.00 units of the Bdiol. When $p_A \to 1$, the initial molar feed ratio of the monomers is equal to the molar composition of the resulting oligoester.

$$\frac{[\text{adipic acid}]_0}{[\text{Bdiol}]_0} = \frac{5.00}{6.00},$$

$$\boldsymbol{W} = 90.14 \times \frac{6.00}{5.00} \times \frac{36.54}{146.16} = 27.0 \text{ g}$$

Answer 2:

From eq. 2, when $p_A \rightarrow 1$, $X = (1 + r) / (1 – r)$. Therefore,

$$11.00 = \{1 + [(36.54 / 146.16) / \boldsymbol{W} / 90.14)] \} / \{1 – [(36.54 / 146.16) / \boldsymbol{W} / 90.14)] \} =$$

$$= [(\boldsymbol{W} / 90.14) + 0.2500] / [(\boldsymbol{W} / 90.14) – 0.2500]$$

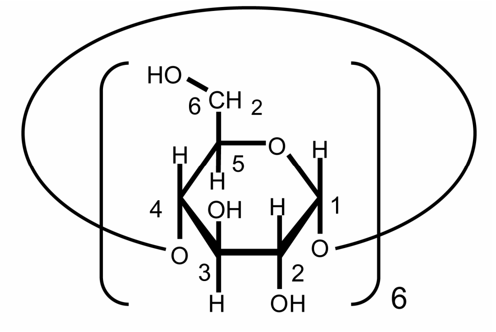
$$11.00 \times [(\boldsymbol{W} / 90.14) – 0.2500] = [(\boldsymbol{W} / 90.14) + 0.2500],$$

$$10.00 \times [(\boldsymbol{W} / 90.14)] = 3.000$$

$$\boldsymbol{W} = 3.000 \times 90.14 / 10.00 = 27.0 \text{ g}$$

PROBLEM 9

α-Cyclodextrin (αCyD), which is a cyclic oligosaccharide of six α(1→4) linked α-D-glucopyranoside units, can be topologically represented as toroids (Figure 1). α-D-glucopyranoside units in αCyD are usually in the most stable chair conformation.



αCyDe

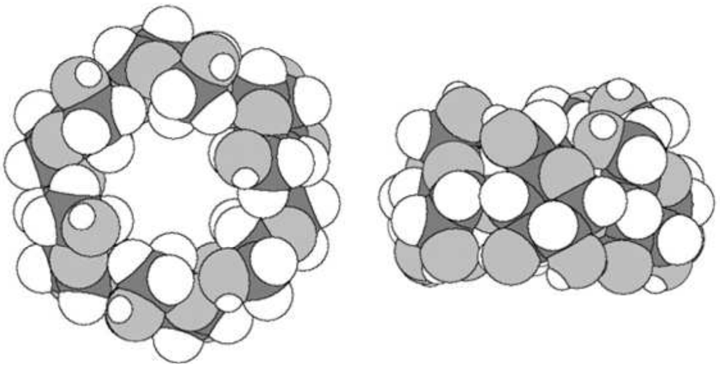
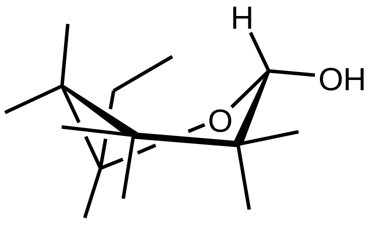
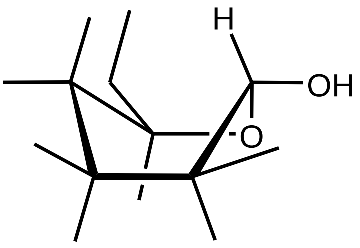


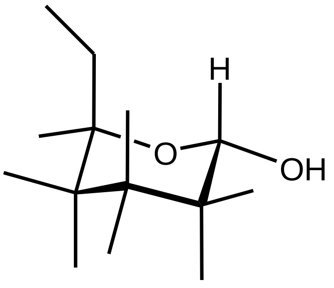
Figure 1. Space filling model of αCyD.
Left: view through the hole.
Right: side view.

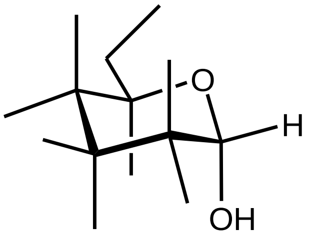
9.1 Give the absolute configuration (*R* or *S*) at stereogenic carbons C-2 and C-5 of D-glucose. Also, draw a stereostructure of the open chain form of D-glucose.

9.2 Choose the most stable conformation from the following four incomplete α-D-glucopyranose formulas. Also, add four OH groups and four H atoms to complete the α-D-glucopyranose formula.



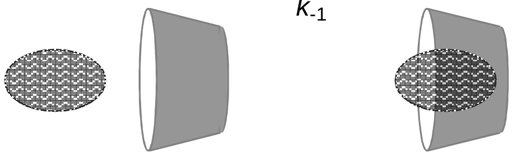






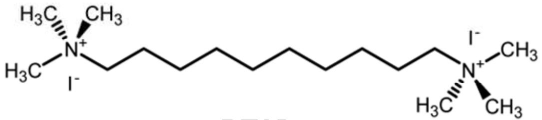
αCyD in water is able to host hydrophobic molecules. When the host : guest (H : G) stoichiometry is 1 : 1, the inclusion complexation can be given by the following equilibrium.

$$\mathrm{G} + \mathrm{H} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{HG} \qquad (1)$$



where k_1 and k_{-1} are the rate constant for the forward and backward reaction, respectively. The complexation of a guest to αCyD causes a chemical shift change in ^{1}H NMR spectra.

Figure 2 shows a part of ^{1}H NMR spectra (signals from H–1 of αCyD) showing the chemical shift change in the presence of varying amounts of BTAD (1,10-bis(trimethylammonium)decane diiodide). The doublet peak at 5.06 ppm is from H–1 of free αCyD, while the doublet at 5.14 ppm is from H–1 of αCyD complexed with BTAD. (Note that the spectra given in Figure 2 were measured in the complexation equilibrium state.)



BTAD

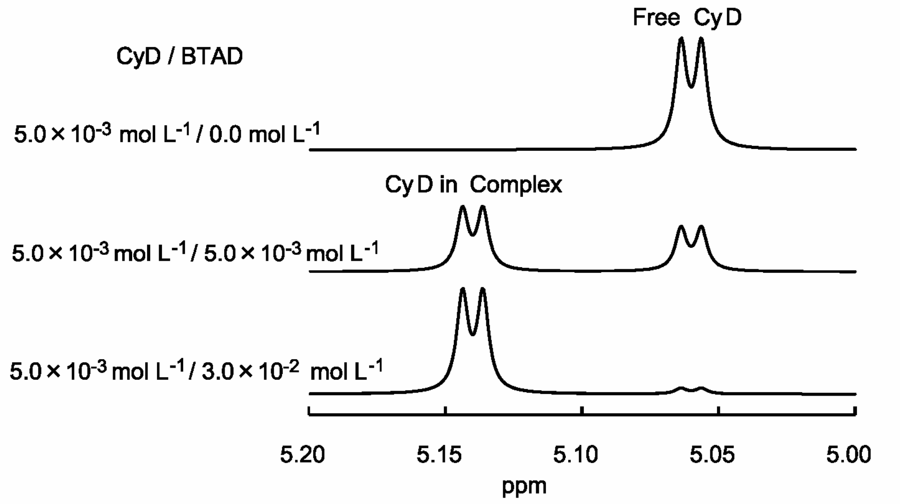
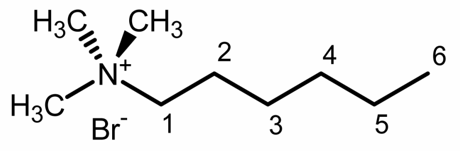


Figure 2.

Expanded ^{1}H NMR spectra (signals from H–1 of αCyD) of solutions with concentration of αCyD equal to $5.0 \cdot 10^{-3}$ mol dm^{-3} and that of BTAD equal from 0 to $3.0 \cdot 10^{-2}$ mol dm^{-3}.

9.3 Consider a solution in which concentrations of αCyD as well as BTAD are equal to $5.0 \cdot 10^{-3}$ mol dm^{-3} and the relative peak areas of the doublets at 5.06 and 5.14 ppm are 0.41 and 0.59, respectively. Calculate (to 2 significant figures) the concentration equilibrium constant, *K,* for the inclusion complexation of αCyD / BTAD.

Complexation of αCyD with hexyltrimethylammonium bromide (HTAB) appears in NMR spectra in a way different from the αCyD/BTAD complexation. Figure 3 shows a part of ^{1}H NMR spectra (H-6 signal of HTAB) in αCyD/HTAB solutions. The signal appears as one triplet (not two triplets), which shifts depending on the concentration of αCyD from the position of free HTAB to the position of αCyD/HTAB in proportion to the fraction of the complex in the solution. The H-6 signals from free HTAB and HTAB complexed with αCyD are triplets at 0.740 ppm and 0.860 ppm, respectively.



HTAB

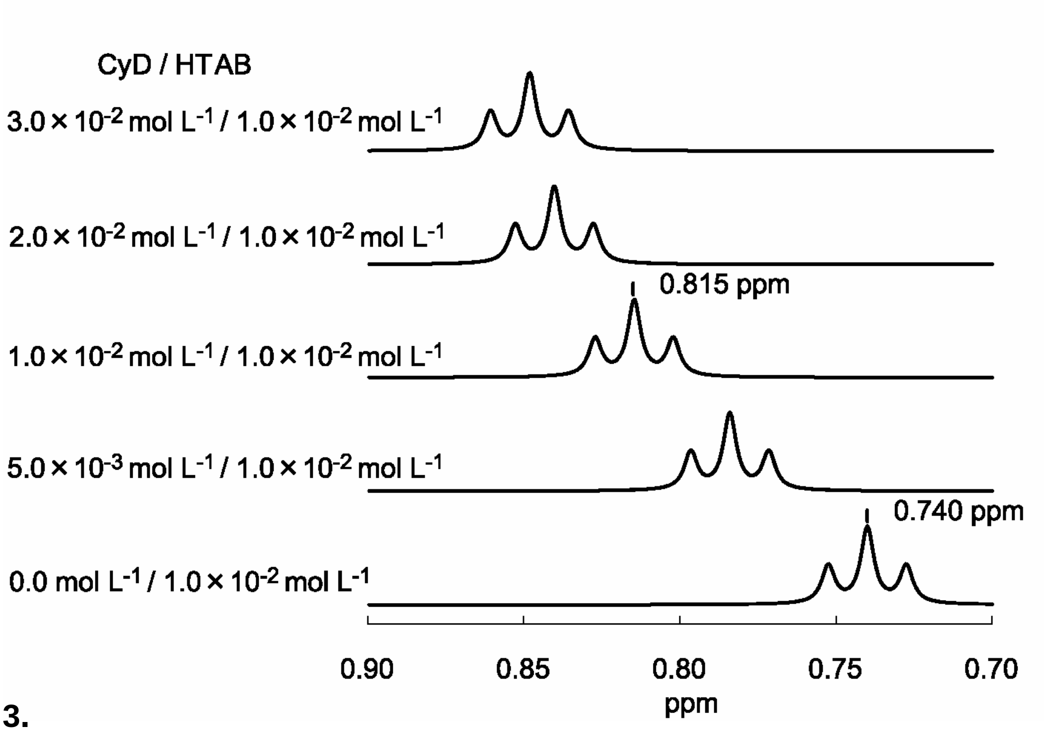


Figure 3.

Expanded ^{1}H NMR spectra (H-6 signal of HTAB) of solutions with concentration of HTAB equal to $1.0 \cdot 10^{-2}$ mol dm^{-3} and that of αCyD equal from 0 to $3.0 \cdot 10^{-2}$ mol dm^{-3}.

9.4 The signal of HTAB in αCyD/HTAB_solutions appears as one triplet that shifts depending on the concentration of αCyD. Choose the rational interpretation(s) just from these spectra.

Hint: When a guest molecule move in and out of αCyD rapidly and repeatedly, only one signal of the guest is observed at the weighted average of the chemical shifts of the free guest and the shift of the guest included in αCyD.

a) k_1 of αCyD/HTAB > k_1 of αCyD/BTAD
b) k_1 of αCyD/HTAB < k_1 of αCyD/BTAD
c) K of αCyD/HTAB > K of αCyD/BTAD
d) K of αCyD/HTAB < K of αCyD/BTAD

9.5 The signals of HTAB in the solution with concentrations of αCyD as well as HTAB equal to $1.0 \cdot 10^{-2}$ mol dm^{-3} are positioned at 0.815 ppm. Calculate (to 2 significant figures) the value of K for the complexation of αCyD/HTAB.

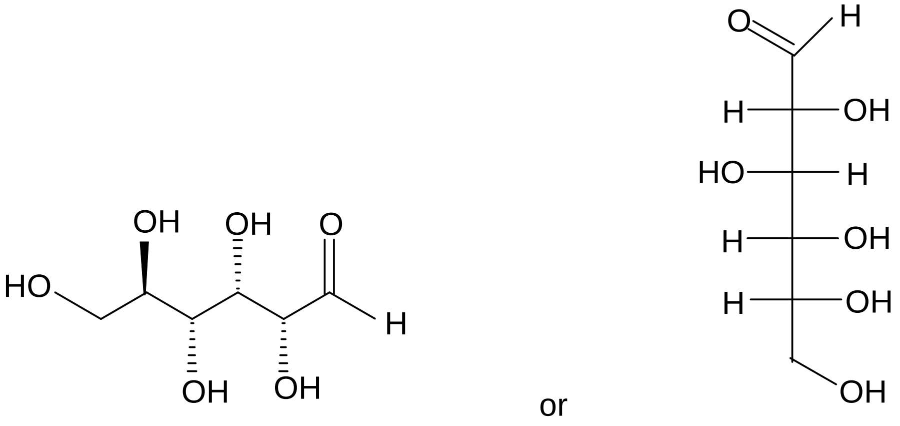
9.6 At 40.0 ºC and 60.0 ºC, K for the complexation of αCyD / HTAB are $3.12 \cdot 10^2$ and $2.09 \cdot 10^2$ respectively. Calculate (to 2 significant figures) the enthalpy change, ΔH^o [kJ mol^{-1}] and the entropy change, ΔS^o [J K^{-1} mol^{-1}]. (Ignore the temperature dependence of ΔH^o and ΔS^o.)

SOLUTION

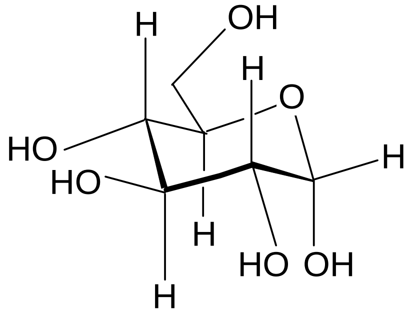
9.1 Absolute configuration at C-2: *R*

Absolute configuration at C-5: *R*

Chain form:



9.2



9.3 $K = \dfrac{[HG]}{[H][G]} = \dfrac{[\alpha\text{CyD}]_0 \times a_{5.14}}{\{[\alpha\text{CyD}]_0 \times a_{5.06} \times \{[\text{BTAD}]_0 - [\alpha\text{CyD}]_0 \times a_{5.14}\}} =$

$$= \frac{5.0 \cdot 10^{-3} \times 0.59}{(5.0 \cdot 10^{-3} \times 0.41)^2} = 7.0 \cdot 10^2$$

$a_{5.06}$: relative area of the peak at 5.06 ppm = mole fraction of free αCyD

$a_{5.14}$: relative area of the peak at 5.14 ppm = mole fraction of αCyD complexed with BTAD

9.4 The correct answer: **a**

9.5 (M = mol dm^{-3})

In $1.0 \cdot 10^{-2}$ M / $1.0 \cdot 10^{-2}$ M αCyD/HTAB

$$f_{10/10} = \frac{s_{10/10} - s_{\text{free}}}{s_{\text{complex}} - s_{\text{free}}} = \frac{0.815 - 0.740}{0.860 - 0.740} = 0.625$$

s_{free} : chemical shift of HTAB in free, and complexed state

s_{complex}: chemical shift of HTAB in a complexed state

$s_{10/10}$: chemical shift of HTAB in 10.0 mM / 10.0 mM αCyD/HTAB

$f_{10/10}$: mole fraction of complexed HTAB in 10.0 mM / 10.0 mM αCyD/HTAB

$$K = \frac{[HG]}{[H][G]} =$$

$$= \frac{[\text{HTAB}]_0 \times f_{10/10}}{\{[\alpha\text{CyD}]_0 - f_{10/10}\,[\text{HTAB}]_0\}\,[\text{HTAB}]_0(1 - f_{10/10})} =$$

$$= \frac{1.0 \cdot 10^{-2} \times 0.625}{[1.0 \cdot 10^{-2} \times (1 - 0.625)]^2} = 4.4 \cdot 10^2$$

$K = 4.4 \cdot 10^2$

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

$\Delta G^o(40.0\ ^\circ\text{C}) = -8.314 \times 313.2 \times \ln(3.12 \cdot 10^2) = -14.94 \cdot 10^3\ \text{J mol}^{-1}$

$\Delta G^o(60.0\ ^\circ\text{C}) = -8.314 \times 333.2 \times \ln(2.09 \cdot 10^2) = -14.79 \cdot 10^3\ \text{J mol}^{-1}$

From $\Delta G^o = \Delta H^o - T\Delta S^o$

$-14.94 \cdot 10^3 = \Delta H^o - 313.2 \times \Delta S^o$

$-14.79 \cdot 10^3 = \Delta H^o - 333.2 \times \Delta S^o$

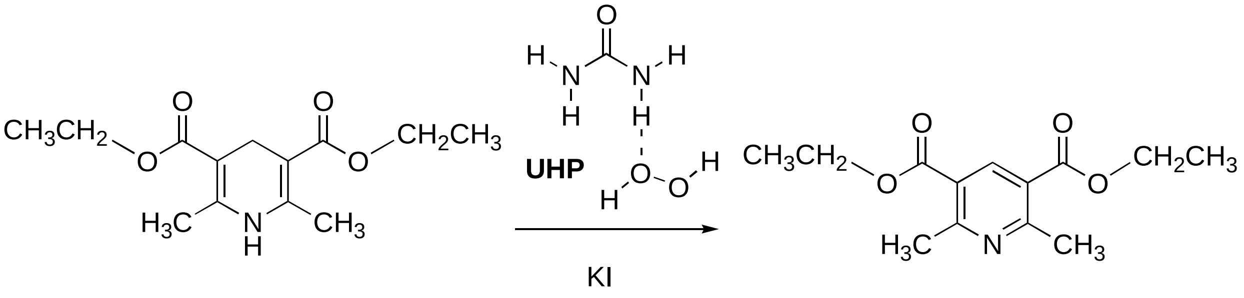
$\Delta S^o = -7.5\ \text{J K}^{-1}\text{mol}^{-1}$; $\Delta H^o = -17\ \text{kJ mol}^{-1}$

PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Reaction of Hantzsch Ester with Urea Hydrogen Peroxide

In this experiment, you are required to synthesize a pyridinedicarboxylate derivative from 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylic acid diethyl ester (1,4-DHP or Hantzsch ester) by oxidation with urea hydrogen peroxide (UHP), an environmentally-friendly oxidant.



1,4-DHP

Chemicals

- Hydrochloric acid, c = 0.5 mol dm^{-3}, 50 cm^3
- 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylic acid diethyl ester, $C_{13}H_{19}NO_4$; (1,4-DHP), powder, 1 g
- 1,4-DHP for TLC, 3 mg
- Ethanol, C_2H_5OH, 10 cm^3
- Ethyl acetate, $CH_3COOC_2H_5$, 25 cm^3
- Heptane, C_7H_{16}, 20 cm^3
- Potassium iodide, KI, 150 mg
- Sodium metabisulfite, $Na_2S_2O_5$, 1 g
- Sodium hydrogen carbonate, saturated aqueous solution, 25 cm^3
- Urea hydrogen peroxide, $CH_4N_2O \cdot H_2O_2$, (UHP), 1 g

Procedures

(1) Place a 22 mm magnetic stirring bar in a 100 cm^3 test tube. Fix the test tube on a magnetic stirrer using a clamp. Add 1,4-DHP (1 g) (labelled as 1,4-DHP powder), and

potassium iodide (150 mg) to the test tube, followed by ethanol (5 cm^3), with a 5 cm^3 graduated pipette.

(2) Add 1 g UHP (wear gloves) and stir the mixture. (Caution: this reaction is exothermic.)

(3) For thin layer chromatography (TLC) analysis, prepare a mixture of ethyl acetate and heptane (1 : 2 in volume) using a measuring glass and place an appropriate amount of the mixture in a TLC developing chamber. Add 1 cm^3 of ethyl acetate to the vial (labelled as 1,4-DHP TLC) to dissolve 1,4-DHP (3 mg).

(4) Check your TLC plates before using. If they are damaged, they can be replaced without penalty. Draw a start line on the lower portion of a TLC plate with a pencil (see Fig. 1.1).

(5) During the reaction, the reaction mixture becomes clear (usually within 20 min). When the reaction mixture becomes clear (the precipitates may form when it cools, but precipitates will not affect the TLC analysis), take a small portion of the mixture using a glass capillary and load it to make two spots in the centre and right positions on the TLC plate. Load an appropriate amount of the 1,4-DHP solution prepared in procedure (3) in the centre and left positions, so that there are three spots on the plate, with the centre spot containing both the reaction mixture and 1,4-DHP (see Fig. 1.1). Develop the TLC plate in the TLC chamber (see Figs. 1.1 and 1.2). Mark the solvent front with the pencil. Visualize the spots using a UV lamp (254 nm) and draw a line around the UV-active spots on the TLC clearly with the pencil. Assess the completion of the reaction based on the TLC results. Repeat the TLC analysis after ten minutes, if you find significant amounts of 1,4-DHP in the reaction mixture. [Note that you will perform TLC analysis again in procedure (8).] Place the last TLC plate in a zipper storage bag marked “A.”

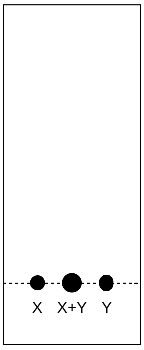


Fig. 1.1 Spots on the TLC plate before development;
X: 1,4-DHP, Y: Reaction mixture.

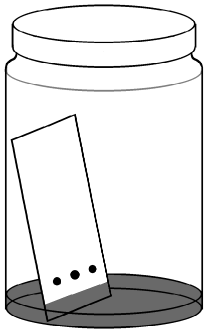


Fig. 1.2 TLC plate placed in the TLC developing chamber.

(6) Set up the suction filtration equipment (see Fig. 1.3). Connect the suction flask to the diaphragm vacuum pump. Place a Büchner funnel fitted with a rubber adapter onto the suction flask. Place a glass microfiber filter sheet on the funnel.

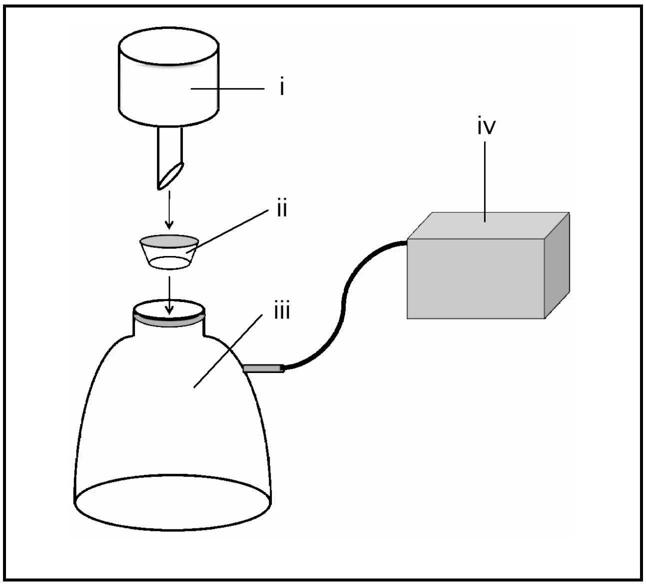


Fig. 1.3 Suction filtration equipment:
i - Büchner funnel; ii - rubber adopter;
iii - suction flask; iv - diaphragm vacuum pump.

(7) Add water (5 cm^3) to the reaction mixture using a 10 cm^3 plastic graduated cylinder. Add sodium metabisulfite (1 g), transfer the contents of the tube (including the stirring bar) into a 200 cm^3 conical beaker and wash the test tube with water (30 cm^3). Place the 200 cm^3 conical beaker on the magnetic stirrer and stir the solution. Add saturated sodium hydrogen carbonate solution in small portions using a 2 cm^3 graduated pipette until the pH of the aqueous phase becomes just over 7 (check the pH with pH test paper). Filter the precipitate formed through the Büchner funnel with suction using the diaphragm vacuum pump, and wash the precipitate with a small portion of water. Suck air through the precipitates for a minute to dry the product.

(8) Transfer the filtrate from the suction flask to a 300 cm^3 conical beaker. Transfer the filtrate (2 cm^3) to a 10 cm^3 test tube using a 2 cm^3 graduated pipette. Place a 10 mm magnetic stirring bar in the test tube and fix it securely with the clamp. Add 1 cm^3 of ethyl acetate to the test tube using a 2 cm^3 graduated pipette and stir the solution vigorously for 30 seconds on the magnetic stirrer. Stop stirring and wait for the solution to separate into two layers. Analyze the upper layer by TLC to see if there is any product remaining in the filtrates. Spot the filtrates on the plate in the same way as procedure (5). Mark the solvent front and the spot(s), if any. Place the TLC plate in a zipper storage bag marked “B.” If you detect the product on the TLC plate, add more saturated sodium hydrogen carbonate solution.

(9) At this stage, if you find a precipitate formed, filter and wash it. If you find no precipitate, skip this filtration process.

(10) Suck air through the precipitate for 10 minutes to dry the product. Place your product and the glass microfiber filter sheet in the crystallization dish. Cover the dish with the lid marked with your code. Avoid placing the stirring bar in the dish. Place the crystallization dish with the lid in a zipper storage bag marked “C.”

1.1 Copy (sketch) the TLC plate in bag “A” on your answer sheet.

1.2 Determine and record the R_f values (to the 2nd decimal place) of the spots on the TLC plate in bag “A.”

1.3 Draw the structural formula of the organic cation before adding sodium hydrogen carbonate.

1.4 What is (are) the final product(s) derived from UHP? Give the chemical formula(e) of the product(s).

1.5 Submit the following:

i) TLC plate in bag “A”.
ii) TLC plate in bag “B”.
iii) Your product and filter paper in the crystallization dish placed in bag “C”.

SOLUTION

1.1 Indication of the solvent front line and the base line is expected.

Some points will be subtracted if:

i) there are less than three spots loaded on the base line,

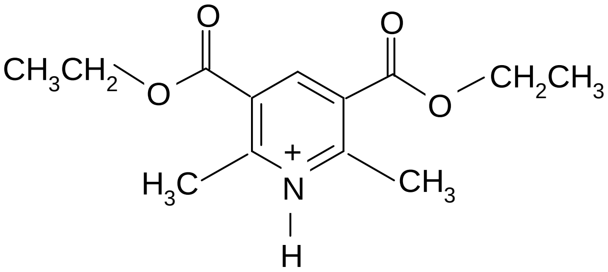
ii) the spots are not separated on the TLC after development,

iii) the solvent front line and/or the base line is missing.

1.2

Spot	R_f value
1,4-DHP	0.32 – 0.42
Product	0.61 – 0.71

1.3



1.4 H_2O and CH_4N_2O

1.5 The following rules for evaluation of the practical results in this problem were suggested by the organizer and approved by the International Jury:

Evaluation of the TLC plates.

Points will be subtracted:

- if the outline to be drawn with a pencil around the UV-active spots, is unclear or missing,
- if the solvent front line and/or base line is missing.

Evaluation of the product and filter paper in the crystallization dish (in bag "C").

i) A technician should weigh the product and calculate the percent yield after drying at 60 °C.

ii) In most cases the sample is pure and dissolved in $CDCl_3$ completely. The special calculation based on the percent yields and an approved graph is applied only if no 1,4-DHP or by-products are observed in the ^{1}H NMR spectrum and the product is completely soluble in $CDCl_3$.

iii) If there are peaks of 1,4-DHP (ca δ 2.19 ppm) and the corresponding pyridine product (ca δ 2.85 ppm) in the ^{1}H NMR spectrum and the percent yield is 100 % or less, the actual percent yield is calculated by an equation proposed by the organizer and approved by the International Jury.

iv) Some points subtraction is suggested:
  - if insoluble material remains after the addition of $CHCl_3$ for ^{1}H NMR measurements,
  - if by-products are detected evidently in the ^{1}H NMR spectrum.

PROBLEM 2 (Practical)

Determination of Fe(II) and Fe(III) by visual colorimetry

In this experiment, you are required to determine Fe(II) and Fe(III) in a given sample solution which simulates a dissolved magnetite ore by visual colorimetric analysis involving a colour reaction between Fe(II) and 2,2'-bipyridine (bpy) to form an intensely red complex, $Fe(bpy)_3^{2+}$.

The amount of $Fe(bpy)_3^{2+}$ complex can be quantified by visual colorimetric measurement using Nessler tubes. This is a quite simple technique that was employed before photoelectric instruments were generally available, but an accuracy of less than ± 5% can be achieved. In this technique, a pair of Nessler tubes is used; one is filled with a reference solution, and the other is filled with a solution to be tested. The depths of colours of the two solutions are balanced by adjusting the heights of liquid columns of the solutions.

When the colours look the same, the concentration can be calculated from that of the reference solution with a known concentration and the height of the column of each solution based on the Lambert-Beer law:

$$A = \varepsilon c\, l$$

where A is the absorbance, c is the concentration, l is the pass length and ε is the molar absorption coefficient. First, you will learn to employ this technique by conducting measurements **A** and **B**, and then you will determine the concentrations of Fe(II) and Fe(III) with measurements **C** and **D**.

Chemicals

- Sample solution
- Standard $Fe(bpy)_3^{2+}$ solution 1 containing 2.0 mg of iron in 1 dm^3 of the solution.
- Standard $Fe(bpy)_3^{2+}$ solution 2 containing 3.0 mg of iron in 1 dm^3 of the solution.
- Acetate buffer solution, pH 4.6, 1 : 1 mixture of acetic acid and sodium acetate.
- Disodium hydrogen phosphate solution, c = 0.1 mol dm^{-3}.
- 2,2'-bipyridine aqueous solution, w = 0.2 %.
- Sodium thioglycolate.

Procedures

(1) Add 5 cm^3 of acetate buffer solution, 5 cm^3 of disodium hydrogen phosphate solution (to mask Fe(III)), 5 cm^3 of 2,2'-bipyridine solution and 10.00 cm^3 of sample solution into a 50 cm^3 volumetric flask using appropriate pipettes for each and dilute the resulting solution with water to the 50 cm^3 mark. Then stopper the flask and mix the solution well. Allow it to stand for at least 20 min to fully develop colour. This solution is named "sample 1."

(2) Add 5 cm^3 of acetate buffer solution, 5 cm^3 of 2,2'-bipyridine solution and 5.00 cm^3 of sample solution into a 50 cm^3 volumetric flask. Then add 20 mg of sodium thioglycolate powder (in excess) to reduce Fe(III) to Fe(II). Dilute the solution with water to the 50 cm^3 mark, stopper the flask and mix the solution well. Allow it to stand for at least 20 min. This solution is named "sample 2."

(3) Perform visual colorimetric measurements A – D based on the "Instructions for visual colorimetric measurement" shown below.

Instructions for visual colorimetric measurement

Set a pair of Nessler tubes on a Nessler tube rack placed on an LED light box (do not remove it from the bag at any time) and turn on the light (see Fig. 2.1). Pour the provided "standard $Fe(bpy)_3^{2+}$ solution 1" into one tube to an appropriate height (70 – 90 mm is recommended) from the bottom (etched marks on the tube indicate fixed heights from the bottom in mm) and use this as a reference for measurements **A** – **D**. Pour the solution to be measured into the other tube, and then compare its depth of colour with that of the reference solution by looking downward through the solutions toward the LED light box.

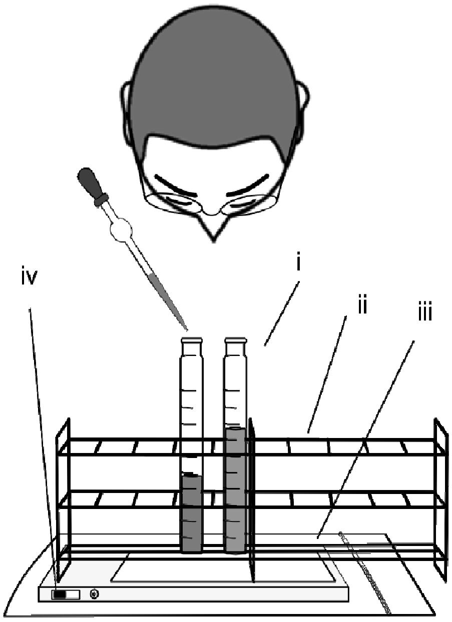


Fig. 2.1
Visual colorimetric measurement:
i: Nessler tube;
Ii: Nessler tube rack; iii: LED light box in a zipper storage bag;
Iv: power switch.

Adjust the height of the liquid column of the test solution by adding or removing the solution with a graduated pipette until the depth of colour in the two tubes is identical. Estimate your reading to at least 1 mm.

Note that the depths of colour in a certain range may be recognized as identical to human eyes. The appropriate value for the height of the test solution, *h*, should be determined by taking the range into the consideration. For example, if you adjust the height of the liquid column of the test solution only by increasing (or decreasing) the volume, you could reach a lower (or higher) value than the true one. A possible way to estimate the true value is to take an average between the values of lower and higher limits.

Measurement A:

Perform a measurement using "standard $Fe(bpy)_3^{2+}$ solution 1" as both the reference and the test solutions. In this measurement, pour the reference solution into a Nessler tube to achieve an appropriate height, and then pour the test solution into the other Nessler tube until the colours of the two solutions match each other. (When the colours match, the heights should ideally be the same.) Then add more test solution until you recognize that the colours have become different from each other. Report both the lower and higher limits of the height of the liquid column of test solution with the same depth of colour as the reference solution.

2.1 Report your results for measurement A using the table provided on the answer sheet.

Measurement B:

Perform a measurement of "standard $Fe(bpy)_3^{2+}$ solution 2" as a test solution using "standard $Fe(bpy)_3^{2+}$ solution 1" as a reference.

2.2 Report your results for measurement B using the table provided on the answer sheet.

Measurement C:

2.3 Perform the measurement of sample 1.

Report your results for measurement C using the table provided on the answer sheet.

Measurement D:

2.4 Perform the measurement of sample 2.

Report your results for measurement D using the table provided on the answer sheet.

2.5 Express the concentration, c, of the test solution, using the concentration of the reference solution, c', and the heights of each liquid column, h and h'.

2.6 Calculate the concentrations of Fe(II) and Fe(III) in the original sample solution in mg dm^{-3}.

SOLUTION

2.1– 2.4

The competitors were requested to summarize their results in four tables for measurements A, B, C, and D, respectively. It was necessary to record the height, *h*', (in mm) of the standard solution and the height, *h*, of the test solution.

A distribution graph was proposed and applied for evaluations of the competitors' results.

2.5 $c = \dfrac{c'\,h'}{h}$

2.6 For Fe^{2+}:

$$c(Fe^{2+}) = \frac{2.0\ \text{mg dm}^{-3} \times h'_C \times 50\ \text{cm}^3}{h_C \times 10\ \text{cm}^3}$$

$c(Fe^{2+})$: concentration, (mg dm^{-3}), of Fe^{2+} in the sample solution,

h_C: experimental height, (mm), of the liquid column of the test solution in the measurements C,

h'_C: experimental height, (mm), of the liquid column of the standard solution in the measurements C.

For Fe^{3+}:

$$c(Fe^{3+}) = \frac{2.0\ \text{mg dm}^{-3} \times h'_D \times 50\ \text{cm}^3}{h_D \times 5\ \text{cm}^3} - c(Fe^{3+})$$

$c(Fe^{3+})$: concentration, (mg dm^{-3}), of Fe^{3+} in the sample solution,

h_D: experimental height, (mm), of the liquid column of the test solution in the measurements D,

h'_D: experimental height, (mm), of the liquid column of the standard solution in the measurements D.

Concentrations of Fe^{2+} and Fe^{3+} used for particular original sample solutions:

	$c(Fe^{2+})$ / mg dm^{-3}	$c(Fe^{3+})$ / mg dm^{-3}
Sample 1	8.16	18.0
Sample 2	8.60	19.0
Sample 3	9.08	17.7

PROBLEM 3 (Practical)

Polymers in Analysis

Polymers can be used in various analyses. In this task, you are first required to analyze a polysaccharide using a polymer-polymer interaction, which will then be utilized to identify polymers in the second part.

I. Analysis of Polysaccharide by Colloid Titration

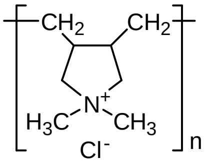
You are provided with a solution of a polysaccharide containing sulfonate (-SO_3^-) and carboxylate (-COO^-) groups. You are asked to determine the concentrations of these two groups by colloid titration under the basic and acidic conditions based on the differences in the protonation behaviour of these acid groups. A back-titration technique is utilized.

When these acid groups are ionized, the polysaccharide becomes a polyanion. Upon addition of polycation, poly(diallyldimethylammonium) (provided as its chloride salt, PDAC), it forms a polyion complex. PDAC solution is standardized using the standard solution of potassium poly(vinyl sulphate) (PVSK). At the endpoint of colloid titration, the number of anionic groups becomes equal to that of cationic groups.

Chemicals

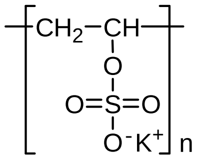
- Polysaccharide solution, 50 cm^3
- Poly(diallyldimethylammonium chloride), (**PDAC**), aqueous solution

  Formula:



- Potassium poly(vinyl sulfate) aqueous solution, c = 0.0025 mol dm^{-3}; (monomer unit concentration)

  Formula:



- sodium hydroxide, aqueous solution, c = 0.5 mol dm^{-3}
- toluidine blue, $C_{15}H_{16}N_3SCl$, (TB), aqueous solution, c = 1 g dm^{-3}
- Solutions X-1 – X- 5 for Part II**.**

Procedure

(1) Take precisely 20 cm^3 of the PDAC solution using a volumetric pipette into a 100 cm^3 conical beaker. Add 2 drops of toluidine blue (TB) into the conical beaker. Titrate the resulting blue solution with the standard solution of PVSK (c = 0.0025 mol dm^{-3} - monomer unit concentration). At the endpoint the colour turns purple. Note that the solution becomes gradually turbid as the endpoint approaches. The endpoint is determined when the colour remains purple for 15 – 20 seconds. Repeat if necessary.

3.1 Report the PVSK solution volume (**z** cm^3) consumed in the standardization of PDAC. Record your reading to 0.05 cm^3.

_____

(2) Take precisely 5 cm^3 of the polysaccharide solution and 20 cm^3 of the PDAC solution using volumetric pipettes into a conical beaker. Add 0.4 cm^3 of NaOH solution (c = 0.5 mol dm^{-3}) and 2 drops of TB to the solution. Titrate the resulting blue solution with the PVSK standard solution in a similar manner. Repeat if necessary.

(The appearance of coagulation may be different, depending on the pH of the solution.)

3.2 Report the PVSK solution volume, (**x** cm^3) consumed in the titration under basic conditions. Record your reading to 0.05 cm^3.

3.3 Mark the acid group(s) ionized under the basic conditions on the answer sheet.

_____

(3) Repeat procedure (2) above with the addition of 0.5 cm^3 of HCl solution (c = 0.5 mol dm^{-3}) instead of NaOH solution (c = 0.5 mol dm^{-3}).

3.4 Report the PVSK solution volume (**y** cm^3) consumed in the titration under acidic conditions. Record your reading to 0.05 cm^3.

3.5 Mark the acid group(s) fully ionized under acidic conditions on the answer sheet.

3.6 Calculate the concentrations of the $-SO_3^-$ (or $-SO_3H$) groups and the $-COO^-$ (or $-COOH$) groups (in mol dm^{-3}) in the given polysaccharide solution.

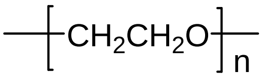
_____

II. Identification of compounds

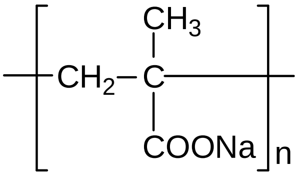
You are provided with five solutions **(1 – 5)** and each solution contains one of the compounds below (all of which are used). The concentration is 0.05 mol dm^{-3} (for polymers, monomer unit concentration). Your task is to identify all the compounds by carrying out the following procedures.

$$HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH$$

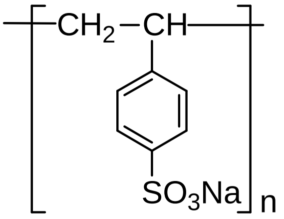
(TEG)



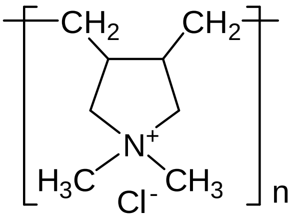
(PEO)



(PMANa)



(PSSNa)



(PDAC)

Abbreviations:

TEG = triethylene glycol;

PEO = poly(ethylene oxide);

PMANa = poly(sodium methacrylate);

PSSNa = poly(sodium 4-styrenesulfonate);

PDAC = poly(diallyldimethylammonium chloride) MW. stands for molecular weight.

Helpful comments

i) Aggregates observed in part I could be observed when mixing two polymer solutions in an appropriate combination in which an interaction takes place between the two polymers. They can be utilized to identify polymer samples.

ii) The volume of a solution measuring 5 mm in height from the bottom of the vial is approximately 1 cm^3. Remember that you have only 10 cm^3 of each solution.

Procedures

(4) Mix similar volumes of two solutions together in a vial.

(5) If necessary, you can acidify the resulting mixture. Ten drops of hydrochloric acid (c = 0.5 mol dm^{-3}) from a plastic Pasteur pipette are sufficient for this purpose.

3.7 Identify the compound in each solution based on the experimental results. Mark one of the five boxes to indicate your identification of the samples.

Sample					
1	☐ TEG	☐ PEO	☐ PMANa	☐ PSSNa	☐ PDAC
2	☐ TEG	☐ PEO	☐ PMANa	☐ PSSNa	☐ PDAC
3	☐ TEG	☐ PEO	☐ PMANa	☐ PSSNa	☐ PDAC
4	☐ TEG	☐ PEO	☐ PMANa	☐ PSSNa	☐ PDAC
5	☐ TEG	☐ PEO	☐ PMANa	☐ PSSNa	☐ PDAC

SOLUTION

I. Analysis of Polysaccharide by Colloid Titration

3.1 V = 20.06 cm^3; z = 20.06

3.2 Sample A: V = 13.14 cm^3 ; x = 13.14
Sample B: V = 12.07 cm^3 x = 12.07
Sample C: V = 10.91 cm^3 x = 10.91

3.3 Under basic conditions: The acid groups are $–SO_3H$ and –COOH.

3.4 Sample A: V = 15.26 cm^3 ; y = 15.26
Sample B: V = 14.61 cm^3 y = 14.61
Sample C: V = 13.59 cm^3 y = 13.59

3.5 Under acidic conditions: The acid group is $–SO_3H$.

3.6 The concentrations (in mol dm$^{–3}$) of:
$–SO_3^-$ (or $–SO_3H$) groups = 0.0005 (z – y)
$–COO^–$ (or –COOH) groups = 0.0005 (y – x)

II. Identification of compounds

PMANa and PSSNa are polyanions and they interact with a polycation (PDAC) to form a precipitate. Under acidic conditions the carboxylate ($–COO^–$) groups in PMANa undergo protonation and PMANa changes to protonated poly(metacrylic acid) (PMA). The resulting carboxy groups (–COOH) interact with the ether oxygen atoms in PEO through hydrogen bonding to form a precipitate. Since the protonated PMA is no longer a polyanion, the precipitate (the complex between PMANa and PDAC) disappears after the addition of HCl.

On the other hand, PSSNa does not exist as a protonated form even under acidic condition.

The expected results of mutual reactions are summarized in the table below. The signs in upper rows correspond to the reactions before addition of HCl while those in lower rows to the reactions after addition of HCl.

	TEG	PEO	PMANa	PSSNa	PDAC
TEG					
PEO	– –				
PMANa	– –	– +			
PSSNa	– –	– –	– –		
PDAC	– –	– –	+ –	+ +	

Note: (+) precipitation is formed; **(–)** no precipitation occurs (or the precipitation disappears)

43rd

8 theoretical problems
3 practical problems

THE FORTY-THIRD
INTERNATIONAL CHEMISTRY OLYMPIAD
9–18 JULY 2011, ANKARA, TURKEY

THEORETICAL PROBLEMS

PROBLEM 1

Nitrogen oxides, common pollutants in the ambient air, are primarily nitric oxide, NO, and nitrogen dioxide, NO_2. Atmospheric nitric oxide is produced mainly during thunderstorms and in the internal combustion engines. At high temperatures NO reacts with H_2 to produce nitrous oxide, N_2O, a greenhouse gas.

$$2\ NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$

To study the kinetics of this reaction at 820 ℃, initial rates for the formation of N_2O were measured using various initial partial pressures of NO and H_2.

Exp.	Initial pressure, torr		Initial rate of production of N_2O, torr s^{-1}
	p_{NO}	p_{H_2}	
1	120.0	60.0	$8.66 \cdot 10^{-2}$
2	60.0	60.0	$2.17 \cdot 10^{-2}$
3	60.0	180.0	$6.62 \cdot 10^{-2}$

Throughout this problem do not use concentrations. Use units of pressure (torr) and time in seconds.

1.1 Determine the experimental rate law and calculate the rate constant.

1.2 Calculate the initial rate of disappearance of NO, if NO with a pressure of $2.00 \cdot 10^2$ torr and H_2 with $1.00 \cdot 10^2$ torr are mixed at 820 ℃.

(If you have been unable to calculate the value for the rate constant, you can use the value of $2 \cdot 10^{-7}$ in appropriate unit.)

1.3 Calculate the time elapsed to reduce the partial pressure of H_2 to the half of its initial value, if NO with a pressure of $8.00 \cdot 10^2$ torr and H_2 with 1.0 torr are mixed at 820 ℃.

(If you have been unable to calculate the value for the rate constant, you can use the value of $2 \cdot 10^{-7}$ in appropriate unit.)

A proposed mechanism for the reaction between NO and H_2 is given below:

$$2\ NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g)$$

$$N_2O_2(g) + H_2(g) \xrightarrow{k_2} N_2O(g) + H_2O(g)$$

1.4 Derive the rate law for the formation of N_2O from the proposed mechanism using the steady-state approximation for the intermediate.

1.5 Under what condition does this rate law reduce to the experimentally determined rate law found in Part 1.1? Tick the relevant answer.

☐ If $k_{-1} << k_2\, p_{H2}$

☐ If $k_{-1} >> k_2\, p_{H2}$

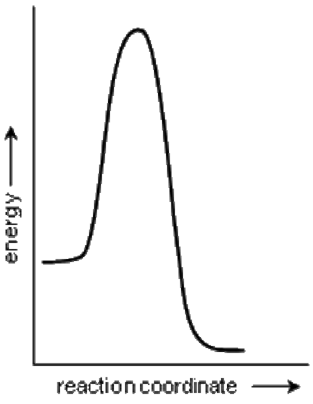
☐ If $k_{-1} > k_2$

☐ If $k_1 > k_{-1}$

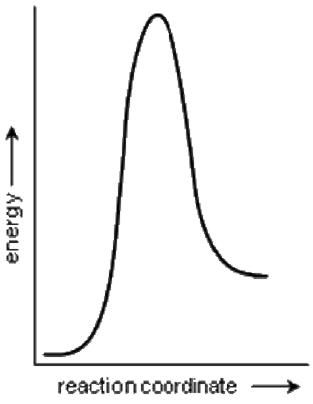
1.6 Express the experimentally determined rate constant k in terms of k_1, k_{-1} and k_2.

1.7 Select the schematic energy diagram that is consistent with the proposed reaction mechanism and experimental rate law.

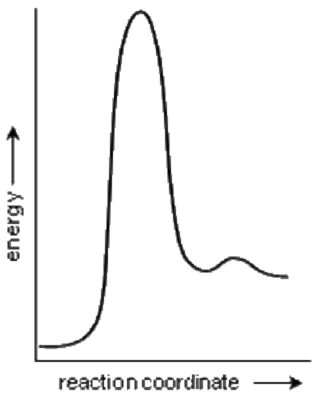
a.



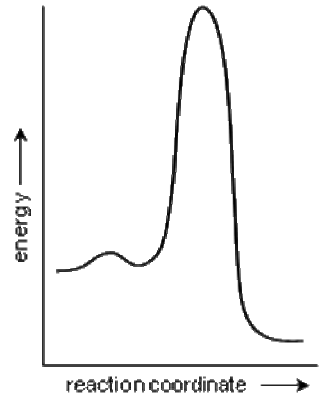
b.



c.



d.


energy
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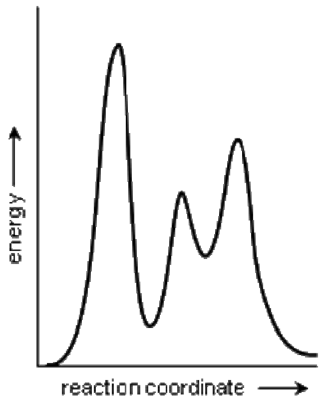
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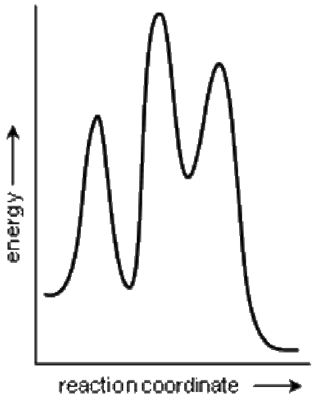

energy
reaction coordinate

SOLUTION

1.1 Rate = $R = k\,(p_{NO})^a\,(p_{H_2})^b$

$$\frac{R_1}{R_2} = \frac{8.66\cdot10^{-2}}{2.17\cdot10^{-2}} = 3.99 = \frac{k\times120^a\times60^b}{k\times60^a\times60^b} \qquad 2^a = 3.99 \;\Rightarrow\; a = 2$$

$$\frac{R_3}{R_2} = \frac{6.62\cdot10^{-2}}{2.17\cdot10^{-2}} = 3.05 = \frac{k\times60^a\times180^b}{k\times60^a\times60^b} \qquad 3^b = 3.05 \;\Rightarrow\; b = 1$$

Rate = $R = k\,(p_{NO})^2\,p_{H_2}$

$$k = \frac{8.66\cdot10^{-2}}{120^2\times60} = 1.00\cdot10^{-7}\ \text{torr}^{-2}\,\text{s}^{-1}$$

1.2 $$\text{Rate} = \frac{\Delta p_{N_2O}}{\Delta t} = -\frac{1}{2}\,\frac{\Delta p_{NO}}{\Delta t} = 1.0\cdot10^{-7}\times200^2\times100 = 0.40\ \text{torr s}^{-1}$$

$$-\frac{\Delta p_{NO}}{\Delta t} = 0.80\ \text{torr s}^{-1}$$

1.3 Rate = $R = k\,(p_{NO})^2\,p_{H_2}$

Since $p_{NO} \gg p_{H_2}$

$$\text{Rate} = k'\,p_{H_2} \;\Rightarrow\; k' = k\,(p_{NO})^2$$

$k' = 1.0\cdot10^{-7}\times(8.00\cdot10^2)^2 = 0.064\ \text{s}^{-1}$

$$t_{1/2} = \frac{\ln 2}{k'} = 10.8\ \text{s}$$

1.4 $$\frac{\Delta p_{N_2O}}{\Delta t} = k_2\,p_{N_2O_2}\,p_{H_2}$$

Steady state approximation for N_2O_2:

$$\frac{\Delta p_{N_2O_2}}{\Delta t} = 0 = k_1\,(p_{NO})^2 - k_{-1}\,p_{N_2O_2} - k_2\,p_{N_2O_2}\,p_{H_2} = 0$$

$$p_{N_2O_2} = \frac{k_1\,(p_{NO})^2}{k_{-1} + k_2\,p_{H_2}}$$

$$\frac{\Delta p_{N_2O}}{\Delta t} = k_2\,p_{H_2}\,\frac{k_1\,(p_{NO})^2}{k_{-1} + k_2\,p_{H_2}}$$

$$\text{Rate} = \frac{\Delta p_{N_2O}}{\Delta t} = k_1 k_2\,\frac{(p_{NO})^2\,p_{H_2}}{k_{-1} + k_2\,p_{H_2}}$$

1.5 The correct answer: If $k_{-1} >> k_2\, p_{H_2}$

1.6 $k = \dfrac{k_1 k_2}{k_{-1}}$

1.7 Energy diagram **d** is correct.

PROBLEM 2

Anhydrous ammonia is an ultra-clean, energy-dense alternative liquid fuel. It produces no greenhouse gases on combustion.

In an experiment, gaseous NH_3 is burned with O_2 in a container of fixed volume according to the equation given below.

$$4\ NH_3(g) + 3\ O_2(g) \rightarrow 2\ N_2(g) + 6\ H_2O(l)$$

The initial and final states are at 298 K. After combustion with 14.40 g of O_2, some of NH_3 remains unreacted.

2.1 Calculate the heat released during the process.

$\Delta_f H^o(NH_3(g)) = -46.11$ kJ mol^{-1} and $\Delta_f H^o(H_2O(l)) = -285.83$ kJ mol^{-1}

To determine the amount of NH_3 gas dissolved in water, produced during the combustion process, a 10.00 cm^3 sample of the aqueous solution was withdrawn from the reaction vessel and added to 15.0 cm^3 of a H_2SO_4 solution (c = 0.0100 mol dm^{-3}). The resulting solution was titrated with a standard NaOH solution (c = 0.0200 mol dm^{-3}) and the equivalence point was reached at 10.64 cm^3.

($K_b(NH_3) = 1.8 \cdot 10^{-5}$; $K_a(HSO_4^-) = 1.1 \cdot 10^{-2}$)

2.2 Calculate pH of the solution in the container after combustion.

2.3 At the end point of titration, NH_4^+ and SO_4^{2-} ions are present in the solution. Write the equations for the relevant equilibria to show how the presence of these two ions affects the pH and calculate their equilibrium constant(s).

2.4 Tick the correct statement for the pH of the solution at the equivalence point.

☐ pH > 7   ☐ pH = 7   ☐ pH < 7

SOLUTION

2.1 $q_v = \Delta E = \Delta H - \Delta n_g RT$

For 1 mole of NH_3:

$\Delta H = 3/2 \times (-285.83) - (-46.11) = -382.64$ kJ

$\Delta n_g = -1.25$ mol

$\Delta E = -382.64 \text{ kJ} - [(-1.25 \text{ mol}) \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}] = -379.5 \text{ kJ}$

$$n(O_2) = \frac{14.4 \text{ g}}{32.0 \text{ g mol}^{-1}} = 0.450 \text{ mol}$$

$n(NH_3)_{\text{reacted}} = 0.450 \text{ mol} \times 4/3 = 0.600 \text{ mol}$

$q_v = \Delta E = 0.600 \text{ mol} \times (-379.5 \text{ kJ mol}^{-1}) = \underline{-227.7 \text{ kJ}}$

2.2 Total $n(H_2SO_4) = 15.00 \text{ cm}^3 \times 0.0100 \text{ mol dm}^{-3} = 0.150$ mmol

$H_2SO_4 + 2\,NaOH \rightarrow Na_2SO_4 + 2\,H_2O$

After back titration with NaOH:

$n(H_2SO_4)_{\text{reacted}} = ½\, n(NaOH)_{\text{reacted}} = ½\,(0.01064 \text{ dm}^3 \times 0.0200 \text{ mol dm}^{-3}) =$

$= 1.064 \cdot 10^{-4} \text{ mol} = 0.1064 \text{ mmol}$

$n(H_2SO_4)_{\text{reacted with NH3}} = 0.0436$ mmol

$2\,NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$

$n(NH_3) = 2 \times n(H_2SO_4)_{\text{reacted with NH3}} = 2 \times 0.0436 \text{ mmol} = 0.0872 \text{ mmol}$

$$c(NH_3) = \frac{0.0872 \text{ mmol}}{0.0100 \text{ dm}^3} = 8.72 \cdot 10^{-3} \text{ mol dm}^{-3}$$

$$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$

$c - x \qquad\qquad x \qquad x$

$$K_b = 1.8 \cdot 10^{-5} = \frac{x^2}{0.00872 - x}$$

$x = [OH^-] = 3.96 \cdot 10^{-4}$

$pOH = 3.41$

$pH = 10.59$

2.3 $SO_4^{2-}(aq) + H_2O(l) \rightleftarrows HSO_4^-(aq) + OH^-(aq)$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \cdot 10^{-14}}{1.1 \cdot 10^{-2}} = 9.1 \cdot 10^{-13}$$

$NH_4^+(aq) + H_2O(l) \rightleftarrows NH_3(aq) + H_3O^+(aq)$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \cdot 10^{-14}}{1.8 \cdot 10^{-5}} = 5.6 \cdot 10^{-10}$$

2.4 The correct answer: $pH < 7.0$

PROBLEM 3

At a temperature of 0 K, the total energy of a gaseous diatomic molecule AB is approximately given by:

$E = E_o + E_{vib}$

where E_o is the electronic energy of the ground state, and E_{vib} is the vibrational energy.

Allowed values of the vibrational energies are given by the expression:

$$E_{\mathbf{vib}} = (v + \frac{1}{2})\,\varepsilon \qquad v = 0, 1, 2, \ldots \qquad \varepsilon = \frac{h}{2\,\pi}\sqrt{\frac{k}{\mu}} \qquad \mu(\mathrm{AB}) = \frac{m_A\, m_B}{m_A + m_B}$$

where h is the Planck's constant, v is the vibrational quantum number, k is the force constant, and μ is the reduced mass of the molecule. At 0 K, it may be safely assumed that v is zero, and E_o and k are independent of isotopic substitution in the molecule.

Deuterium, D, is an isotope of hydrogen atom with mass number 2. For the H_2 molecule, k is 575.11 N m^{-1}, and the isotopic molar masses of H and D are 1.0078 and 2.0141 g mol^{-1}, respectively.

At a temperature of 0 K: $\varepsilon_{H_2} = 1.1546\,\varepsilon_{HD}$ and $\varepsilon_{D_2} = 0.8167\ \varepsilon_{HD}$.

3.1 Calculate the enthalpy change, ΔH, in kJ·mol^{-1} for the following reaction at 0 K:

$H_2(g) + D_2(g) \rightarrow 2\ HD(g)$

3.2 Calculate the frequency in s^{-1} of infrared photons that can be absorbed by HD molecule.

(If you have been unable to calculate the value for ε_{HD} then use 8.000 · 10^{-20} J for the calculation.)

The allowed electronic energies of H atom are given by the expression:

$E = -\frac{R_H}{n^2}$, $n = 1, 2, \ldots$ where R_H = 13.5984 eV, and 1 eV = 1.602 · 10^{-19} J

The total energy of H_2 molecule in its ground state is –31.675 eV, relative to the same reference as that of hydrogen atom.

3.3 Calculate the dissociation energy, DE, in eV of a hydrogen molecule in its ground state such that both H atoms are produced in their ground states.

3.4 A molecule H_2 in the ground state dissociates into its atoms after absorbing a photon of wavelength 77.0 nm. Determine all possibilities for the electronic states of hydrogen atoms produced. For each case calculate the total kinetic energy, KE, in eV of the dissociated hydrogen atoms.

3.5 Calculate the electron affinity, EA, of H_2^+ ion in eV if its dissociation energy is 2.650 eV. If you have been unable to calculate the value for the dissociation energy of H_2 then use 4.500 eV for the calculation.)

SOLUTION

3.1 $H_2(g) + D_2(g) \rightarrow 2\ HD(g) \qquad \Delta H = ?$

$\Delta H = \Delta E + \Delta n_g\, R\, T$

$\Delta n_g = 0$, thus $\Delta H = \Delta E$

$\Delta E = 2\,E(HD) - E(H_2) - E(D_2)$

$E_{vib} = \frac{1}{2}\varepsilon$ as $v =$ 0 at 0 K.

$$\Delta E = 2\left(E_0 + \frac{\varepsilon_{HD}}{2}\right) - \left(E_0 + \frac{\varepsilon_{H_2}}{2}\right) - \left(E_0 + \frac{\varepsilon_{D_2}}{2}\right) = \varepsilon_{HD} - \frac{1}{2}(\varepsilon_{H_2} + \varepsilon_{D_2})$$

$$\Delta E = \varepsilon_{HD}(1 - \frac{1}{2}(1.1546 + 0.8167)) = 0.01435\ \varepsilon_{HD}$$

$$\mu(HD) = \frac{m_H\, m_D}{m_H + m_D} =$$

$$= \frac{\dfrac{1.0078\cdot 10^{-3}\text{ kg mol}^{-1} \times 2.0141\cdot 10^{-3}\text{ kg mol}^{-1}}{N_A^2}}{\dfrac{1.0078\cdot 10^{-3}\text{ kg mol}^{-1} + 2.0141\cdot 10^{-3}\text{ kg mol}^{-1}}{N_A}} = 1.1154\cdot 10^{-27}\text{ kg}$$

For one molecule HD:

$$\varepsilon_{HD} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{6.6261\cdot 10^{-34}\text{ J s}}{2\pi}\sqrt{\frac{575.11\text{ N m}^{-1}}{1.1154\cdot 10^{-27}\text{ kg}}} = 7.5724\cdot 10^{-20}\text{ J}$$

For 1 mol of HD:

$$\varepsilon_{HD} = 7.5724\cdot 10^{-20}\text{ J} \times N_A = 7.5724\cdot 10^{-20}\text{ J} \times 6.0221\cdot 10^{23}\text{ mol}^{-1} = 45\,600\text{ kJ mol}^{-1}$$

$$\Delta H = \Delta E = 0.01435\,\varepsilon_{HD} = 0.6544\text{ kJ mol}^{-1}$$

3.2 $h\nu = \Delta E$

$$\Delta E = E_{\nu 1} - E_{\nu 0} = \left(\frac{3}{2} - \frac{1}{2}\right)\varepsilon_{HD} = \varepsilon_{HD}$$

$$h\nu = \varepsilon_{HD} \quad \Rightarrow \quad \nu = \frac{\varepsilon_{HD}}{h}$$

From part 3.1:

$$\varepsilon_{HD} = 7.5724\cdot 10^{-20}\text{ J}$$

Thus: $\nu = \dfrac{7.5724 \cdot 10^{-20}\ \text{J}}{6.6261 \cdot 10^{-34}\ \text{J s}} = 1.1428 \cdot 10^{-14}\ \text{s}$

3.3 $H_2 \rightarrow 2\ H$

For n = 1: ΔE = 2 (–13.5984) – (–31.675) = 4.478 eV

3.4 $H_2 + h\nu \rightarrow H + H$

	H	H
n =	1	1
	1	2
	2	1
	2	2
	.	.
	.	.
	.	.

The energy of H_2 molecule in its ground state is –31.675 eV.

λ = 77.0 nm

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{6.6261 \cdot 10^{-34} \times 3.00 \cdot 10^{8}}{77.0 \cdot 10^{-9}} = 2.58 \cdot 10^{-18}\ \text{J}$$

$$E_{\text{photon}} = \frac{6.6261 \cdot 10^{-34}}{1.602 \cdot 10^{-19}} = 16.1\ \text{eV}$$

$$\Delta E = E_{n_1} + E_{n_2} - E_{n_{H_2}} = -\frac{R_H}{n_1^2} - \frac{R_H}{n_2^2} - (31.675) < 16.1\,\text{eV}$$

---

n_1 = 1 n_2 = 1

$$\Delta E = -\frac{13.5984}{1^2} - \frac{13.5984}{1^2} + 31.675 = 4.478\ \text{eV}$$

KE = 16.1 – 4.478 = 11.6 eV

---

n_1 = 1, n_2 = 2 or n_1 = 2, n_2 = 1

$$\Delta E = -\frac{13.5984}{1^2} - \frac{13.5984}{2^2} + 31.675 = 14.677\ \text{eV}$$

KE = 16.1 – 14.677 = 1.4 eV

$n_1 = 2, \quad n_2 = 2$

$$\Delta E = -\frac{13.5984}{2^2} - \frac{13.5984}{2^2} + 31.675 = 24.880 \text{ eV} > 16.1 \text{ eV}$$

K.E. = 16.1 – 14.677 = 1.4 eV

Thus, the possibilities are:

$H_2 + h\nu \rightarrow H + H$

n =	1	1
	1	2
	2	1

3.5 IP(H) = $\Delta E_{n \to \infty} = -\frac{13.5984}{\infty^2} - \frac{13.5984}{1^2} = 13.598 \text{ eV}$ (ionization potential)

$H_2^+ + e \rightarrow H_2 \qquad EA(H_2^+) = - IP(H_2)$

$H_2^+ \rightarrow H^+ + H \qquad DE(H_2^+) = 2.650 \text{ eV}$

$H \rightarrow H^+ + e \qquad IP(H) = 13.598 \text{ eV}$

$H_2 \rightarrow H + H \qquad DE(H_2) = 4.478 \text{ eV}$

$$EA(H_2^+) = DE(H_2^+) - IP(H) - DE(H_2) = 2.650 - 13.598 - 4.478 = -15.426 \text{ eV}$$

Electron affinity H_2^+ = – 15.426 eV

PROBLEM 4

For sustainable energy, hydrogen appears to be the best energy carrier. The most efficient way of using hydrogen is generation of electrical energy in a fuel cell. However, storing hydrogen in large quantities is a challenge in fuel cell applications. Among the chemical hydrides considered as solid hydrogen storage materials, sodium borohydride ($NaBH_4$), being non-toxic, stable and environmentally benign, appears to be the most promising one. The hydrolysis of sodium borohydride that releases H_2 gas is a slow reaction at ambient temperature and, therefore, needs to be catalyzed.

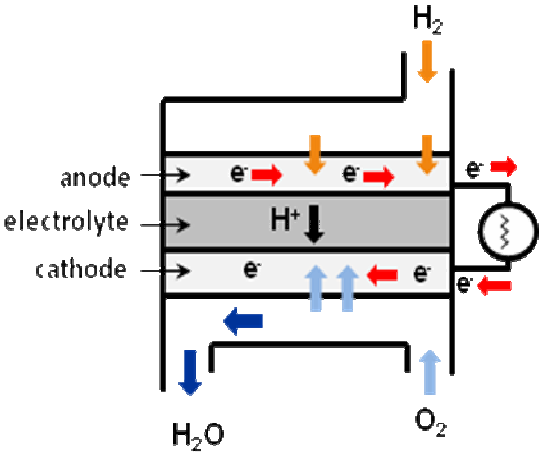
$$NaBH_4(aq) + 2\,H_2O(l) \xrightarrow{\text{catalyst}} Na^+(aq) + BO_2^-(aq) + 4\,H_2(g)$$

Colloidal ruthenium(0) nanoclusters are the most active catalysts in this hydrolysis even at room temperature and lead to a complete H_2 release from sodium borohydride. Kinetic studies show that the catalytic hydrolysis of $NaBH_4$ is a first order reaction with respect to the catalyst, but a zero order with respect to the substrate. The rate of hydrogen production per mole of ruthenium is 92 mol $H_2\cdot(\text{mol Ru})^{-1}\cdot\text{min}^{-1}$ at 25 °C.

4.1 Calculate the amount of ruthenium catalyst (in mg) which must be added to 0.100 dm^3 of $NaBH_4$ solution with a concentration of 1.0 mol dm^{-3} to supply the hydrogen gas at a rate of 0.100 $dm^3\cdot min^{-1}$ at 25 °C and 1.0 atm, that is required for a portable fuel cell.

4.2 For how many minutes will this system supply hydrogen gas at this rate?

4.3 The Arrhenius activation energy for this catalytic hydrolysis of sodium borohydride is E_a = 42.0 kJ mol^{-1}. Calculate the temperature required to achieve the same rate of hydrogen evolution by using a half of the amount of ruthenium catalyst used at 25.0 °C.



4.4 A fuel cell (see figure) is made up of three segments sandwiched together: the anode, the electrolyte, and the cathode. Hydrogen is used as fuel and oxygen as oxidant. Two chemical reactions occur at the interfaces of the three different segments:

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

$H_2(g) + 2\ OH^-(aq) \rightarrow 2\ H_2O(l) + 2\ e^-$

The net result of the two reactions is

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

The hydrogen for the fuel cell is supplied from the hydrolysis of sodium borohydride. Calculate the standard potential for the cathode half reaction if the standard reduction potential for the anode half reaction is –0.83 V and $\Delta_f G^o(H_2O(l))$ is –237 kJ mol^{-1}.

4.5 Calculate the volume of air at a temperature of 25 °C and a pressure of 1.0 atm needed to generate a constant current of 2.5 A for 3.0 hours in this fuel cell. Assume that air contains 20 % by volume O_2(g).

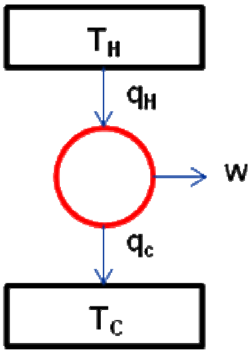
4.6 The efficiency of a fuel cell is given by the ratio of the work produced to the heat dissipated by the cell reaction. Thus, the maximum efficiency for a fuel cell is given by:

$$\eta_{\text{fuel cell}} = \frac{\text{work}}{\text{heat}}$$

Calculate the maximum efficiency for the fuel cell using the data given below at 25 °C and a standard pressure.

	$S°$ (J mol^{-1} K^{-1})
$H_2(g)$	130.7
$O_2(g)$	205.2
$H_2O(l)$	70.0

The second law of thermodynamics states that it is impossible to convert all of the heat, q_H, from a high-temperature reservoir at T_H into work. At least, some of the energy, q_C, must be transferred to a low-temperature reservoir at T_C. Thus, a heat engine with 100% efficiency is thermodynamically impossible. When the heat engine is working reversibly, as in a Carnot cycle, the efficiency will be a maximum.



For a heat engine working reversibly between two reservoirs the following relations are applied:

$$q_H = w + q_C$$

and

$$\frac{q_H}{T_H} = \frac{q_C}{T_C}$$

4.7 <u>What should be the temperature</u> of the hot reservoir, T_H, of a Carnot heat engine to maintain the efficiency of the fuel cell calculated in part 4.6, if the temperature of cold reservoir T_C is 40 °C?

(If you have been unable to calculate the value for the efficiency then use the value 0.80 for the calculation.)

SOLUTION

4.1 $n(H_2) = \dfrac{0.100\ \text{dm}^3\ \text{min}^{-1} \times 101.325\ \text{kPa}}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times\ 298\ \text{K}} = 4.1 \cdot 10^{-3}\ \text{mol min}^{-1}$

$$n(\text{Ru}) = \frac{4.1 \cdot 10^{-3}\ \text{mol H}_2\ \text{min}^{-1}}{\dfrac{92\ \text{mol H}_2\ \text{min}^{-1}}{1\ \text{mol Ru}}} = 4.5 \cdot 10^{-5}\ \text{mol}$$

$m(\text{Ru}) = 4.5 \cdot 10^{-5}\ \text{mol} \times 101.07\ \text{g mol}^{-1} = 4.5 \cdot 10^{-3}\ \text{g} = 4.5\ \text{mg}$

4.2 $n(NaBH_4) = 1.0\ \text{mol dm}^{-3} \times 0.100\ \text{dm}^3 = 0.10\ \text{mol}$

0.04 mol of H_2 are released from 0.10 mol $NaBH_4$.

Thus:

$$t = \frac{0.40\ \ \text{mol H}_2}{4.1 \cdot 10^{-3}\ \ \text{mol H}_2\ \text{min}^{-1}} = 98\ \text{min}$$

4.3 Rate = k [Ru] = $A\, e^{-E_a / RT}$ [Ru]

$$\frac{e^{-E_a / R \times 298}}{e^{-E_a / RT}} = \frac{1}{2}$$

$$-\frac{E_a}{R}\left(\frac{1}{298} - \frac{1}{T}\right) = \ln\frac{1}{2}$$

$$\frac{4.20 \cdot 10^4\ \text{J mol}^{-1}}{8.314\ \text{J mol}^{-1}\text{K}^{-1}}\left(\frac{1}{298} - \frac{1}{T}\right) = \ln 2$$

T = 311 K or 38 °C

4.4 Since $\Delta G^o = -\, n\, F\, E^o$

$2\ (-2.37 \cdot 10^5) = -\ 4 \times 96485 \times E^0_{\text{cell}}$ $\qquad E^0_{\text{cell}} = 1.23\ \text{V}$

$1.23\ \text{V} = E^0_{\text{cathode}} - (-0.83\ \text{V})$

$E^0_{\text{cathode}} = 0.40\ \text{V}$

4.5 2.5 A × 3 × 3600 s = 27000 C

$$n(O_2) = 27000\ \text{C} \times \frac{1\ \text{mol}}{4 \times 96485\ \text{C}} = 0.070\ \text{mol}$$

$V(O_2) = \dfrac{0.070\ \text{mol} \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}}{101.325\ \text{kPa}} = 1.7\ \text{dm}^3$ $\qquad V(\text{air}) = 8.6\ \text{dm}^3$

4.6 $\Delta_{rxn}G^o = \Delta_{rxn}H^o - T\,\Delta_{rxn}S^o$

$\Delta_{rxn}S^o = 2\,S^o\,(H_2O_{(l)}) - [\,2S^o\,(H_2(g)) + S^o(O_2\,(g))\,] = 2 \times 70.0 - (2 \times 130.7 + 205.2)$

$= -326.6$ J mol^{-1} K^{-1}

$\Delta_{rxn}H^o = \Delta_{rxn}G^o + T\,\Delta_{rxn}S^o = -\,474 + 298.15 \times (-326.6 \cdot 10^{-3}) = -571.4$ kJ

maximum w = $\Delta_{rxn}G^o = -\,474$ kJ

$$\eta = \frac{-\,474000\text{ J}}{-\,571400\text{ J}} = 0.83$$

4.7 $$\eta_{\text{engine}} = \frac{w}{q_H} = \frac{q_H - q_C}{q_H} = 1 - \frac{q_C}{q_H}$$

Since $\dfrac{q_H}{T_H} = \dfrac{q_C}{T_C} \qquad \dfrac{q_C}{q_H} = \dfrac{T_C}{T_H}$

Thus: $\eta_{\text{engine}} = 1 - \dfrac{T_C}{T_H}$

$0.83 = 1 - \dfrac{313}{T_H}$

$T_H = 1.8 \cdot 10^3$ K or $T_H \approx 1.5 \cdot 10^3$ °C

PROBLEM 5

Polynitrogen compounds have great potential for being used as high energy density materials. They are thermodynamically unstable. Huge amount of energy is released from their decomposition or reactions leading to more stable products. The only known polynitrogen species are N_2, N_3^- and N_5^+, isolated in 1772, 1890 and 1999, respectively, and recently reported cyclic anion, N_5^-.

5.1 Write the lesis structure for N_5^+ with three energetically favourable resonance forms. Indicate the lone pairs and formal charges. Draw the molecular geometry of N_5^+.

5.2 Write the Lewis structures for cyclic N_5^- with five energetically favourable resonance forms. Indicate the lone pairs and formal charges. Draw the molecular geometry of cyclic N_5^-.

5.3 The synthesis of $[N_5^+][AsF_6^-]$, a white ionic solid, was achieved by reacting $[N_2F^+][AsF_6^-]$ with hydrazoic acid, HN_3, in liquid HF at –78 °C. Write the balanced chemical equation for this reaction.

The preparation of $[N_2F^+][AsF_6^-]$ requires the reaction of N_2F_2 with strong Lewis acid AsF_5 as follows:

$x\,C(\text{graphite}) + AsF_5 \rightarrow C_x \cdot AsF_5$ (graphite intercalate with x = 10 – 12)

$2\,C_x \cdot AsF_5 + N_2F_4 \rightarrow 2\,[C_x^+][AsF_6^-] + \textit{trans}\text{-}N_2F_2$

$\textit{trans}\text{-}N_2F_2 + AsF_5 \rightarrow [N_2F^+][AsF_6^-]$

In the synthesis of N_2F_2, the *trans* isomer is formed which is thermodynamically less stable than *cis*-N_2F_2. However, conversion of *trans*-N_2F_2 to *cis*-N_2F_2 requires surmounting a high energy barrier of 251 kJ mol^{-1}, so that equilibration between the *cis* and the *trans* isomers does not significantly take place without a suitable catalyst.

When *trans*-N_2F_2 is maintained in a closed container for six days at room temperature in the presence of a small amount of SbF_5 as a catalyst, *cis*-*trans* thermal equilibrium is established.

$$\textit{trans}\text{-}N_2F_2 \xrightleftharpoons{25\ ^{\circ}\mathrm{C}} \textit{cis}\text{-}N_2F_2$$

The standard enthalpies of formation of *trans*- and *cis*-N_2F_2 are 67.31 and 62.03 kJ mol$^{–1}$, respectively, and their standard entropies at 25 °C are 262.10 and 266.50 J K$^{–1}$ mol^{-1}, respectively.

5.4 Find the ratio of the number of *cis*-N_2F_2 molecules over that of the *trans*-N_2F_2 molecules in an equilibrium mixture at 25 °C.

5.5 Write the Lewis structures showing the geometry of N_2F^+ ion and those of *trans*- and *cis*-isomers of N_2F_2. Include all lone pairs and formal charges. Suggest an appropriate hybridization for each nitrogen atom in N_2F_2 and N_2F^+.

Solid $[N_5^+][AsF_6^-]$ is marginally stable at room temperature but reacts explosively with water to produce arsenic pentafluoride, hydrogen fluoride, molecular nitrogen and oxygen.

5.6 Write a balanced equation for the reaction between $[N_5^+][AsF_6^-]$ and water.

Conversion of $[N_5^+][SbF_6^-]$ into other N_5^+ salts can be achieved by a metathesis reaction:

$[N_5^+][SbF_6^-] + [M^+][X^-] \longrightarrow [N_5^+][X^-] + [M^+][SbF_6^-]$

where $M^+ = Na^+$, K^+, Cs^+, and X^- = large anion such as SnF_6^{2-} and $B(CF_3)_4^-$.

Since $[Cs^+][SbF_6^-]$ has a low solubility in anhydrous HF, and $[K^+][SbF_6^-]$ has a low solubility in SO_2, these two solvents were used extensively to carry out metathesis reactions at –78 °C and –64 °C, respectively.

5.7 Write the balanced equation for the preparation of $[N_5^+]_2[SnF_6^{2-}]$ and $[N_5^+][B(CF_3)_4^-]$ in solution starting with $[Cs^+]_2[SnF_6^{2-}]$ and $[K^+][B(CF_3)_4^-]$, respectively. Indicate the appropriate solvent.

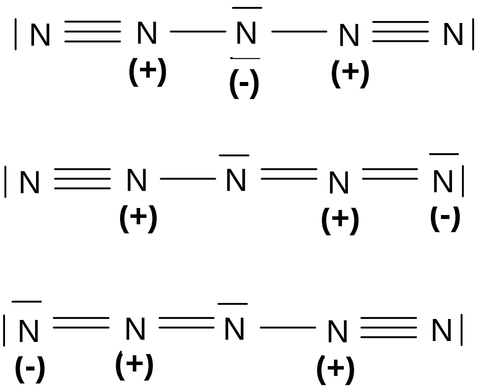
When $[N_5^+]_2[SnF_6^{2-}]$ decomposes under carefully controlled conditions at 25 – 30 °C, $[N_5^+][SnF_5^-]$ and N_5F are formed. The $[N_5^+][SnF_5^-]$ salt is a white solid and has a thermal stability comparable to that of $[N_5^+][SbF_6^-]$ (50 – 60 °C). The solution ^{119}Sn NMR spectrum has shown that the SnF_5^- anion in this compound is, in fact, a mixture of dimeric and tetrameric polyanions. In both of these polyanions the coordination number of Sn atom is 6 and there are bridging fluorine atoms.

5.8 Draw the structures of dimeric and tetrameric polyanions.

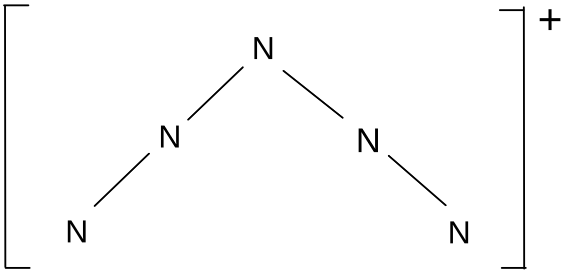
SOLUTION

5.1 Formula**:** N_5^+

Lewis structure:

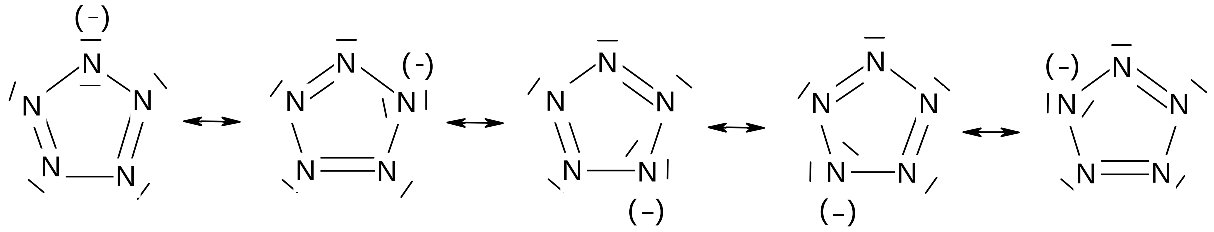


Molecular geometry:

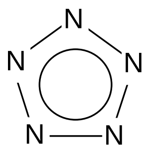


5.2 Cyclic N_5^+:

Lewis structure:



Molecular geometry:



5.3 $[N_2F^+][AsF_6^-] + HN_3 \xrightarrow[\text{in HF}(l)]{-78\ °C} [N_5^+][AsF_6^-] + HF$

5.4 The desired ratio is the value of the equilibrium constant K of the trans $\rightleftarrows$ cis reaction shown above:

$$K = \frac{[cis]}{[trans]}$$

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

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

$$\Delta H^{\,o} = 62.03 - 67.31 = -5.28 \text{ kJ mol}^{-1}$$

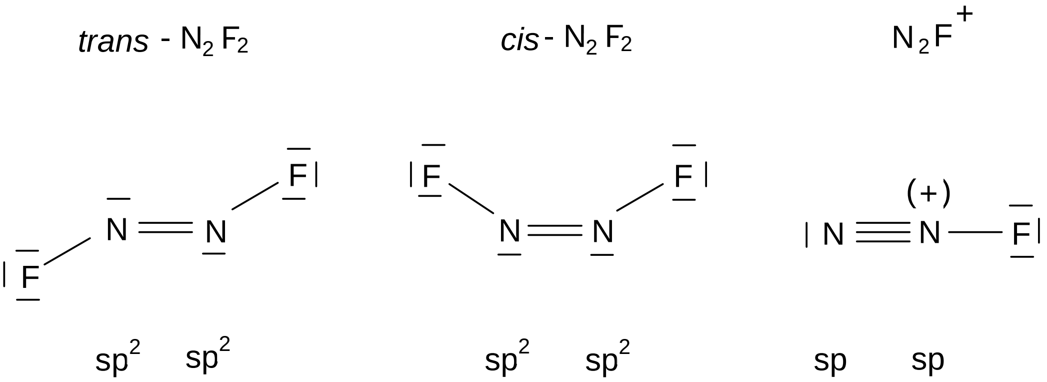
$$\Delta \text{S}^o = 266.50 - 262.10 = 4.40 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$\Delta \text{G}^o = -5.28{\cdot}10^3 - (298 \times 4.40) = -6.59 \cdot 10^3 \text{ J mol}^{-1}$$

$$K = e^{-\Delta G^o / RT} = = e^{-(-6.59\ \cdot 10^3)/(8.314 \times 298)} = 14.3$$

$$K = \frac{[cis]}{[trans]} = 14.3 \text{ at } 25\ ℃$$

5.5



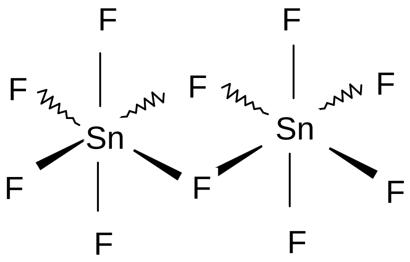
5.6 $4\,[N_5^+][AsF_6^-] + 2\,H_2O \rightarrow 4\ AsF_5 + 4\,HF + 10\,N_2 + O_2$

5.7 $2\,[N_5^+][AsF_6^-] + Cs_2SnF_6 \xrightarrow{HF,\ -78\ ℃} [N_5^+]_2[SnF_6^{2-}] + 2\,CsSbF_6$

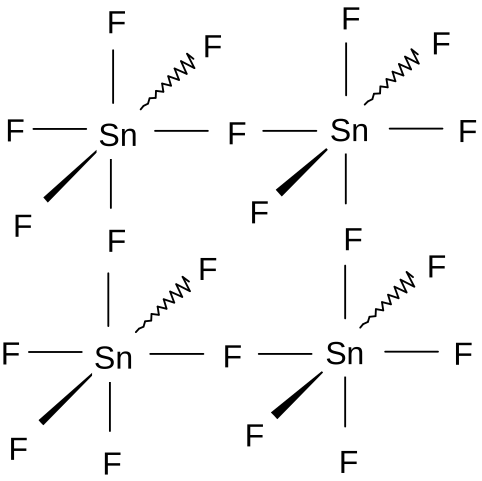
$[N_5^+]\,[SbF_6{}^-] + K^+[B(CF_3)_4^-] \xrightarrow{SO_2,\ -64\ ℃} [N_5^+]\,[B(CF_3)_4^-] + 2\,KSbF_6$

5.8

dimer, $Sn_2F_{10}^{2-}$



tetramer, $Sn_4F_{20}^{4-}$



PROBLEM 6

Extraction of gold using sodium cyanide, a very poisonous chemical, causes environmental problems and gives rise to serious public concern about the use of this so called "cyanide process". Thiosulfate leaching of gold has been considered as an alternative. In this process, the main reagent is ammonium thiosulfate, $(NH_4)_2S_2O_3$, which is relatively non-toxic. Although this process appears to be environmentally benign, the chemistry involved is very complex and needs to be studied thoroughly. The solution used for leaching gold contains $S_2O_3^{2-}$, Cu^{2+}, NH_3, and dissolved O_2. The solution must have a pH greater than 8.5 to allow free ammonia to be present.

According to the proposed mechanism, a local voltaic micro-cell is formed on the surface of gold particles during the leaching process and operates as follows:

Anode:

$Au(s) + 2\ NH_3(aq) \longrightarrow [Au(NH_3)_2]^+(aq) + e^-$

$[Au(NH_3)_2]^+(aq) + 2\ S_2O_3^{2-}(aq) \longrightarrow [Au(S_2O_3)_2]^{3-}(aq) + 2\ NH_3(aq)$

Cathode:

$[Cu(NH_3)_4]^{2+}(aq) + e^- \longrightarrow [Cu(NH_3)_2]^+(aq) + 2\ NH_3(aq)$

$[Cu(NH_3)_2]^+(aq) + 3\ S_2O_3^{2-}(aq) \longrightarrow [Cu(S_2O_3)_3]^{5-}(aq) + 2\ NH_3(aq)$

6.1 Write the overall cell reaction for this voltaic cell.

6.2 In the presence of ammonia $[Cu(S_2O_3)_3]^{5-}$ is oxidized by O_2 back to $[Cu(NH_3)_4]^{2+}$. Write a balanced equation for this oxidation-reduction reaction in basic solution.

6.3 In this leaching process, the $[Cu(NH_3)_4]^{2+}$ complex ion functions as catalyst and speeds up the dissolution of gold. Write the net overall oxidation-reduction reaction for dissolution of the gold metal, which is catalyzed by $[Cu(NH_3)_4]^{2+}$ complex ion.

6.4 Draw the coordination geometries of the metal in $[Au(NH_3)_2]^+$ and $[Au(S_2O_3)_2]^{3-}$ complex ions, indicating the coordinating atoms.

The formation constants, K_f, of $[Au(NH_3)_2]^+$ and $[Au(S_2O_3)_2]^{3-}$ complexes are $1.00 \cdot 10^{26}$ and $1.00 \cdot 10^{28}$, respectively. Consider a leaching solution in which the equilibrium concentrations of the species are as follows:

$[S_2O_3^{2-}] = 0.100$; $[NH_3] = 0.100$ and the total concentration of gold(I) species = $5.50 \cdot 10^{-5}$ mol dm^{-3}.

6.5 Calculate the percentage of gold(I) ion that exists in the form of thiosulfate complex.

When the concentration of O_2 is not high enough and pH > 10, $S_2O_3^{2-}$ reduces $[Cu(NH_3)_4]^{2+}$ to $[Cu(S_2O_3)_3]^{5-}$ with the formation of tetrathionate ion $S_4O_6^{2-}$:

$$2\ [Cu(NH_3)_4]^{2+}(aq) + 8\ S_2O_3^{2-}\ (aq) \rightarrow 2\ [Cu(S_2O_3)_3]^{5-}\ (aq) + S_4O_6^{2-}\ (aq) + 8\ NH_3(aq)$$

In basic solution tetrathionate disproportionates to trithionate, $S_3O_6^{2-}$, and thiosulfate.

6.6 Write a balanced equation for this disproportionation reaction.

6.7 When the O_2 concentration is too high, $S_2O_3^{2-}$ is oxidized by oxygen to yield trithionate and sulfate ions. Write a balanced equation for this reaction.

SOLUTION

6.1 Net anode half reaction:

$Au(s) + 2\ S_2O_3^{2-}(aq) \rightarrow [Au(S_2O_3)_2]^{3-}(aq) + e^-$

Net cathode half reaction:

$[Cu(NH_3)_4]^{2+}(aq) + 3\ S_2O_3^{2-}(aq) + e^- \rightarrow [Cu(S_2O_3)_3]^{5-}(aq) + 4\ NH_3(aq)$

erall cell reaction:

$Au(s) + [Cu(NH_3)_4]^{2+}(aq) + 5\ S_2O_3^{2-}(aq) \rightarrow [Au(S_2O_3)_2]^{3-}(aq) + [Cu(S_2O_3)_3]^{5-}(aq)$
$+ 4\ NH_3(aq)$

6.2 Oxidation half reaction:

$[Cu(S_2O_3)_3]^{5-}(aq) + 4\ NH_3(aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq) + 3\ S_2O_3^{2-}(aq) + e^-$

Reduction half reaction:

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

Redox reaction:

$4\ [Cu(S_2O_3)_3]^{5-}(aq) + 16\ NH_3(aq) + O_2(g) + 2\ H_2O(l) \rightarrow$
$\rightarrow 4\ [Cu(NH_3)_4]^{2+}(aq) + 12\ S_2O_3^{2-}(aq) + 4\ OH^-(aq)$

6.3 $Au(s) + [Cu(NH_3)_4]^{2+}(aq) + 5\ S_2O_3^{2-}(aq) \rightarrow [Au(S_2O_3)_2]^{3-}(aq) + [Cu(S_2O_3)_3]^{5-}(aq) +$
$+ 4\ NH_3(aq)$

$4\ [Cu(S_2O_3)_3]^{5-}(aq) + 16\ NH_3(aq) + O_2(g) + 2\ H_2O(l) \rightarrow$
$\rightarrow 4\ [Cu(NH_3)_4]^{2+}(aq) + 12\ S_2O_3^{2-}(aq) + 4\ OH^-(aq)$

Summarizing the above equations:

$4\ Au(s) + 8\ S_2O_3^{2-}(aq) + O_2(g) + 2\ H_2O(l) \rightarrow 4\ [Au(S_2O_3)_2]^{3-}(aq) + 4\ OH^-(aq)$

6.4	$[Au(NH_3)_2]^+$	$[Au(S_2O_3)_2]^{3-}$
Coordination geometry:	$[H_3N\text{-}Au\text{-}NH_3\ ]^+$	$[O_3S\text{-}S\text{-}Au\text{-}S\text{-}SO_3\ ]^{3-}$

6.5 $Au^+(aq) + 2\ NH_3(aq) \rightarrow [Au(NH_3)_2]^+(aq)$ $K_{f,1} = 1.00\ .\ 10^{26}$

$Au^+(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow [Au(S_2O_3)_2]^{3-}(aq)$ $K_{f,2} = 1.00\ .\ 10^{28}$

$[Au(NH_3)_2]^+(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow [Au(S_2O_3)_2]^{3-}(aq) + 2\ NH_3(aq)$

$$K_{eq} = \frac{K_{f,2}}{K_{f,1}} = 1.00 \cdot 10^2$$

$[Au(NH_3)_2]^+ + [Au(S_2O_3)_2]^{3-} = 5.50 \cdot 10^{-5}$ mol dm^{-3}

$$K_{eq} = \frac{(0.100)^2\ x}{(5.50 \cdot 10^{-5} - x)\ (0.100)^2} = 1.00 \cdot 10^2$$

$x = 5.445 \cdot 10^{-5}$

$$\frac{5.445 \cdot 10^{-5}}{5.50 \cdot 10^{-5}} \times 100 = 99.0\ \%$$

Thus, 99.0 % of Au(I) is in the form of $[Au(S_2O_3)_2]^{3-}$.

6.6 $S_4O_6^{2-}(aq) + 2\ e^- \rightarrow 2\ S_2O_3^{2-}(aq)$

$12\ OH^-(aq) + 3\ S_4O_6^{2-}(aq) \rightarrow 4\ S_3O_6^{2-}(aq) + 6\ H_2O(l) + 10\ e^-$

$4\ S_4O_6^{2-}(aq) + 6\ OH^-(aq) \rightarrow 5\ S_2O_3^{2-}(aq) + 2\ S_3O_6^{2-}(aq) + 3\ H_2O(l)$

disproportionation

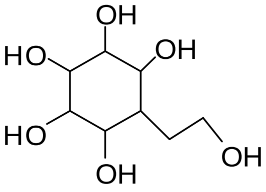
6.7 $2\ S_2O_3^{2-}(aq) + 2\ O_2(g) \rightarrow SO_4^{2-}(aq) + S_3O_6^{2-}(aq)$

PROBLEM 7

Synthesis of a carbasugar

Carbohydrates are essential components of living cells and a source of energy for animals. They include simple sugars with small molecules as well as macromolecular substances. When the ring oxygen (endocyclic oxygen) in sugars is replaced by a methylene group, the compounds formed are called as *pseudosugars* or *carbasugars*. Since carbasugars are hydrolytically stable towards acids and enzymes, several carbasugars have found application in the field of glycosidase inhibition.

The total syntheses of two isomeric carbasugars having skeleton **1** are described below.

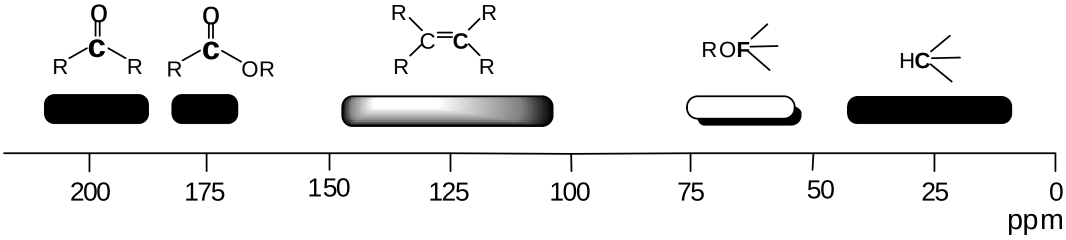


1

The total synthesis of **1** starts with a reduction of benzene by sodium in liquid ammonia to give **A**. The C-13 NMR spectrum of **A** consists of two signals at 124.0 and 26.0 ppm.

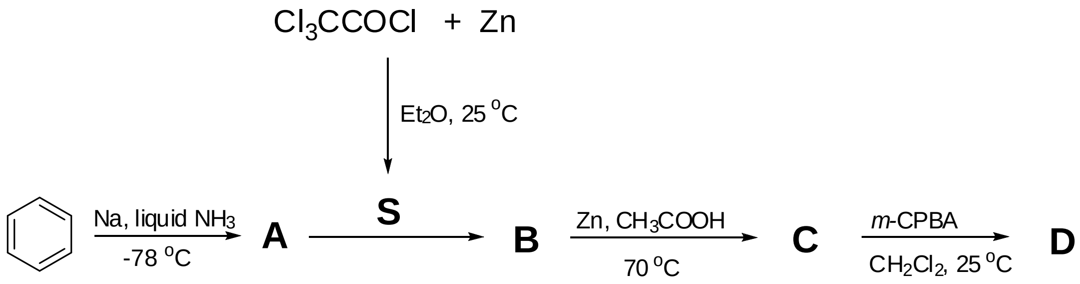
Trichloroacetyl chloride in the presence of Zn gives a reactive species **S** (see the Scheme 7.1). One equivalent of **S** undergoes [2+2]cycloaddition with **A** to form a racemic product **B**. The reaction of **B** with Zn in acetic acid gives **C**. Compound **C** contains only carbon, hydrogen and oxygen. The C-13 NMR spectrum of **C** exhibits three sp^2 carbon signals at 210.0, 126.5 and 125.3 ppm.

The reaction of **C** with one equivalent *m*-chloroperbenzoic acid (*m*-CPBA) in methylene chloride gives **D** as a major product. The C-13 NMR spectrum of **D** exhibits also three signals in the sp^2 region at 177.0, 125.8, 124.0 ppm.



^{13}C-NMR chemical shift ranges of typical functional groups

Scheme 7.1:



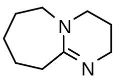
7.1 Draw the structures of **A**, **B**, **C**, **D**, and the intermediate **S**.

Reduction of **D** with $LiAlH_4$ yields **E** which reacts with an excess of acetyl chloride in pyridine to give **F** (Scheme 7.2).

Scheme 7.2:

$$\mathbf{D} \xrightarrow[25\,^{o}C]{LiAlH_4,\ Et_2O} \mathbf{E} \xrightarrow[Pyridine,\ 25\,^{o}C]{CH_3COCl} \mathbf{F} \xrightarrow[CH_2Cl_2,\ 0\,^{o}C]{Br_2} \mathbf{G_1} + \mathbf{G_2} \xrightarrow[Benzene,\ reflux]{DBU\ (2\ eq)} \mathbf{H}$$

DBU =



7.2 Draw the structures (use one enantiomer) of **E** and **F** using dashed-wedged line notation. Assign the configurations (*R* or *S*) at the asymmetric carbon atoms in **E**.

The compound **F** (use the drawn enantiomer) reacts with bromine to give the stereoisomers $\mathbf{G_1}$ and $\mathbf{G_2}$.

7.3 Draw the structures of $\mathbf{G_1}$and $\mathbf{G_2}$ using dashed-wedged line notation.

A mixture of $\mathbf{G_1}$ and $\mathbf{G_2}$ reacts with two equivalents of 1,8-diazabicyclo- [5.4.0]undec-7-ene (DBU), which is a strong amine base, to afford **H**.

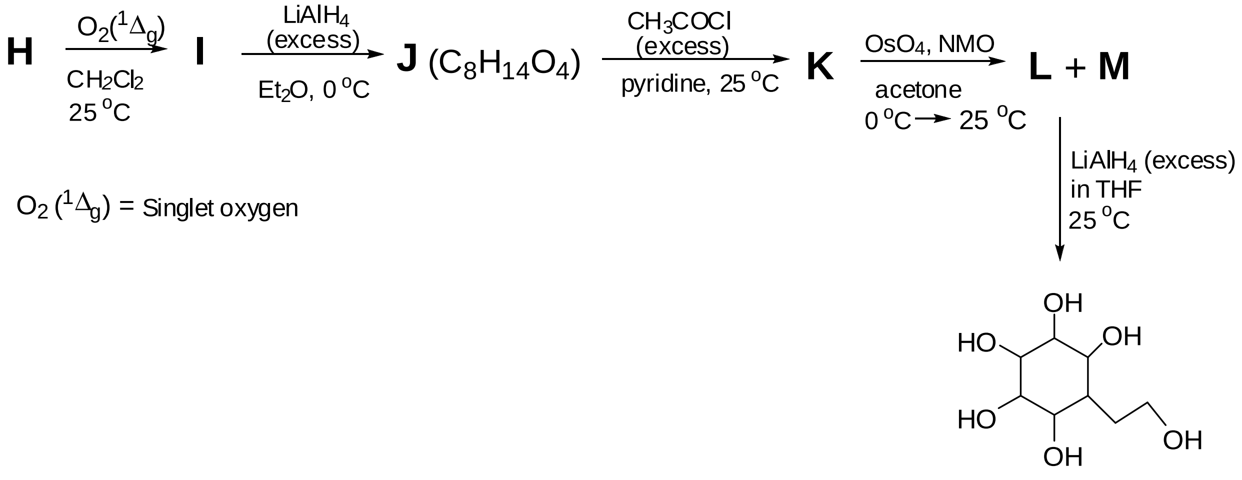
7.4 Draw the structure of **H** using dashed-wedged line notation.

Reaction of **H** with singlet oxygen (in situ generated) affords **I**. Although two isomers are theoretically possible, **I** is formed as the single isomer due to steric hindrance and electronic repulsion.

The reaction of **I** with excess of $LiAlH_4$ results in the formation of **J** (see the Scheme 7.3). The C-13 NMR spectrum of **J** shows 8 signals, two in the sp^2 region.

Reaction of **J** with excess acetyl chloride in the presence of pyridine yields **K**. Subsequent reaction of **K** with OsO_4 in the presence of 4-methylmorpholine 4-oxide (NMO) gives stereoisomers **L** and **M.** Upon reduction with excess $LiAlH_4$, **L** and **M** give the stereoisomers **1a** and **1b**, respectively.

Scheme 7.3:



O2 ($^1\Delta_g$) = Singlet oxygen

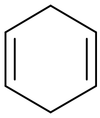
1a and **1b**

7.5 Draw the structures of **I, J, K, L, M, 1a**, and **1b** using dashed-wedged line notation.

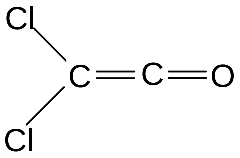
SOLUTION

7.1

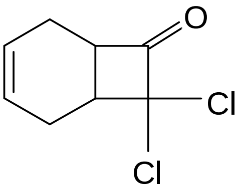
A



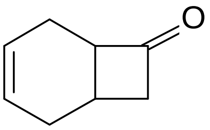
S



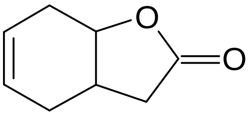
B



C

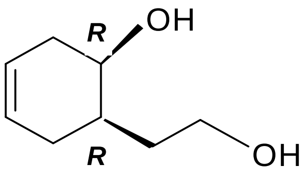


D

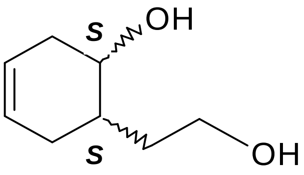


7.2

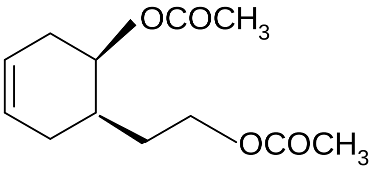
E



or



F



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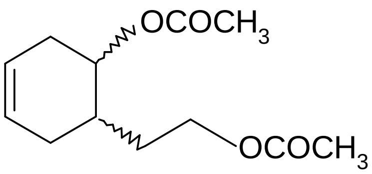
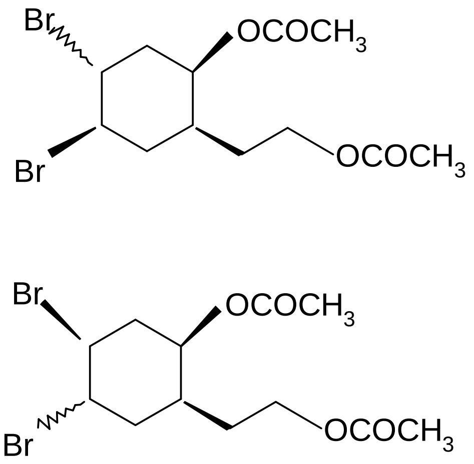


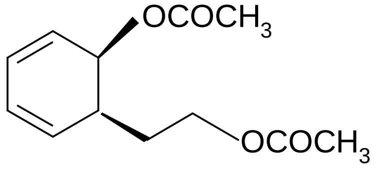
7.3

G_1 and **G_2**



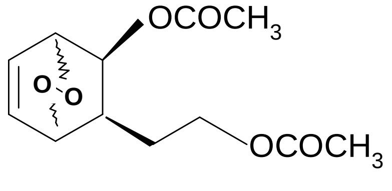
7.4

H

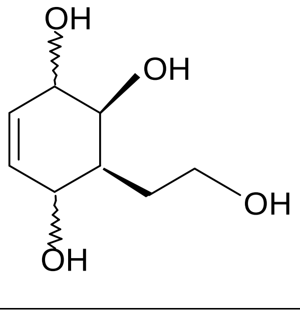


7.5

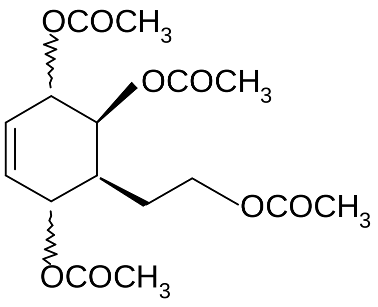
I



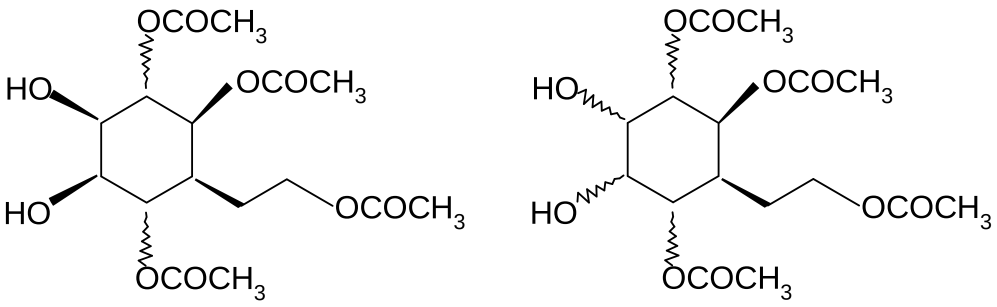
J



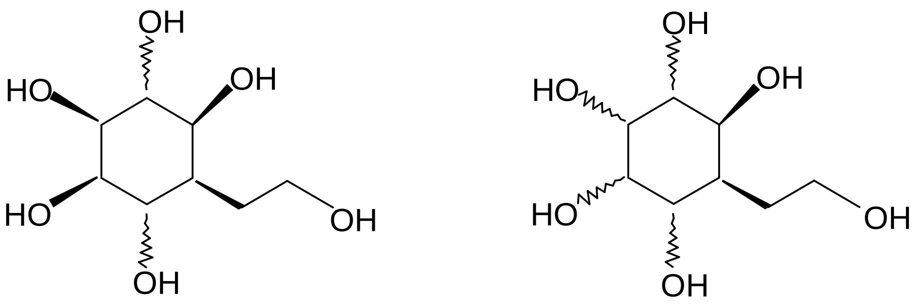
K



L and **M**



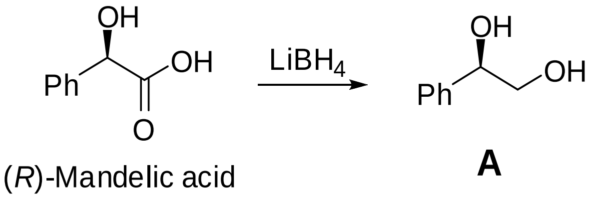
1a and **1b**



PROBLEM 8

Click chemistry is a chemical concept introduced by K. B. Sharpless in 2001 and describes a set of chemical reactions that generate substances quickly, reliably and quantitatively by joining molecules through small units under mild conditions. This methodology has recently been applied as a key step in the following synthesis of bicyclic compounds.

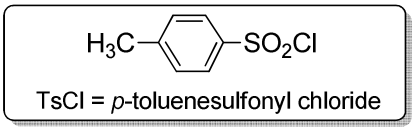
Mandelic acid is a versatile natural compound and widely used as a “chiral pool” in synthesis. The reduction of (*R*)-mandelic acid with $LiBH_4$ affords **A**.



Reaction of **A** with one equivalent of *p*-toluenesulfonyl chloride gives **B** (Scheme 8.1). Heating **B** in pyridine yields **C**. During this transformation, compounds **B** and **C** retain their absolute configurations.

Scheme 8.1:

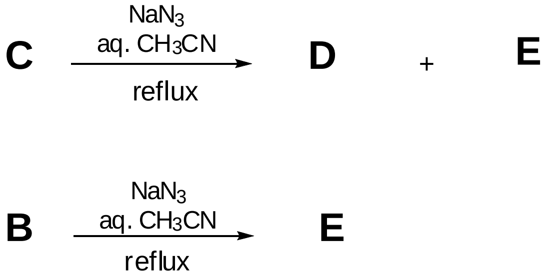
$$\mathbf{A} \xrightarrow[CH_2Cl_2,\ 0\ ^{o}C]{TsCl\ (1\ eq),\ Et_3N\ (1.2\ eq)} \mathbf{B} \xrightarrow{Pyridine,\ heat} \mathbf{C}$$



8.1 Draw the structures of **B** and **C** with the correct stereochemistry. Use dashed-wedged line notation throughout this problem.

Reaction of **C** with sodium azide in aqueous acetonitrile gives a mixture of enantiopure regioisomers **D** and **E** in a ratio of 3 : 1 (Scheme 8.2). On the other hand, the compound **B** affords **E** as the sole product under the same condition.

Scheme 8.2:



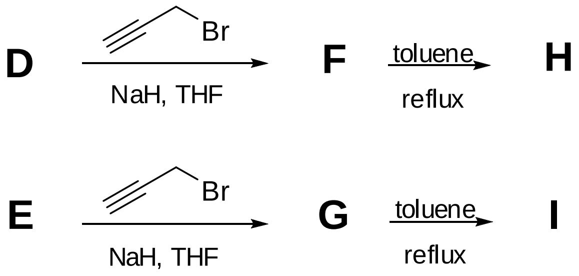
$$\mathbf{C}\ \xrightarrow[\text{reflux}]{\text{NaN}_3,\ \text{aq. CH}_3\text{CN}}\ \mathbf{D}\ +\ \mathbf{E}$$

$$\mathbf{B}\ \xrightarrow[\text{reflux}]{\text{NaN}_3,\ \text{aq. CH}_3\text{CN}}\ \mathbf{E}$$

8.2 Draw the structures of **D** and **E** with the correct stereochemistry.

Part I: Compounds **D** and **E** are separately subjected to NaH mediated reaction with 3-bromoprop-1-yne to afford **F** and **G**, respectively (Scheme 8.3). Heating **F** and **G** separately in toluene gives the bicyclic products **H** and **I**, respectively.

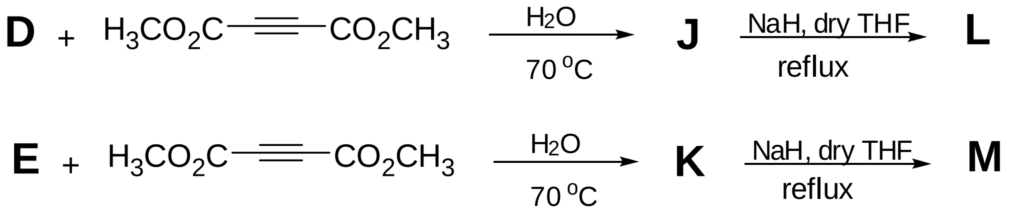
Scheme 8.3:



8.3 Draw the structure of compounds **F**, **G**, **H** and **I** with the correct stereochemistry.

Part II: Reaction of **D** and **E** separately with dimethyl acetylenedicarboxylate in water at 70 °C forms the optically active monocyclic regioisomers **J** and **K**, respectively (Scheme 8.4). Subsequent treatment of **J** and **K** with NaH gives final bicyclic products **L** and **M**, respectively, both having the formula $C_{13}H_{11}N_3O_4$.

Scheme 8.4:



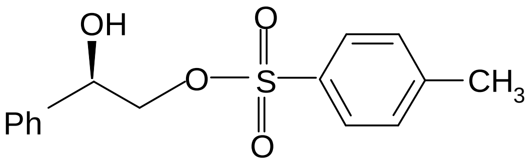
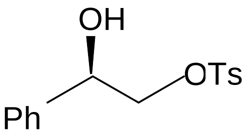
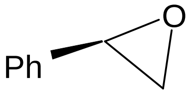
$$\mathbf{D}\ +\ H_3CO_2C{\equiv}CO_2CH_3\ \xrightarrow[70\,^{o}C]{H_2O}\ \mathbf{J}\ \xrightarrow[\text{reflux}]{\text{NaH, dry THF}}\ \mathbf{L}$$

$$\mathbf{E}\ +\ H_3CO_2C{\equiv}CO_2CH_3\ \xrightarrow[70\,^{o}C]{H_2O}\ \mathbf{K}\ \xrightarrow[\text{reflux}]{\text{NaH, dry THF}}\ \mathbf{M}$$

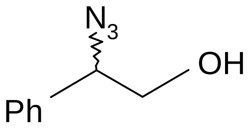
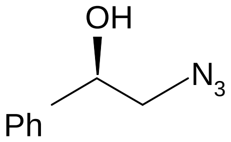
8.4 Draw the structures of compound **J**, **K**, **L** and **M** with the correct stereochemistry.

SOLUTION

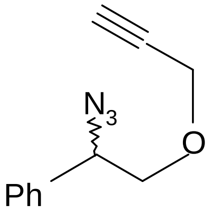
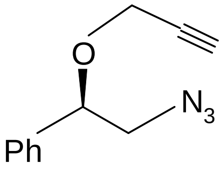
8.1

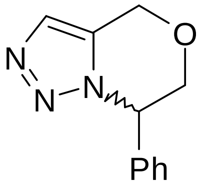
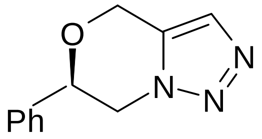
B	**C**
 or 	

8.2

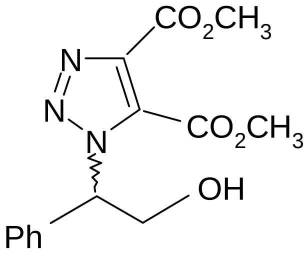
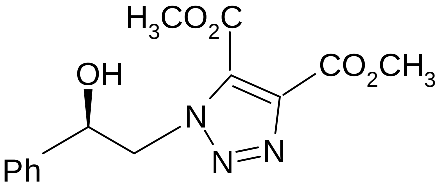
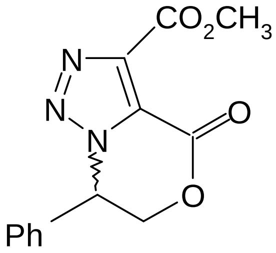
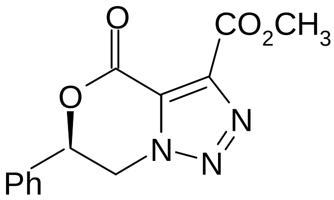
D	**E**
	

8.3

F	**G**
	

H	**I**
	

8.4

J	**K**
	
L	**M**
	

PRACTICAL PROBLEMS

PROBLEM 1 (practical)

Analysis of Chloride Mixtures

Introduction

Composition of a solution containing only $MgCl_2$ and NaCl can be determined by an indirect titration method by performing a precipitation titration to determine the total amount of chloride present, followed by a complex formation titration to determine the amount of magnesium ions. A common precipitation titration technique used to determine the amount of chloride ions present in a solution is the Fajans method. In this argentometric procedure, silver nitrate is used as the titrant to precipitate the chloride ions present in the solution. The end point is detected through the use of an adsorption indicator, typically dichlorofluorescein, a weak organic acid. Prior to the end point, silver chloride particles are negatively charged because of the adsorption of excess chloride ions present in solution. The indicator anions are repelled by the negatively charged surface of the silver chloride particles imparting a yellow-green colour to the solution. Beyond the equivalence point, however, silver chloride particles adsorb silver ions. Thus a positively charged layer is formed and it attracts the dichlorofluoresceinate ions displaying a pink-red colour. Dextrin is used to stabilize the silver chloride particles against the coagulation.

On the other hand, the amount of magnesium ions present in a solution can be determined by complexometric titration with ethylenediaminetetraacetic acid, EDTA. As a hexadentate ligand, EDTA forms chelates with all metal ions, except alkali metal ions, in a 1 : 1 mole ratio regardless of the charge of the cation. Eriochrome Black T (EBT) is a common indicator used for EDTA titrations. When pH > 7.00 EBT imparts a blue colour to the solution in the absence of metal ions and forms a red colour when coordinated to metal ions.

In this experiment the chloride content of the solution containing $MgCl_2$ and NaCl will be determined by Fajans method. Magnesium ion concentration will be determined by EDTA titration.

A 100 cm^3 solution prepared by dissolving $MgCl_2$ and NaCl in water is given as the unknown sample. The task is to determine the mass concentration (in g/100 cm^3) of both $MgCl_2$ and NaCl in the unknown solution.

Reagents

- Unknown solution, 100 cm^3
- Dextrin in Eppendorf tubes (3) in a zipper bag
- Dichlorofluorescein, indicator
- $AgNO_3$ solution, *c* = 0.1 mol dm^{-3} *), 100 cm^3
- EDTA solution, *c* = 0.01 mol dm^{-3} *), 100 cm^3
- pH 10 buffer (NH_3/NH_4Cl), 5 cm^3
- Eriochrome Black T, indicator

---

*) The exact value of the concentration is given on the label.

A. Determination of total chloride concentration by Fajans method

1. Using a 10 cm^3 pipette, transfer 10.0 cm^3 aliquot from the bottle labelled as unknown solution into a 250 cm^3 Erlenmeyer flask. Complete the volume to approximately 100 cm^3 by adding distilled water.
2. Take one of the Eppendorf tubes given in the zipper bag labelled as “dextrin” and transfer all its content into the Erlenmeyer flask.
3. Add 5 drops of dichlorofluorescein indicator solution.
4. Record the exact concentration of $AgNO_3$ in standard solution.
5. Fill one of the burettes with the standard $AgNO_3$ solution.
6. Titrate the unknown solution until the whole solution has pink-red colour.
7. Record the volume of $AgNO_3$ used in cm^3.
8. Use the same Erlenmeyer flask when repeating the titration. Before doing this, pour the content of Erlenmeyer flask into the “Aqueous Waste” container and rinse it twice with distilled water.

B. Determination of Mg^{2+} by direct titration with EDTA

1. Fill the second burette with the standard EDTA solution.
2. Record the exact concentration of EDTA in standard solution.

3. Using a 25 cm^3 pipette, transfer a 25.0 cm^3 aliquot of the unknown solution into a 250 cm^3 Erlenmeyer flask. Complete the volume to approximately 100 cm^3 by adding distilled water.
4. Using a 1 cm^3 pipette, add 1.0 cm^3 of pH 10 buffer.
5. Add 3 – 4 drops of EBT indicator solution.

6. Titrate the unknown solution with standard EDTA solution until the colour changes from red to blue.
7. Record the volume of EDTA solution used, in cm^3.
8. Use the same Erlenmeyer flask when repeating the titration. Before doing this, pour the content of Erlenmeyer flask into the "Aqueous Waste" container and rinse it twice with water.

Treatment of Data

1.1 Determine the amount of Cl^- ions (in mmol) in 100 cm^3 of the unknown solution.

1.2 Determine the amount of Mg^{2+} ions (in mmol) in 100 cm^3 of the unknown solution.

1.3 Calculate the concentration of both $MgCl_2$ and NaCl in g/100 cm^3 in the unknown solution.

SOLUTION

1.1 – 1.3

- Some distribution graphs were proposed by the organizer and approved by the International Jury that could be applied for evaluating of accuracy of the titrations and, consequently, for awarding points.
- For determinations of amounts of substance of Cl^- and Mg^{2+} ions, as well concentrations of both $MgCl_2$ and NaCl in the unknown solution, simple stoichiometric calculations can be applied.

PROBLEM 2 (practical)

Hydrogen generation from ammonia borane

Hydrogen has been considered as a clean and environmentally benign new energy carrier in the way towards a sustainable energy future. An effective and safe storage of hydrogen is one of the key issues of the hydrogen economy. Among the chemical hydrides, considered as potent solid hydrogen storage materials, ammonia-borane ($H_3N\cdot BH_3$) has been attracting a great deal of attention due to its high hydrogen content and stability under fuel cell operating conditions. Ammonia borane can release hydrogen upon hydrolysis, (Equation 1):

$$H_3N.BH_3(aq) + 2\ H_2O(l) \rightarrow NH_4BO_2(aq) + 3\ H_2(g) \qquad (1)$$

Aqueous solution of ammonia borane is stable and its hydrolysis occurs only in the presence of a suitable catalyst. Recent studies have shown that palladium(0) nanoclusters stabilized by water soluble polymers are highly active catalyst in the hydrolysis of ammonia borane. Palladium(0) nanoclusters are generated in situ by the reduction of potassium tetrachloropalladate(II) with ammonia borane in the presence of poly(4-styrenesulfonic acid-co-maleic acid).

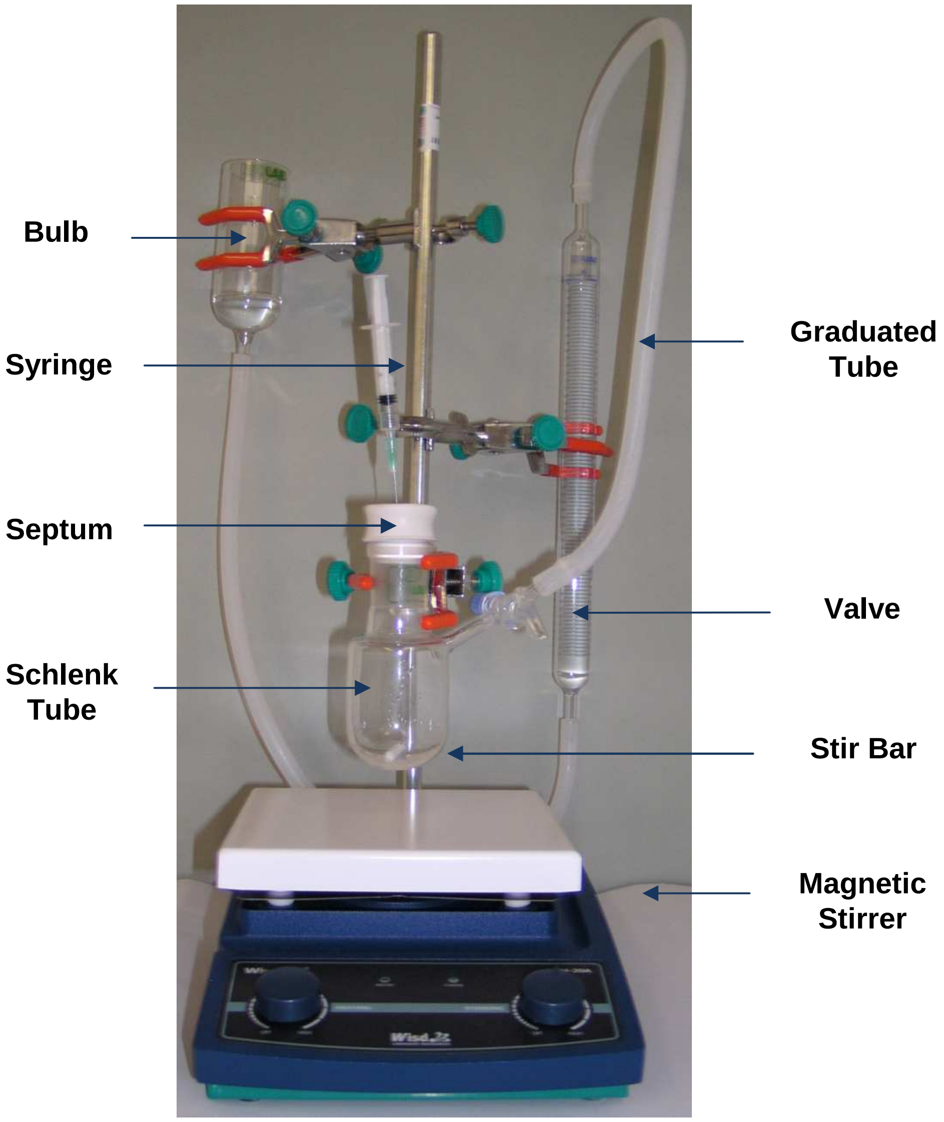
In this experiment, the catalytic hydrolysis of ammonia borane will be carried out starting with potassium tetrachloropalladate(II) in a solution containing poly(4-styrenesulfonic acid-co-maleic acid). Potassium tetrachloropalladate(II) will be used as precatalyst, which will be reduced by ammonia borane and palladium(0) nanoclusters will be formed and stabilized by poly(4-styrenesulfonic acid-co-maleic acid). These nanoclusters will catalyze the hydrolysis of ammonia borane.

Chemicals

- Solution A: H_3NBH_3 , 29.5 mg dissolved in 10 cm^3 H_2O,
- Solution B: poly(4-styrenesulfonic acid-co-maleic acid), 137.7 mg in 9 cm^3 H_2O,
- Solution C: Potassium tetrachloropalladate(II), $K_2[PdCl_4]$, 6.7 mg in 1 cm^3 H_2O.

I. Preparation of the Experimental Set-up

1. Check that the experimental setup, shown below, is held on a support, the graduated tube is connected to the Schlenk tube by Tygon tubing, and a stir bar is in the Schlenk tube.
2. Make sure that the septum is off and the valve is open.
3. By changing the bulb height adjust the water level in the graduated tube to zero.
4. Close the valve on the Schlenk tube.



Experimental Set-up

II. Hydrolysis of ammonia borane

A. In the absence of catalyst

1. Transfer all of the ammonia-borane solution (Solution A) from the glass vial to the Schlenk tube through the funnel,
2. Add the polymer solution (Solution B) from the glass vial to the Schlenk tube through the funnel.
3. Close the Schlenk tube with the septum, turn the stirring on at 600 rpm (as marked on the stirrer), and open the valve connecting to the graduated tube. Record the water level as V_o at time zero. Start the timer.
4. Every minute read the total volume of gas produced and write in the Table given on the answer sheet. Do this for 10 minutes. Stop the timer.

B. In the presence of catalyst

1. While stirring, transfer all of the potassium tetrachloropalladate(II) solution (Solution C) from the glass vial to the Schlenk tube by injecting through the septum using a 2.0 cm^3 syringe. Keep the syringe inserted in the septum throughout the experiment. Start the timer.
2. Every minute read the total volume of gas produced and write in the Table given on the answer sheet. Do this for 10 minutes. Stop the timer.

Treatment of Data

A. Reaction of ammonia-borane without catalyst

2.1 Plot the volume of gas recorded versus time in Graph 2.1.

2.2 Report the volume of gas evolved as $V_{\text{uncatalyzed}}$.

B. Reaction of ammonia-borane with catalyst

2.3 Plot the volume of the gas generated versus time in Graph 2.2.

2.4 Calculate the maximum amount of substance (mol) and the maximum volume (cm^3) of hydrogen gas which will be evolved theoretically from the hydrolysis of 29.5 mg ammonia borane with a purity of 97 % w/w at 25 °C. The atmospheric pressure is 690 torr.

2.5 Calculate the rate of hydrogen generation in your experiment

i) in cm^3 H_2/ min.

ii) in mmol H_2/min by assuming that the temperature is 25 °C. The atmospheric pressure is 690 torr.

2.6 Based on your experiment calculate the rate of hydrogen production per mole of palladium in (mol H_2)×(mol Pd)$^{-1}$×(min)$^{-1}$. The purity of potassium tetrachloropalladate(II) is 98 % w/w.

SOLUTION

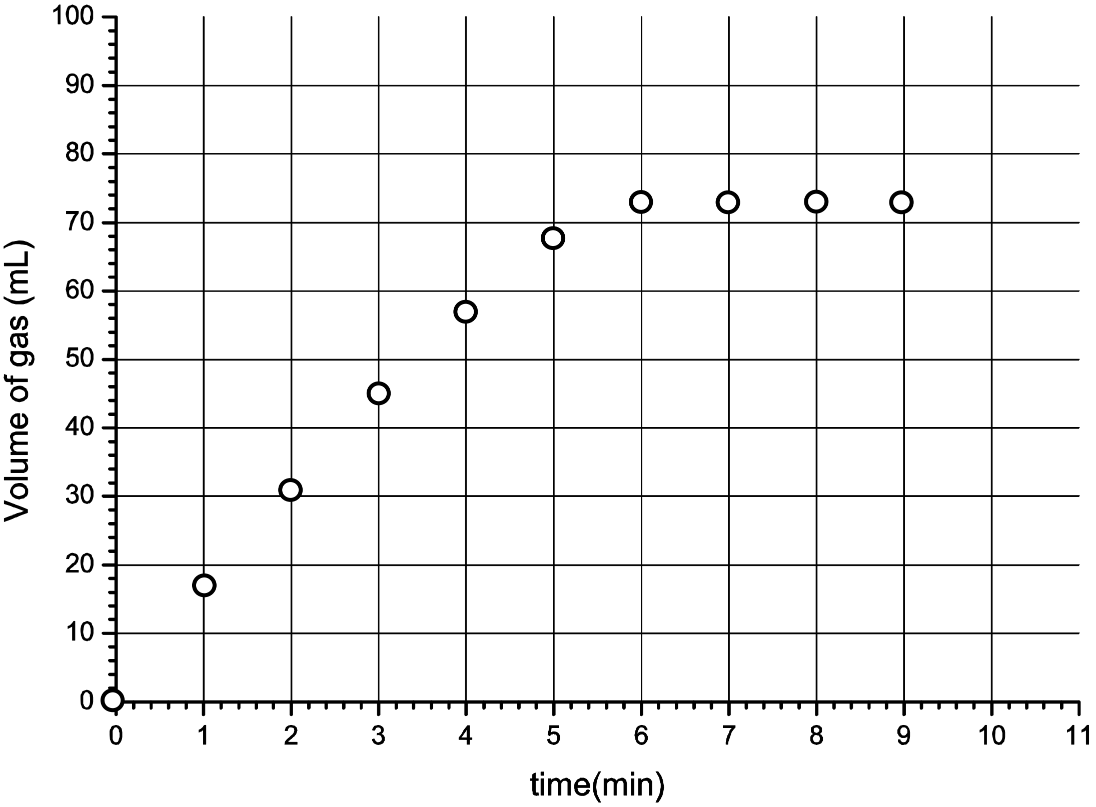
2.1 **Part A.** The volume of the gas evolved stays within a range of 0 – 2 cm^3 (maximum).

2.2 $V(H_2)_{uncatalyzed} = 0\ cm^3$

2.3 **Part B.** The gas volume versus time data for the reaction of ammonia borane in the presence of catalyst, are given in the table below.

Time (min)	0	1	2	3	4	5	6	7	8	9
Volume (cm^3)	0	17	31	45	57	68	73	73	73	73

Graph of gas volume versus time in the presence of catalyst:



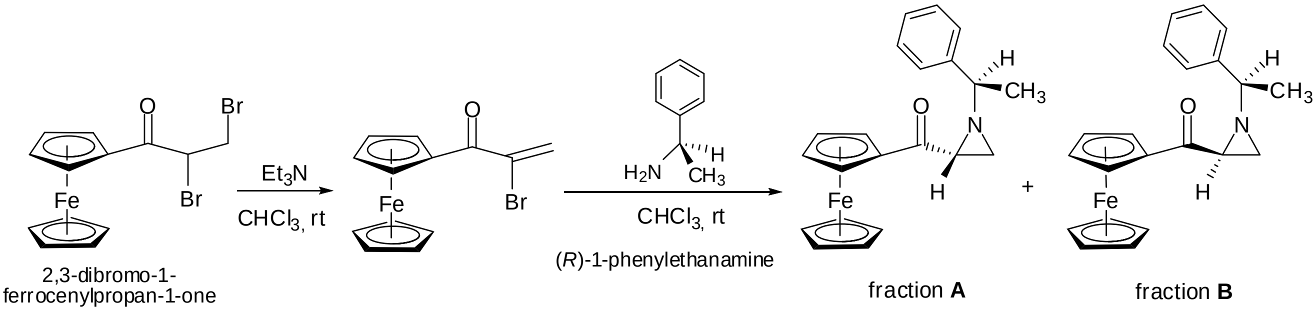
2.4 – 2.6

The required calculations are based on the experimental data obtained in practical problem 2. The well known relations between the mass, molar mass, amount of substance, and the volume of a gaseous substance at a certain pressure and temperature, as well as the experimental volume data in dependence on time (part 2.3) should be used to solve the tasks 2.4 – 2.6.

PROBLEM 3 (practical)

Synthesis, purification and separation of a diastereomeric mixture

Nature has many compounds in the form of a single enantiomer or diastereomer such as sugars, amino acids, steroids, etc. Some of these compounds are biologically active and used as drugs. Therefore, the asymmetric synthesis of organic compounds is important. One of the methods for the asymmetric synthesis of organic compounds employes a metal-catalyst, in which the metal is coordinated to a chiral organic molecule named as chiral ligand. In this experiment two chiral ligands will be synthesized.



Chemicals

- 2,3-dibromo-1-ferrocenylpropan-1-one, 0.50 mmol, labelled as "Rxn RB"
- Triethylamine, 1.0 mmol in 1.0 cm^3 of $CHCl_3$, label: "V 1"
- (*R*)-1-phenylethanamine, 1.0 mmol in 0.5 cm^3 of $CHCl_3$, label: "V 2"
- 2,3-dibromo-1-ferrocenylpropan-1-one, reference starting material for TLC, label: "SM"
- Heptane : ethyl acetate mixture in a volume ration 3 : 2, 500 cm^3, label: "ELUENT",

A. Synthesis

1. Using a syringe, transfer through the septum the triethylamine solution in vial 1 (V 1) to the 10 cm^3 round bottom reaction flask (Rxn RB) containing 0.50 mmol 2,3-dibromo-1-ferrocenylpropan-1-one.
2. Stir the mixture at room temperature for 30 minutes using the magnetic stirrer at 600 rpm (as marked on the stirrer).
3. After 30 minutes, transfer through the septum the (*R*)-1-phenylethanamine solution in vial 2 (V2) to the reaction flask using the same syringe.
4. Stir the mixture for additional 60 minutes at room temperature.

5. After 60 minutes turn off the magnetic stirrer and perform a thin layer chromatography, TLC, analysis as follows:
   - i) Check your TLC plates before use. Damaged plates will be replaced upon request without penalty.
   - ii) Draw a start line on the lower portion of TLC plate with a pencil (Fig. 3.1).
   - iii) Apply starting material from the vial labelled as SM two times to the spot on the left and then two times to the spot in the middle of plate. To the same plate, apply the reaction mixture (RM) taken from the reaction flask once to the spot on the right and then once to the spot in the middle as shown in Figure 3.1 (use a different capillary tube for each sample).
   - iv) Develop TLC plate in the TLC chamber with the eluent. Mark the solvent front with the pencil (Fig. 3.2).
   - v) When the TLC plate is dry, place it in a zipper storage bag marked as TLC1.

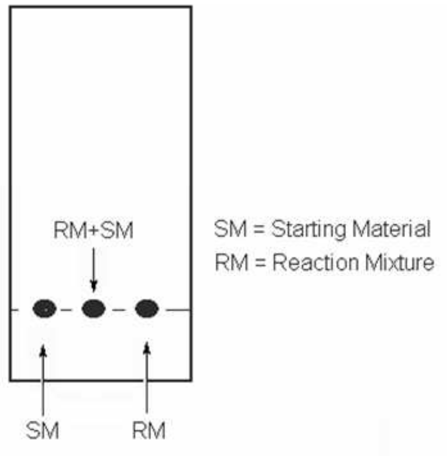


Figure 3.1. TLC plate

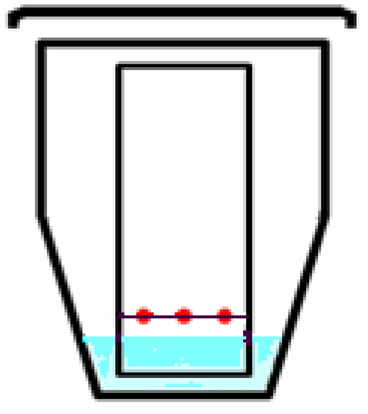


Fig. 3.2 TLC plate placed in the TLC developing chamber.

B. Flash Column Chromatography

1. Remove the stopper, open the valve, and bring the eluent level at top of column to the upper level of silica gel. (Fig. 3.3).
2. Close the valve and load the content of reaction flask on the top of flash column using a Pasteur pipette.
3. Rinse the reaction flask with 0.5 cm^3 eluent taken from the bottle labelled as ELUENT using a clean syringe. Using the same Pasteur pipette, load the washings also on the top of column.
4. Open the valve of the column and let the solvent run down to the upper level of silica gel.

5. Close the valve and add 1.0 cm^3 eluent by a Pasteur pipette. Open the valve. When the eluent is at the upper level of silica gel, add 2 - 3 cm^3 eluent slowly without closing the valve.
6. Fill the column by adding more eluent.

   CAUTION: Be careful during the addition of eluent; do not disturb silica gel.

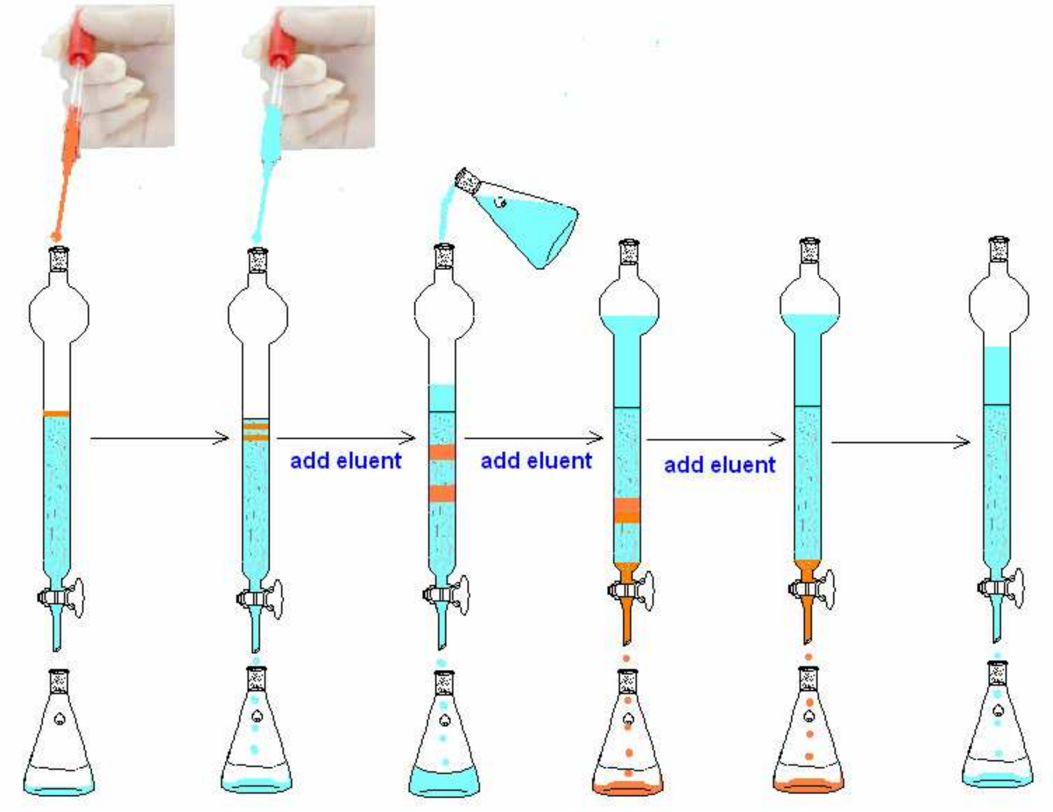


Figure 3.3. Flash Column Chromatography

7. In order to speed up the purification, apply little pressure by connecting the pressure applying bulb with an adapter on top of the column.

   CAUTION: Be careful not to apply too much pressure. Add eluent time to time to avoid silica gel run dry.
8. You are expected to collect two major fractions **A** and **B**. Discard any material which elutes before major fraction **A** and between **A** and **B** into the container labeled as Organic Waste.

9. Collect the first major fraction into a 100 cm^3 Erlenmeyer flask and label it as fraction **A**.
10. Collect the second major fraction into a 250 cm^3 Erlenmeyer flask and label it as fraction **B**.
11. After collecting fraction **B** stop the elution by closing the valve.

C. Analysis. Perform

1 Perform another TLC by applying the starting material (**SM**) two times to the spot on the left, apply fraction **A** two times to the spot in the middle, and then fraction **B** five times to the spot on the right. After development, when the TLC plate is dry, place it in a zipper storage bag marked **TLC2**.

2. Measure the volume of fraction **A** using 50 cm^3 graduated cylinder and record the volume to your answer sheet.
3. Measure the volume of fraction **B** using 250 cm^3 graduated cylinder and record the volume to your answer sheet.
4. Using a 2 cm^3 pipette transfer 2.0 cm^3 of fraction **A** into the 10 cm^3 volumetric flask and complete the volume to 10 cm^3 by adding eluent. After shaking the flask, fill out the UV-visible cell (at least ¾ of its volume) by using a Pasteur pipette. Ask the assistant to measure the absorbance at 450 nm using the spectrophotometer and record the result to your answer sheet.
5. Using fraction **B**, fill out (at least ¾ of its volume) the other UV-visible cell by a Pasteur pipette (no need for dilution). Ask the assistant to measure the absorbance at 450 nm using the spectrophotometer and record the result to your answer sheet.

Treatment of Data

3.1 Copy (sketch) the TLC1 plate on your answer sheet.

3.2 Copy (sketch) the TLC2 plate on your answer sheet.

3.3 Calculate and record the R_f values of the spots (fraction **A**, fraction **B**, and starting material **SM**) using the TLC2 plate.

3.4 The molar extinction coefficient, molar absorptivity, ε, is 404 M^{-1}cm^{-1} for **A** and 400 M^{-1}cm^{-1} for **B** at 450 nm (M = mol dm^{-3}). Calculate in percent:

i) the yield of fraction **A** based on the starting material.

ii) the yield of fraction **B** based on the starting material.

SOLUTION

3.1 – 3.2

Maximum points are given:

- for the appearance of three spots loaded on the base line,
- for the well developed and separated spots on the TLC,
- for the solvent front line and the base line,
- for the accurate presentation of the sketch of the TLC,
- in part 3.2, moreover, for the absence of fraction **B** in fraction **A** and vice versa.

3.3 Maximum points if calculated and recorded R_f values fall within those given in the following table:

Spots	R_f value
Fraction **A**	0.40 – 0.50
Fraction **B**	0.20 – 0.30
Starting material **SM**	0.65 – 0.75

3.4 Points were awarded in accordance with some distribution graphs proposed by the organizer and approved by the International Jury. The graphs were applied for fraction **A** and **B**, when evaluating their volumes, absorbance and yields.

44th

International Chemistry Olympiad

8 theoretical problems
2 practical problems

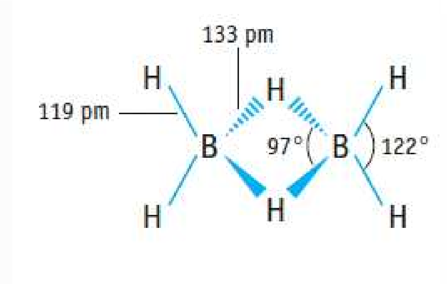
THE FORTY-FOURTH
INTERNATIONAL CHEMISTRY OLYMPIAD
21–30 JULY 2012, WASHINGTON, U.S.A.

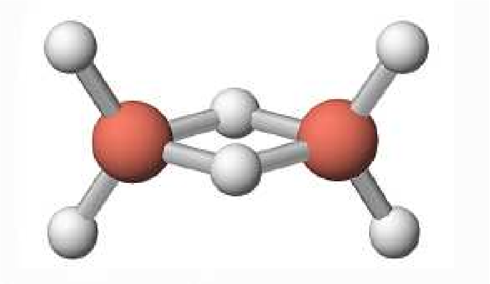
THEORETICAL PROBLEMS

PROBLEM 1

A. Boron Hydrides and Other Boron Compounds

Boron hydride chemistry was first developed by Alfred Stock (1876 - 1946). More than 20 neutral molecular boron hydrides with the general formula B_xH_y have been characterized. The simplest boron hydride is B_2H_6, diborane.





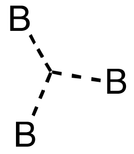
1.1 Using the data below derive the molecular formulae for two other members of this series of boron hydrides, **A** and **B**.

Substance	State (25 ˚C, 1 bar)	Mass Percent of Boron	Molar mass (g mol^{-1})
A	Liquid	83.1	65.1
B	Solid	88.5	122.2

William Lipscomb received the Nobel Prize in Chemistry in 1976 for “studies on the structures of boron hydrides illuminating the problems of chemical bonding.” Lipscomb recognized that, in all boron hydrides, each B atom has a normal 2-electron bond to at least one H atom (B–H). However, additional bonds of several types occur, and he developed a scheme for describing the structure of a borane by giving it a styx number where:

s = number of B–H–B bridges in the molecule,

t = the number of 3-center BBB bonds in the molecule,



y = the number of two-center B–B bonds in the molecule,

x = the number of BH_2 groups in the molecule.

The *styx* number for B_2H_6 is 2002.

1.2 Propose a structure for tetraborane, B_4H_{10}, with a *styx* number of 4012.

1.3 A boron-based compound is composed of boron, carbon, chlorine, and oxygen. Spectral measurements indicate that the molecule has two types of B atoms, with tetrahedral and trigonal planar geometry, in a 1 : 3 ratio, respectively. These spectra are also consistent with a CO triple bond. The molecular formula of the compound is B_4CCl_6O. Suggest a structure for its molecule.

B. Thermochemistry of Boron Compounds

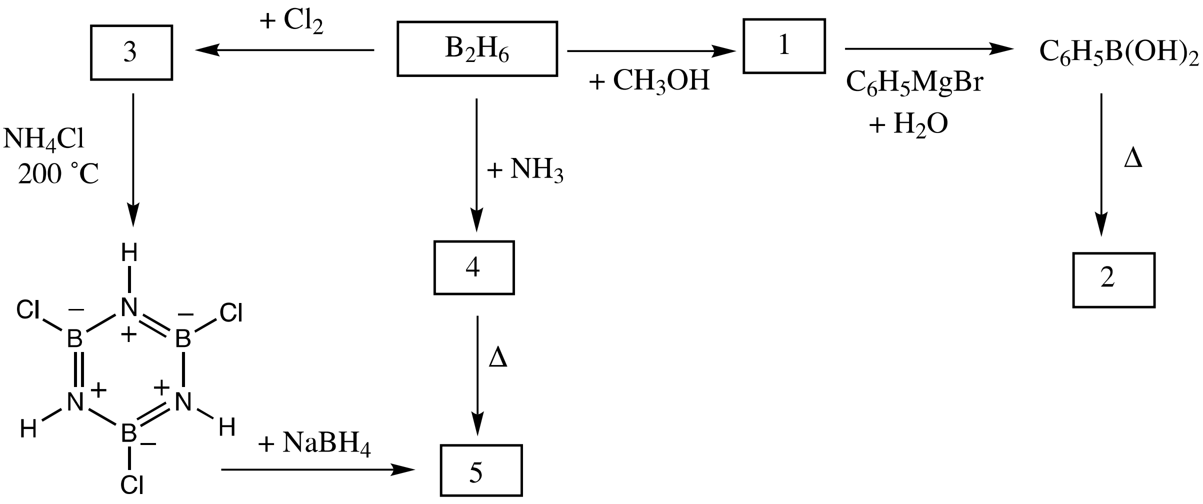
1.4 Estimate the B-B single bond dissociation enthalpy in $B_2Cl_4(g)$ using the following information:

Bond	Bond dissociation enthalpy (kJ mol^{-1})
B–Cl	443
Cl–Cl	242

Compound	$\Delta_f H°$ (kJ mol^{-1})
$BCl_3(g)$	–403
$B_2Cl_4(g)$	–489

C. Chemistry of Diborane

1.5 Give the structure for each numbered compound in the scheme below. Each numbered compound is a boron-containing compound.



NOTES:

i. The boiling point of compound 5 is 55 °C.

ii. Excess reagents used in all reactions.

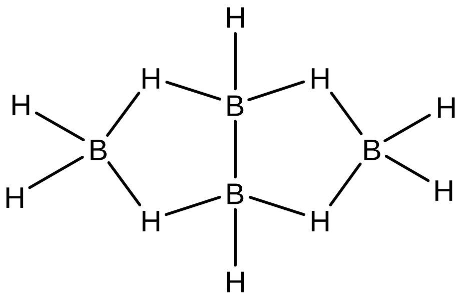
iii. The freezing point depression for 0.312 g of compound 2 in 25.0 g of benzene, is 0.205 °C. The freezing point depression constant for benzene is 5.12 kg K mol^{-1}.

SOLUTION

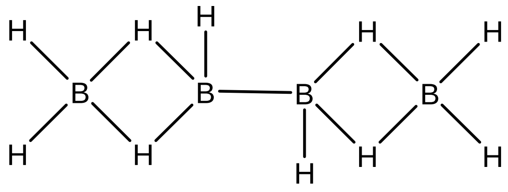
1.1 **A** = B_5H_{11}

B = $B_{10}H_{14}$

1.2



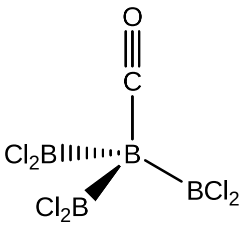
actual structure



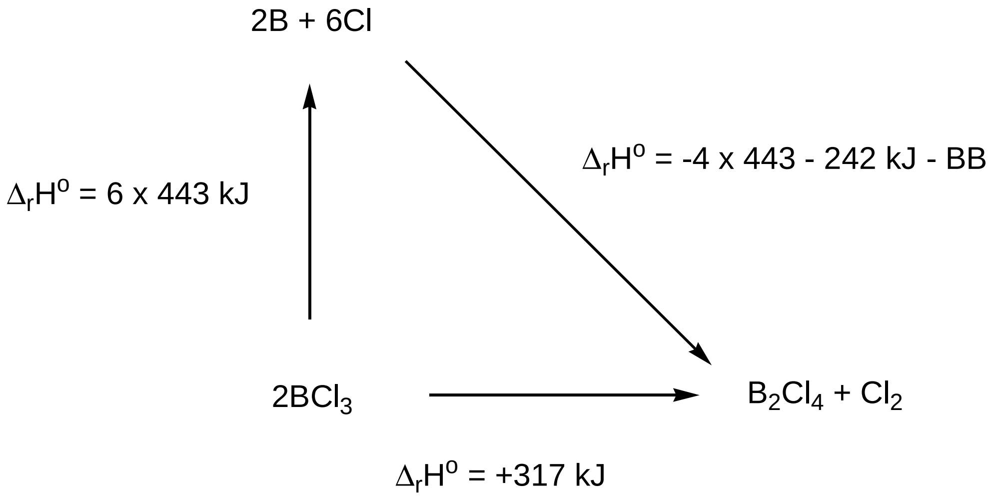
unknown but acceptable structure

1.3

Structure:

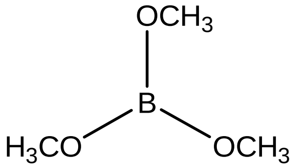
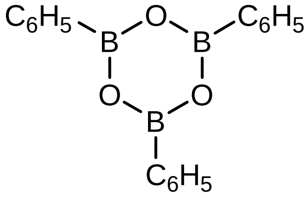
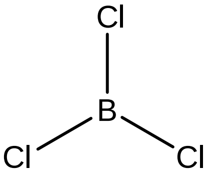
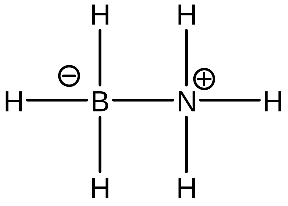
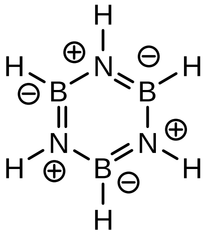


1.4



A Born-Haber cycle gives a B–B bond dissociation enthalpy of 327 kJ mol^{-1}.

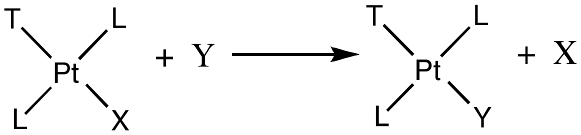
1.5

Number	Formula	Molecular Structure of the Compound
1	$B(OCH_3)_3$	
2	$B_3O_3(C_6H_5)_3$	 A dimer or tetramer $[C_6H_5BO]_x$ are also acceptable (x = 2, 4).
3	BCl_3	
4	BNH_6	 Formal charges are not necessary.
5	$B_3N_3H_6$	 Formal charges are not necessary.

PROBLEM 2

A. Platinum(II) Compounds, Isomers, and the *Trans* Effect.

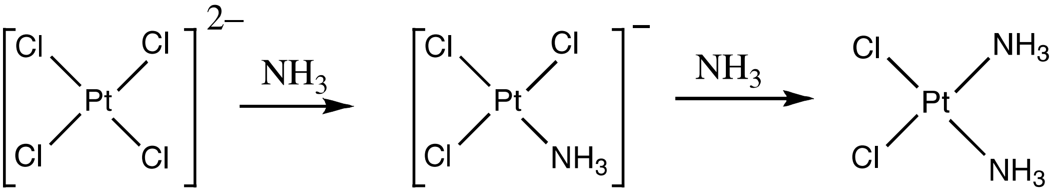
Platinum and other Group 10 metals form square planar complexes and the mechanisms of their reactions have been studied extensively. For example, it is known that substitution reactions of these complexes proceed with retention of stereochemistry.



It is also known that the rate of substitution of ligand X by Y depends on the nature of the ligand *trans* to X, that is, on ligand T. This is known as the ***trans* effect.** When T is one of the molecules or ions in the following list, the rate of substitution at the trans position decreases from left to right.

$$CN^- > H^- > NO_2^-, I^- > Br^-, Cl^- > \text{pyridine}, NH_3, OH^-, H_2O$$

The preparations of *cis*- and *trans*-$Pt(NH_3)_2Cl_2$ depend on the *trans* affect. The preparation of the *cis* isomer, a cancer chemotherapy agent commonly called cisplatin, involves the reaction of K_2PtCl_4 with ammonia.



2.1 Draw all possible stereoisomers for square planar platinum(II) compounds with the formula $Pt(py)(NH_3)BrCl$ (where py = pyridine, C_5H_5N).

2.2 Write reaction schemes including intermediate(s), if any, to show the preparation in aqueous solution for each of the stereoisomers of $[Pt(NH_3)(NO_2)Cl_2]^-$ using, as reagents, $PtCl_4^{2-}$, NH_3, and NO_2^-. The reactions are controlled kinetically by the *trans* effect.

B. Kinetic Studies of Substitution Reactions of Square Planar Complexes

Substitutions of the ligand X by Y in square planar complexes

$$ML_3X + Y \rightarrow ML_3Y + X$$

can occur in either or both of two ways:

i) *Direct substitution:* The incoming ligand Y attaches to the central metal, forming a five-coordinate complex, which then rapidly eliminates a ligand, X, to give the product, ML_3Y.

$$ML_3X \xrightarrow[**]{+\,Y} [ML_3XY] \xrightarrow{-\,X} ML_3Y$$

** = rate determining step, rate constant = k_Y

ii) *Solvent-assisted substitution:* A solvent molecule S attaches to the central metal to give ML_3XS, which eliminates the X to give ML_3S. Y rapidly displaces S to give ML_3Y.

$$ML_3X \xrightarrow[**]{+\,S} [ML_3XS] \xrightarrow{-\,X} [ML_3S] \xrightarrow[-\,S]{+\,Y} ML_3Y$$

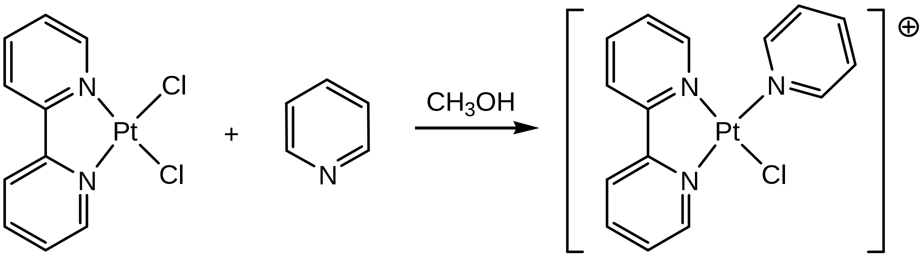
** = rate determining step, k_S = rate constant

The overall rate law for such substitutions is

$$\text{Rate} = k_s\,[ML_3X] + k_Y\,[Y]\,[ML_3X]$$

When [Y] >> [ML_3X], then Rate = k_{obs} [ML_3X].

The values of k_s and k_Y depend on the reactants and solvent involved. One example is the displacement of the Cl^- ligand in a square planar platinum(II) complex, ML_2X_2, by pyridine (C_5H_5N). (The ML_3X scheme above applies to ML_2X_2.)



Data for reaction at 25 °C in methanol where [pyridine] >> the concentration of the platinum complex, are given in the table below.

Concentration of pyridine (mol dm^{-3})	k_{obs} (s^{-1})
0.122	$7.20 \cdot 10^{-4}$
0.061	$3.45 \cdot 10^{-4}$
0.030	$1.75 \cdot 10^{-4}$

2.3 Calculate the values of k_S and k_Y. Give the proper unit for each constant.

(A grid is given if you wish to use it.)

2.4 When [pyridine] = 0.10 mol dm^{-3}, which of the following is true? (Tick the box next to the correct answer.)

☐ Most pyridine product is formed by the solvent-assisted (k_S) substitution pathway.

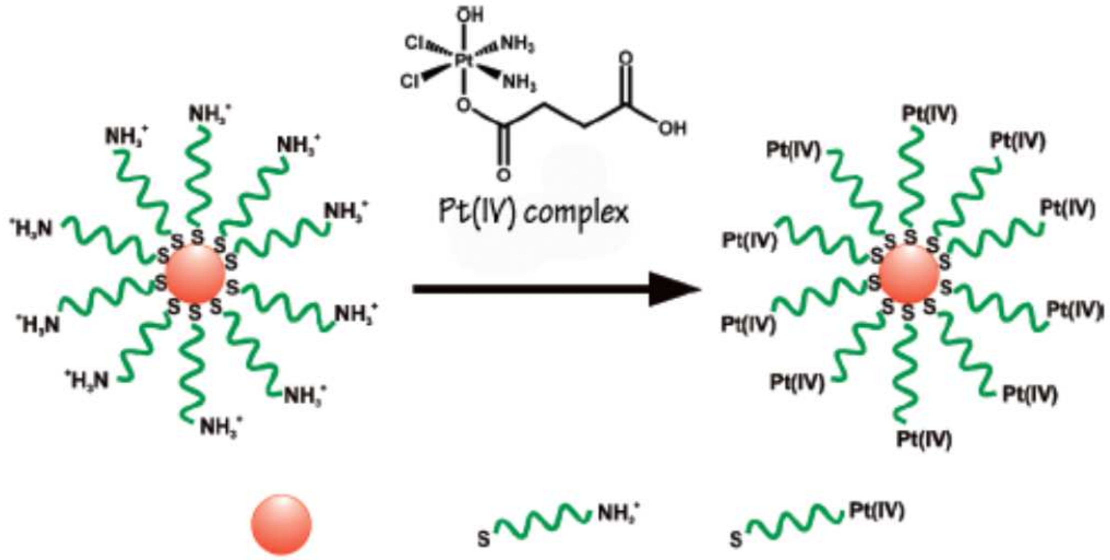
☐ Most pyridine product is formed by the direct substitution (k_Y) pathway

☐ Comparable amounts of product are formed by the two pathways.

☐ No conclusions may be drawn regarding the relative amounts of product produced by the two pathways.

C. A chemotherapy agent

In an effort to better target cisplatin to cancer cells, Professor Lippard's group at MIT attached a platinum(IV) complex to oligonucleotides bound to gold nanoparticles.



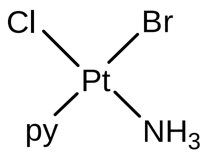
Gold nanoparticle Oligonucleotide Pt(IV) complex attached

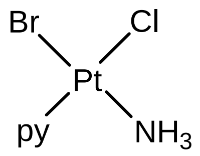
2.5 Experiments showed that the diameter of a gold nanoparticle was 13 nm. Attached to this nanoparticle are 90 oligonucleotide groups, with 98 % of them being bound to a Pt(IV) complex. Suppose that the reaction vessel used for treating cells with the Pt(IV) nanoparticle reagent had a volume of 1.0 cm^3 and the concentration of the solution was $1.0 \cdot 10^{-6}$ mol dm^{-3} in Pt. Calculate the mass of platinum and that of gold used in this experiment.

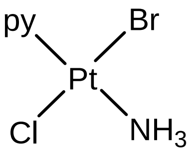
(The density of gold = 19.3 g cm^{-3}, the volume of a sphere = $(4/3)\pi r^3 = 4.18879\ r^3$.)

SOLUTION

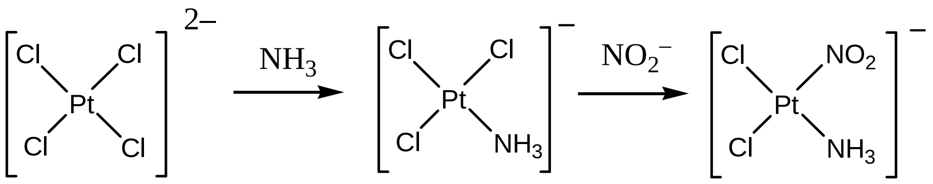
2.1



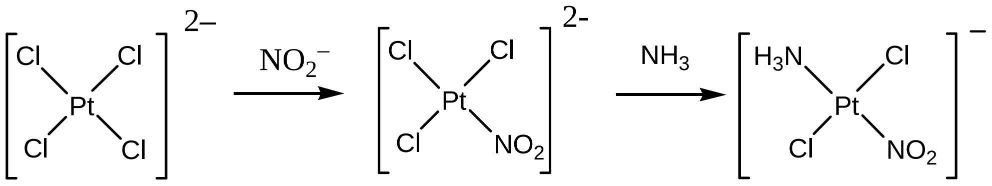




2.2 *cis*-isomer:



trans-isomer:



2.3

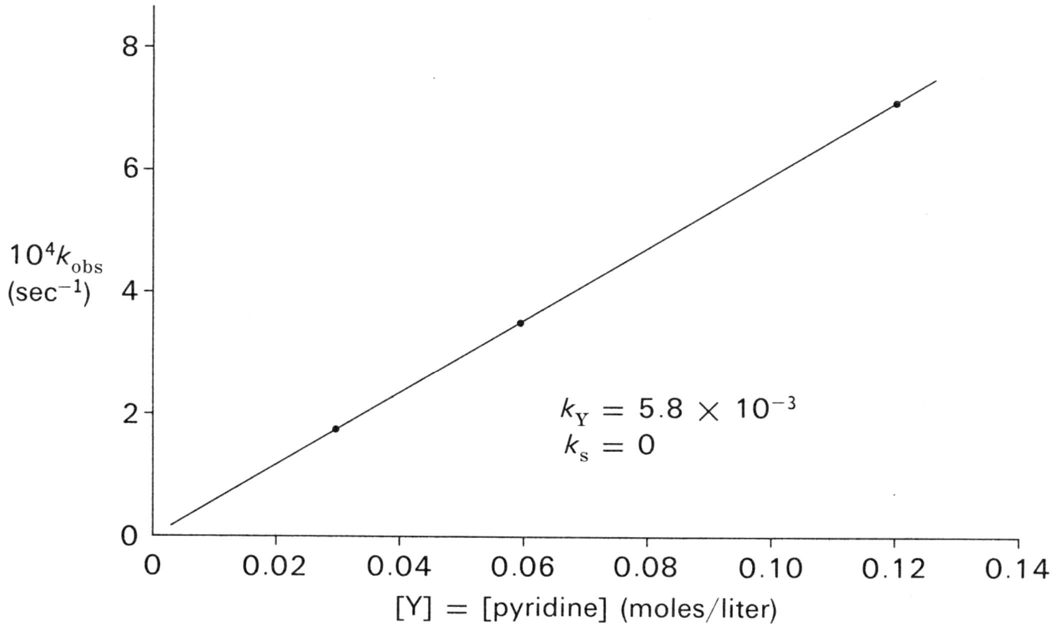


Fig. 2.3 Verification of the rate law $k_{obs} = k_s + k_Y$[pyridine] for the reaction of Pt(bipy)Cl$_2$ with pyridine to give Pt(bipy)(py)Cl$^+$. Data taken from L. Cattalini, A. Orio, and A. Doni, *Inorg. Chem.*, **5**, 1517 (1966).

$k_Y = 5.8 \cdot 10^{-3}\ s^{-1}mol^{-1}\ dm^3$

$k_S = 0\ s^{-1}$ (allow small range of values, ± $0.2 \cdot 10^{-3}$)

2.4 ☑ Most pyridine product is formed by the direct substitution (k_Y) pathway.

2.5 Mass of platinum

$n(Pt) = 1.0 \cdot 10^{-6}\ mol\ dm^{-3} \times 0.001\ dm^3 = 1.0 \cdot 10^{-9}\ mol$

This is equivalent to $2.0 \cdot 10^{-7}$ g Pt.

Mass of gold

- (90 groups/nanoparticle)(0.98 Pt bound complexes)
  = 88 Pt complexes/nanoparticle or 88 Pt atoms per nanoparticle
- $1.0 \cdot 10^{-9}$ mol Pt is equivalent to $6.0 \cdot 10^{14}$ Pt atoms
- ($6.0 \cdot 10^{14}$ Pt atoms)(1 nanoparticle/88 Pt atoms) = $6.8 \cdot 10^{12}$ nanoparticles
- Size of gold nanoparticles:
  Radius = $6.5 \cdot 10^{-7}$ cm and volume of gold nanoparticle = $1.2 \cdot 10^{-18}$ cm^3
  Mass of gold nanoparticle = $2.3 \cdot 10^{-17}$ g
  Amount of gold in a nanoparticle = $1.2 \cdot 10^{-19}$ mol
  Atoms of gold in a nanoparticle = $7.1 \cdot 10^4$ atoms
- Mass of gold:
  Total number of gold atoms = ($6.8 \cdot 10^{12}$ particles)($7.1 \cdot 10^4$ atoms/particle)
  = $4.8 \cdot 10^{17}$ atoms of gold
  Equivalent to $1.5 \cdot 10^{-4}$ g of gold

PROBLEM 3

Thiomolybdate ions are derived from molybdate ions, MoO_4^{2-}, by replacing oxygen atoms with sulfur atoms. In nature, thiomolybdate ions are found in such places as the deep waters of the Black Sea, where biological sulfate reduction generates H_2S. The molybdate to thiomolybdate transformation leads to rapid loss of dissolved Mo from seawater to underlying sediments, depleting the ocean in Mo, a trace element essential for life.

The following equilibria control the relative concentrations of molybdate and thiomolybdate ions in dilute aqueous solution:

$MoS_4^{2-} + H_2O(l) \rightleftharpoons MoOS_3^{2-} + H_2S(aq)$ $\quad K_1 = 1.3 \cdot 10^{-5}$

$MoOS_3^{2-} + H_2O(l) \rightleftharpoons MoO_2S_2^{2-} + H_2S(aq)$ $\quad K_2 = 1.0 \cdot 10^{-5}$

$MoO_2S_2^{2-} + H_2O(l) \rightleftharpoons MoO_3S^{2-} + H_2S(aq)$ $\quad K_3 = 1.6 \cdot 10^{-5}$

$MoO_3S^{2-} + H_2O(l) \rightleftharpoons MoO_4^{2-} + H_2S(aq)$ $\quad K_4 = 6.5 \cdot 10^{-6}$

3.1 If at equilibrium the concentrations of MoO_4^{2-} and $H_2S(aq)$ are equal to $1 \cdot 10^{-7}$ and $1 \cdot 10^{-6}$, respectively, what would be the equilibrium concentration of MoS_4^{2-}?

Solutions containing $MoO_2S_2^{2-}$, $MoOS_3^{2-}$ and MoS_4^{2-} display absorption peaks in the visible wavelength range at 395 and 468 nm. The other ions, as well as H_2S, absorb negligibly in the visible wavelength range. The molar absorptivities (ε) at these two wavelengths are given in the following table:

	ε at 468 nm dm^3 mol^{-1} cm^{-1}	ε at 395 nm dm^3 mol^{-1} cm^{-1}
MoS_4^{2-}	11870	120
$MoOS_3^{2-}$	0	9030
$MoO_2S_2^{2-}$	0	3230

3.2 A solution *not* at equilibrium contains a mixture of MoS_4^{2-}, $MoOS_3^{2-}$ and $MoO_2S_2^{2-}$ and no other Mo-containing species. The total concentration of all species containing Mo is $6.0 \cdot 10^{-6}$ mol dm^{-3}. In a 10.0 cm absorption cell, the absorbance of the solution at 468 nm is 0.365 and that at 395 nm is 0.213. Calculate the concentrations of all three Mo-containing anions in this mixture.

A solution with initial concentration of MoS_4^{2-} equal to $2.0 \cdot 10^{-7}$ mol dm^{-3} hydrolyzes in a closed system. The H_2S product accumulates until equilibrium is reached. When calculating the final equilibrium concentrations of H_2S(aq), and all five Mo-containing anions (that is, MoO_4^{2-}, $MoOS_3^{2-}$, $MoO_2S_2^{2-}$, $MoOS_3^{2-}$ and MoS_4^{2-}) ignore the possibility that H_2S might ionize to HS^- under certain pH conditions.

3.3 Write the six independent equations that determine the system.

3.4 Calculate the above mentioned six concentrations making reasonable approximations, giving your answers to two significant figures.

SOLUTION

3.1 Multiplying the mass action laws for the four given reactions produces:

$$\frac{[\mathrm{MoO_4^{2-}}]\,[\mathrm{H_2S}]^4}{[\mathrm{MoS_4^{2-}}]} = \frac{1\cdot 10^{-7}\ (1\cdot 10^{-6})^4}{[\mathrm{MoS_4^{2-}}]} = 1.4\cdot 10^{-20}$$

$$[\mathrm{MoS_4^{2-}}] = 7\cdot 10^{-12}$$

3.2 $\mathrm{MoS_4^{2-}}$ concentration is determined by absorbance at 468 nm:

$0.365 = 11870 \times 10.0 \times c(\mathrm{MoS_4^{2-}})$

$c(\mathrm{MoS_4^{2-}}) = 3.08\cdot 10^{-6}$ mol dm^{-3}

From conservation of Mo:

$c(\mathrm{MoOS_3^{2-}}) + c(\mathrm{MoO_2S_2^{2-}}) = c(\mathrm{Mo})_{\mathrm{Total}} - c(\mathrm{MoS_4^{2-}}) =$

$= (6.0\cdot 10^{-6} - 3.08\cdot 10^{-6})$ mol dm^{-3} $= 2.9\cdot 10^{-6}$ mol dm^{-3}

By rearrangement:

$c(\mathrm{MoO_2S_2^{2-}}) = 2.9\cdot 10^{-6}$ mol dm^{-3} $- c(\mathrm{MoOS_3^{2-}})$

From optical absorbance at 395 nm (quantities in the equations are without dimensions):

$0.213 = (120 \times 10.0 \times 3.08\cdot 10^{-6}) + (9030 \times 10.0 \times c(\mathrm{MoOS_3^{2-}})) +$

$+ (3230 \times 10.0 \times c(\mathrm{MoO_2S_2^{2-}}))$

$0.213 = (120 \times 10.0 \times 3.08\cdot 10^{-6}) + (9030 \times 10.0 \times c(\mathrm{MoOS_3^{2-}})) +$

$+ (3230)(10.0)(2.9\cdot 10^{-6} - c(\mathrm{MoOS_3^{2-}}))$

$c(\mathrm{MoOS_3^{2-}}) = 2.0\cdot 10^{-6}$ mol dm^{-3}

$c(\mathrm{MoO_2S_2^{2-}}) = 2.9\cdot 10^{-6} - c(\mathrm{MoOS_3^{2-}}) = 0.9\cdot 10^{-6}$ mol dm^{-3}

3.3 Mass balance for Mo:

$2.0\cdot 10^{-7} = c(\mathrm{MoS_4^{2-}}) + c(\mathrm{MoOS_3^{2-}}) + c(\mathrm{MoO_2S_2^{2-}}) + c(\mathrm{MoO_3S^{2-}}) + c(\mathrm{MoO_4^{2-}})$ (1)

Mass balance for S:

$8.0\cdot 10^{-7} = 4\ c(\mathrm{MoS_4^{2-}}) + 3\ c(\mathrm{MoOS_3^{2-}}) + 2\ c(\mathrm{MoO_2S_2^{2-}}) + c(\mathrm{MoO_3S^{2-}}) + (\mathrm{H_2S})$ (2)

Equilibrium constants:

$$1.3\cdot10^{-5}=\frac{[\mathrm{MoOS_3^{2-}}][\mathrm{H_2S}]}{[\mathrm{MoS_4^{2-}}]} \qquad (3)$$

$$1.0\cdot10^{-5}=\frac{[\mathrm{MoO_2S_2}^{2-}][\mathrm{H_2S}]}{[\mathrm{MoOS_3^{2-}}]} \qquad (4)$$

$$1.6\cdot10^{-5}=\frac{[\mathrm{MoO_3S^{2-}}][\mathrm{H_2S}]}{[\mathrm{MoO_2S_2^{2-}}]} \qquad (5)$$

$$6.5\cdot10^{-6}=\frac{[\mathrm{MoO_4^{2-}}][\mathrm{H_2S}]}{[\mathrm{MoO_3S^{2-}}]} \qquad (6)$$

3.4 It is likely that multiple approaches will be found for solving these equations. Here is one approach:

The maximum possible H_2S concentration is $8.0\cdot10^{-7}$ mol dm^{-3} if complete hydrolysis occurs. At this H_2S concentration, MoO_3S^{2-} is only about 12 % of $c(\mathrm{MoO_4^{2-}})$ and the remaining thio anions are much less abundant. Because the problem justifies a solution that is precise only to two significant figures, the mass balance equations can be truncated as follows:

$2.0\cdot10^{-7}=[\mathrm{MoO_3S^{2-}}]+[\mathrm{MoO_4^{2-}}]$ (Mo mass balance)

$8.0\cdot10^{-7}=[\mathrm{MoO_3S^{2-}}]+[\mathrm{H_2S}]$ (S mass balance)

Subtracting the first from the second equation and rearranging gives:

$[\mathrm{MoO_4^{2-}}]=[\mathrm{H_2S}]-6.0\cdot10^{-7}$

Likewise, the S mass balance can be rearranged,

$[\mathrm{MoO_3S^{2-}}]=8.0\cdot10^{-7}-[\mathrm{H_2S}]$

Employing the equilibrium constant for the reaction involving MoO_4^{2-} and MoO_3S^{2-}:

$$6.5\cdot10^{-6}=\frac{[\mathrm{MoO_4^{2-}}][\mathrm{H_2S}]}{[\mathrm{MoO_3S^{2-}}]}=\frac{([\mathrm{H_2S}]-6.0\cdot10^{-7})\,[\mathrm{H_2S}]}{8.0\cdot10^{-7}-[\mathrm{H_2S}]}$$

Rearrangement and solution by the quadratic formula gives (H_2S). Back substitution gives the remaining concentrations.

Results:

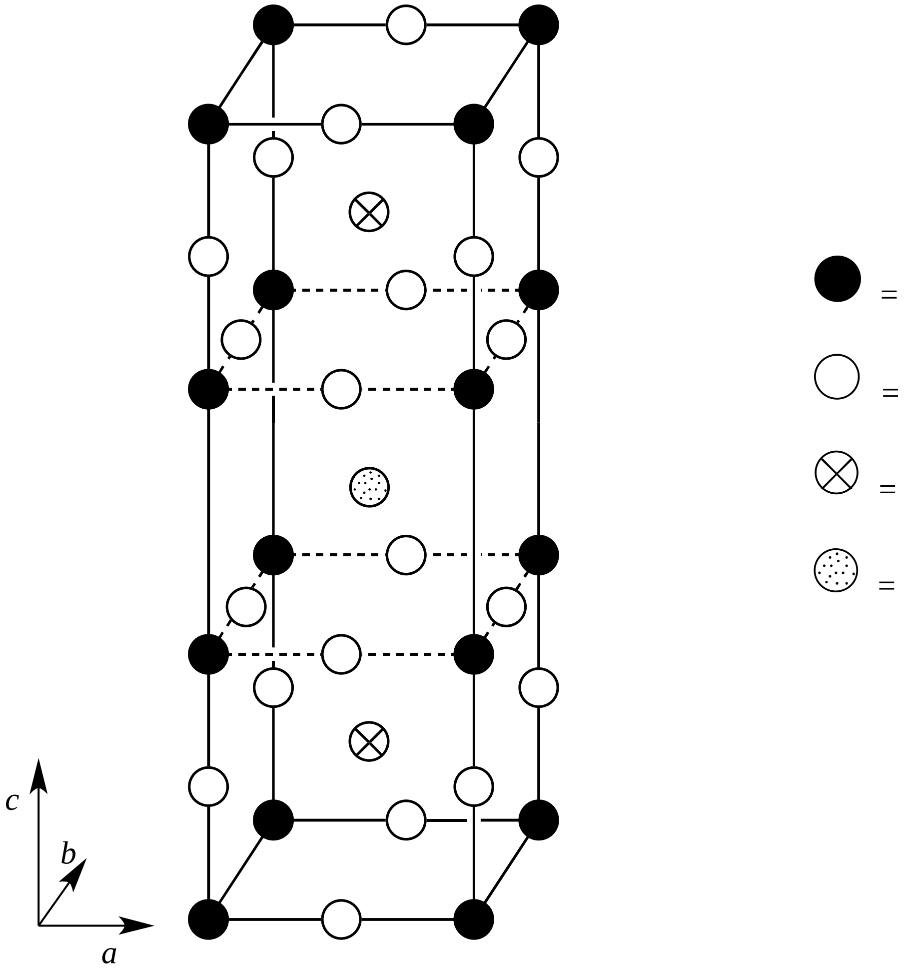
$[\mathrm{H_2S}]=7.8\cdot10^{-7}$; $[\mathrm{MoO_4^{2-}}]=1.8\cdot10^{-7}$; $[\mathrm{MoO_3S^{2-}}]=2.1\cdot10^{-8}$;

$[\mathrm{MoO_2S_2^{2-}}]=1.0\cdot10^{-9}$; $[\mathrm{MoOS_3^{2-}}]=8.1\cdot10^{-11}$; $[\mathrm{MoS_4^{2-}}]=4.9\cdot10^{-12}$.

PROBLEM 4

In the 1980's a class of ceramic materials was discovered that exhibits superconductivity at the unusually high temperature of 90 K. One such material contains yttrium, barium, copper and oxygen and is called "YBCO". It has a nominal composition of $YBa_2Cu_3O_7$, but its actual composition is variable according to the formula $YBa_2Cu_3O_{7-\delta}$ ($0 < \delta < 0.5$).

4.1 One unit cell of the idealized crystal structure of YBCO is shown below. Identify which circles correspond to which elements in the structure.



The true structure is actually orthorhombic ($a \neq b \neq c$), but it is approximately tetragonal, with $a \approx b \approx (c/3)$.

4.2 A sample of YBCO with δ = 0.25 was subjected to X-ray diffraction using CuKα radiation (λ = 154.2 pm). The lowest-angle diffraction peak was observed at 2θ = 7.450º. Assuming that $a = b = (c/3)$, calculate the values of a and c.

4.3 Estimate the density of this sample of YBCO (with δ = 0.25) in g cm^{-3}. If you were unable to calculate the values for a and c from part 4.2, then use a = 500 pm and c = 1500 pm.

When YBCO is dissolved in aqueous HCl (c = 1.0 mol dm^{-3}) bubbles of gas are observed (identified as O_2 by gas chromatography). After boiling for 10 min to expel the dissolved gases, the solution reacts with excess KI solution, turning yellow-brown. This solution can be titrated with thiosulfate solution to a starch endpoint. If YBCO is added under Ar directly to a solution in which concentrations of both KI and HCl are equal to 1.0 mol dm^{-3}, the solution turns yellow-brown but no gas evolution is observed.

4.4 Write a balanced net ionic equation for the reaction when solid $YBa_2Cu_3O_{7-\delta}$ dissolves in aqueous HCl with evolution of O_2.

4.5 Write a balanced net ionic equation for the reaction when the solution from 4.4 reacts with excess KI in acidic solution after the dissolved oxygen is expelled.

4.6 Write a balanced net ionic equation for the reaction when the solution from 4.5 is titrated with thiosulfate ($S_2O_3^{2-}$).

4.7 Write a balanced net ionic equation for the reaction when solid $YBa_2Cu_3O_{7-\delta}$ dissolves in aqueous HCl containing excess KI in an Ar atmosphere.

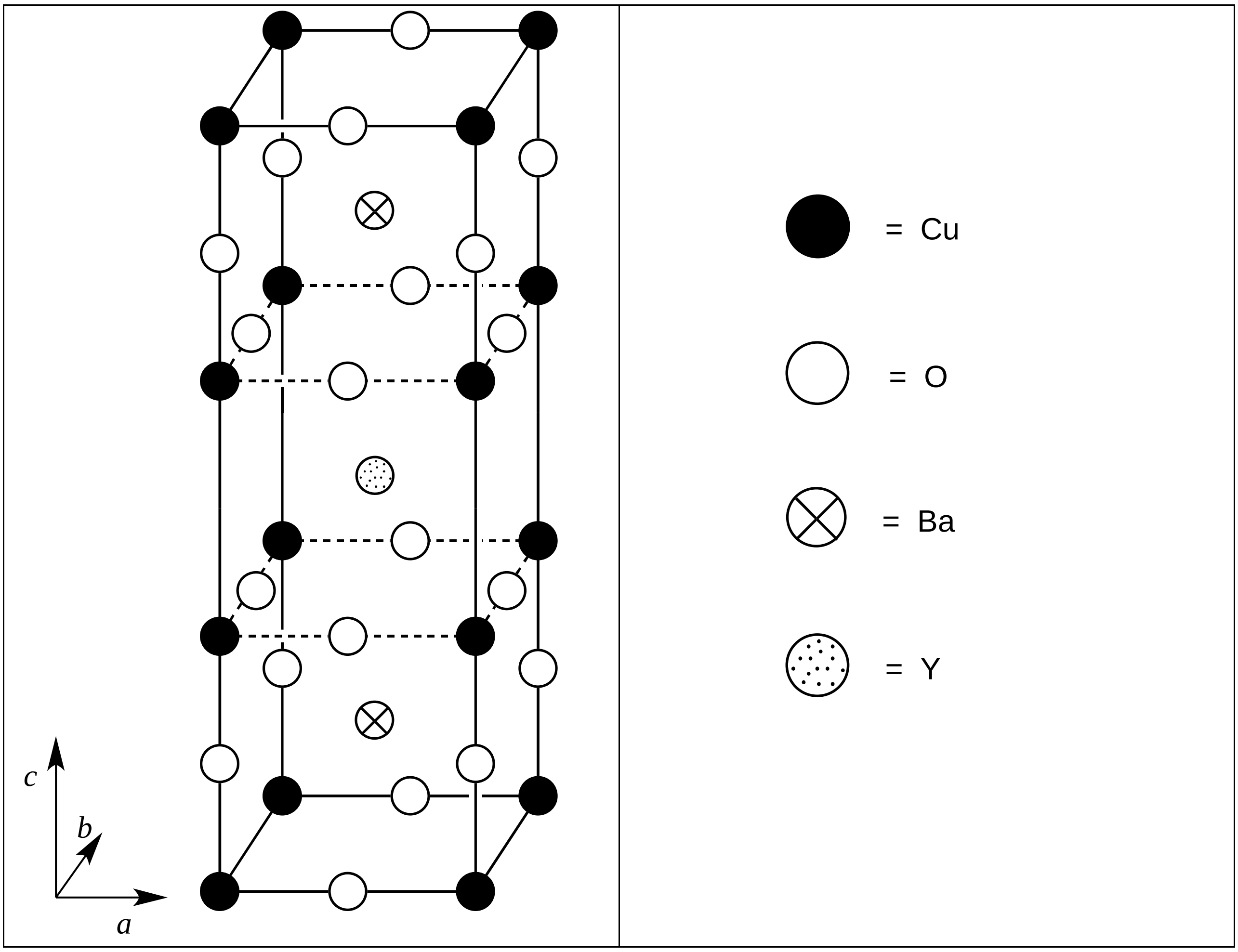
Two identical samples of YBCO with an unknown value of δ were prepared. The first sample was dissolved in 5 cm^3 of aqueous HCl (c = 1.0 mol dm^{-3}), evolving O_2. After boiling to expel gases, cooling, and addition of 10 cm^3 of KI solution (c = 0.7 mol dm^{-3}) under Ar, titration with thiosulfate to the starch endpoint required $1.542 \cdot 10^{-4}$ mol thiosulfate. The second sample of YBCO was added under Ar directly to 7 cm^3 of a solution in which c(KI) = 1.0 mol dm^{-3} and c(HCl) = 0.7 mol dm^{-3}. Titration of this solution required $1.696 \cdot 10^{-4}$ mol thiosulfate to reach the endpoint.

4.8 Calculate the amount of substance of Cu (in mol) in each of these samples of YBCO.

4.9 Calculate the value of δ for these samples of YBCO.

SOLUTION

4.1



4.2 $\sin\theta = n\lambda / 2d$

$d = (1)(154.2\text{ pm}) / 2\sin(3.725\,^\circ)$

$d = 1187\text{ pm}$

lowest-angle = > d = longest axis = c

$c = 1187\text{ pm}$

$a = c / 3 = 396\text{ pm}$

$a = 396\text{ pm}$

4.3 $V_{\text{unit cell}} = a \times b \times c = 3a^3 = 3\,(396\text{ pm})^3 = 1.863 \cdot 10^{-22}\text{ cm}^3$

$$m_{\text{unit cell}} = \frac{88.91\ +\ 2\times137.33\ +\ 3\times63.55\ +\ 6.75\times16.00}{N_A}$$

$$m_{\text{unit cell}} = \frac{662.22\ \text{g mol}^{-1}}{6.0221 \cdot 10^{23}\ \text{mol}^{-1}} = 1.100 \cdot 10^{-21}\ \text{g}$$

$$\text{density} = \frac{1.100 \cdot 10^{-21}\ \text{g}}{1.863 \cdot 10^{-22}\ \text{cm}^3} = 5.90\ \text{g cm}^{-3}$$

4.4 $YBa_2Cu_3O_{7-\delta}(s) + 13\ H^+(aq) \rightarrow$

$\rightarrow Y^{3+}(aq) + 2\ Ba^{2+}(aq) + 3\ Cu^{2+}(aq) + (0.25\ [1 - 2\delta])\ O_2(g) + 6.5\ H_2O(l)$

4.5 $2\ Cu^{2+}(aq) + 5\ I^-(aq) \rightarrow 2\ CuI(s) + I_3^-(aq)$

or

$2\ Cu^{2+}(aq) + 4\ I^-(aq) \rightarrow 2\ CuI(s) + I_2(aq)$

4.6 $I_3^-(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow 3\ I^-(aq) + S_4O_6^{2-}(aq)$

or

$I_2(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow 2\ I^-(aq) + S_4O_6^{2-}(aq)$

4.7 $YBa_2Cu_3O_{7-\delta}(s) + (14 - 2\ \delta)\ H^+(aq) + (9 - 3\ \delta)\ I^-(aq) \rightarrow$

$\rightarrow Y^{3+}(aq) + 2\ Ba^{2+}(aq) + 3\ CuI(s) + (7 - \delta)\ H_2O(l) + (2 - \delta)\ I_3^-(aq)$

or

$YBa_2Cu_3O_{7-\delta}(s) + (14 - 2\ \delta)\ H^+(aq) + (7 - 2\ \delta)\ I^-(aq) \rightarrow$

$\rightarrow Y^{3+}(aq) + 2\ Ba^{2+}(aq) + 3\ CuI(s) + (7 - \delta)\ H_2O(l) + (2 - \delta)\ I_2(aq)$

4.8 $n(Cu) = n(\text{thiosulfate})$ in the first titration

$n(Cu) = 1.542 \cdot 10^{-4}$ mol

4.9 Total $n(Cu) = 1.542 \cdot 10^{-4}$ mol

$n(Cu^{III}) = (1.696 \cdot 10^{-4}\ \text{mol}) - (1.542 \cdot 10^{-4}\ \text{mol}) = 1.54 \cdot 10^{-5}$ mol

Thus: 90 % of Cu is present as Cu(II) and 10 % as Cu(III).

From charge balance:

$2(7 - \delta) = 3 + (2 \times 2) + 3 \times [(0.90 \times 2) + (0.10 \times 3)] = 13.30$

$\delta = 0.35$

Alternatively, using the balanced equations in (d):

In the 1st titration, each mol YBCO corresponds 1.5 mol I_3^- and 3 mol $S_2O_3^{2-}$

In the 2nd titration, each mol YBCO corresponds (2 – δ) mol I_3^- and (4 – 2 δ) mol $S_2O_3^{2-}$

Thus,

$$\frac{1.542 \times 10^{-4}\text{ mol}}{1.696 \times 10^{-4}\text{ mol}} = \frac{3}{4-2\delta} = \frac{1.5}{2-\delta}$$

$2 - \delta = 1.650$

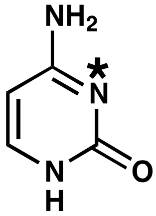
$\delta = 0.35$

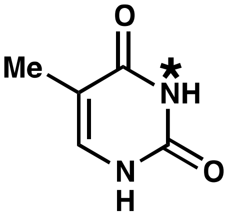
PROBLEM 5

Deoxyribonucleic Acid (DNA) is one of the fundamental molecules of life. This question will consider ways that DNA's molecular structure may be modified, both naturally and in ways devised by humankind.

Consider the pyrimidine bases, cytosine (**C**) and thymine (**T**). The N-3 atom (indicated by *) of one of these bases is a common nucleophilic site in single strand DNA alkylation, while the other is not.

5.1 Select (circle) which base, **C** or **T**, has the more nucleophilic N-3 atom.

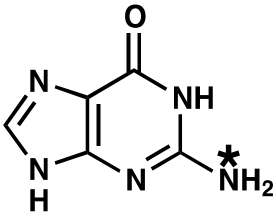

C

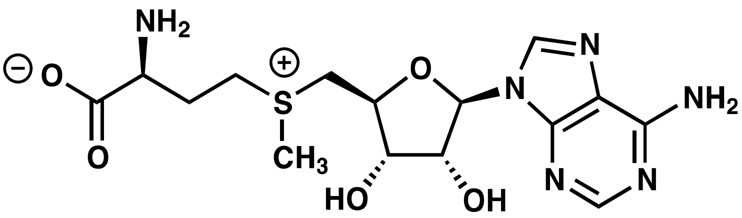

T

5.2. Draw two complementary resonance structures of the molecule you select to justify your answer.

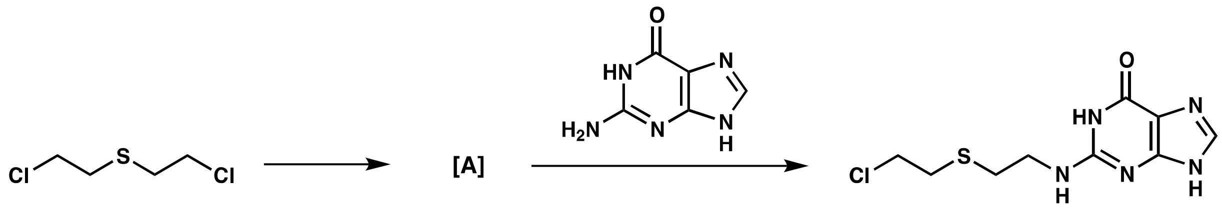
One common modification of DNA in nature is methylation of the indicated (*) position of guanine (**G**) by S-adenosyl methionine (**SAM**).

5.3 Draw the structures of both of the products of the reaction between guanine and SAM.


G


SAM

One of the earliest man-made DNA alkylating agents was mustard gas. Mustard gas acts by first undergoing an intramolecular reaction to form intermediate **A** which directly alkylates DNA, to give a nucleic acid product such as that shown in the part above.

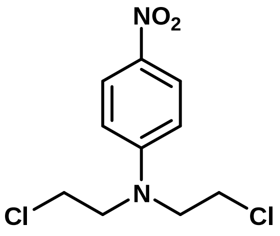


5.4 Draw the structure for reactive intermediate **A**.

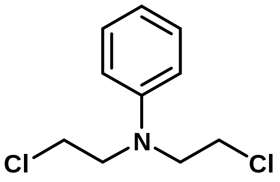
The nitrogen mustards react via an analogous pathway to the sulfur mustard of previous part. The reactivity of the compound may be modified depending on the third substituent on the nitrogen atom. The reactivity of nitrogen mustards increases with increasing nucleophilicity of the central nitrogen atom.

5.5 Select the most and least reactive from each of following groups of nitrogen mustards.

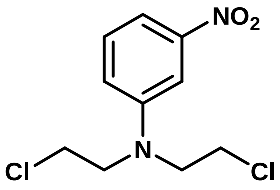
a)



I

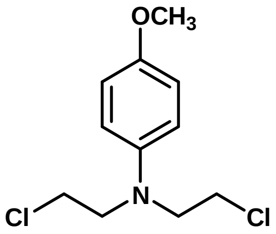


II

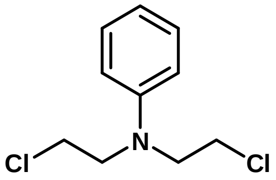


III

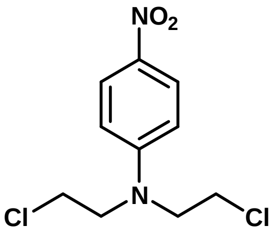
b)



I

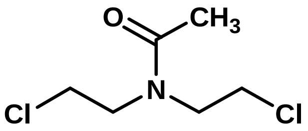


II

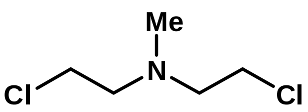


III

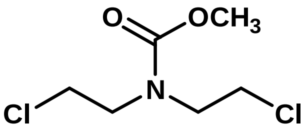
c)



I



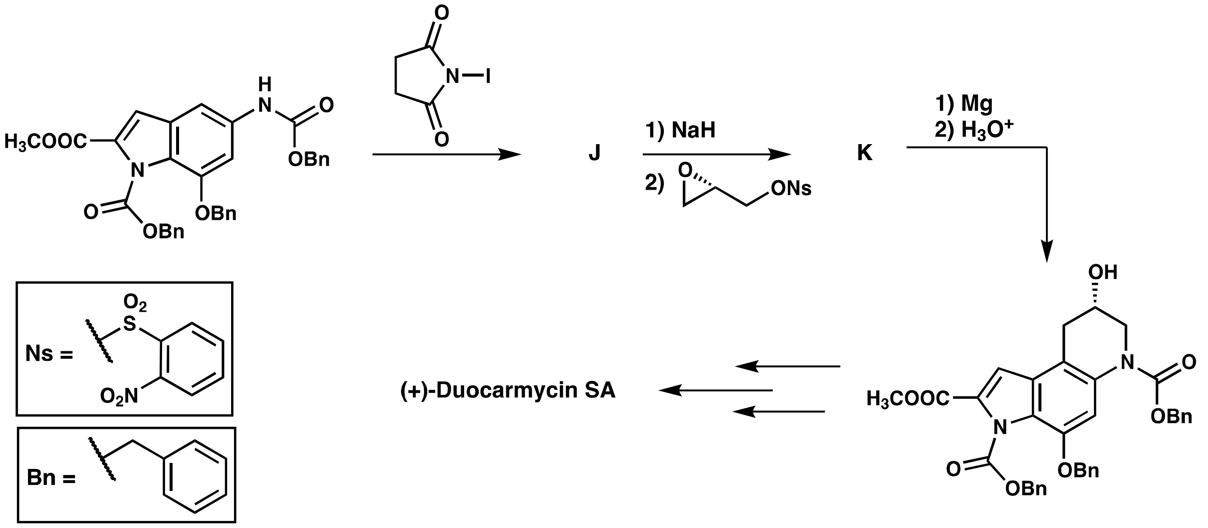
II



III

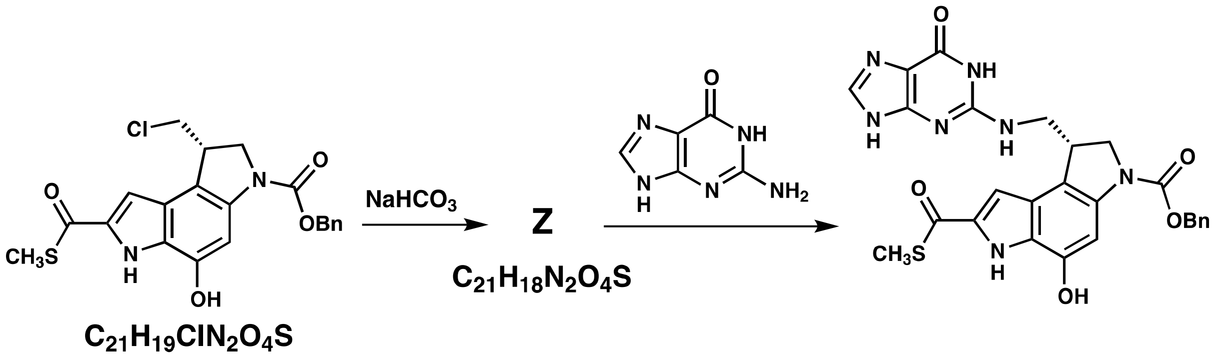
Some classes of natural products act as DNA alkylators, and in this way, they have the potential to serve as cancer therapies due to their antitumor activity. One such class is the duocarmycins. Shown below are steps from an asymmetric total synthesis of the natural product.

5.6 Draw the structures of isolable compounds **J** and **K** in the following scheme:



Related small molecules were synthesized to study the way in which the duocarmycins work. One such example is the thioester shown below.

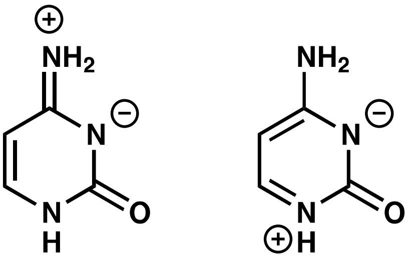
5.7 Draw the structure of reactive intermediate **Z**.



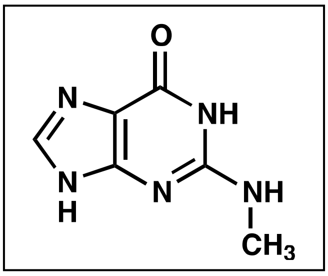
SOLUTION

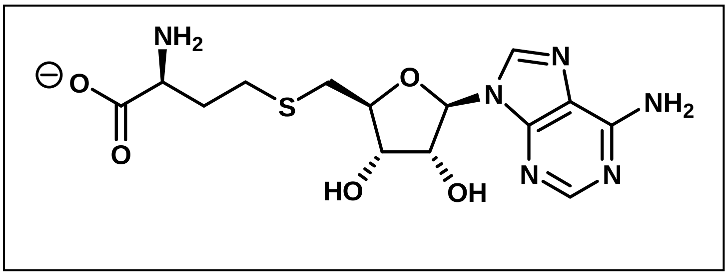
5.1 **C** is correct.

5.2

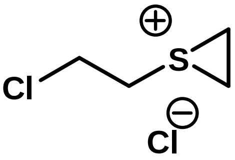


5.3





5.4



A

5.5

a) Most reactive: **II**

Least reactive: **I**

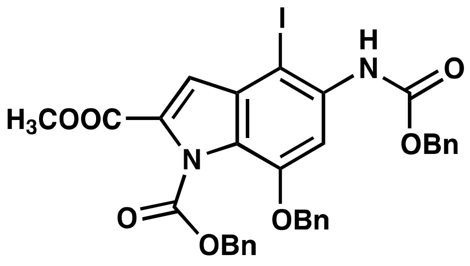
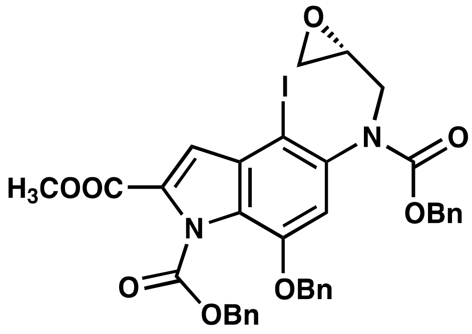
b) Most reactive: **I**

Least reactive: **III**

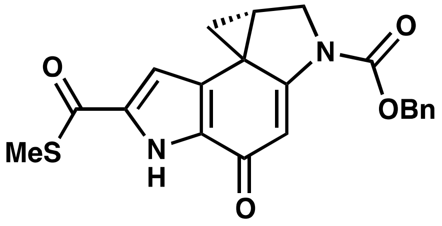
c) Most reactive: **II**

Least reactive: **I**

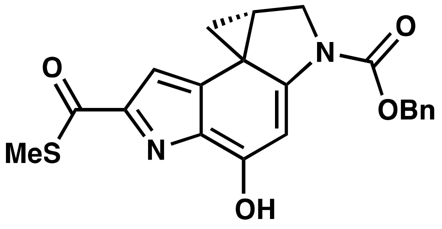
5.6

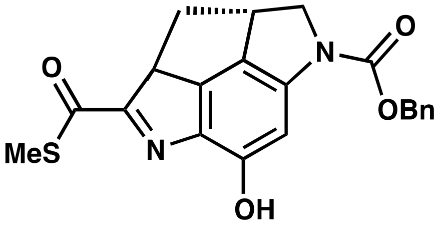
J	K
	

5.7



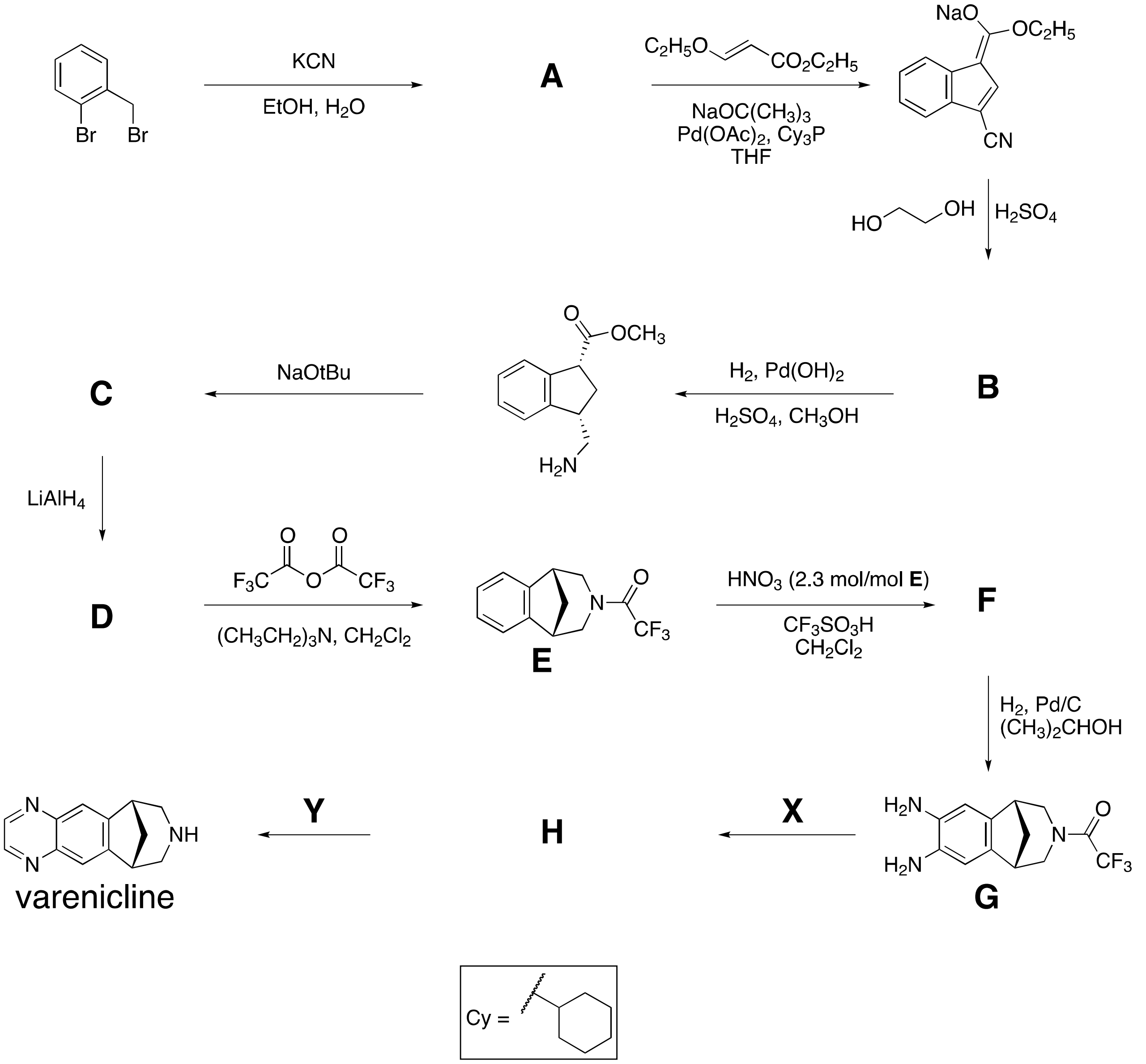
Z





PROBLEM 6

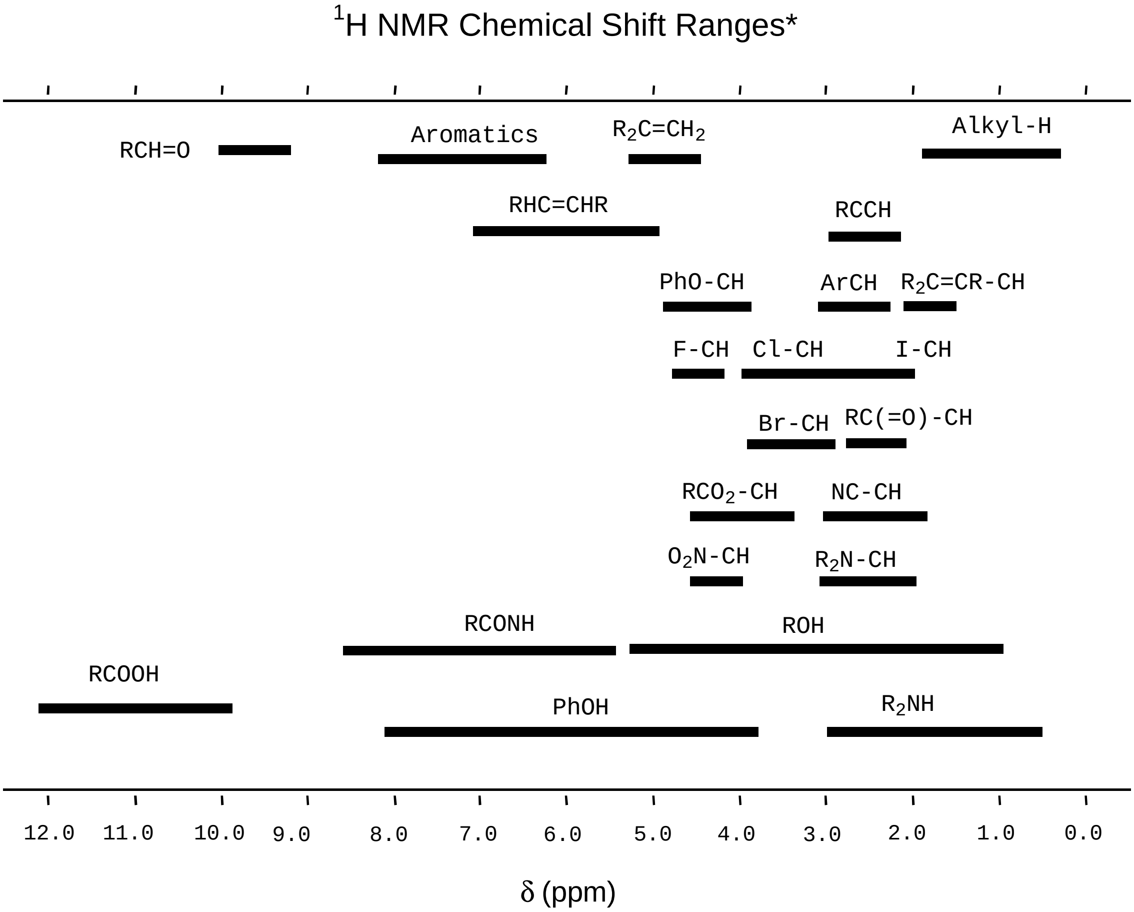
Varenicline has been developed as an oral treatment for smoking addiction and can be synthesized by the route shown below. All compounds indicated by a letter (**A** – **H**) are uncharged, isolable species.



6.1 Suggest a structure for compound **A**.

6.2 Suggest a structure for compound **B** consistent with the following ^{1}H-NMR data:

δ 7.75 (singlet, 1H), 7.74 (doublet, 1H, J = 7.9 Hz), 7.50 (doublet, 1H, J = 7.1 Hz), 7.22 (multiplet, 2 nonequivalent H), 4.97 (triplet, 2H, J = 7.8 Hz), 4.85 (triplet, 2H, J = 7.8 Hz).



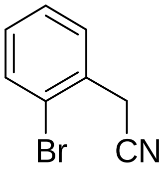
6.3 Suggest a structure for compounds **C**, **D**, and **F**.

6.4 Suggest reagents **X** and **Y** to convert compound **G** into *varenicline,* and provide the isolable intermediate **H** along this route.

SOLUTION

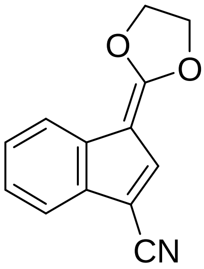
6.1

A

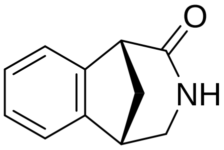
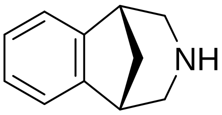
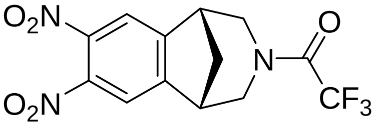


6.2

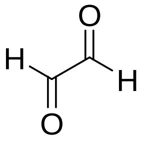
B



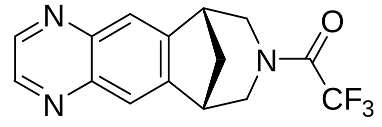
6.3

C	**D**
	
F 	

6.4

X	**Y**
	Aqueous NaOH or any other amide hydrolyzing reagents

H

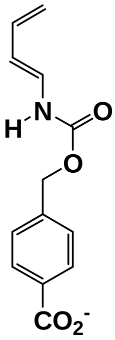


PROBLEM 7

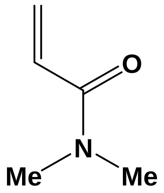
An artificial enzyme was designed to bind the two substrate molecules shown below (diene and dienophile) and catalyze a Diels-Alder reaction between them.

a. There are eight potential products from a Diels-Alder reaction involving these two molecules in the reaction without any enzyme.

7.1 Draw the structures of **any** two of the potential products that are **regioisomers** of each other, in the boxes that are given below. Use wedges (▬) and dashes (┅) to show the stereochemistry of each product in your drawings. Use **R** and **R′** shown below to represent the substituents in the molecules that are not directly involved in the reaction.

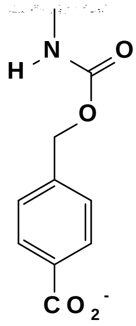


diene

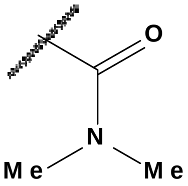


dienophile

R



R '



7.2 Draw the structures of **any** two of the potential products that are **enantiomers** of each other, in the boxes that are given below. Use wedges (▬) and dashes (┅) to show the stereochemistry of each product in your drawings. Use **R** and **R′** as in part (7.1).

7.3 Draw the structures of **any** two of the potential products that are **diastereomers** of each other, in the boxes that are given below. Use wedges (▬) and dashes (┅) to show the stereochemistry of each product in your drawings. Use **R** and **R′** as in part (7.1).

b. The rate and regioselectivity of a Diels-Alder reaction depend on the degree of electronic complementarity between the two reactants. The structures of the diene and the dienophile from part **a** are given below.

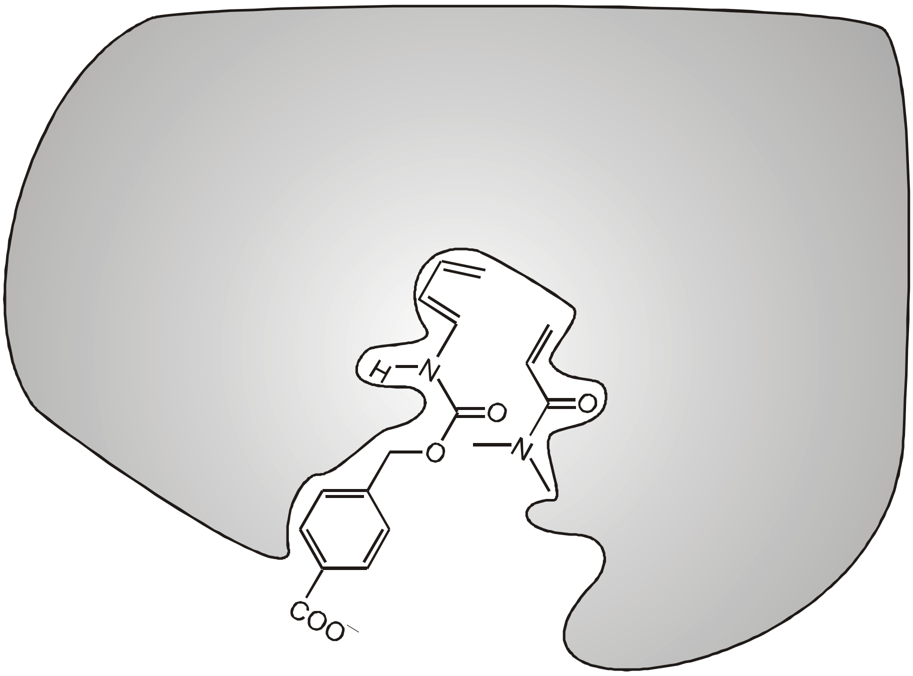
7.4 Circle the carbon atom in the diene that has increased electron density and therefore can act as an electron donor during the reaction. Draw one resonance structure of the diene in the box to support your answer. Indicate all non-zero formal charges on the atoms in the resonance structure that you draw.

7.5 Circle the carbon atom in the dienophile that has decreased electron density and therefore can act as an electron acceptor during the reaction. Draw one resonance structure of the dienophile in the box to support your answer. Indicate all non-zero formal charges on the atoms in the resonance structure that you draw.

7.6 Based on your assignments in parts (7.4) and (7.5), predict the regiochemistry of the uncatalyzed Diels-Alder reaction of the diene and dienophile by drawing the major product. You need not show the stereochemistry of the product in your drawing.

c. The figure below shows the Diels-Alder reactants as they are bound before they enter the transition state for product formation in the active site of the artificial enzyme. The gray area represents a cross-section through the enzyme. The dienophile is **below** the cross-section plane whereas the diene is **above** the cross-section plane, when the two molecules are bound in the active site that is shown.

7.7 Draw the structure of the product of the enzyme-catalyzed reaction in the box given below. Show the stereochemistry of the product in your drawing and use **R** and **R′** as you did for question **a**.



d. Consider the following statements about enzymes (artificial or natural). For each statement, indicate whether that statement is True or False (draw a circle around “True” or “False”).

7.8 Enzymes bind more tightly to the transition state than to the reactants or products of the reaction.

True False

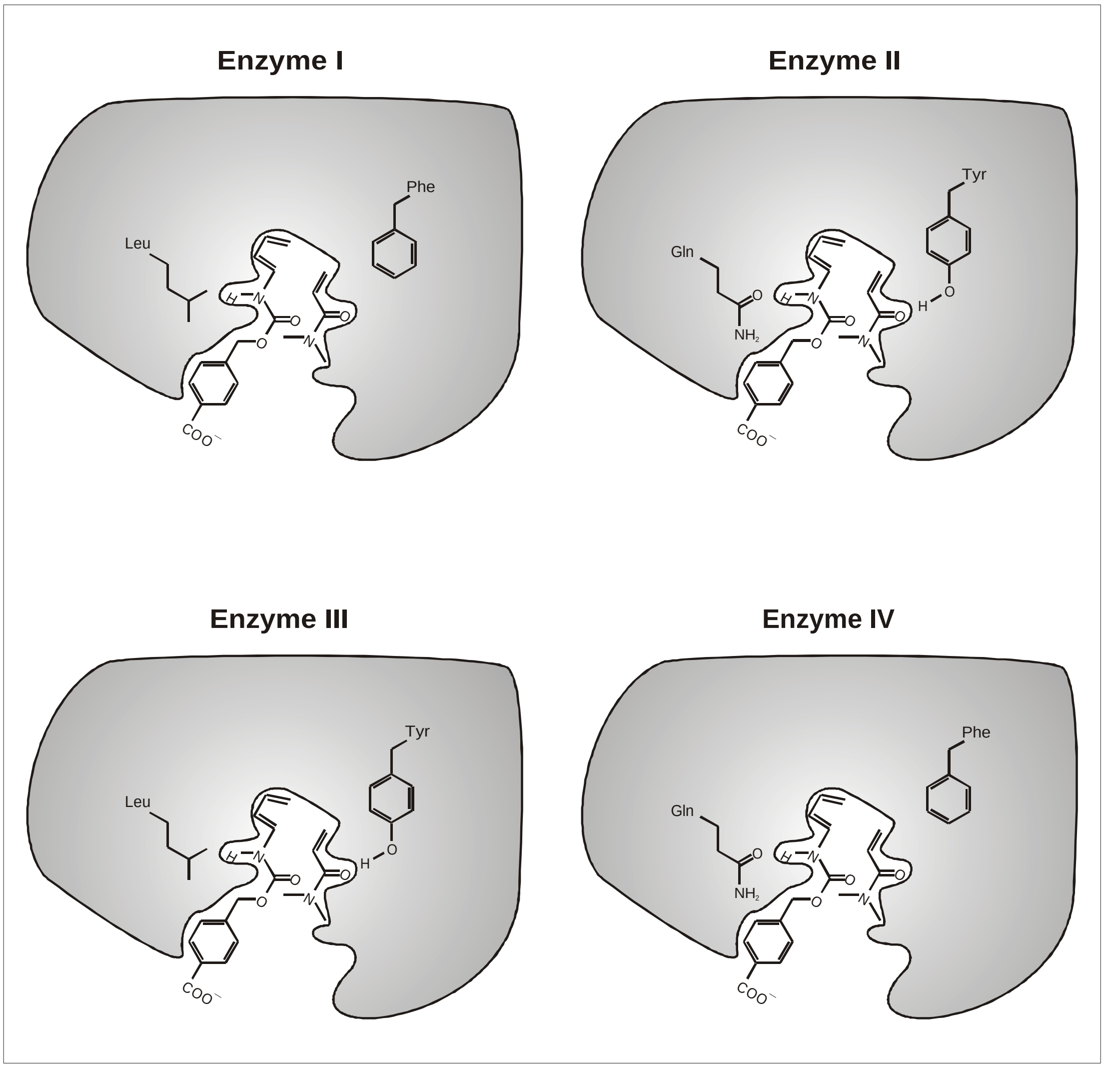
7.9 Enzymes alter the equilibrium constant of the reaction to favour the product.

True False

7.10 Enzymatic catalysis always increases the entropy of activation of the reaction compared to the uncatalyzed reaction.

True False

e. Modified versions of the artificial enzymes with different catalytic activities were prepared (enzymes I, II, III, and IV, shown in the figure below).

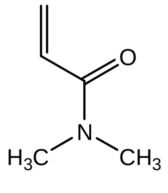


Enzyme I **Enzyme II** **Enzyme III** **Enzyme IV**

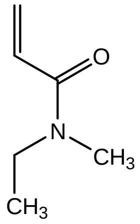
Two amino acid residues that differ among the different enzymes are shown. Assume that the enzyme functional groups shown are located in close proximity to the matching fragments of the reagents when they form the transition state in the enzyme active site.

7.11 Of these four enzymes <u>which one</u> would cause the greatest increase in the rate of the Diels-Alder reaction compared to the uncatalyzed reaction?

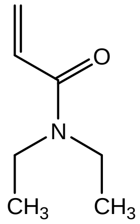
<u>f.</u> The substrate specificity of the artificial enzymes **V** and **VI** (see below) was tested by using the dienophile reactants **1 - 6**, shown below.



1



2



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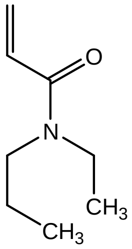

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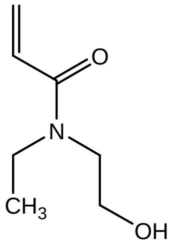

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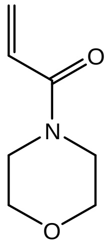
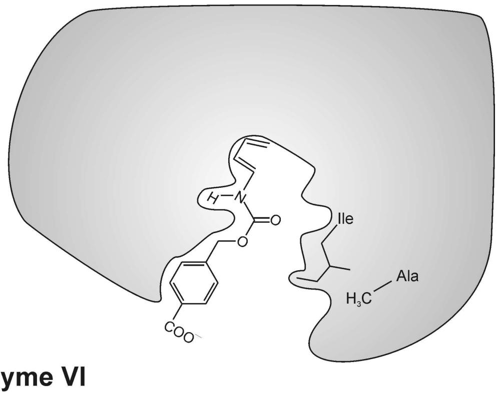


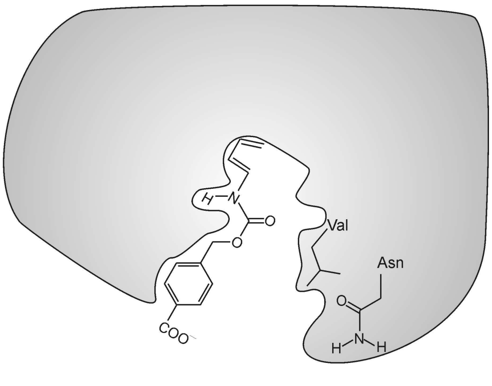
6

7.12 Dienophile **#1** reacted most rapidly in the reaction catalyzed by artificial **enzyme V** (see below). However, artificial **enzyme VI** catalyzed the reaction most rapidly with a different dienophile. Of the six dienophiles shown above, <u>which one</u> would react most rapidly in the Diels-Alder reaction catalyzed by **enzyme VI**?

Enzyme V

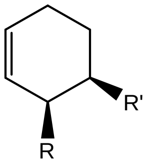
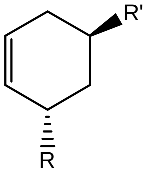


Enzyme VI

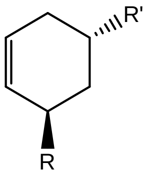
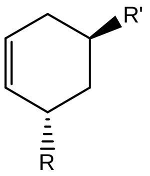


SOLUTION

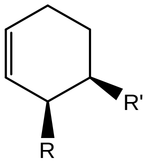
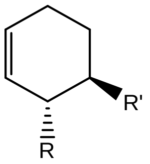
7.1

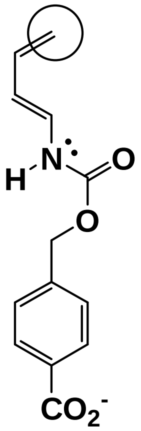
7.2

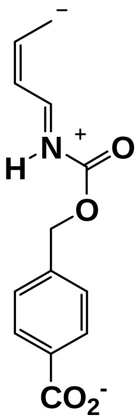
	

7.3

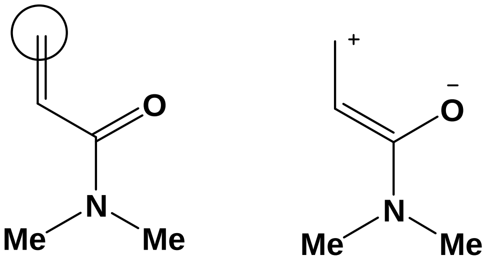
	

7.4

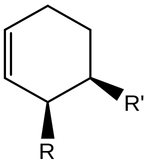




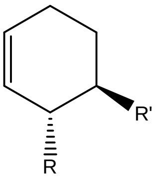
7.5



7.6



7.7



7.8 True

7.9 False

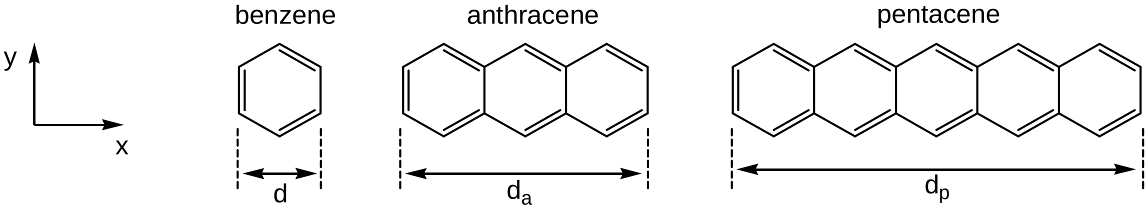
7.10 False

7.11 Enzyme **II**

7.12 Dienophile **5**

PROBLEM 8

Polycyclic aromatic hydrocarbons (PAHs) are atmospheric pollutants, components of organic light emitting diodes and components of the interstellar medium. This problem deals with so-called linear PAHs, i.e., those being just one benzene ring wide whereas the length is varied. Specific examples are benzene, anthracene and pentacene whose structures are shown below. Their physical and chemical properties depend on the extent to which the π electron cloud is delocalized over the molecule.



8.1 The distance across the benzene ring is d = 240 pm. Use this information to estimate the distances along the horizontal (x) axis for anthracene and pentacene, d_a and d_p, respectively.

Assume for simplicity that the π electrons of benzene can be modelled as being confined to a square. Within this model, the conjugated π electrons of PAHs may be considered as free particles in a two dimensional rectangular box in the x-y plane.

For electrons in a two-dimensional box along the x- and y-axes, the quantized energy states of the electrons are given by

$$E = \left(\frac{n_x^{\,2}}{L_x^{\,2}} + \frac{n_y^{\,2}}{L_y^{\,2}}\right)\frac{h^2}{8m_e}$$

In this equation, n_x and n_y are the quantum numbers for the energy state and are integers between 1 and ∞, h is Planck's constant, m_e is the mass of the electron and L_x and L_y are the dimensions of the box.

For this problem, treat the π electrons of the PAHs as particles in a two dimensional box. In this case, the quantum numbers n_x and n_y are independent.

8.2 Assume that the benzene unit has x and y dimensions that are each of length d. Derive a general formula for the quantized energies of linear PAHs as a function of quantum numbers n_x and n_y, the length d, the number of fused rings w, and the fundamental constants h and m_e.

The energy level diagram below for pentacene shows qualitatively the energies and quantum numbers n_x, n_y, for all levels occupied by π electrons and the lowest unoccupied energy level, with the electrons of opposite spins represented as the arrows pointing up or down. The levels are labelled with quantum numbers (n_x; n_y).

Pentacene:

__ (3; 2)
↑↓ (9; 1)
↑↓ (2; 2)
↑↓ (1; 2)
↑↓ (8; 1)
↑↓ (7; 1)
↑↓ (6; 1)
↑↓ (5; 1)
↑↓ (4; 1)
↑↓ (3; 1)
↑↓ (2; 1)
↑↓ (1; 1)

8.3 The energy level diagram for anthracene is shown below. Note that some energy levels may have the same energy. Draw the correct number of up and down arrows to represent the π electrons in this diagram. Also, the blanks in parentheses within this diagram are the quantum numbers n_x, n_y, which you need to determine. Fill these blanks with the pertinent values of n_x, n_y for each filled and the lowest unfilled energy level(s).

Anthracene:

__ (__; __)

__ (__; __) __ (__; __)

__ (__; __)

__ (__; __)

__ (__; __)

__ (__; __)

__ (__; __)

__ (__; __)

__ (__; __)

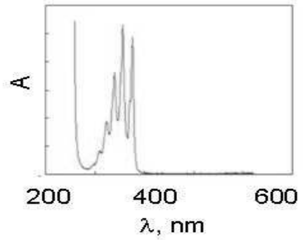
8.4 Use this model to create an energy level diagram for benzene and fill the pertinent energy levels with electrons. Include energy levels up to an including the lowest unoccupied energy level. Label each energy level in your diagrams with the corresponding n_x, n_y. Do not assume that the particle-in-a-square-box model used here gives the same energy levels as other models.

Often the reactivity of PAHs correlates inversely with the energy gap ΔE between the highest energy level occupied by π electrons and the lowest unoccupied energy level.

8.5 Calculate the energy gap ΔE (in joules) between the highest occupied and lowest unoccupied energy levels for benzene, anthracene and pentacene. Use your result from parts 8.3 and 8.4 for anthracene or benzene, respectively, or use (2, 2) for the highest occupied energy level and (3, 2) for the lowest unoccupied energy level for these two molecules (these may not be the true values).

8.6 Rank benzene (**B**), anthracene (**A**), and pentacene (**P**) in order of increasing reactivity by placing the corresponding letters from left to right in the box below.

8.7 The electronic absorption spectra (molar absorptivity vs. wavelength) for anthracene (**A**), benzene (**B**), and pentacene (**P**) are shown below. Based on a qualitative understanding of the particle in the box model, indicate which molecule corresponds to which spectrum by writing the appropriate letter in the box to its right.



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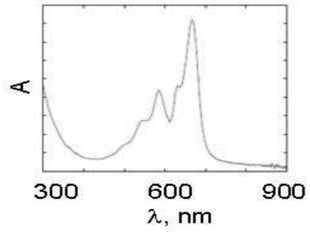

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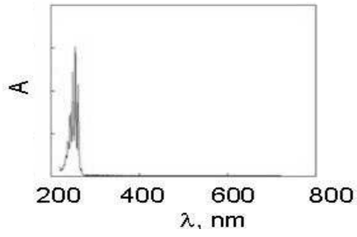
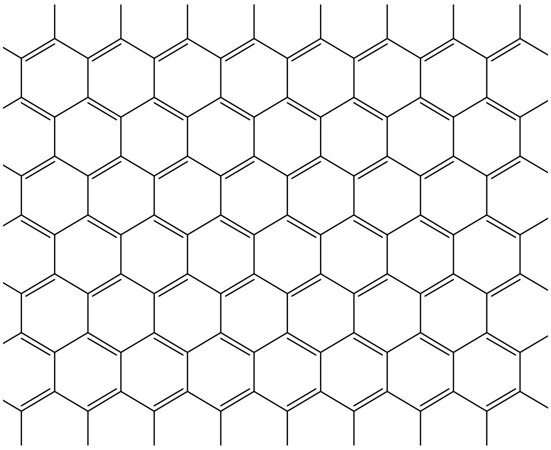


☐

Graphene is a sheet of carbon atoms arranged in a two-dimensional honeycomb pattern. It can be considered as an extreme case of a polyaromatic hydrocarbon with essentially infinite length in the two dimensions. The Nobel Prize for Physics was awarded in 2010 to Andrei Geim and Konstantin Novoselov for groundbreaking experiments on graphene.

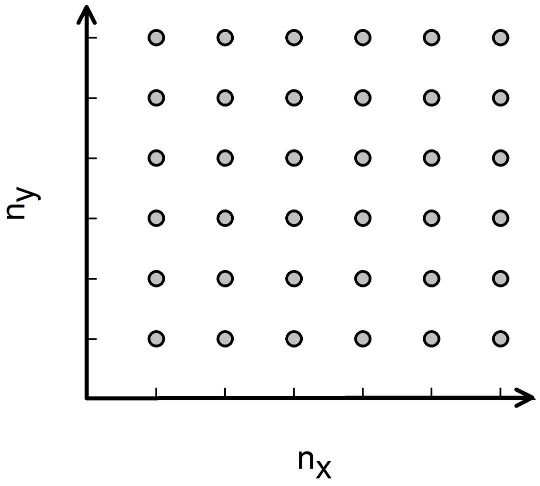
Consider a sheet of graphene with planar dimensions of L_x = 25 nm by L_y = 25 nm. A section of this sheet is shown below. The area of one hexagonal 6-carbon unit is ~52 400 pm^2.

8.8 Calculate the number of π electrons in a (25 nm × 25 nm) sheet of graphene. For this problem you can ignore edge electrons (i. e. those outside the full hexagons in the picture).



We can think about the π electrons in graphene as being free electrons in a 2-dimensional box. In systems containing large numbers of electrons, there is no single highest occupied energy level. Instead, there are many states of nearly the same energy above which the remaining are empty. These highest occupied states determine the so-called Fermi level. The Fermi level in graphene consists of multiple combinations of n_x and n_y quantum numbers.

8.9 Determine the energy of the Fermi level for the 25 nm × 25 nm square of graphene relative to the lowest filled level. The lowest filled level has a non-zero energy; however, it is negligible, and can be assumed to be zero. To solve this problem it might be helpful to represent the (n_x, n_y) quantum states as points on a 2-D grid (as shown below) and consider how the energy levels are filled with pairs of electrons. For the number of electrons use your result from part 8.8 or use a value of 1000 (this may not be the true value).



8.10 The conductivity of graphene-like materials correlates inversely with the energy gap between the lowest unoccupied and highest occupied energy levels. Use your analysis and understanding of π electrons in PAHs and graphene to predict whether the conductivity of a 25 nm × 25 nm square of graphene, at a given temperature, is less than, equal to or greater than the conductivity of a 1 m × 1 m square of graphene (which is the largest obtained to date). Circle the correct answer:

less equal greater

SOLUTION

8.1 For anthracene: $d_a = 3 \times 240$ pm = 720 pm

For pentacene: $d_p = 5 \times 240$ pm = 1200 pm

8.2

$$E = \left(\frac{n_y^{\ 2}}{d^2} + \frac{n_x^{\ 2}}{w^2 d^2} \right) \frac{h^2}{8\,m_e} = \left(n_y^{\ 2} + \frac{n_x^{\ 2}}{w^2} \right) \frac{h^2}{8\,m_e d^2}$$

8.3 Anthracene:

__ (__; __)

__ (_6_; _1_) __ (_3_; _2_)

↑↓ (_2_; _2_)

↑↓ (_1_; _2_)

↑↓ (_5_; _1_)

↑↓ (_4_; _1_)

↑↓ (_3_; _1_)

↑↓ (_2_; _1_)

↑↓ (_1_; _1_)

8.4 Benzene:

__ (_2_; _2_)

↑↓ (_2_; _1_) ↑↓ (_1_; _2_)

↑↓ (_1_; _1_)

8.5

ΔE for benzene: $\Delta E = E(2;2) - E(1;2) = 3\,\frac{h^2}{8\,m_e d^2} = 3.14 \cdot 10^{-18}\,\text{J}$

Alternate solution:

$\Delta E = E(3;2) - E(2;2) = 5\,\frac{h^2}{8\,m_e d^2} = 5.23 \cdot 10^{-18}\,\text{J}$

ΔE for anthracene: $\Delta E = E(6;1) - E(2;2) = \frac{5}{9}\left(\frac{h^2}{8\, m_e d^2}\right) = 5.81 \cdot 10^{-19}\ \text{J}$

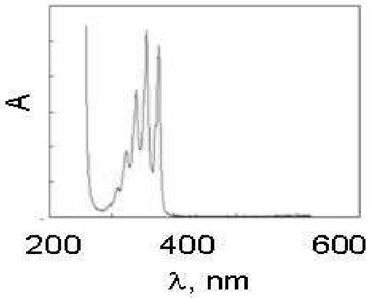
Alternate solution:

$$\Delta E = E(3;2) - E(2;2) = \frac{5}{9}\left(\frac{h^2}{8\, m_e d^2}\right) = 5.81 \cdot 10^{-19}\ \text{J}$$

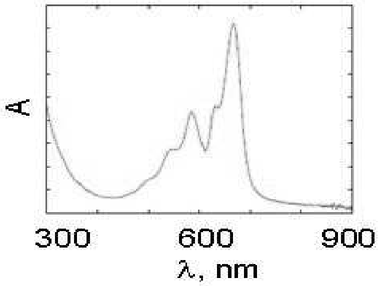
ΔE for pentacene: $\Delta E = E(3;2) - E(9;1) = \frac{3}{25}\left(\frac{h^2}{8\, m_e d^2}\right) = 1.26 \cdot 10^{-19}\ \text{J}$

8.6 (least reactive) **B** < **A** < **P** (most reactive)

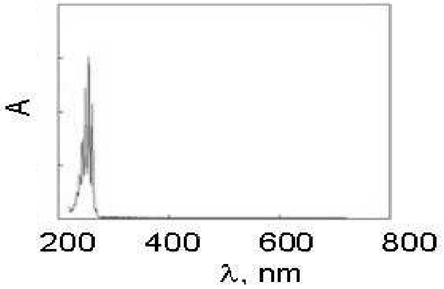
8.7



A



P



B

8.8 The number of hexagonal units in the graphene sheet:

$$N_{units} = \frac{\text{Area}_{\text{graphene}}}{\text{Area}_{\text{unit}}} = \frac{(25000\ \text{pm})^2}{52400\ \text{pm}^2} = 12\,000\ \text{units}$$

Since each carbon atom in a graphene sheet is shared by three hexagonal units, each unit of the area 52 400 pm^2 contains 6/3 = 2 carbon atoms contributing 2 π electrons total.

Therefore, 12 000 units contribute 12 000 pairs of π electrons.

Correct answer: 24 000 π electrons.

8.9 Two electrons fill each state, so the Fermi level has 12 000 filled levels. This corresponds to the number of (n_x, n_y) pairs that are occupied.

Since $L_x = L_y$ and the lowest energy level's energy is approximated as zero,

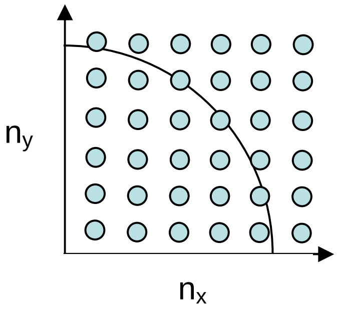
$$\Delta E = E_{\text{highest occupied}} = (n_x^{\ 2} + n_y^{\ 2})\frac{h^2}{8\,m_e L^2}$$

This is rearranged to the equation of a circle.

$$R^2 = (n_x^{\ 2} + n_y^{\ 2}) = \frac{E\,8 m_e L^2}{h^2} = \text{constant}$$

The area of the populated grid is

$$\text{Area}_{\text{grid}} = \frac{\pi R^2}{4}$$



The area of each quantum number pair is 1.

Therefore, the number of points is given as

$$N_{\text{points}} = \frac{\text{Area}_{\text{grid}}}{\text{Area}_{\text{pair}}} = \frac{\pi R^2}{4} = N_{\text{states}} = 12\,000\,.$$

Rearranging and solving for energy yields the Fermi energy.

$$N_{\text{states}} = \frac{\pi R^2}{4} = \frac{\pi 8 m_e L^2 E}{4 h^2} = 12\,000$$

$$E = \frac{4h^2 \times 12\,000}{\pi 8 m_e L^2} = 1.48 \cdot 10^{-18}\ \text{J}$$

Alternate solution:

$$N_{\text{states}} = \frac{\pi R^2}{4} = \frac{\pi 8 m_e L^2 E}{4 h^2} = 1000$$

$$E = \frac{4h^2 \times 1000}{\pi 8 m_e L^2} = 1.23 \cdot 10^{-19}\ \text{J}$$

8.10 Less is correct.

The energy gaps decrease with the graphene sample size increase and the conductivity increases as the energy gap decreases.

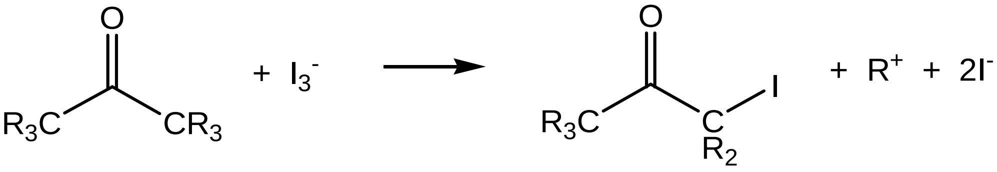
PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Kinetics, Isotope Effect, and Mechanism of Iodination of Acetone

Discoveries about the mechanisms of chemical reactions underlie advances in catalysis and synthesis. One of the most powerful tools for probing reaction mechanisms is the study of kinetics because the ways in which reaction rates vary with reaction conditions follow directly from the mechanism of reaction. A second powerful tool is the study of isotopically substituted molecules. While isotopes impart similar reactivity, there are slight differences in reaction rates as a function of nuclear mass.

In this task you will use both kinetics and isotope effects to provide information about the iodination of acetone in acidic aqueous solution:



R = H or D

The reaction takes place with a rate law

$$\text{Rate} = k\,[\text{acetone}]^m\,[\text{I}_3^-]^n\,[\text{H}^+]^p$$

where the rate constant k and the integer reaction orders m, n, and p are for you to determine. You will also compare the reactivity of acetone with that of acetone-d_6, where the six atoms of protium (^{1}H) have been replaced by deuterium (^{2}H, D), to determine the isotope effect (k_H / k_D) of the reaction. From these data you will make inferences about the mechanism of this reaction.

Please read the whole description of this task and plan your work before you begin.

Chemicals

- HCl, aqueous solution, c = ~2 mol dm$^{-3\,*)}$, 50 cm^3
- KI$_3$, aqueous solution, c = ~0.01 mol dm$^{-3\,*)}$, 10 cm^3 , labelled “I$_2$”,
- Acetone, $(CH_3)_2CO$, M = 58.08 g mol^{-1}, density = 0.791 g cm^{-3}, 10 cm^3,

- Acetone-d_6, $(CD_3)_2CO$, M = 64.12 g mol^{-1}, density = 0.872 g cm^{-3}, 3.0 cm^3

[*)] The exact concentration is indicated on the label.

Procedure

Reaction rates are dependent on temperature. Record the temperature in the room you are working in (ask the room assistant).

Measure the volumes of hydrochloric acid, distilled water, and potassium triiodide solution (labelled as "I_2") that you choose into the reaction vessel. The initial concentrations of the reagents in the reaction mixtures should be in the ranges given below (you need not explore the full ranges given, but your values should not be significantly outside these ranges):

$[H^+]$: between 0.2 and 1.0 mol dm^{-3}
$[I_3^-]$: between 0.0005 and 0.002 mol dm^{-3}
[acetone]: between 0.5 and 1.5 mol dm^{-3}

To initiate the reaction, add the chosen volume of acetone to the solution containing the other reagents, quickly cap the reaction vessel, start the timer, shake the vial vigorously one time, then put it aside on a white background. Report the volumes of reagents that you use in table 1.1. When setting up and running a reaction do not hold or touch the vial below the level of liquid in it. The progress of the reaction can be monitored visually by watching the disappearance of the yellow-brown colour of the triiodide ion. Record the time required for the colour to disappear. When the reaction is complete, set aside the vessel, and leave it sealed so that you do not expose yourself to iodoacetone vapours.

Repeat as often as desired with different concentrations of reagents. Report the concentrations of the reagents that you use in table 1.3.

Hint: Change one concentration at a time.

Once you have studied the rate of reaction of acetone, you should examine the rate of reaction of acetone-d_6. Note that while you have an ample supply of acetone, you will be given only 3.0 cm^3 of acetone-d_6 because of the greater expense of the isotopically labelled material. Therefore, any refilling of acetone-d_6 will be accompanied by a one point penalty. When you need to use this reagent, raise your hand and the lab supervisor will open the sealed ampoule for you. The reactions of deuterium-substituted compounds are generally slower than those of protium-substituted compounds. You would thus be well advised to use reaction conditions that promote faster reactions when working with $(CD_3)_2CO$.

When you have finished your work:

a) empty the water bottle and place it along with any unused equipment back to the box labelled "Kit #1",

b) place used pipettes and sealed used vials in designated containers under the hoods,

c) use a container labelled "Broken Glass Disposal" to dispose of all parts of the empty ampoule.

You may clean up your area after the STOP command has been given.

1.1 Record your results for acetone, $(CH_3)_2CO$, in the table below. *You need not fill the entire table.*

Table 1.1

Run #	Volume HCl solution, cm^3	Volume H_2O, cm^3	Volume I_3^- solution, cm^3	Volume $(CH_3)_2CO$, cm^3	Time to disappearance of I_3^-, s
1					
2					
3					
etc.					

1.2 Record your results for acetone-*d*$_6$, $(CD_3)_2CO$, in the table below. *You need not fill the entire table.*

Table 1.2

Run #	Volume HCl solution, cm^3	Volume H_2O, cm^3	Volume I_3^- solution, cm^3	Volume $(CD_3)_2CO$, cm^3	Time to disappearance of I_3^-, s
1d					
2d					
3d					
etc.					

1.3 Use the following tables to calculate concentrations and average rates for the reactions you studied. Assume that the volume of each reaction mixture is equal to the sum of volumes of its constituent solutions. You need not use all of your runs in your calculation of *k* (parts 1.5 and 1.6), but you must indicate which run or runs you used in your calculation by checking the appropriate box in the right-hand column.

Table 1.3

$(CH_3)_2CO$:

Run #	Initial $[H^+]$, mol dm^{-3}	Initial $[I_3^-]$, mol dm^{-3}	Initial $[(CH_3)_2CO]$, mol dm^{-3}	Average rate of disappearance of I_3^-, mol dm^{-3} s^{-1}	Run used in calculating k_H? **Yes**	**No**
1					☐	☐
2					☐	☐
3					☐	☐
etc.						

Table 1.4

$(CD_3)_2CO$:

Run #	Initial $[H^+]$, mol dm^{-3}	Initial $[I_3^-]$, mol dm^{-3}	Initial $[(CD_3)_2CO]$, mol dm^{-3}	Average rate of disappearance of I_3^-, mol dm^{-3} s^{-1}	Run used in calculating k_D? **Yes**	**No**
1d					☐	☐
2d					☐	☐
3d					☐	☐

1.4 Give the integer reaction order in acetone, triiodide, and hydrogen ion.

$$\text{rate} = -\frac{d[I_3^-]}{dt} = k\,[(CH_3)_2CO]^m\,[I_3^-]^n\,[H^+]^p$$

m =

n =

p =

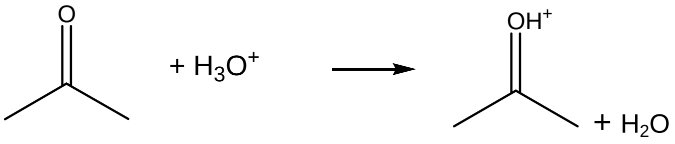
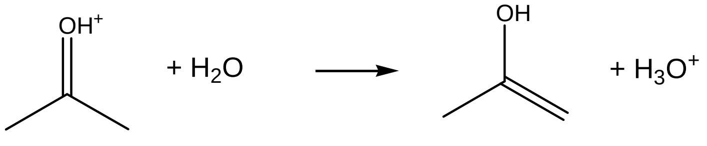
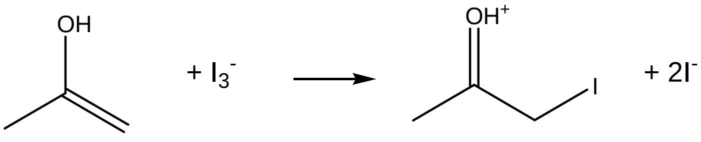
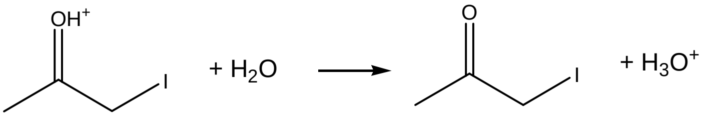
1.5 Calculate the rate constant k_H for the reaction of acetone, $(CH_3)_2CO$, and indicate the units.

1.6 Calculate the rate constant k_D for the reaction of acetone-d_6, $(CD_3)_2CO$, and calculate the value of k_H / k_D (the isotope effect of the reaction).

From the kinetic and isotope effect data you may draw certain conclusions about the reaction mechanism. Shown below is a reasonable mechanism for the iodination of acetone. One reaction is the rate-determining step with all previous steps rapidly achieving an equilibrium that strongly favours the reactants.

1.7 In the box in the **first column** on the right next to each step, place a check mark (✓) if your *experimentally measured rate law* (part **1.4**) is **consistent** with that step being rate-determining and a mark (**X**) if your measured rate law is **inconsistent** with that step being rate-determining.

In the box in the second column on the right next to each step, place a check mark (✓) if your *experimentally measured isotope effect* (part 1.6) is **consistent** with that step being rate-determining and a mark **X** if your measured isotope effect is **inconsistent** with that step being rate-determining.

	Rate determining step consistent with rate law?	Rate determining step consistent with isotope effect?
		
		
		
		

SOLUTION

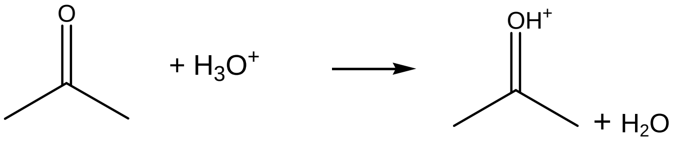
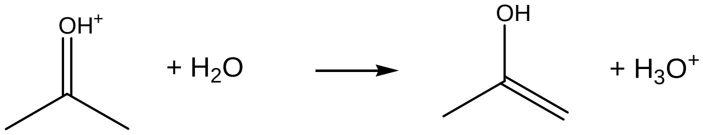
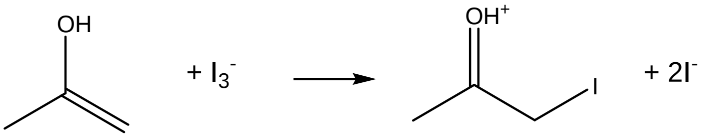
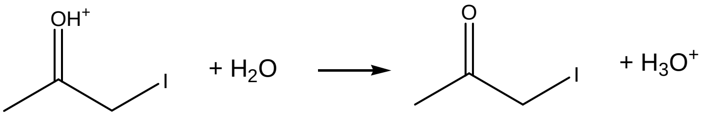
1.4 m = 1; n = 0; p = 1

1.5 $k_H = 2.8 \pm 0.4 \cdot 10^{-5}$ dm^3 mol^{-1} s^{-1}

1.6 $k_D = 4.3 \pm 0.6 \cdot 10^{-6}$ dm^3 mol^{-1} s^{-1}

k_H **/** $k_D = 6.5 \pm 0.4$

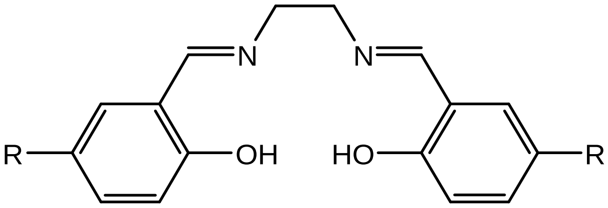
1.7

	Rate determining step consistent with rate law?	Rate determining step consistent with isotope effect?
	✓	X
	✓	✓
	X	X
	X	X

PROBLEM 2 (Practical)

Synthesis of a Salen Manganese Complex and Determining Formula of the Product

Transition metal complexes of the 3*d*-block elements derived from the bis(salicylidene)ethylenediamine (salen) ligand have proven to be efficient catalysts of various redox reactions in organic synthesis.



(salen)H$_2$, R = H

(salen*)H$_2$, R = H, COOH, or SO_3H

The ability of the salen ligand to stabilize higher oxidation states of 3*d*-block elements is important in this sphere of chemistry. In particular, compounds of manganese in oxidation states from II to V could be generated depending on the reaction conditions when the manganese salen complex is prepared. In this task you are required to prepare a manganese salen complex by reacting (salen)H$_2$ with Mn(II) acetate in ethanol in the air in the presence of lithium chloride. Under these conditions, you might have obtained a complex of the formula (salen)MnCl$_x$, where x = 0, 1, 2, or 3.

You are expected to:

i) determine the mass of the product,

ii) characterize the purity of the material prepared using thin-layer chromatography (TLC),

iii) determine the metal oxidation state in the complex using an iodometric redox titration.

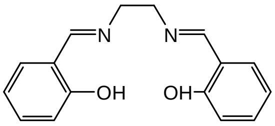
For the redox titration, you will be given a solution of a previously prepared analogue of your compound, (salen*)MnCl$_x$, where manganese has the same oxidation state as in the product and the substituent R on the benzene ring is either H, COOH, or SO_3H.

Please read the whole description of this task and plan your work before you begin. Some operations have to be performed in parallel in order to complete it in time.

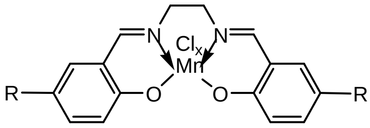
Chemicals

Note: The exact values of masses and concentrations of the particular chemicals are indicated on the labels.

- **(salen)H_2**, ~1.0 g in a vial



- $Mn(OOCCH_3)_2 \cdot 4\ H_2O$, ~1.9 g in a vial
- Lithium chloride, solution in ethanol, c = 1 mol dm^{-3}
- Ethanol
- Acetone
- (salen*)$MnCl_x$, ~32 cm^3 of a solution with a mass concentration of ~3.5 mg cm^{-3}



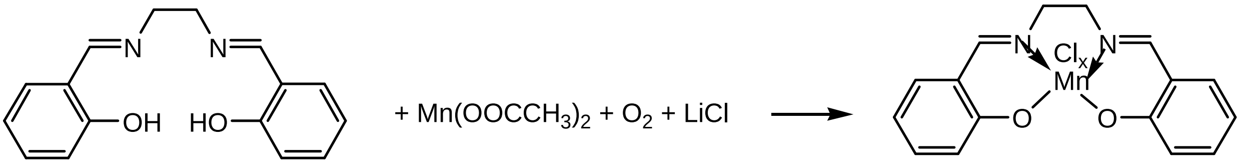
Both R groups are equal and can be either H, or COOH or SO_3H.

- KI_3, 50 cm^3 of an aqueous solution in a bottle, labelled "I_2", c = ~0.010 mol dm^{-3}.
- Ascorbic acid, 20 cm^3 of an aqueous solution, c = ~0.030 mol dm^{-3}.
- Starch, w = 0.01, 2 cm^3 solution in water,

Procedure:

A. Synthesis of (salen)$MnCl_x$

B.



(salen)$MnCl_x$

(1) Place 2-3 crystals of (salen)H_2 aside in a small vial to be used for the TLC experiment later.

(2) Transfer the pre-weighed ~1.0 g sample of (salen)H_2 provided into a 250 cm^3 Erlenmeyer flask charged with a stirring bar. Combine the reagent with 35 cm^3 of absolute ethanol.

(3) Place the flask on a hot plate/stirrer. Heat the contents with constant stirring until the solid dissolves (usually, dissolution is complete when the ethanol is about to boil). Then decrease the temperature setting to maintain the mixture close but below its boiling point. Do not boil the mixture so that the neck of the flask remains cool. If the flask is too hot to hold with bare hands, use a folded paper towel.

(4) Remove the flask from the hotplate and add to its content a pre-weighed ~1.9 g sample of $Mn(OAc)_2 \cdot 4\ H_2O$. A dark brown colour will develop. Return the flask to the hotplate immediately and continue heating and stirring for 15 min. Do not boil the mixture so that the neck of the flask remains cool.

(5) Remove the flask from the hotplate and add to its contents the provided solution of LiCl (c = 1 mol dm^{-3}) in ethanol (12 cm^3, an excess). Return the flask to the hotplate and continue heating and stirring for 10 min. Do not boil the mixture so that the neck of the flask remains cool.

(6) After this time remove the flask from the hotplate and place it in an ice bath for crystallization for 30 min. Every 5 min gently scratch the walls of the flask from inside under the liquid level with a glass rod to accelerate crystallization of (salen)$MnCl_x$. The first crystals may appear immediately upon cooling or after a period of only 10 – 15 minutes.

(7) Use vacuum line located inside the hood (the corresponding valve is labelled "Vacuum") and suction filter the crystalline solid formed using the small Hirsch funnel and a suction flask. Use a transfer pipette to wash the solid with few drops of acetone without disconnecting the flask from the vacuum line, and leave it on the filter (with the suction on) for 10 – 15 min to air-dry.

(8) Transfer the solid product into a pre-weighed vial labelled "Product", then determine and record its mass, m_p, in the box below. Record also the mass of the following reagents used in the synthesis: (salen)H_2, m_S, and $Mn(OOCCH_3)_2 \cdot 4\ H_2O$, m_{Mn}.

(9) Place the labelled vial with product into a zipper bag.

You are required to fill in the following table:

Mass of the empty vial for the product: _______________ g

Mass of the vial with the dried product: _______________ g

Mass of the product, m_p: _______________ g

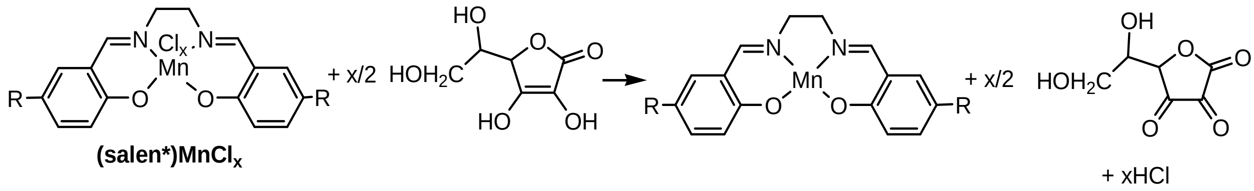
Mass of $(salen)H_2$ from label on the vial (copy from the label), m_S:

_______________ g

Mass of $Mn(OOCCH_3)_2 \cdot 4\ H_2O$ from label on the vial (copy from the label), m_{Mn}:

_______________ g

B. Volumetric analysis of a sample of (salen*)MnCl$_x$ provided



R = H, COOH, or SO_3H

Procedure:

(1) Dispense 10.00 cm^3 of the provided (salen*)MnCl$_x$ solution into a 125 cm^3 Erlenmeyer flask using the volumetric pipette.

(2) Add 5.00 cm^3 of the ascorbic acid solution to this solution and mix well. Allow the solution to stand for 3 – 4 minutes.

(3) To avoid oxidation of ascorbic acid with O_2 do not delay and titrate the solution immediately with the KI_3 solution using 5 drops of a 1 % starch solution as indicator. The blue or blue-green endpoint should persist for at least 30 sec.

(4) If time permits, perform 1 – 2 replicate titrations to improve the accuracy of your determination.

Place results of your titration experiment(s) in table 2.1.

Table 2.1. Results of the titration experiment(s).

#	Initial volume reading in burette of KI_3 solution, cm^3	Final volume reading in burette of KI_3 solution, cm^3	Volume of KI_3 solution consumed, cm^3
1			
2			

2.1 Indicate the volume (selected or averaged) of KI_3 solution consumed in cm^3 that you will use for calculations of molar mass of (salen*)$MnCl_x$.

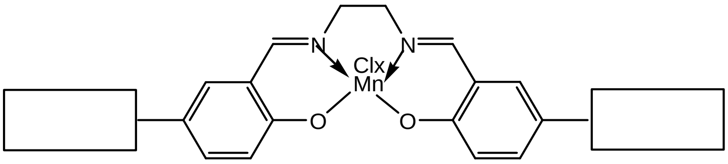
Concentrations of (salen*)$MnCl_x$ (in mg cm^{-3}) and ascorbic acid (in mol dm^{-3}) are given on the labels of the particular bottles.

2.2 From your titration data and referring to the table 2.2 deduce:

i) the value of *x*,

ii) oxidation state of manganese,

iii) the identity of the substituent on the salen ligand (R = H, COOH, SO_3H). Show them in the template below.



x = ________

Manganese oxidation state: ______________

Table 2.2

R	x	(Theoretical molar mass)/x, g mol^{-1}
H	1	357
H	2	196
H	3	143
COOH	1	445
COOH	2	240

Table 2.2 continued

COOH	3	172
SO_3H	1	517
SO_3H	2	276
SO_3H	3	196

C. TLC characterization of (salen)MnCl$_x$

(1) Dissolve a few crystals of the (salen)MnCl$_x$ that you have prepared in a few drops of absolute ethanol using a small vial and a plastic transfer pipette for ethanol.

(2) Dissolve a few crystals of (salen)H$_2$ in few drops of absolute ethanol using another small vial.

(3) If necessary, use scissors (available from lab assistant upon request) to trim the TLC plate so it is an appropriate height for the TLC chamber.

(4) Fold or trim a large circle of filter paper, and place it in the beaker so that it takes almost the full height of the beaker. This is required to saturate the chamber with ethanol vapour. Add ethanol to the beaker to wet the filter and cover the bottom with a 3 – 4 mm thick layer of the solvent. Close the beaker with watch glass.

(5) Mark the start.

(6) Using the capillary tubes provided spot the TLC plate with both solutions.

(7) Run a TLC in the beaker covered with a watch glass for 10 – 15 min.

(8) Mark the solvent front as well as the coloured spots on the TLC plate using a pencil.

(9) Dry the TLC plate in air and place it back into a zipper bag.

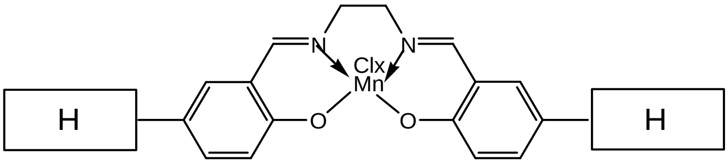
2.3 Calculate the R_f for both (salen)H$_2$ and (salen)MnCl$_x$.

2.4 Sketch the TLC plate on your answer sheet.

2.5 Determine and record the R_f values for (salen)H$_2$ and (salen)MnCl$_x$.

SOLUTION

2.2



x = 1

Manganese oxidation state: 3

2.4 Evaluation of the TLC plate:

Maximum points:

- for the appearance of two spots on the start line,
- for the start and solvent front lines,
- for the clearly visible spots.

2.5 The relevant R_F values:

Compound	R_f
(salen)H_2	0.58 – 0.68
(salen)$MnCl_x$	0.30 – 0.40

45th

8 theoretical problems
3 practical problems

THE FORTY-FIFTH
INTERNATIONAL CHEMISTRY OLYMPIAD
15–24 JULY 2013, MOSCOW, RUSSIAN FEDERATION

THEORETICAL PROBLEMS

PROBLEM 1

Clathrate gun

The only gun that is able to kill all living people in one shot

On the floors of oceans and seas there are vast reserves of methane in the form of clathrate compounds called methane hydrates. These reserves can be mined and serve as a source of energy or raw materials for organic synthesis. However, scientists are seriously worried about the possibility of spontaneous decomposition of hydrates caused by the raising ocean temperature. It is believed that if a sufficient amount of methane is released into the atmosphere, the oceans will warm up quicker due to the greenhouse effect, further accelerating the decomposition of clathrates. Due to the explosion of the resulting methane-air mixture and/or changes in the composition of the atmosphere, all living creatures may become extinct. This apocalyptic scenario is called a clathrate gun.

Upon decomposition of 1.00 g of a methane hydrate with a fixed composition at 25 °C and atmospheric (101.3 kPa) pressure, 205 cm^3 of methane is released.

1.1 Determine *n* (not necessarily integer) in the formula of methane hydrate, $CH_4 \cdot n\ H_2O$.

Real methane hydrate has a non-stoichiometric composition close to $CH_4 \cdot 6\ H_2O$. At atmospheric pressure, methane hydrate decomposes at –81 °C. However, under high pressures (e.g. on the ocean floor) it is stable at much higher temperatures.

Decomposition of methane hydrate produces gaseous methane and solid or liquid water depending on temperature.

1.2 Write down the equation of decomposition of 1 mol of $CH_4 \cdot 6\, H_2O$ producing solid water (ice) $H_2O(s)$.

The enthalpy of this process equals 17.47 kJ mol^{-1}. Assume that the enthalpies do not depend on temperature and pressure, the volume change upon decomposition of hydrate is equal to the volume of released methane, and methane is an ideal gas.

1.3 At what external pressure does decomposition of methane hydrate into methane and ice take place at –5 °C?

1.4 What is the minimum possible depth of pure liquid water at which methane hydrates can be stable?

To answer this question, you should first deduce at which minimum temperature methane hydrate can coexist with liquid water. Choose the correct answer.

☐ 272.9 K ☐ 273.15 K ☐ 273.4 K

Large methane hydrate stocks on the floor of Baikal lake, the largest freshwater lake in Russia and in the world, have been discovered in July 2009 by the crew of a deep-submergence vehicle «Mir-2». During the ascent from the depth of 1400 m methane hydrate samples started to decompose at the depth of 372 m.

1.5 Determine the temperature in Baikal lake at the depth of 372 m. The enthalpy of fusion of ice is equal to 6.01 kJ mol^{-1}.

Total amount of methane in hydrates on the Earth is no less than $5 \cdot 10^{11}$ tons.

1.6 By how many degrees would the Earth atmosphere heat up, if such amount of methane is burned by reacting with atmospheric oxygen?

The enthalpy of combustion of methane is –889 kJ mol^{-1}, the total heat capacity of the Earth's atmosphere is about $4 \cdot 10^{21}$ J K^{-1}.

SOLUTION

1.1 By the ideal gas law, the amount of methane ν is equal:

$$\nu = \frac{pV}{RT} = \frac{101300 \times 205 \cdot 10^{-6}}{8.314 \times 298.15} = 8.38 \cdot 10^{-3}\,\text{mol},$$

Then the amount of water in hydrate $\nu = \dfrac{1 - 8.38 \cdot 10^{-3} \times 16}{18} = 4.81 \cdot 10^{-2}$ mol.

The ratio of amounts of water and methane is $\dfrac{4.81 \cdot 10^{-2}}{8.38 \cdot 10^{-3}} \approx 5.75$, i. e. the composition of methane hydrate is $CH_4 \cdot 5.75\ H_2O$ or $x\ CH_4 \cdot 5.75x\ H_2O$, where x is any natural number.

1.2 $CH_4 \cdot 6\ H_2O = CH_4 + 6\ H_2O$

1.3 Decomposition of methane hydrate can be viewed as a phase transition that obeys the Clausius-Clapeyron equation:

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}.$$

$$\Delta V = \frac{RT}{p} + \frac{6\,M(H_2O_{(s)})}{\rho(H_2O_{(s)})} - \frac{M(CH_4 \cdot 6\,H_2O)}{\rho(CH_4 \cdot 6\,H_2O)}.$$

The difference between two last terms is negligibly small in comparison with the first term. Thus, we can write the following equation:

$$\frac{1}{p}dp = \frac{\Delta H}{RT^2}dT$$

The dependence of the pressure on temperature is thus given by

$$p = p_0\,exp\left(\frac{\Delta H}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right).$$

Substituting T_0 = 192.15 K, T = 268.15 K, p_0 = 1 atm, we find that p = 22 atm or 2.2 MPa.

The correct answer: p = 2.2 MPa

1.4 The correct answer is: ☑ 272.9 K.

At the minimum possible depth, the sum of pressures of atmosphere and water column is equal to the dissociation pressure of methane hydrate. The temperature should be as low as possible, but it cannot be less than the melting point of water at the corresponding pressure. Thus, the temperature and pressure should correspond to the point of coexistence of water, ice, methane hydrate and gaseous methane. Since the melting point of water decreases with increasing pressure, the correct answer is 272.9 K.

Substituting T = 272.9 K into the equation from the previous question, we obtain p = 2.58 MPa. The height of the water column can be calculated using the formula $h = \dfrac{p - p_{atm}}{g\ \rho(H_2O)}$, where g = 9.8 m s^{-2}. From here $h \approx 250$ m.

1.5 From the Hess's law, the enthalpy of the process

$CH_4 \cdot 6\ H_2O = CH_4 + 6\ H_2O(l)$

is equal to 17.47 + (6 × 6.01) = 53.53 kJ mol^{-1}.

From the previous question we know that an equilibrium between methane, water and methane hydrate is established at T_o = 272.9 K and p_o = 2.58 MPa.

Thus, we can calculate the temperature of decomposition T at a pressure *of* $p = 9.8 \times 1000 \times 372 + 101000 = 3746600$ Pa using the equation:

$$\frac{1}{T} = \frac{1}{T_o} + \frac{R}{\Delta H} ln \frac{p_o}{p}\ .$$

The temperature obtained is T = 277.3 K or about 4 °C (which is in agreement with the measured temperature of Baikal water at such depth).

1.6 Upon burning of methane,

$$\frac{500 \times 10^9 \times 10^3}{0.016} \times 889 \cdot 10^3 = 2.78 \cdot 10^{22}\ \text{J}$$

of heat is released. The Earth atmosphere will heat up by

$$\frac{2.78 \cdot 10^{22}}{4 \cdot 10^{21}} \approx 7\ \text{K}$$

ΔT = 7 K

PROBLEM 2

Break down photosynthesis – the Hill reaction

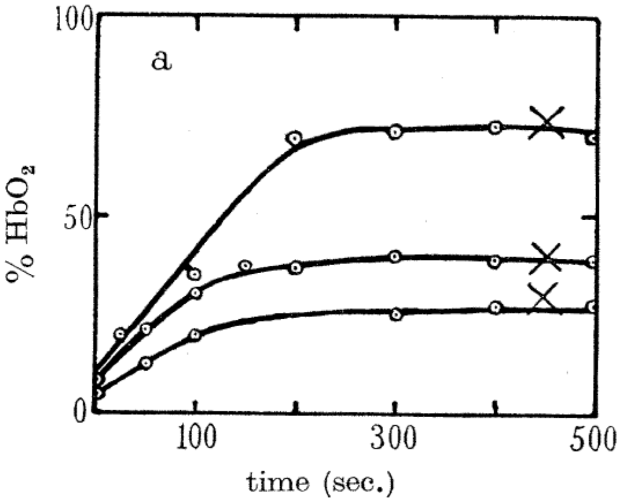
In the history of photosynthesis research, there were some breakthrough experiments which added much to our knowledge of this very complex process. One of such experiments was performed in 1930s by an English biochemist Robert Hill. In this problem, we consider some of his data together with the data of more recent experiments.

2.1 In plants, under illumination, carbon dioxide is reduced to carbohydrates (denote as $\{CH_2O\}$) and oxygen is produced. Write the overall equation of photosynthesis in plants.

Much of the photosynthesis takes place in chloroplasts – organelles found in plant cells and containing chlorophyll – the light-absorbing substance. Hill isolated chloroplasts from the cells by grinding the leaves in the sucrose solutions. The cell-free chloroplasts did not produce oxygen under illumination even in the presence of CO_2. However, upon adding potassium ferrioxalate $K_3[Fe(C_2O_4)_3]$ (with the excess of potassium oxalate) to the chloroplast suspension Hill observed oxygen liberation under illumination even without CO_2.

2.2 Hill's experiment enabled to determine the source of oxygen during photosynthesis. Write the formulas of the oxidant and the reducing agent in the photosynthesis inside the plant cells and in the cell-free chloroplasts (the Hill reaction).

Hill measured the amount of evolved oxygen using muscle haemoglobin (Hill denoted it Hb) which binds all molecular oxygen in a 1 : 1 ratio to form HbO_2. The initial concentration of Hb was $0.6 \cdot 10^{-4}$ mol dm^{-3}. Kinetic curves corresponding to different ferrioxalate concentrations are shown in the figure (the upper curve corresponds to $2.0 \cdot 10^{-4}$ mol dm^{-3}).



The fraction of bound haemoglobin HbO_2 (with respect to the initial amount of Hb) as a function of time. Crosses denote the end of the reaction

(Figure 2a from the original Hill's paper: *R. Hill. Oxygen produced by isolated chloroplasts. – Proc. R. Soc. B, 1939, v. 127, pp. 192-210.*)

2.3 **a.** From the figure, estimate the Fe / O_2 mole ratio at the end of the reaction. Do not take into account the iron from Hb.

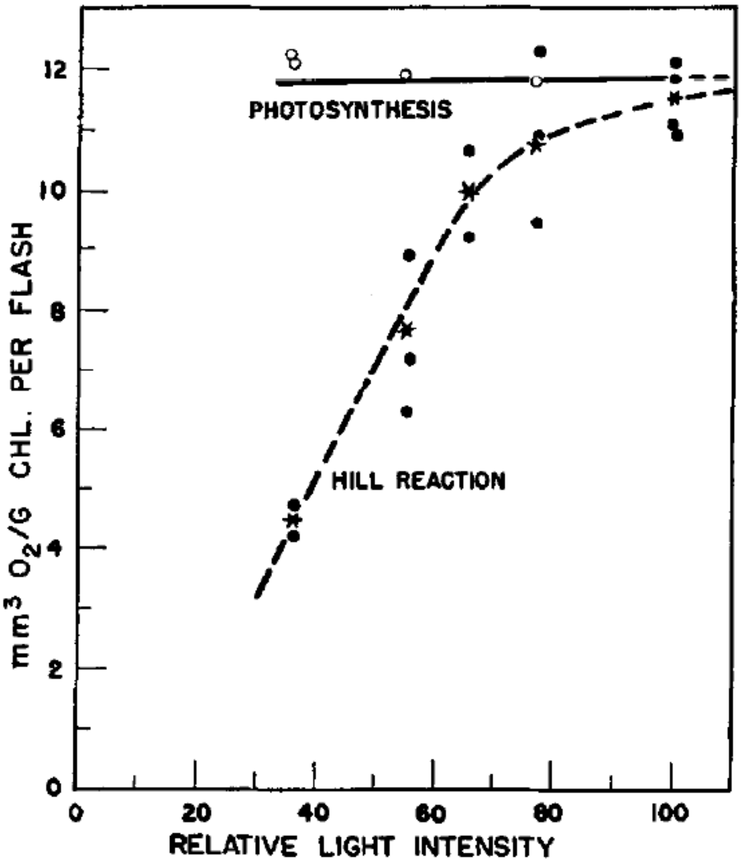
b. Write the equation of Hill reaction assuming that it proceeds with a high yield.

c. Using the table of standard electrode potentials, determine the Gibbs energy of the Hill reaction at T = 298 K, oxygen pressure 1 mm Hg, pH = 8 and standard concentrations of other species. Is this reaction spontaneous at such conditions?

Half-reaction	E°, V
$O_2 + 4\,H^+ + 4\,e \rightarrow 2\,H_2O$	+1.23
$CO_2 + 4\,H^+ + 8\,e \rightarrow \{CH_2O\} + H_2O$	–0.01
$Fe^{3+} + e \rightarrow Fe^{2+}$	+0.77
$Fe^{3+} + 3\,e \rightarrow Fe^0$	–0.04
$[Fe(C_2O_4)_3]^{3-} + e \rightarrow [Fe(C_2O_4)_3]^{4-}$	+0.05
$[Fe(C_2O_4)_3]^{4-} + 2\,e \rightarrow Fe + 3\,C_2O_4^{2-}$	–0.59

Now, the name "Hill reaction" denotes photochemical oxidation of water by any oxidant other than carbon dioxide which is sensitized by plant cells or isolated chloroplasts.

In another experiment (1952), quinone in an acid solution was used as an oxidant in the Hill reaction initiated by light flashes in the *Chlorella* algae. Experimental data are shown in the figure. The volume of oxygen (in mm^3, at temperature 10 ^{o}C and pressure 740 mm Hg) per one gram of chlorophyll per one flash was determined as a function of light intensity for natural photosynthesis and for isolated chloroplasts. It was found that the maximum yield of oxygen is the same for natural photosynthesis and the Hill reaction.



(Figure 1 from: *H. Ehrmantraut, E. Rabinovitch. Kinetics of Hill reaction. – Archives of Biochemistry and Biophysics, 1952, v. 38, pp. 67-84*)

2.4 **a.** Determine the reaction order of a photochemical Hill reaction with respect to light intensity at low and high intensity. For each case choose one of the following three values: 0, 1 or 2.

b. How many chlorophyll molecules participate in the formation of one oxygen molecule in the saturation limit of the Hill reaction? (The molecular mass of chlorophyll is about 900 Da).

The quantum requirement of the light redox reactions is defined as the average number of light photons (not necessarily integer) needed for the transfer of one electron from a reducing agent to an oxidant. The isolated chloroplasts were irradiated during 2 hours by a monochromatic light (wavelength 672 nm) with the energy input 0.503 mJ s^{-1}, and the total volume of oxygen formed was 47.6 mm^3 (under the same conditions as in question 4).

2.5 Calculate the quantum requirement for the Hill reaction.

2.6 Try to make conclusions from the above experiments (questions 2.2 – 2.5). Tick the relevant boxes.

	Yes	**No**
In natural photosynthesis, water oxidation and CO_2 reduction are separated in space.		
In chloroplasts, O_2 is produced from CO_2.		
Oxidation of water in chloroplasts requires light illumination.		
Most of chlorophylls in chloroplasts participate directly in the photochemical O_2 production.		
In isolated chloroplasts, every absorbed photon causes transfer of one electron.		

SOLUTION

2.1 $H_2O + CO_2 = \{CH_2O\} + O_2$

2.2

Natural photosynthesis		Hill reaction	
Oxidant	Reducing agent	Oxidant	Reducing agent
CO_2	H_2O	$K_3[Fe(C_2O_4)_3]$	H_2O

2.3

a. The upper curve in the saturation limit gives ~ 75 % of HbO_2

$$\frac{n(\text{Fe})}{n(\text{O}_2)} = \frac{c(\text{Fe})}{c(\text{HbO}_2)} = \frac{2.0 \cdot 10^{-4}}{(0.75 \times 0.6 \cdot 10^{-4})} = \frac{4.4}{1}$$

b. Ratio ~ 4 : 1 shows that Fe(III) is reduced to Fe(II), which in the presence of excess oxalate exists as a complex:

$2\ H_2O + 4\ [Fe(C_2O_4)_3]^{3-} \rightarrow O_2 + 4\ [Fe(C_2O_4)_3]^{4-} + 4\ H^+$

c. Calculations:

$[Fe(C_2O_4)_3]^{3-} + e \rightarrow [Fe(C_2O_4)_3]^{4-}$ $\quad E_1° = 0.05$ V

$O_2 + 4\ H^+ + 4\ e \rightarrow 2\ H_2O$ $\quad E_2° = 1.23$ V

emf: $E° = E_1° - E_2° = -1.18$ V

$$\Delta G = \Delta G^o + RT \ln(p_{O_2}[H^+]^4) =$$

$$= -4 \times 96\,500 \times (-1.18) + 8.314 \times 298 \times \ln\left(\frac{1}{750}(1 \cdot 10^{-8})^4\right) =$$

$$= 2.57 \cdot 10^5 \text{ J mol}^{-1} = 257 \text{ kJ mol}^{-1}$$

The reaction is highly endoergic and, hence, not spontaneous.
Light is necessary.

2.4 **a.** Reaction order:

– at low intensity: 1

– at high intensity: 0.

b. $n(\text{Chl})/n(O_2) = 1/900 / [(12 \cdot 10^{-6} \times (740/760) \times 101.3) / (8.314 \times 283)] =$

$= 2200$

2.5 Total energy absorbed: $E = 0.503 \cdot 10^{-3} \times 3600 \times 2 = 3.62$ J

Energy of one mole of photons:

$$E_\text{m} = \frac{h\,c\,N_A}{\lambda} =$$

$$= \frac{6.63 \cdot 10^{-34} \times 3.00 \cdot 10^{8} \times 6.02 \cdot 10^{23}}{672 \cdot 10^{-9}} = 1.78 \cdot 10^{5}\ \text{J mol}^{-1}$$

$n(\text{phot}) = E / E_\text{m} = 2.03 \cdot 10^{-5}$ mol

$$n(O_2) = \frac{pV}{RT} = \frac{\frac{740}{760} \times 101.3 \times 47.6 \cdot 10^{-6}}{8.314 \times 283} = 2.00 \cdot 10^{-6}\ \text{mol.}$$

Formation of one mole of O_2 requires the transfer of 4 electrons:

$n(e) = 8.00 \cdot 10^{-6}$ mol

Quantum requirement: $\dfrac{n(\text{phot})}{n(\text{e})} = 2.5$

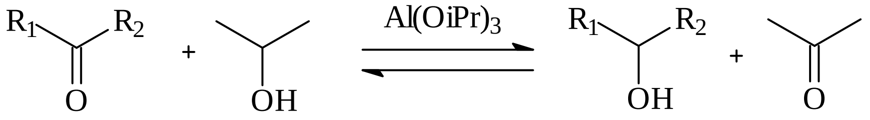
2.6

	Yes	**No**
In natural photosynthesis, water oxidation and CO_2 reduction are separated in space.	✓	
In chloroplasts, O_2 is produced from CO_2.		✓
Oxidation of water in chloroplasts requires light illumination.	✓	
Most of chlorophylls in chloroplasts participate directly in the photochemical O_2 production.		✓
In isolated chloroplasts, every absorbed photon causes transfer of one electron.		✓

PROBLEM 3

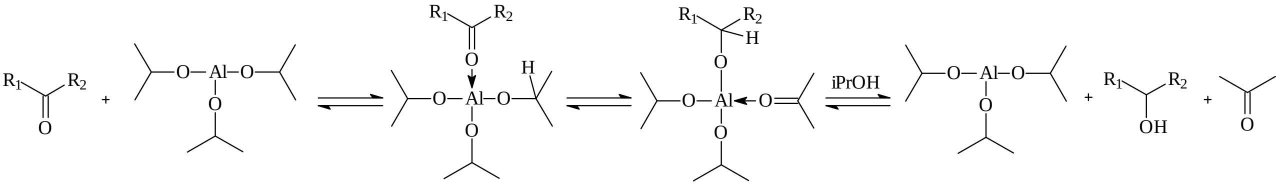
Meerwein-Schmidt-Ponndorf-Verley reaction

Meerwein-Schmidt-Ponndorf-Verley (MSPV) reaction is a useful tool for reduction of carbonyl compounds to alcohols. The reaction is the reduction of carbonyl compounds by low molecular weight alcohols in the presence of alkoxides of aluminium or other metals:



(1)

The mechanism of the reaction includes coordination of carbonyl compound by aluminium alkoxide, hydride transfer in the inner sphere of the complex and subsequent transalkoxylation. It can be schematically represented as follows (transalkoxylation is shown as a one-step process for brevity):



(2)

The reaction is reversible and shifting the equilibrium to the desired product requires some excess of the reductant. In some cases (e. g. in the case of reduction of aromatic aldehydes and ketones) the equilibrium constant is so large that the reverse reaction can be neglected.

The table below contains standard entropies and standard enthalpies of formation of liquid substances at 298 K. The boiling points of the substances at 1 bar are also given.

Substance	$\Delta_f H^o_{298}$, kJ mol^{-1}	S^o_{298}, J mol^{-1} K^{-1}	t_{vap}, ^{o}C
Acetone	–248.4	200.4	56
Isopropanol	–318.1	180.6	82
Cyclohexanone	–271.2	229.0	156
Cyclohexanol	–348.2	203.4	161

3.1 a Calculate the minimum isopropanol to cyclohexanone mass ratio which is required to reach a 99 % yield of reaction at 298 K. Assume that:

i) the reaction mixture eventually gets at equilibrium,

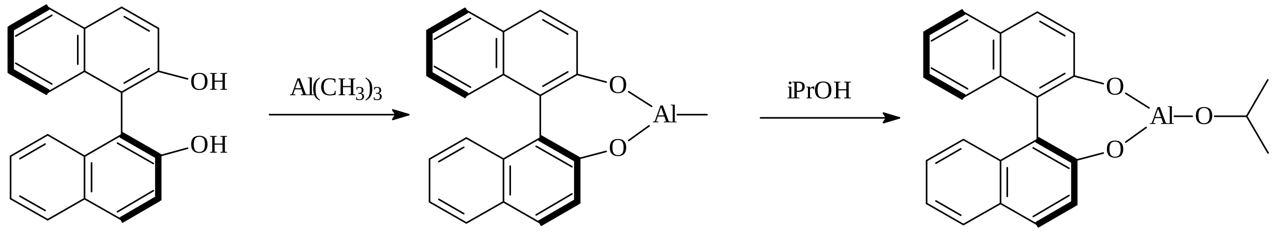
ii) no products are initially present.

3.1 b Choose the appropriate way(s) to increase the cyclohexanol yield. Tick the relevant boxes.

Increase the temperature up to 50 °C using a reflux	
Increase the temperature up to 60 °C, evaporating (distilling) the acetone	
Add some ethanol to the reaction mixture	
Add some ethanal to the reaction mixture	

3.2 Often the rate-limiting step in the MSPV reaction is the hydride transfer or the alcoholysis of the alkoxide after hydride transfer. For these two cases, using the above mechanism (2), derive an expression for the rate of reaction as a function of current concentrations of a carbonyl compound, isopropanol and a catalyst. In both cases determine the rate orders in the reactants and the catalyst. Assume that all reaction steps before the limiting step are fast and reversible. Use equilibrium approximation, if necessary. For brevity use the following notation: **A** for carbonyl compound, **B** for isopropanol, **C** for catalyst. Denote intermediates as you wish.

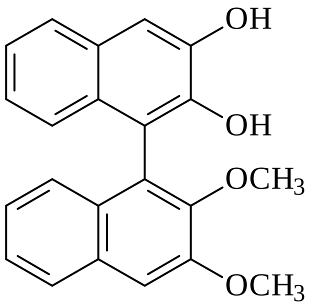
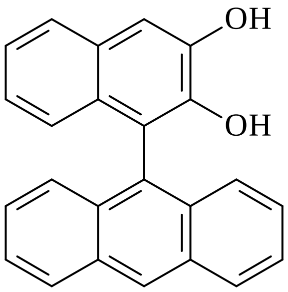
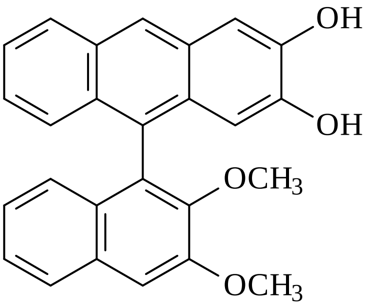
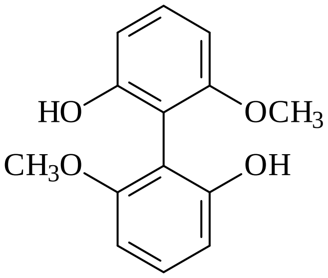
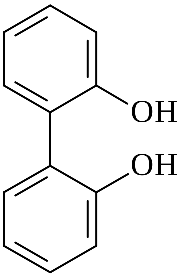
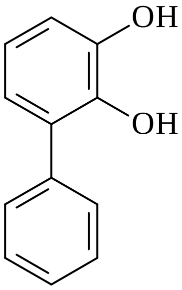
MSPV reaction can be used to obtain chiral alcohols, if the chiral catalyst is employed. For instance, Campbell et al. used the catalyst based on the chiral 2,2'-dihydroxy-1,1'-binaphtyl (BINOL), which is synthesized *in situ* from binaphtol and trimethylaluminium:



(BINOL)Al(OiPr) (3)

The chirality of BINOL is due to the sterically hindered rotation around the C-C bond. Though perfectly stable at room temperature, BINOL may racemize when heated.

3.3 Which of the phenols below can form stable (at room temperature) enantiomers so that they can be used in the same fashion to produce a chiral catalyst? Tick the relevant boxes.

Substance	Can be used	Substance	Can be used
			
			
			

Enantiomeric excess, *ee*, is used to characterize the enantiomeric purity of the substance. This quantity equals to the ratio of the difference of concentrations of enantiomers *R* and *S* to their sum:

$$ee = \frac{[\mathrm{R}] - [\mathrm{S}]}{[\mathrm{R}] + [\mathrm{S}]}$$

Enantiomeric excess of the pure *R* isomer is unity, *ee* of the racemic mixture is zero.

3.4 When using the enantiomerically pure (BINOL)Al(OiPr) as a catalyst for reduction of α-bromoacetophenone, the *ee* of the product equals 81 %. What is the *ee* of the product if the catalyst *ee* equals 50 %? Provide your calculation with an illustration or derivation of the final formula.

SOLUTION

3.1 a

The reaction enthalpy is:

$$\Delta_r H^o_{298} = \Delta_f H^o_{298}(C_3H_6O) + \Delta_f H^o_{298}(C_6H_{12}O) – \Delta_f H^o_{298}(C_3H_8O) – \Delta_f H^o_{298}(C_6H_{10}O) =$$

$$= (–248.4) + (–348.2) – (–318.1) – (–271.2) = – 7.3 \text{ kJ mol}^{–1}$$

The reaction entropy is:

$$\Delta_r S^o_{298} = S^o_{298}(C_3H_6O) + S^o_{298}(C_6H_{12}O) – S^o_{298}(C_3H_8O) – S^o_{298}(C_6H_{10}O) =$$

$$= 200.4 + 203.4 – 180.6 – 229.0 = –5.8 \text{ J mol}^{–1} \text{ K}^{–1}$$

The reaction Gibbs energy is:

$$\Delta_r G^o_{298} = \Delta_r H^o_{298} – T\, \Delta_r S^o_{298} = –5.6 \text{ kJ mol}^{–1}$$

The equilibrium constant equals

$$K = \exp(–\Delta_r G^o_{298}/RT) = 9.6$$

The expression for equilibrium constant is as follows:

$$K = \frac{x(C_3H_6O)\ x(C_6H_{12}O)}{x(C_3H_8O)\ x(C_6H_{10}O)} = \frac{\nu(C_3H_6O)\ \nu(C_6H_{12}O)}{\nu(C_3H_8O)\ \nu(C_6H_{10}O)},$$

where x is the molar fraction of a substance in the equilibrium mixture, ν is an amount of a substance in the mixture. Denote the initial amount of cyclohexanone as y. The yield of the reaction is 99 %, i. e. 99 % of cyclohexanone must react. Hence, in equilibrium the amounts of $C_6H_{10}O$ and $C_6H_{12}O$ are $0.01y$ and $0.99y$, respectively. Denote the initial amount of isopropanol z. Due to the reaction stoichiometry the amounts of C_3H_6O and C_3H_8O in equilibrium are $0.99y$ and $(z – 0.99y)$, respectively. Substituting these amounts in the expression for equilibrium constant one gets:

$$K = \frac{0.99y \times 0.99y}{0.01y \times (z - 0.99y)} = \frac{98.01}{\left(\frac{z}{y} - 0.99\right)} = 9.6$$

The solution is:

$$\frac{z}{y} = 11.2$$

Hence, the mole ratio $\nu(C_3H_8O)$: $\nu(C_6H_{10}O)$ is 11.2. The mass ratio can be calculated as follows:

$$\frac{m(C_3H_8O)}{m(C_6H_{10}O)} = \frac{\nu(C_3H_8O)\ M(C_3H_8O)}{\nu(C_6H_{10}O)\ M(C_6H_{10}O)} = \frac{11.2 \times 60}{98} = 6.9$$

3.1 b

Increase the temperature up to 50 °C using a reflux	
Increase the temperature up to 60 °C, evaporating (distilling) the acetone	✓
Add some ethanol to the reaction mixture	✓
Add some ethanal to the reaction mixture	

3.2 *<u>i) Rate-limiting step is the hydride transfer</u>*

Kinetic scheme:

$A + C \rightleftarrows A{\cdot}C$ fast, K

$A{\cdot}C \rightarrow A'{\cdot}C'$ rate-determining, k

Expression for equilibrium constant:

$$K = \frac{[A \cdot C]}{[A][C]}$$

The rate of the rate determining step is:

$$r = k[A \cdot C]$$

Final expression:

$$r = k[A \cdot C] = kK\,[A][C]$$

Answer:

Order in carbonyl compound: 1

Order in isopropanol: 0

Order in the catalyst: 1

ii) Rate-limiting step is the transalkoxylation of the alcoholate by isopropanol

Kinetic scheme:

$A + C \rightleftarrows A{\cdot}C$	fast, K_1
$A{\cdot}C \rightleftarrows A'{\cdot}C'$	fast, K_2
$A'{\cdot}C' + B \rightarrow P$	rate-determining, k

Expression for equilibrium constants:

$$K_1 = \frac{[A \cdot C]}{[A][C]}$$

$$K_2 = \frac{[A' \cdot C']}{[A \cdot C]}$$

The rate of reaction is:

$$r = k[A' \cdot C'][B]$$

Final expression:

$$r = k[A' \cdot C'][B] = k K_1 K_2 [A][B][C]$$

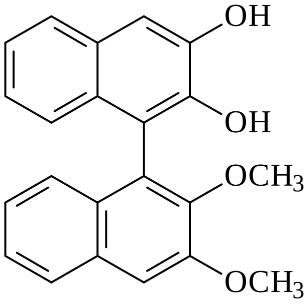
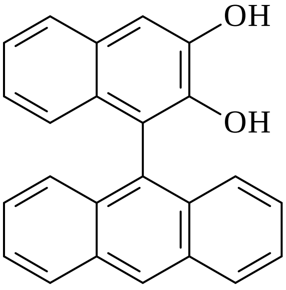
Answer:

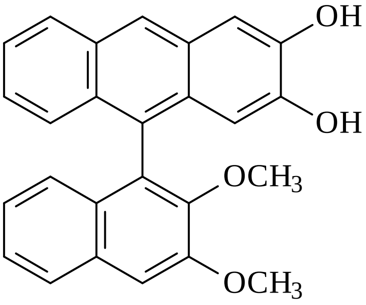
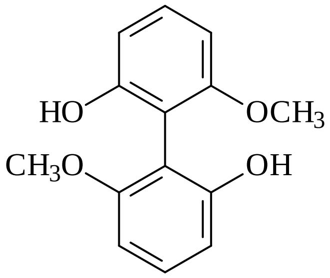
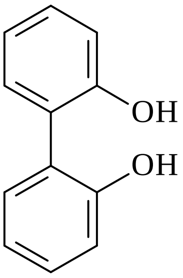
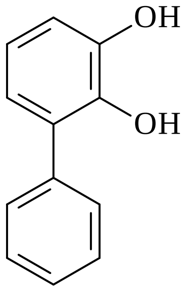
Order in carbonyl compound: 1

Order in isopropanol: 1

Order in the catalyst: 1

3.3

Substance	Can be used	Substance	Can be used
	✓		

	✓		✓
			

3.4

Solution 1

The total kinetic scheme is:

$$\begin{tikzcd}
(S)\text{ catalyst} \arrow[r, "k"] \arrow[dr, "k'"] & (S)\text{ product} \\
(R)\text{ catalyst} \arrow[r, "k"'] \arrow[ur, "k'"'] & (R)\text{ product}
\end{tikzcd}$$

According to the scheme, the *R* : *S* ratio is

$$\frac{[\text{(R)product}]}{[\text{(S)product}]} = \frac{k[\text{(R)catalyst}] + k'[\text{(S)catalyst}]}{k[\text{(S)catalyst}] + k'[\text{(R)catalyst}]}$$

After inserting this expression into *ee* definition one gets:

$$ee_{\text{product}} = \frac{[\text{(R)product}] - [\text{(S)product}]}{[\text{(R)product}] + [\text{(S)product}]} = \frac{\dfrac{[\text{(R)product}]}{[\text{(S)product}]} - 1}{\dfrac{[\text{(R)product}]}{[\text{(S)product}]} + 1} =$$

$$= \frac{\left(k[\text{(R)catalyst}] + k'[\text{(S)catalyst}]\right) - \left(k[\text{(S)catalyst}] + k'[\text{(R)catalyst}]\right)}{\left(k[\text{(R)catalyst}] + k'[\text{(S)catalyst}]\right) + \left(k[\text{(S)catalyst}] + k'[\text{(R)catalyst}]\right)} =$$

$$= \frac{[\text{(R)catalyst}] - [\text{(S)catalyst}]}{[\text{(R)catalyst}] + [\text{(S)catalyst}]} \times \frac{k - k'}{k + k'} = ee_{\text{catalyst}} \frac{k - k'}{k + k'}$$

That is, the *ee* of the product is proportional to the *ee* of the catalyst:

$$ee_{\text{product}} = ee_{\text{catalyst}} \frac{k - k'}{k + k'}$$

Applying numbers one gets:

$$ee_{\text{product}} = 0.50 \times 0.81 = 0.41$$

Solution 2

$$50\,\%\, ee \equiv \begin{cases} 50\,\%\,\text{rac.} \\ 50\,\%\,\text{R} \end{cases}$$

$$\text{R cat.} \rightarrow 90.5\,\%\,\text{R} + 9.5\,\%\,\text{S}$$

$$\text{rac. cat.} \rightarrow 50\,\%\,\text{R} + 50\,\%\,\text{S}$$

$$\%\text{ of R prod.} = 0.5 \times 0.905 + 0.5 \times 0.5 = 0.7025$$

$$\%\text{ of S prod.} = 0.5 \times 0.095 + 0.5 \times 0.5 = 0.2975$$

$$ee\text{ prod.} = 0.7025 - 0.2975 = 0.405$$

Answer: 41 %

PROBLEM 4

A simple inorganic experiment

Compound **A** which contains metal **X** is a colourless crystalline solid and highly soluble in water. It is used as a reagent in analysis and gives in alkali media a binary compound **B** containing 6.9 % (mass) of oxygen. Under heating **A** decomposes with a mass loss of 36.5 %.

4.1 Determine the metal **X** and compounds **A** and **B**.

Upon adding some amount of sodium thiosulfate to the solution of **A** the colour immediately becomes red, then changes to reddish-brown, and after some minutes a dark-brown precipitate **C** forms (reaction 1). The solution over it is colourless. Being heated on air at 600 ºC, **C** gives a grey powder **X** (reaction 2), so as 0.90 g of residue can be obtained from 1.10 g of **C**. A gas evolved by heating **C** in vacuum (reaction 3) can be absorbed by calcium hydroxide suspension (reaction 4). Being stored for a long time under saturated solution of barium perchlorate in $HClO_4$ (c = 0.1 mol dm^{-3}), the colour of the precipitate becomes lighter, while the use of magnesium perchlorate does not give such an effect.

4.2 What is **C**? Write the equations of the reactions 1 – 4.

The compound **C** being stored under the mother liquor (containing an excess of **A**) changes its colour to yellow due to the transformation into **D**. If barium ions are added to the suspension of **C** in the mother liquor, a mixture of **D** and of a white precipitate is formed.

4.3 Propose the formula of **D**, taking into account that it contains 77.5 mass % of **X**. Give the equation of **D** formation.

SOLUTION

4.1 A general formula of a binary compound is XO_n. The molar ratios of X and O should be:

$$\frac{93.1}{A_r(\mathrm{X})} : \frac{6.9}{16} = \frac{1}{n},$$

where $A_r(\mathrm{X})$ is a relative atomic mass of metal **X** and n = 0.5; 1; 1.5; 2; etc.

n = 0.5 gives $A_r(\mathrm{X})$ = 107.9. That is the relative atomic mass of silver.

X: Ag, **B**: Ag_2O.

The heating of silver salts generally results in reduction of the metal. According to the mass loss, the molar mass of **A** is 170 g mol^{-1} and corresponds to silver nitrate: **A** – $AgNO_3$.

4.2 The residue formed by heating on air is metallic silver, as the silver compounds readily decompose. Substance **C** contains silver and probably sulfur and oxygen as it evolves sulfur oxide by heating in vacuum.

1.10 g of **C** contains 0.90 g of Ag, thus, 1 mol of Ag is in 132 g of **C**. The mass of the elements other than Ag is 132 -108 = 24 g which corresponds to ½ S and ½ O. Thus, the empirical formula is $AgS_{1/2}O_{1/2}$ or Ag_2SO.

The light brown colour of the precipitate after the addition of barium salt means the formation of barium sulfate which is insoluble in acids. The sulfate groups on the surface of the precipitate are substituted by perchlorate ions from solution. Thus, based on the formula Ag_2SO and assuming the presence of sulfate, the formula $Ag_8S_3SO_4$ can be suggested.

The equations are listed below:

Equation 1:

$$16\ AgNO_3 + 6\ Na_2S_2O_3 + 6\ H_2O \rightarrow 2\ [Ag_8S_3]SO_4\downarrow + 4\ Na_2SO_4 + 4\ NaNO_3 + 12\ HNO_3$$

Equation 2:

$$[Ag_8S_3]SO_4 + 2\ O_2 \rightarrow 8\ Ag + 4\ SO_2$$

Equation 3:

$$[Ag_8S_3]SO_4 \rightarrow 2\ Ag_2S + 4\ Ag + 2\ SO_2.$$

Equation 4:

$$SO_2 + Ca(OH)_2 = CaSO_3 + H_2O \quad \text{or}$$

$$2\ SO_2 + Ca(OH)_2 = Ca(HSO_3)_2$$

4.3 We can assume that the sulfate ions in **C** are substituted by nitrate ions.

For a formula unit containing *n* silver atoms, molar mass is 108 *n* / 0.775 = 139.35 *n*. For *n* = 3 we get *M* = 418 g mol^{-1}. It corresponds to 418 – (108 × 3) = 94 that is NO_3 + S. Thus, the formula of **D** is $[Ag_3S]NO_3$.

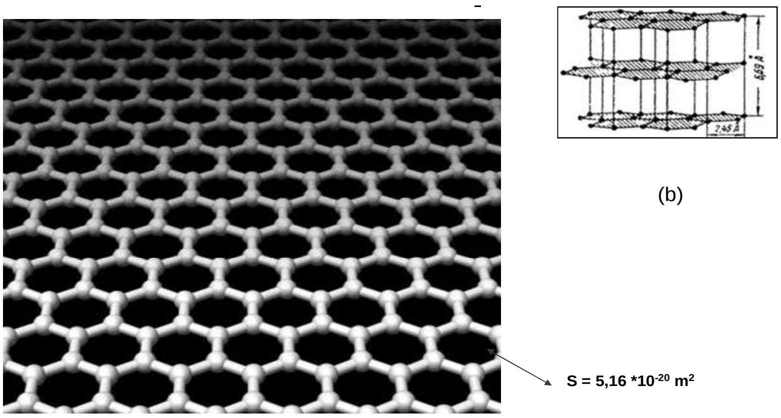
Equation:

$[Ag_8S_3]SO_4 + AgNO_3 + 2\ NaNO_3 \rightarrow 3\ [Ag_3S]NO_3 + Na_2SO_4$

PROBLEM 5

Simple estimates of graphene properties

Graphene is a two-dimensional, one atom thick carbon material (Fig. 1 a). Many layers of graphene stack together to form graphite (Fig. 1 b).



(a) (b)

Fig. 1. (a) The structure of graphene. Spheres are carbon atoms. They are arranged in hexagons. The area of one carbon hexagon is $5.16 \cdot 10^{-20}$ m^2.
(b) Crystal lattice of graphite. Three graphene layers are shown.

Such atomic structure was long considered to be unstable. However, in 2004 Andrey Geim and Konstantin Novoselov have reported production of the first samples of this unusual material. This groundbreaking invention was awarded by Nobel prize in 2010.

Experimental studies of graphene are still restricted. Production of massive portions of the new substance still is a challenging synthetic problem. Many properties of graphene were estimated. Usually, there is not enough information for rigorous calculations, so we have to make assumptions and neglect unimportant factors. In this problem, you will estimate the adsorption properties of graphene.

5.1 Estimate the specific surface of graphene open for adsorption in units m^2 g^{-1}. Consider that graphene plane is separated from any other solid or liquid substance.

The single layer of nitrogen molecules adsorbed on the outer surface of graphite is shown in Fig. 2. Assume that the same arrangement of nitrogen molecules is formed on a graphene surface.

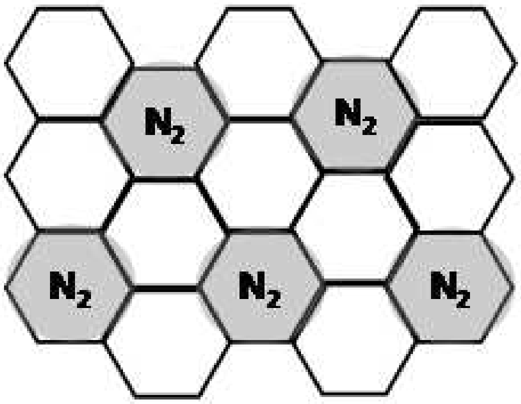


Fig. 2. Nitrogen molecules N_2 (grey circles) on the outer surface of graphite

5.2 How many grams of nitrogen can be adsorbed on 1 gram of graphene assuming that the graphene layer is placed onto the surface of a solid support? Estimate the volume occupied by these nitrogen molecules after the complete desorption from 1 g of graphene (pressure 1 bar, temperature 298 K).

Let us consider adsorption as a common chemical equilibrium

$$A_{\text{gas}} \rightleftarrows A_{\text{ads}}\,, \qquad (1)$$

(A_{gas} are molecules A in the gaseous state, A_{ads} are the same molecules on the surface) with the equilibrium constant K:

$$K = \frac{n_{A_{\text{ads}}}(\text{mol m}^{-2})}{p_{A_{\text{gas}}}(\text{bar})}$$

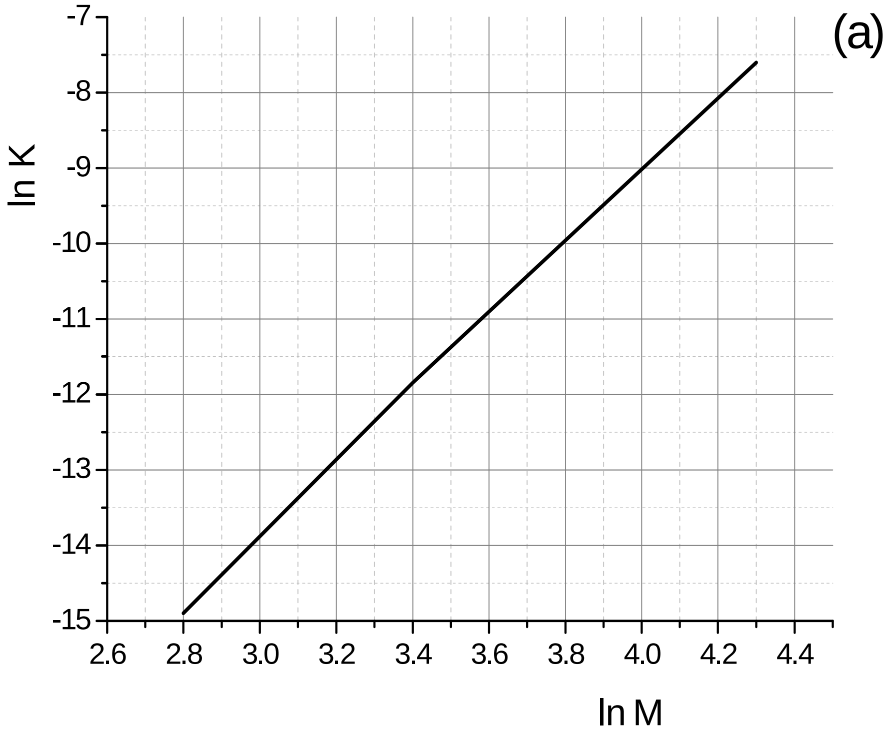
(Such an assumption holds if a small number of molecules is adsorbed on the surface.)

Adsorption properties of graphene can be estimated from the data for adsorption on a regular three-dimensional graphite. The enthalpy of adsorption (ΔH^o of reaction (1)) of any molecule A on graphene is on average by 10 % less negative compared to that on graphite. On graphite, the adsorbed molecule is bound more strongly due to the interaction with the lower graphene layers in the lattice (Fig. 1b) and hence the enthalpy of adsorption is more negative. The standard entropies of adsorption on graphene and graphite are assumed to be the same.

5.3 How many moles, *n*, of CCl_4 are adsorbed on 1 g of graphene at $p(CCl_4) = 10^{-4}$ bar if $2.0 \cdot 10^{-7}$ mol of CCl_4 are adsorbed on 1 m^2 of graphite at $p(CCl_4) = 6.6{\cdot}10^{-5}$ bar? Assume that graphene is placed onto the surface of a solid support and the interaction of CCl_4 with the support does not change the enthalpy of adsorption of CCl_4 on graphene.The temperature in both cases is 293 K. ΔH^0 of adsorption of CCl_4 on graphite is –35.1 kJ/mol.

The graphene films are expected to be sensitive gas detectors. If 10^9 particles of a gas are adsorbed on 1 cm^2 of a graphene surface this is enough to measure an electrical resistivity change of the graphene layer and to detect the presence of a gas in the environment.

5.4 Determine the minimal content of ethane, C_2H_6, in the air (in mol. %) at atmospheric pressure (*T* = 293 K) at which a graphene sensor will detect this gas. The known data for the adsorption of alkanes on graphite are shown in Fig 3. Assume that air doesn't affect the adsorption properties of ethane.



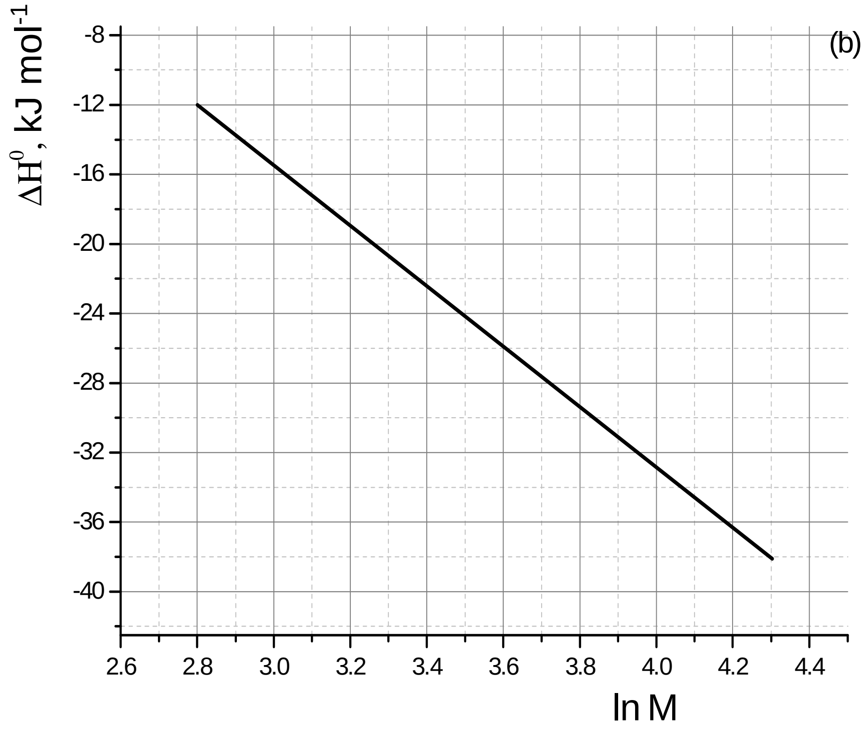


Fig. 3
Thermodynamic properties for adsorption of alkanes on a graphite surface.
(a) ln K [mol m^{-2} bar^{-1}] as a function of ln M (M - molar mass of alkane in g mol^{-1});
(b) ΔH^o of adsorption as a function of ln M.
Linear dependences are assumed in both cases

SOLUTION

5.1 The area of a hexagon is $S = 5.16 \cdot 10^{-20}$ m^2.

Calculations:

The number of hexagons per gram of carbon, n, is

$$n = N_A \times \frac{3}{6} \times \frac{1}{12} = 6.022 \cdot 10^{23} \times 0.5 \times \frac{1}{12} = 2.51 \cdot 10^{22}$$

The area per gram is

$$S_{\text{total}} = S \times n \times 2 = 5.16 \cdot 10^{-20} \times 2.51 \cdot 10^{22} \times 2 = 2590 \text{ m}^2 \text{ g}^{-1}$$

In the case of two-dimensional material both sides of the layer are open for adsorption and have to be taken into consideration. The total area of hexagons should be multiplied by two!

5.2 Graphene is on the solid support and only one side of the plane works. One molecule of nitrogen falls on six atoms of carbon (three hexagons) (see Fig. 2).

Mass of nitrogen adsorbed per gram of graphene:

$$\frac{m_{N_2}}{m_C} = \frac{1 \times 28}{6 \times 12} = 0.39; \quad m_{N_2} = 0.39 \text{ g}$$

The volume of nitrogen isw

$$V_{N_2} = \frac{\frac{m}{M} RT}{p} = \frac{\frac{0.39}{28} \times 8.314 \times 298}{100} = 0.34 \text{ dm}^3 .$$

5.3 The equilibrium constant for the adsorption on graphite surface is

$$K(\text{graphite}) = \frac{n(\text{CCl}_4 \text{ on graphite})}{p(\text{CCl}_4)} = \frac{2.0 \cdot 10^{-7}}{6.6 \cdot 10^{-5}} = 3.0 \cdot 10^{-3} \text{ mol m}^{-2} \text{ bar}^{-1}$$

The equilibrium constant need to be re-calculated for the graphene surface. There is a 10 % difference in enthalpies of adsorption on graphene and on graphite, respectively, while the entropies are the same. Thus:

$$\frac{K(\text{graphene})}{K(\text{graphite})} = e^{\frac{-(\Delta H_{\text{graphene}} - \Delta H_{\text{graphite}})}{RT}} = e^{\frac{-3510}{8.314 \times 293}} = 0.24$$

$$K(\text{graphene}) = 0.24\, K(\text{graphite}) = 7.2 \cdot 10^{-4} \text{ mol m}^{-2} \text{ bar}^{-1}$$

The adsorption of CCl_4 on graphene is calculated based on the equilibrium constant for graphene surface and the area of graphene surface in m^2 g^{-1}. One side of the graphene layer works in this case,

$$S_{\text{total}} = 2590\,/\,2 = 1295\ \text{m}^2\ \text{g}^{-1}$$

$$n\,[\text{mol g}^{-1}] = K(\text{graphene})\,[\text{mol m}^{-2}\,\text{bar}^{-1}] \times p(\text{CCl}_4)\,[\text{bar}] \times S(\text{graphene})\,[\text{m}^2\,\text{g}^{-1}] =$$
$$= (7.2\cdot 10^{-4}) \times 1\cdot 10^{-4} \times 1295 = 9.3\cdot 10^{-5}\ \text{mol g}^{-1}$$

The area of the graphene surface (the number!) determined in question 5.1 is used here.

5.4 The lower limit of detectable concentration of a substance on the graphene surface is

$$n\,[\text{mol m}^{-2}] = \frac{\dfrac{1\cdot 10^{9}}{6.02\cdot 10^{23}}}{1\cdot 10^{-4}} = 1.7\cdot 10^{-11}$$

The equilibrium constant and the enthalpy of adsorption of ethane on graphite are given in Fig. 3:

$M = 30$; ln $M = 3.4$; ln $K = -11.8$; $\Delta H^o = -22.5$ kJ mol^{-1}

$$K_{C_2H_6} = 7.5\cdot 10^{-6}\ \text{mol m}^{-2}\,\text{bar}^{-1}$$

This equilibrium constant needs to be re-calculated to the graphene surface (as in question 5.2).

$$K_{C_2H_6}(\text{graphene}) = K_{C_2H_6}(\text{graphite}) \times e^{-2250/(8.314\times 293)} =$$
$$= 7.5\cdot 10^{-6} \times 0.4 = 3.0\cdot 10^{-6}\ \text{mol m}^{-2}\ \text{bar}^{-1}$$

The partial pressure of ethane is

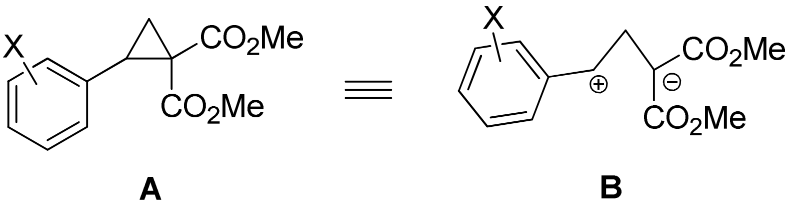
$$p(C_2H_6) = \frac{n(C_2H_6\ \text{on graphene})}{K_{C_2H_6}(\text{graphene})} = \frac{1.7\cdot 10^{-11}}{3.0\cdot 10^{-6}} = 5.7\cdot 10^{-6}\ \text{bar}$$

Content of C_2H_6: $\dfrac{5.7\cdot 10^{-6}}{1.013} \times 100\,\% = 5.6\cdot 10^{-4}\,\%$

PROBLEM 6

Cyclopropanes. So simple. So fancy…

Cyclopropanes bearing donor and acceptor substituents at the neighbouring C-atoms, for example, **A**, demonstrate high reactivity behaving similar to 1,3-zwitterion **B**.



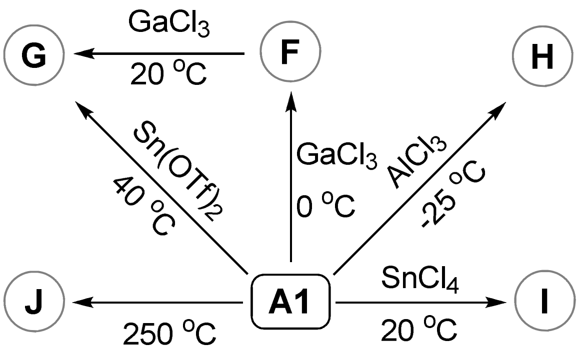
Thus, **A1** (X = 4-OMe) undergoes the three-membered ring opening in the Lewis acid-catalyzed reaction with 1,3-dimethoxybenzene as a nucleophile giving the product **C**.

6.1 Write down structural formula of **C**.

A1 participates in cycloadditions, annulations, oligomerizations, and other processes. Thus, [3+2]-cycloaddition between **A1** and 4-methoxybenzaldehyde leads to a five-membered ring in **D**. Complete decarboxylation of **D** produces **E** ($C_{18}H_{20}O_3$), the molecule of the latter having a plane of symmetry.

6.2 Write down structural formulae of **D** and **E** indicating their stereochemistry.

Also, **A** can undergo various transformations in the absence of any reaction partners except catalysts. Some transformations typical of **A1** are shown in the Scheme below.



OTf = OSO_2CF_3

To determine the structures of **F – J**, a set of physico-chemical data was obtained (see Table for some results). It was found that:

a) **F** and **G** are structural isomers of **A1**;

b) **G** is formed as the most stable stereoisomer;

c) **H** and **I** are structural isomers;

d) **H** is formed as a single diastereomer with C_2 axis of symmetry (the molecule looks the same after rotation through the angle of 180°);

e) **I** is formed as a mixture of two diastereomers;

f) **J** is naphthalene derivative.

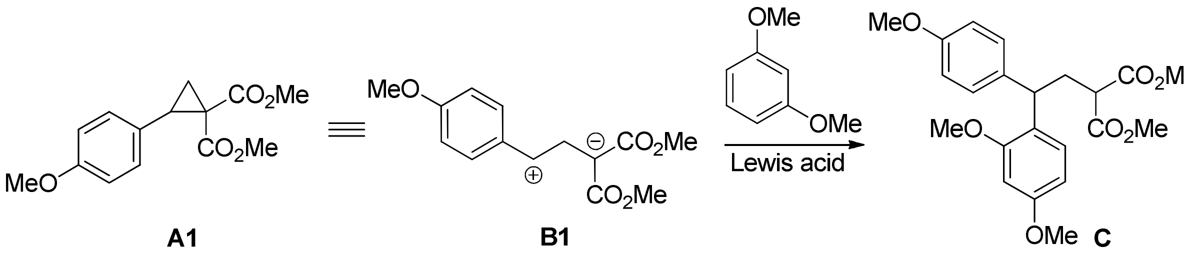
In the process leading to **I**, one molecule of **A1** demonstrates the described above common reactivity (analogous to that of **B**). The other molecule of **A1** behaves differently. Also, the latter behaviour is demonstrated by cyclopropane **A2** (dimethyl 2-(3,4,5-trimethoxyphenyl)cylopropane-1,1-dicarboxylate) when treated with $SnCl_4$ in CH_3NO_2 affording **K** as a mixture of two diastereomers. The major isomer has the centre of symmetry. Similar reactivity is shown by **A2** in $Sn(OTf)_2$-catalyzed reaction with **G** furnishing **L**.

6.3 Write down the structural formulae of **F – J,** and those of **L** and the major isomer of **K**.

	Ratio of the number of hydrogen-containing groups					**Composition**
	Non-aromatic				Aromatic	
	CH	CH_2	CH_3	OH		
F	1	1	1+1+1	0	4 in total	C 63.62%, H 6.11%
G	1+1+1	0	2+1	0	4 in total	C 63.62%, H 6.11%
H	1	1	1+1+1	0	4 in total	C 63.62%, H 6.11%
I	1+1+1	1+1	2+1+1+1+1	0	7 in total	C 63.62%, H 6.11%
J	0	0	1+1	1	5 in total	C 67.22%, H 5.22%
K	1+1	1	2+1+1+1	0	1	C 59.24%, H 6.23%
L	1+1+1+1+1	1	2+2+1+1+1+1	0	5 in total	C 61.21%, H 6.18%

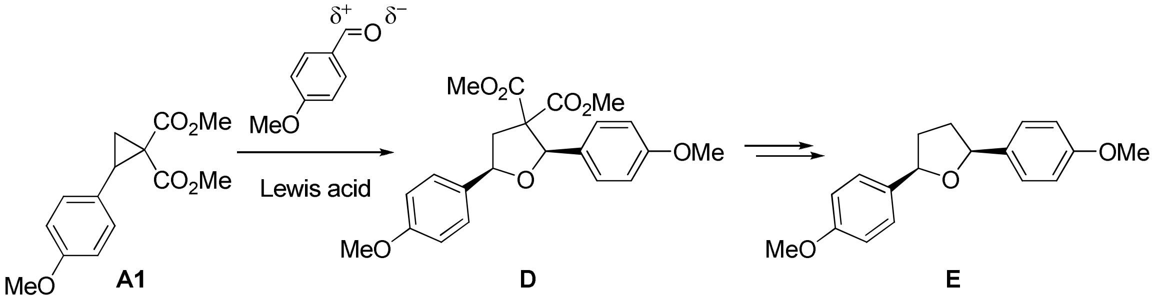
SOLUTION

6.1



Reaction of **A1** with 1,3-dimethoxybenzene as a nucleophile proceeds as Friedel-Crafts alkylation. Electrophiles attacks onto *ortho-/para*-position. Attack onto C4 position of arene proceeds easier than attack onto sterically more hindered C2 atom.

6.2



Compound **A1** reacts similarly to 1,3-zwitterion **B1**. It is the 3-atom component. Therefore, 4-methoxybenzaldehyde is a two-atom component.

Benzene ring is not prone to react as two-atom component. So, C=O group participates in the reaction. Accounting for its polarization, carbonyl oxygen reacts with a positive end of 1,3-zwitterion **B1**.

The product has *cis*-geometry. Therefore, compound **D** is *cis*-dimethyl 2,5-diaryltetrahydrofuran-3,3-dicarboxylate. Decarboxylation of compound **D** produces 2,5-bis(4-methoxyphenyl)tetrahydrofuran **E** (accounting for its molecular formula). It has *cis*-arrangement of aryl groups as **E** has a plane of symmetry.

6.3 Compounds **F** and **G** are isomers of **A1**. **G** has three CH groups instead of the cyclopropane fragment, two equivalent ester groups and unchanged aromatic fragment.

Thus, **G** is $ArCH=CHCH(CO_2Me)_2$ which is formed by cyclopropane-to-alkene isomerization as (*E*)-isomer (more stable than *Z*-isomer).

Compound **F** has CH_2 and CH groups, two different ester groups and unchanged aromatic fragment. **F** is formed from **A1** and undergoes secondary isomerization into **G**. Therefore, **F** is $ArCH_2CH=C(CO_2Me)_2$.

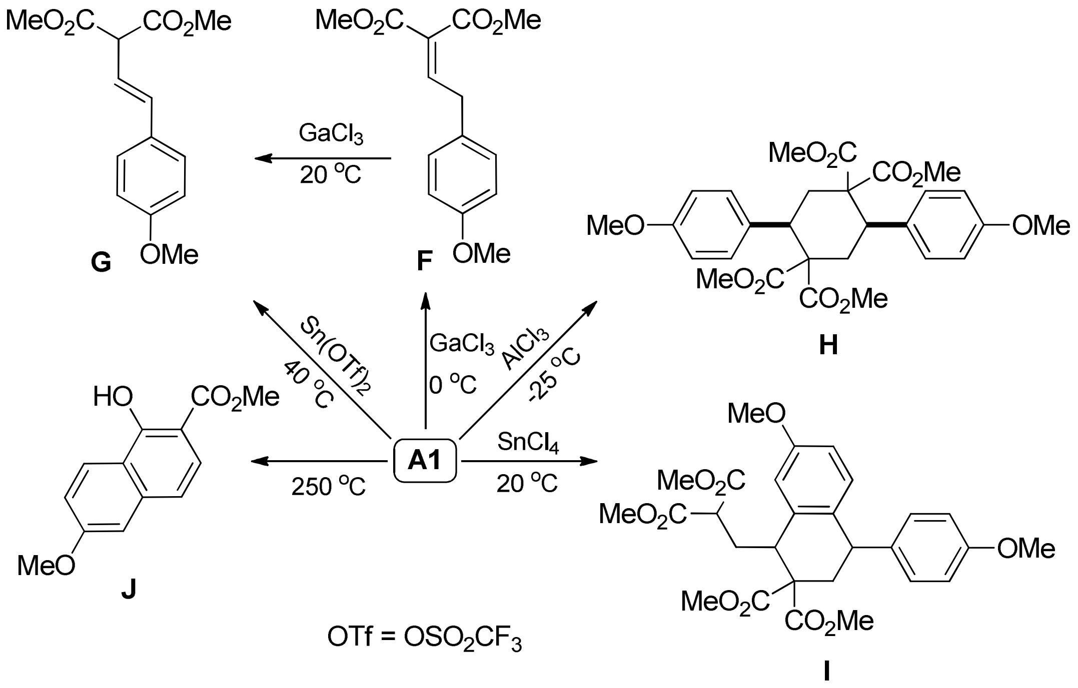
Compound **I** has twice as many protons as **A1**. It means that isomeric **H** and **I** are dimers of **A1**. Indeed, in problem it is directly stated that two molecules of **A1** react when **I** is formed.

Compound **H** is highly symmetric. The aromatic fragment is not changed during its formation. Therefore, **H** is a result of the symmetric dimerization of **A1** when positive end of **B1** of one molecule reacts with negative end of **B1** of another molecule, and *vice versa.* Such dimerization produces cyclohexane. Its *cis*-isomer has C_2 axis of symmetry; *trans*-isomer has centre of symmetry. Therefore, **H** is *cis*-isomer.

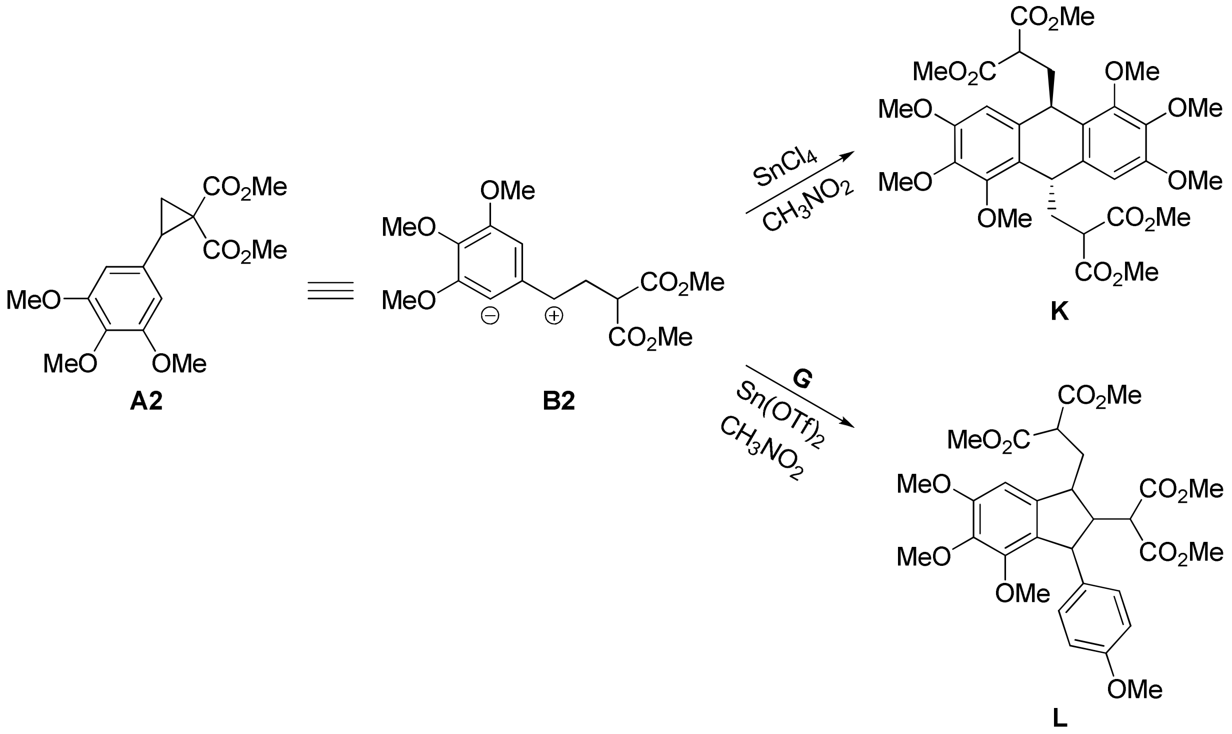
According to the symmetry and table data, **K** is a symmetric dimer of **A2**. Moreover, aromatic/non-aromatic protons ratio in **K** is less than that in **A2**. Accounting for question 1, it is possible to deduce that benzylic carbon atom of one **A2** molecules reacts as electrophiles with *ortho*-position of aromatic fragment (nucleophilic centre) of another molecule, and *vice versa*. In this reaction **A2** reacts as an equivalent of 1,3-zwitterion **B2**. Therefore, **K** is 9,10-dihydroanthracene derivative. The major isomer has the centre of symmetry, *i.e.*, it has *trans*-arrangement of alkyl substituents.

Compound **I** has seven aromatic protons, *i.e.*, it has one aromatic proton less than **H** in which arene fragments are intact. In the process leading to **I**, one molecule of **A1** reacts as an equivalent of **B1**, another **A1** reacts as an equivalent of **B2**. In other words, one new C-C bond in **I** is formed *via* Friedel-Crafts alkylation of aromatic group in the first **A1** molecule by positive end of 1,3-zwitterion producing from the second **A1** molecule. Another C-C bond is formed *via* coupling of electrophilic benzylic carbon of the first **A1** molecule with nucleophilic malonate carbon of the second **A1** molecule. Therefore, **I** is tetraline derivative.

J has 12 protons. From composition data its molecular formula can be determined as $C_{13}H_{12}O_4$, *i.e.* it has one C atom, four H atoms, and one O atom less than **A1**. Moreover, **J** has no aliphatic hydrogens except the protons of methyl and OH groups. It is possible if a new aromatic ring is formed *via* intramolecular Friedel-Crafts reaction. For it, **A1** is isomerized under heating into (*Z*)-isomer of **G** followed by intramolecular acylation of aromatic moiety producing 1-hydroxy-7-methoxy-naphthalene-2-carboxylate (**J**).



Compound **L** has 36 protons. From composition data its molecular formula is $C_{30}H_{36}O_{12}$. It corresponds to combination of **A2** and **G**. Since **A2** reacts as an equivalent of **B2**, it can be supposed that electrophilic centre of **B2** attacks C=C bond of **G** in accordance with Markovnikov's rule followed by reaction between the formed cationic centre and *ortho*-carbon atom of trimethoxyphenyl substituent producing indane derivative **L**.


A2
B2
SnCl4
CH3NO2
K
G
Sn(OTf)2
CH3NO2
L

PROBLEM 7

Diverse permanganatometry

The amount of many reducing agents can be determined by permanganatometric titration in alkaline medium allowing permanganate ion reduction to manganate.

7.1 Write down the ionic reaction equation for titration of formate with permanganate in an aqueous NaOH solution with a concentration of ~0.5 mol dm^{-3}.

Titration with permanganate in alkaline medium is often supplemented by addition of a barium salt, which leads to precipitation of manganate as $BaMnO_4$.

7.2 Which side redox processes involving manganate is suppressed by the barium salt? Write down an example of equation of the corresponding reaction.

A volume of 10.00 cm^3 (V_{Mn}) of $KMnO_4$ solution with a concentration of 0.0400 mol dm^{-3} (c_{Mn}) was placed in each of flasks **A**, **B**, and **C** and different reactions were conducted in each flask.

A sample solution containing crotonic acid (CA) CH_3–CH=CH–COOH, an alkali and barium nitrate (both in an excess) were added to flask **A**, and the reaction mixture was incubated for 45 min. It is known that crotonic acid loses 10 electrons under the experiment conditions.

7.3 a Write down the total ionic equation for the reaction.

A volume of 8.00 cm^3 (V_{CN}) of potassium cyanide solution (c_{CN} = 0.0100 mol dm^{-3}) was then added to the incubated mixture. This resulted in completion of the following reaction:

$$2\,Ba^{2+} + 2\,MnO_4^- + CN^- + 2\,OH^- \rightarrow 2\,BaMnO_4 + CNO^- + H_2O$$

$BaMnO_4$ precipitate was then filtered off, and the excess of cyanide in the filtrate was titrated with $AgNO_3$ solution (c_{Ag} = 0.0050 mol dm^{-3}) till detectable precipitation was observed. Note that both CN^- and CNO^- are analogs of halide ions, but CNO^- affords soluble silver salt.

7.3 b Give the formula for the complex formed when Ag^+ ions were initially added to the cyanide solution (until the precipitate was formed).

7.3 c Give the formula of the precipitate formed.

7.3 d Derive the formula for calculating the amount of substance of crotonic acid in the sample solution. Calculate the mass of crotonic acid (in mg) if 5.40 cm^3 (V_{Ag}) of the silver salt solution was consumed for the titration to the endpoint.

Another sample of crotonic acid and alkali (in an excess) were added to flask **B**, this mixture lacking barium salt. An excess of KI (instead of cyanide) was added as a reducing agent. The mixture was then acidified and the iodine evolved was titrated with a thiosulfate solution (c_S = 0.1000 mol dm^{-3}). 4.90 cm^3 (V_{S1}) of the titrant was used to reach the endpoint.

7.4 Derive the formula for calculating the amount of substance of crotonic acid in this experiment. Calculate the mass of crotonic acid (in mg).

A sample containing tin(II) was added to flask **C**, and the medium was adjusted to weak alkaline. Tin(II) was quantitatively oxidized to $Sn(OH)_6^{2-}$, whereas a precipitate formed as a result of permanganate reduction. The precipitate was isolated, washed off, dried at 250 °C, weighed (the mass of the water-free precipitate (m_{prec}), representing a binary compound, was of 28.6 mg), and dissolved in H_2SO_4 in the presence of an excess of potassium iodide. The evolved iodine was titrated with 0.1000 M thiosulfate solution. 2.5 cm^3 (V_{S2}) of the latter was consumed to attain the endpoint.

7.5 a Write down the reaction of precipitation. Confirm it with calculations.

7.5 b Calculate the mass of tin in the sample (in mg) referred to the metal.

SOLUTION

7.1 $2\ MnO_4^- + HCOO^- + 3\ OH^- \rightarrow 2\ MnO_4^{2-} + CO_3^{2-} + 2\ H_2O$

7.2 $MnO_4^{2-} + 2\ H_2O + 2\ e^- \rightarrow MnO_2 + 4\ OH^-$

or

$3\ MnO_4^{2-} + 2\ H_2O \rightarrow MnO_2 + 2\ MnO_4^- + 4\ OH^-$

7.3 a $C_4H_5O_2^- + 10\ MnO_4^- + 14\ OH^- + 12\ Ba^{2+} \rightarrow$

$\rightarrow 10\ BaMnO_4 + CH_3COO^- + 2\ BaCO_3 + 8\ H_2O$

7.3 b Before the endpoint was attained:

$[Ag(CN)_2]^-$

7.3 c After the endpoint:

$Ag^+ + Ag(CN)_2^- = Ag[Ag(CN)_2]\downarrow$ or $Ag^+ + CN^- = AgCN\downarrow$

Thus: $Ag[Ag(CN)_2]$ or AgCN is the correct answer.

7.3 d Permanganate left after the reaction with crotonic acid: $c_{Mn}V_{Mn} - 10\ n_{CA}$ (mmol).

Cyanide consumed for the residual permanganate: ½ ($c_{Mn}V_{Mn} - 10\ n_{CA}$) (mmol).

Cyanide excess: $c_{CN}V_{CN} - ½\ (c_{Mn}V_{Mn} - 10\ n_{CA})$

For the correct silver-cyanide stoichiometry (1 : 2):

$2\ c_{Ag}V_{Ag} = c_{CN}V_{CN} - ½\ (c_{Mn}V_{Mn} - 10\ n_{CA})$.

Thus: $n_{CA} = \dfrac{2\ c_{Ag}V_{Ag} - c_{CN}V_{CN} + ½\ c_{Mn}V_{Mn}}{5}$

$$n_{CA} = \frac{2 \times 0.005 \times 5.40 - 0.0100 \times 8.00 + 0.5 \times 0.0400 \times 10.00}{5} = 0.0348 \text{ mmol},$$

Then:

$m_{CA} = 0.0348 \times 86.09 = 3.00$ mg ($M_{CA} = 86.09$ g mol^{-1}).

For the wrong silver-cyanide stoichiometry (1 : 1):

$c_{Ag}V_{Ag} = c_{CN}V_{CN} - ½\ (c_{Mn}V_{Mn} - 10\ n_{CA})$

$$n_{CA} = \frac{c_{Ag}V_{Ag} - c_{CN}V_{CN} + ½\, c_{Mn}V_{Mn}}{5}$$

$$n_{CA} = \frac{0.005 \times 5.40 - 0.0100 \times 8.00 + 0.5 \times 0.0400 \times 10.00}{5} = 0.0290\ \text{mmol}$$

Then:

$m_{CA} = 0.0290 \times 86.09 = 2.49$ mg

7.4 Schematically:

$$10\ MnO_4^- + 1\ \text{Crotonate} \rightarrow 10\ MnO_4^{2-} + \text{ products}$$

Permanganate left after the reaction with crotonic acid: $c_{Mn}V_{Mn} - 10\ n_{CA}$ (mmol)

Manganate formed: $10\ n_{CA}$ (mmol)

Reactions occurred after iodide addition:

$$2\ MnO_4^- + 10\ I^- + 16\ H^+ \rightarrow 2\ Mn^{2+} + 5\ I_2 + 8\ H_2O \quad \text{and}$$

$$MnO_4^{2-} + 4\ I^- + 8\ H^+ \rightarrow Mn^{2+} + 2\ I_2 + 4\ H_2O$$

Amount of substance of the iodine evolved (mmol I_2):

$$2.5\ n_{KMnO_4\ \text{left}} + 2\ n_{K_2MnO_4} = 2.5\ (c_{Mn}\ V_{Mn} - 10\ n_{CA}) + 2 \times 10\ n_{CA}$$

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

$$n_{Na_2S_2O_3} = 2\ n_{I_2} = 5\ (c_{Mn}V_{Mn} - 10\ n_{CA}) + 40\ n_{CA}$$

Thus:

$5\ (c_{Mn}V_{Mn} - 10\ n_{CA}) + 40\ n_{CA} = c_S V_{S1}$,

and

$n_{CA} = ½\ c_{Mn}V_{Mn} - 0.1\ c_S V_{S1}$

$n_{CA} = (0.5 \times 0.0400 \times 10.00) - (0.1 \times 0.1000 \times 4.90) = 0.151$ mmol,

$m_{CA} = n_{CA}\ M_{CA} = 13.00$ mg.

7.5 a Oxidation of tin(II) with permanganate in weak alkaline medium led to an insoluble binary manganese compound. Drying conditions suggest it is either one of manganese oxides or their mixture.

The amount of equivalent is just the same for thiosulfate, iodine and the precipitate.

$n_{eq} = V_{s2}\, c_S = 0.1000 \times 2.5 = 0.25$ mmol

$M_{eq} = 28.6$ mg / 0.25 mmol = 114.4 g mol^{-1}.

This is the so called molar mass of the equivalent of the precipitate.

Let us consider possible cases.

- If MnO_2 was formed

  (scheme: $MnO_4^- + Sn^{2+} \rightarrow MnO_2\downarrow + Sn^{4+}$)

  $MnO_2 + 4\ H^+ + 2\ I^- \rightarrow I_2 + Mn^{2+} + 2\ H_2O$,

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

  The molar mass of its equivalent in the reaction with iodide would be: 86.94 / 2 = 43.47 g mol^{-1}.
- If Mn_2O_3 was formed ($Mn_2O_3 + 2\ I^- + 6\ H^+ \rightarrow I_2 + 2\ Mn^{2+} + 3\ H_2O$), the molar mass of its equivalent in the reaction with iodide would be: 157.88 / 4 = 78.9 g mol^{-1}.
- In the experiment, the molar mass of the equivalent is even higher, thus manganese compounds not oxidizing iodide, can be present in the precipitate, i. e. manganese(II). The only possible variant is manganese(II, III) oxide ($Mn_3O_4 + 2\ I^- + 8\ H^+ \rightarrow I_2 + 3\ Mn^{2+} + 4\ H_2O$). The molar mass of the latter: 228.9 / 2 = 114.4 g mol^{-1}.

Reaction:

$$6\,MnO_4^- + 13\,[Sn(OH)_4]^{2-} + 16\,H_2O \rightarrow 2\,Mn_3O_4\downarrow + 13\,[Sn(OH)_6]^{2-} + 6\,OH^-$$

7.5 b Amount of substance of tin equals 13 / 2 of that of Mn_3O_4, or

$n_{Sn} = 28.6 / 228.9 \times 13 / 2 = 0.812$ mmol

$m_{Sn} = 96.4$ mg.

PROBLEM 8

Unique life of archaea

Archaea (or archaebacteria) are single-celled microorganisms. They significantly differ from bacteria and eukaryotes at the molecular level.

Enzymatic reaction of methylamine with water is the major energy source for some archaea. In a particular experiment, an archaea strain was cultivated at pH 7 under anaerobic (oxygen free) conditions with the nutrient medium containing $^{13}CH_3NH_2$ as the only energy source. After a certain incubation period, the gas over the archaea culture was sampled and analyzed. It was found that the gas contains two substances, **A** and **B**, in a molar ratio of 1 : 3 correspondingly (the sample density relative to H_2 is 12.0).

8.1 Calculate the volume fractions (in %) of **A** and **B** in the mixture.

8.2 Determine **A** and **B** if there are no nitrogen atoms in the gas collected.

8.3 Write down the equation of enzymatic reaction of methylamine with water described in the above experiment using predominant form of each species.

Enzymes containing the residue of α-amino acid **X**, are found in many archaea capable of methylamine utilization. It is known that **X**:

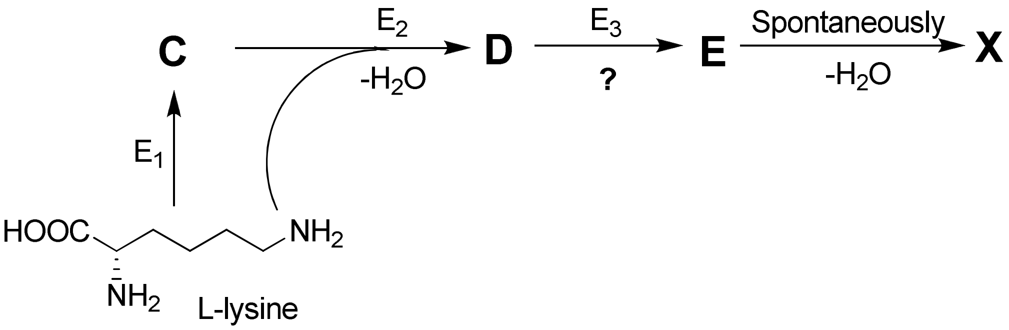
- is composed of atoms of 4 elements;
- contains 18.8 mass % of oxygen;
- possesses the single individual tRNA and is incorporated into proteins of archaea during translation.

Amino acid *L*-lysine (see the structure in scheme below) was identified as the **X** precursor in archaea. All carbon and nitrogen atoms found in **X** originate from two starting lysine molecules. Different isotope-labelled *L*-lysines were introduced into a model system to clarify the biosynthetic pathways of **X**. The results are summarized in the table.

Isotope composition of *L*-lysine	Molar mass (rounded to integer) of the **X** residue [RCH(NH_2)CO], bound to tRNA, (g mol^{-1})
Normal	238
All carbons ^{13}C, all nitrogens ^{15}N	253
ε-amino group with ^{15}N	239

8.4 Determine the molecular formula of **X**.

X is biosynthesized in archaea according to the following scheme (E_1, E_2, and E_3 – enzymes):



At the first step, lysine is transformed into its structural isomer (α–amino acid, **C**), whereas **D** contains a peptide bond, and **E** a formyl group –CHO. All reaction coefficients in the above scheme are equal to 1.

8.5 i) Give the chemical formula of **C**, **D** and **E**.

ii) From the reaction types given hereunder, choose (tick) **only one** corresponding to the enzyme E_3 catalyzed reaction.

☐ Oxidative deamination

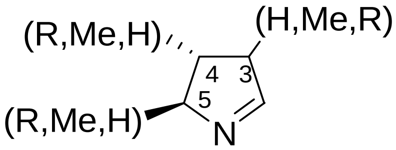
☐ Decarboxylation

☐ Intermolecular deamination

☐ Hydroxylation

☐ Peptide bond hydrolysis

X contains the following fragment:

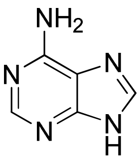


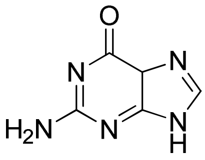
R is a massive substituent (M > 100 g mol^{-1}). The 3rd carbon atom is non-asymmetric. The 4th and 5th carbon atoms are stereogenic centres. All carbon atoms in the cycle are bound with at least one hydrogen atom. Each substituent (H, Me and R) is found only once.

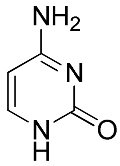
8.6 Determine the positions of substituents H, Me, and R.

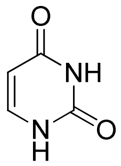
8.7 Draw structural formulae of **C** and **X** with stereochemical details. Mark every stereocenter of **X** with either *R* or *S*.

Only one codon is responsible for the incorporation of **X** residues into proteins in archaea. The nitrogen bases forming this codon contain two exocyclic amino groups and three exocyclic oxygen atoms in total.


adenine


guanine


cytosine


uracyl

8.8 Determine the nucleotide composition of the codon by filling in the hereunder table. Write down the number of each nitrogen base in the codon encoding **X**. Tick only one box in each line.

Nitrogen base	The number of bases in the codon				
	1	2	3	0 or 1	1 or 2
A					
C					
G					
U					

The fragment of mRNA coding sequence given below contains the codons encoding **X** residue incorporation into an archaea enzyme:

5'…AAUAGAAUUAGCGGAACAGAGGGUGAC…3'

8.9 a Using the table of the genetic code, decide how many amino acid residues are incorporated into the enzyme chain due to this fragment translation.

8.9 b Write down the amino acid sequence translated from this fragment. Note that more than one **X** residue is found in the fragment.

Fill in the boxes below with the amino acid abbreviations (from N- to C-terminus).

Note that the number of boxes is excessive. If there is more than one possibility, write all separated by "/". If the translation is stopped in a particular position, write "STOP" and leave all the boxes to the right empty.

(a) RNA codons for the twenty amino acids

First base	Second base				Third base
	U	**C**	**A**	**G**	
U	Phe	Ser	Tyr	Cys	**U**
	Phe	Ser	Tyr	Cys	**C**
	Leu	Ser	STOP	STOP	**A**
	Leu	Ser	STOP	Trp	**G**
C	Leu	Pro	His	Arg	**U**
	Leu	Pro	His	Arg	**C**
	Leu	Pro	Gln	Arg	**A**
	Leu	Pro	Gln	Arg	**G**
A	Ile	Thr	Asn	Ser	**U**
	Ile	Thr	Asn	Ser	**C**
	Ile	Thr	Lys	Arg	**A**
	Met (start)	Thr	Lys	Arg	**G**
G	Val	Ala	Asp	Gly	**U**
	Val	Ala	Asp	Gly	**C**
	Val	Ala	Glu	Gly	**A**
	Val	Ala	Glu	Gly	**G**

Amino Acids Abbreviations:

Ala = Alanine
Arg = Arginine
Asp = Aspartic acid
Asn = Aaparagine
Cys = Cysteine
Glu = Glutamic Acid
Gln = Glutamine
Gly = Glycine
His = Histidine
Ile = Isoleucine
Leu = Leucine
Lys = Lysine
Met = Methionine
Phe = Phenylalanine
Pro = Proline
Ser = Serine
Thr = Threonine
Trp = Tryptophan
Tyr = Tyrosine
Val = Valine

SOLUTION

8.1 Volume ratio of gases **A** and **B** is equal to their mole ratio (1 : 3).

Volume fractions of **A** and **B** are 25 and 75 %, respectively.

8.2 Molecular mass of the mixture of **A** and **B** is equal to 12.0 × 2.0 = 24.0 g mol^{-1}.

The variant of two gases, both with molar masses of 24.0 g mol^{-1}, is impossible. Thus, one of the gases is lighter whereas the other one is heavier.

Reaction of ^{13}C-methylamine with water under anaerobic conditions can theoretically lead to two nitrogen-free gases with a molar mass lower than 24.0 g mol^{-1}: H_2 or $^{13}CH_4$. Further considerations are summed up in the table.

Light gas	Volume fraction of the light gas, %	Molar mass of the heavy gas, (g mol^{-1})
H_2	25	31.3
	75	90.0
$^{13}CH_4$	25	26.3
	75	45.0

At neutral pH values typical of living cells, ammonia exists in the form of ammonium ion and does not transfer into gaseous phase. Thus, the only possible variant is:

A: $^{13}C^{16}O_2$ and **B**: $^{13}C^{1}H_4$.

8.3 $4\ {}^{13}CH_3NH_3^+ + 2\,H_2O \rightarrow 3\ {}^{13}CH_4 + {}^{13}CO_2 + 4\,NH_4^+$

8.4 The molar mass of **X**: 238 + 17 (OH-group) = 255 g mol^{-1}

The number of oxygen atoms in **X**: $\dfrac{255 \times 0.188}{16.00} = 3$

Two molecules of lysine contain 12 carbon and 4 nitrogen atoms, 16 atoms in total.

From comparison of lines 1 and 2 of the table follows that 15 of 16 carbon and nitrogen atoms are found in **X**.

From comparison of lines 1 and 3 of the table: 1 of 2 ε-amino nitrogen atoms is lost during **X** biosynthesis.

X contains 12 carbon atoms and 3 nitrogen atoms.

The rest of the molar mass: 255 – (12 × 12) – (3 ×14) – (3 × 16) = 21 g mol^{-1}

is due to hydrogen (21 atoms). Thus, **X** is $C_{12}H_{21}N_3O_3$.

8.5 i)

C	**D**	**E**
$C_6H_{14}N_2O_2$	$C_{12}H_{26}N_4O_3$	$C_{12}H_{23}N_3O_4$

C is an isomer of lysine, and thus 2 × $C_6H_{14}N_2O_2$ = $C_{12}H_{28}N_4O_4$ enters the reaction of **D** synthesis.

One molecule of water is formed at each of the steps:

C + lysine → **D** ($C_{12}H_{28}N_4O_4 - H_2O = C_{12}H_{26}N_4O_3$)

and

E → **X** **(**$C_{12}H_{21}N_3O_3 + H_2O = C_{12}H_{23}N_3O_4$)].

ii)

From the possibilities listed the oxidative deamination is correct.

(☑ Oxidative deamination)

Loss/gain of atoms at **D** → **E** step:

$C_{12}H_{24}N_4O_3$ – $C_{12}H_{21}N_3O_4$, minus NH_3, plus O. Thus, it is oxidative deamination:

R-CH_2-NH_2 + [O] → R-CH=O + NH_3 (schematically).

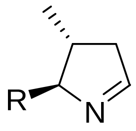
8.6 A hydrogen atom bound to the 4th or 5th C atom would mean a loss of chirality, thus it is unambiguously attributed to the 3rd C atom.

It is needed to decide about the amino group forerunning the heterocyclic nitrogen atom to attribute the positions of the other two substituents.

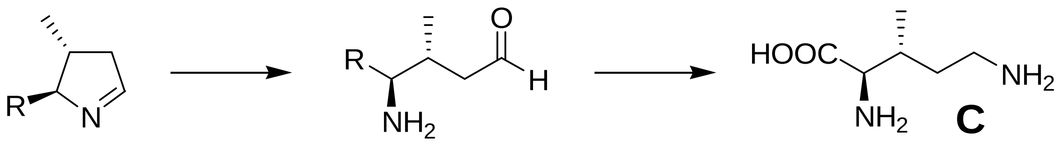
A nitrogen atom is included in the cycle due to the reaction of an amino and formyl group, the latter appearing as a result of the oxidative deamination.

The size of the cycle suggests it was the α–amino group, thus:

in the 3rd position – H; the 4th position – Me; the 5th position – R.

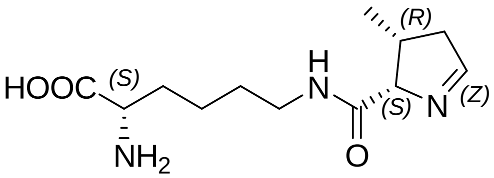


8.7 Moving backwards (**X** → **D**) one gets that **C** is (*3R*)-3-methyl-*D*-ornithine:



Stereochemistry of **C** can be derived from that of the above cyclic fragment with an account that no isomerization occurs on the way from **C** to **X**.

Both amino groups of lysine can form the peptide bond with the carboxylic group of **C**. Still, involvement of only the ε-amino group will provide **X** as α-amino acid. **X** is pyrrolysine, the 22nd amino acid of the genetic code:



X

8.8

Nitrogen base	The number of bases in the codon				
	1	2	3	0 or 1	1 or 2
A	✓				
C				✓	
G				✓	
U	✓				

A has 1 amino group and 0 oxygen atoms,

C has 1 amino group and 1 oxygen atom,

G has 1 amino group and 1 oxygen atom,

U has 0 amino groups and 2 oxygen atoms,

2 amino groups per 3 bases suggest one U.

There are 2 amino groups and 1 oxygen atom per two bases left. A is one of these.

Either G or C is the last one.

8.9 a The fragment contains only four U, which can be used as the starting point to determine the reading frame. There should be only one A in the triplet. UGA and UAG are the options, the latter met twice. Both are STOP codons in the table. But the fragment of mRNA represents coding sequence! Within definite nucleotide motives, the STOP codons can be responsible for amino acid incorporation into proteins. Therefore, 8 amino acids encoded in the fragment (if UGA is STOP codon, then 7 amino acids residues:

…AA|UAG|AAU|UAG|CGG|AAC|AGA|GGG|UGA|C…

Number of amino acids = 8

8.9 b Since only one codon is responsible for the incorporation of **X** residues into proteins in archaea, it is UGA or UAG. There are more than one **X** residue in the polypeptide fragment, thus it is UAG (met twice), while UGA encodes Sec.

X	Asn	X	Arg	Asn	Arg	Gly	Sec		

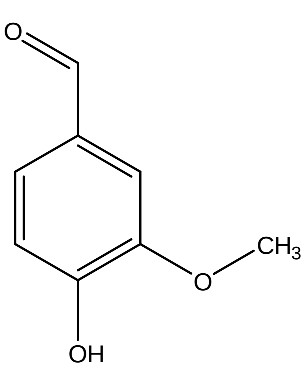
PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

Synthesis of 2,4-dinitrophenylhydrazones

Hydrazones belong to the class of *imines*, which contain a nitrogen-nitrogen single bond adjacent to a carbon-nitrogen double bond. Hydrazones are formed when NH_2-containing hydrazine reacts with aldehydes or ketones under appropriate conditions. Because the hydrazone derivatives of the carbonyl compounds are often stable, crystalline, highly coloured solids, they are used to confirm the identity of aldehydes and ketones.

In this task you will have to identify two substituted benzaldehydes (shown below) by studying the products of their reactions with 2,4-dinitrophenylhydrazine.



Reagents

- 2,4-Dinitrophenylhydrazine
- Sulfuric acid, concentrated
- Aldehyde solution, 1 mmol in ethanol
- Ethanol
- NaOH solution
- Acetone

Procedure

Equip one 50 cm^3 beaker with a magnetic bar. Fix the beaker on the stirrer using the metal ring attached to the stand. Place the content of vial (200 mg of 2,4-dinitrophenylhydrazine) into the beaker and start stirring carefully. Only in the presence of your lab assistant, carefully pour one sample of concentrated sulfuric acid (1 cm^3) onto the solid. Using pipettes add 1.6 cm^3 of water and 4 cm^3 of ethanol to the reaction mixture. Then using a pipette add dropwise the content of the aldehyde solution bottle (either “aldehyde 1” or “aldehyde 2”, each contains 1.00 mmol of the aldehyde). Bright precipitate starts forming at once. Continue stirring for 10 min, then add 10 cm^3 of water and stir for another 3 min.

Separation and purification of the product

Using scissors carefully cut out a filter paper circle, *ca.* 1 cm bigger in diameter than that of the glass filter. Wet the filter circle with water, and carefully put it on the filtering surface. The paper filter should fit evenly and tightly. If you fail to cut out an even circle, take a new filter from the table of common use and repeat cutting out. Assemble apparatus. Remove the stirring bar from the beaker using the spatula and transfer the reaction product onto the filter. Turn on the water-jet pump and filter out the precipitate. Put a little amount of water in the beaker and transfer the leftover product onto the filter. Wash the solid on the filter with water until the pH of the drops coming out the funnel are neutral. Then wash the solid twice with ethanol using no more than 3 cm^3 each time. (Note: Hydrazone is slightly soluble in ethanol.)

Dry out the solid on the filter with working water-jet pump, loosening and squeezing the product with a glass rod from time to time. After ca*.* 20 - 30 min transfer carefully the dried powder into the self-made filter paper box for the final drying in the air. Put the box with the product in a safe place (e.g. on the shelf). Turn off the water-jet pump when you do not use it!

As soon as your products seem dry, we advise you weigh them to avoid queuing at the balances. To collect the products, use the plastic tubes with your student code. Fill in the answer box below.

Note: The products you synthesized will be further re-examined by lab staff.

Repeat the above procedures with the other aldehyde.

Plastic tube **1**	Plastic tube **2**
Mass of empty tube __________ mg Mass of tube with product______ mg Mass of product __________ mg	Mass of empty tube _________ mg Mass of tube with product ______ mg Mass of product _________ mg

Tasks:

1.1 Write down the structures of 2,4-dinitrophenylhydrazine and both products.

1.2 What kind of stereoisomerism (if any) is possible for these hydrazones? Tick the appropriate box.

☐ R/S ☐ E/Z ☐ threo/erythro ☐ manno/gluco ☐ D/L

1.3 What is the role of sulfuric acid in 2,4-dinitrophenylhydrazone formation? Tick the appropriate box.

☐ stoichiometric reagent ☐ catalyst ☐ reducing agent ☐ oxidizing agent

1.4 How would the rate of the reaction change, if the synthesis is carried out in neutral medium? Tick the appropriate box.

☐ highly increase ☐ slightly increase
☐ no change ☐ the reaction would proceed very slow

1.5 How would the rate of the reaction change, if it is carried out in alkaline medium? Tick the appropriate box.

☐ highly increase ☐ slightly increase
☐ no change ☐ the reaction would not proceed

Characterization

Place small amount ("on the tip of a spatula") of each product in an individual 25 cm^3 beaker. Add 10 cm^3 of acetone to each beaker. The best results will be obtained if the colours and their intensities in each beaker are similarly yellow. Pour 5 cm^3 of $NaHCO_3$ solution into each beaker. Stir the resulting mixtures with the glass rod using different ends.

1.6 Record your observations of the solutions colour change. Tick the appropriate box.

☐ The colour does not change in either beaker.

☐ The colour changes significantly in both beakers.

☐ The colour changes significantly only in one beaker.

Add 2 cm^3 of NaOH solution to each of the resultant mixtures from the question **1.6**. Stir the reaction mixtures with the glass rod.

1.7 Record your observations of the solutions colour change in the box.

☐ The colour does not change in either beaker.

☐ The colour changes significantly in both beakers.

☐ The colour changes significantly only in one beaker.

1.8 What structural features of your products explain the colour change in the reaction with $NaHCO_3$? Tick the appropriate box.

☐ the presence of MeO group at position 4 in the benzene ring;

☐ the presence of MeO group at position 3 in the benzene ring;

☐ the presence of the OH group at position 4 in the benzene ring;

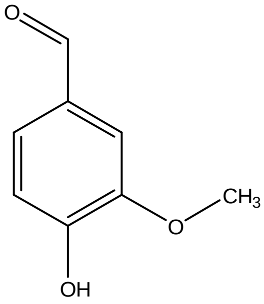
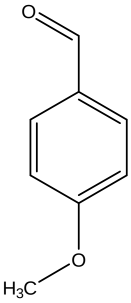
☐ the presence of both MeO and OH groups.

1.9 Which of the listed processes is responsible for the colour change observed in the reaction of 2,4-dinitrophenylhydrazones with aqueous NaOH? Tick the appropriate box.

☐ alkaline hydrolysis ☐ dehydration ☐ hydration

☐ deprotonation ☐ dehydrogenation

1.10 Draw the structures of the main organic species present in each test reaction medium in the answer boxes below.

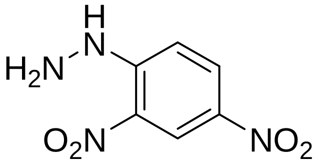
Initial aldehyde: 	Initial aldehyde: 

$NaHCO_3$	$NaHCO_3$
NaOH	NaOH

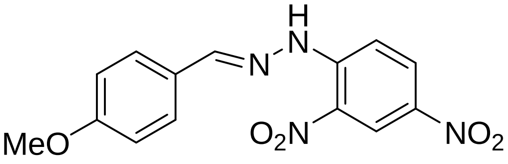
1.11 Put the numbers **1** or **2** under each structure. Calculate the percent yields of both hydrazones

SOLUTION

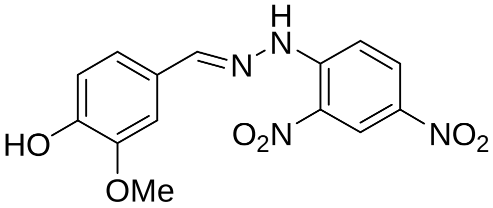
1.1 2,4-dinitrophenylhydrazine



Product 1:



Product 2:



1.2 ☑ E/Z

1.3 ☑ catalyst

1.4 ☑ the reaction would proceed very slow

1.5 ☑ the reaction would not proceed

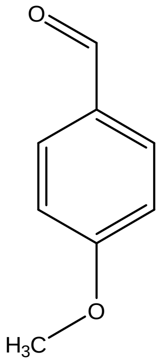
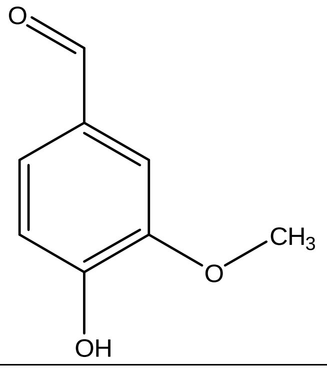
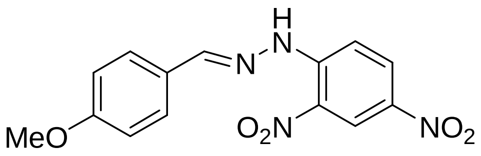
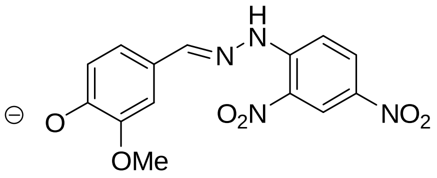
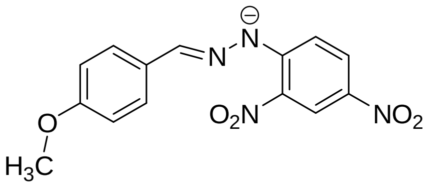
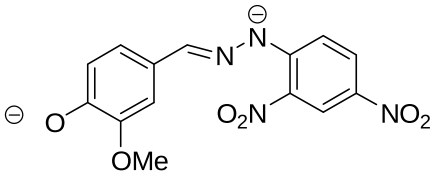
1.6 ☑ The colour changes significantly only in one beaker.

1.7 ☑ The colour changes significantly in both beakers.

1.8 ☑ the presence of the OH group at position 4 in the benzene ring;

1.9 ☑ deprotonation

1.10

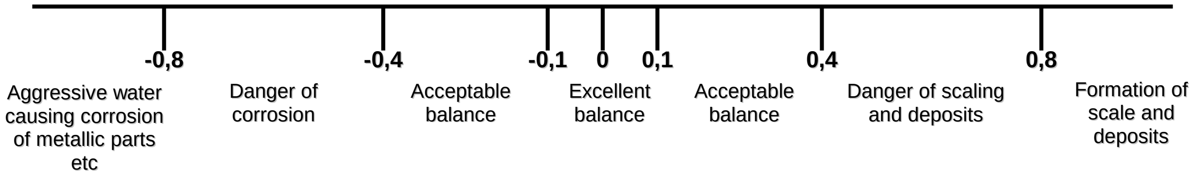
Initial aldehyde: 	Initial aldehyde: 
Product 1 in $NaHCO_3$ 	Product 2 in $NaHCO_3$ 
Product 1 in NaOH 	Product 2 in NaOH 

PROBLEM 2 (Practical)

Determination of the Langelier Saturation Index of a pool water

The Langelier Saturation Index (LI) is a measure of swimming pool water corrosivity as well as its ability to dissolve or deposit calcium carbonate. If LI is approximately zero, the water is considered "balanced". If the index LI is a positive number, the water tends to deposit calcium carbonate and is scale-forming. If the index LI is a negative number, the water is corrosive and dissolves calcium carbonate. The LI is a combination of the physical values factors taken from Table 1 and can be calculated by the formula:

$$\text{LI} = \text{pH} + \text{FT} + \text{FD} + \text{FA} - \text{FTDS}$$



pH : pH value
FT : Temperature factor
FD : Calcium hardness (CH) factor
FA : Total alkalinity (TA) factor
FTDS: Total dissolved solids (TDS) factor

Table 2.1 Values and corresponding factors

Temperature, °C	FT	Calcium hardness (CH), mg dm^{-3} $CaCO_3$	FD	Total alkalinity (TA), mg dm^3 $CaCO_3$	FA	Total dissolved solids (TDS), mg dm^{-3} NaCl	FTDS
0	0.0	5	0.3	5	0.7	0	12.0
3	0.1	25	1.0	25	1.4	-	-
8	0.2	50	1.3	50	1.7	1000	12.1
12	0.3	75	1.5	75	1.9	-	-
16	0.4	100	1.6	100	2.0	2000	12.2
19	0.5	150	1.8	125	2.1	-	-
24	0.6	200	1.9	150	2.2	3000	12.25
29	0.7	250	2.0	200	2.3	-	-

Table 2.1 continued

34	0.8	300	2.1	300	2.5	4000	12.3
41	0.9	400	2.2	400	2.6	-	-
53	1.0	600	2.35	800	2.9	5000	12.35
-	-	800	2.5	1000	3.0	-	-
-	-	1000	2.6	-	-	6000	12.4

In this task you will have to determine the LI value of a given water sample. Note that hardness is expressed as the equivalent to the concentration of $CaCO_3$ (expressed in mg dm^{-3}). Total alkalinity, being the acid equivalent to the total amount of carbonate and hydrogen carbonate, can also be expressed in mg dm^{-3} of $CaCO_3$, whereas TDS is recalculated as concentration of NaCl (mg dm^3).

Chemicals

- EDTA, standard aqueous solution, c = 0.0443 mol dm$^{–3}$,
- HCl, standard aqueous solution, c = 0.0535 mol dm$^{–3}$,
- Methyl orange, 0.1% in water,
- Murexide, indicator, solid mixture with NaCl (1 : 250 by mass),
- Sample of water.

Procedures

Calcium hardness is determined by complexometric titration with EDTA (Na_2H_2Y). This is performed in a strongly alkaline medium to mask magnesium (large amounts of Mg^{2+} interfere due to the co-precipitation of calcium with $Mg(OH)_2$; moreover, the complexometric indicator is also adsorbed on $Mg(OH)_2$, which impairs the observation of its colour change). When the alkali is added, titration should be carried out immediately to avoid the deposition of $CaCO_3$.

2.1 Write down equation of the reaction occurring during titration with Na_2H_2Y.

Procedure for determination of calcium

a) Put the standard solution of EDTA (precise exact concentration c = 0.0443 mol dm$^{–3}$) in the burette.

b) Pipette a 20 cm^3 aliquot of the water sample into an Erlenmeyer flask.

c) Add 3 cm^3 of NaOH solution (c = 2 mol dm$^{–3}$) with the 10 cm^3 measuring cylinder.

d) Add murexide indicator with spatula to obtain noticeably pink solution.

e) Within few minutes titrate the mixture with EDTA solution until the indicator colour changes from pink to purple.

2.2 Fill in the table 2.2.

Table 2.2

Volume of EDTA solution	Titration No			
Initial reading of the burette, cm^3				
Final reading of the burette, cm^3				
Consumed volume, cm^3				

Accepted volume, cm^3:

2.3 Calculate the hardness of the water sample in mg dm^{-3} of $CaCO_3$. Write down the result in Table 2.4 (see question 2.11).

Measurement of pH

Locate a pH meter in the lab (or ask your lab assistant).

a) Place about 70 -- 90 cm^3 of the water sample into a clean Erlenmeyer flask.

b) Remove the protective cap from the pH-meter (keep the cap standing, since there is solution in it).

c) Rinse the electrode with distilled water using a plastic wash bottle.

d) Turn the pH meter on by sliding the ON/OFF switch.

e) Immerse the electrode in the solution to be tested and stir gently by swirling the flask.

f) Place the flask on the table and wait until the reading stabilizes (not more than 1 min).

g) Read and record the pH value.

h) Switch the pH meter off, rinse the electrode with distilled water and place the protective cap back.

2.4 Write down the pH value in Table 2.4 (see question 2.11).

2.5 Which form of carbonic acid predominates in your water sample?

Confirm your choice with calculation and tick one box.

☐ Carbonate ☐ Hydrogen carbonate ☐ Carbonic acid

Note: The dissociation constants of carbonic acid are as follows:

$K_1 = 4.5 \cdot 10^{-7}$;

$K_2 = 4.8 \cdot 10^{-11}$.

2.6 Write down the ionic equation of the predominant reaction of titration of the water sample with HCl solution.

Determination of the total alkalinity

To obtain the value of the total alkalinity the water sample should be titrated to H_2CO_3. An acid-base indicator used is methyl orange, which starts changing its colour from yellow to orange at pH of about 4.5.

a) Rinse the burette with distilled water and fill it with the standard HCl solution (exact concentration of HCl is 0.0535 mol dm^{-3}).

b) Pipette a 50.0 cm^3 aliquot of water sample into an Erlenmeyer flask and add 3 drops of methyl orange solution.

c) If the sample is orange prior to addition of the acid the total alkalinity is zero. If the solution is yellow titrate it with the standard acid solution until the first noticeable colour change towards orange is observed. Record the volume of the titrant used.

2.7 Fill in the Table 2.3.

Table 2.3

Volume of the standard HCl solution	Titration No			
Initial reading of the burette, cm^3				
Final reading of the burette, cm^3				
Consumed volume, cm^3				
Accepted volume, cm^3 ______				

2.8 Calculate the total alkalinity (in mg dm^{-3} $CaCO_3$). Write down the result in Table 2.4 (see question 2.11).

2.9 Temperature measurement

Read the thermometer located at the table of common use and write down the value into Table 2.4 (see question 2.11).

2.10 TDS determination in the water sample with the test strip.

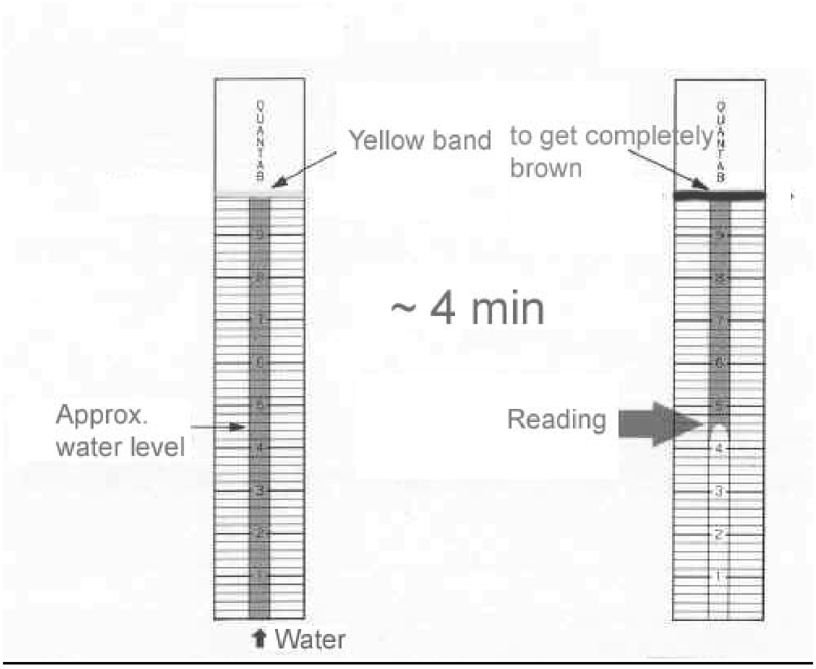
a) Fill a beaker with the water sample to a level of about 3 cm of height. Immerse the strip into water; be sure that the yellow band on the top of the strip does not touch the liquid.

b) Wait for 3 - 4 minutes until the yellow band turns completely brown. Take the reading as shown in the picture hereunder. Give it to one decimal digit.

c) Report the reading.

d) Find your TDS concentration as that of NaCl in mg dm^{-3} in the table to the right of the picture.

e) Write down the concentration of NaCl in Table 2.4 (see question 2.11).



Reading	NaCl conc., mg dm^{-3}
1.4	360
1.6	370
1.8	420
2.0	430
2.2	470
2.4	530
2.6	590
2.8	660
3.0	730
3.2	800
3.4	880
3.6	960
3.8	1050
4.0	1140
4.2	1240
4.4	1340
4.6	1450
4.8	1570
5.0	1700

2.11 Fill in all the blank boxes in the Table 2.4. Calculate LI and write down the result in Table 2.4. Take the values of the factors to the accuracy of two decimal digits.

Table 2.4. Calculation of LI of the water sample

Water sample Number ______					
CH, mg dm^{-3} $CaCO_3$	TA, mg dm^{-3} $CaCO_3$	*t*, °C	pH	TDS, mg dm^{-3} NaCl	**LI**
FD	FA	FT		FTDS	

Theoretical questions. Water balance correction.

If LI significantly deviates from zero, it is needed to be adjusted to zero.

Imagine you are given a sample of pool water analyzed as you have done above. The results of the analysis are as follows: CH = 550 mg dm^{-3}, FD = 2.31, TA = 180 mg dm^{-3}, FA = 2.26, t = 24 °C, FT = 0.6; TDS = 1000 mg dm^{-3}, FTDS = 12.1, pH = 7.9, LI = 0.97. The pool serviceman added 10 cm^3 of 0.0100 mol dm^{-3} solutions of reagents ($NaHCO_3$, NaOH, $NaHSO_4$, $CaCl_2$, EDTA (disodium salt dihydrate) and HCl) to 200 cm^3 of different pool water samples (one reagent for one sample).

2.12 Decide whether $CaSO_4$ is deposited upon addition of $NaHSO_4$.

Yes ☐ No ☐

Tick one box and confirm your choice with calculation.

Note: $CaSO_4$ solubility product is $5\cdot10^{-5}$. Assume that no precipitate of $CaCO_3$ is formed upon addition of any of the above reagents.

2.13 Fill in the hereunder table 2.5 by showing the trends of changes resulting from addition of each reagent to this particular water sample (use "+" if the factor increases, "–" if it decreases, and "0" if it does not change).

Table 2.5

Reagent	pH	FA	FD	FTDS	LI
$NaHCO_3$					
NaOH					
$NaHSO_4$					
$CaCl_2$					
Na_2H_2Y					
HCl					

SOLUTION

2.1 $H_2Y^{2-} + Ca^{2+} = CaY^{2-} + 2\ H^+$

Reactions with other forms of EDTA are also acceptable.

2.5 We observe pH ~8 ⇒ this is carbonic acid - hydrogen carbonate buffer, then:

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{K_1}{[H^+]} = 45$$

i.e. ~ 98 % of hydrogen carbonate

☐ Carbonate ☑ Hydrogen carbonate ☐ Carbonic acid

2.6 $HCO_3^- + H^+ = H_2CO_3$ (or $H_2O + CO_2$)

2.12 $[Ca^{2+}] = \frac{V_{EDTA} \times c_{EDTA}}{20}\ \frac{200}{200+10} = \frac{2.2 \times 0.05}{\frac{20 \times 200}{210}} = 0.00524\ \text{mol dm}^{-3}$

When $NaHSO_4$ is added, $[SO_4^{2-}] = \frac{0.01 \times 10}{(200+10)} = 0.000476\ \text{mol dm}^{-3}$

Then $[Ca^{2+}]\ [SO_4^{2-}] = 0.00524 \times 0.000476 = 2.5 \cdot 10^{-6} < K_{sp}$

⇒ no precipitate of $CaSO_4$ is formed.

Your answer (tick one) Yes ☐ No ☑

2.13

Reagent	pH	FA	FD	FTDS	LI
$NaHCO_3$	+	+	0	+	+
NaOH	+	+	0	+	+
$NaHSO_4$	–	–	0	+	–
$CaCl_2$	0	0	+	+	+
Na_2H_2Y	–	–	–	+	–
HCl	–	–	0	0	–

PROBLEM 3 (Practical)

Determination of molecular mass by viscometry

Viscosity coefficient is a measure of fluid resistance to flow. It can be determined by measuring the rate of liquid flow through a thin capillary. Polymer solution viscosity grows with increasing concentration. At constant concentration, stronger solvent-polymer interactions result in more expanded polymer coils and, therefore, in higher viscosity. Provided the density of the diluted solution of a polymer is equal to that of the solvent, the reduced viscosity η_{red} of the polymer solution with concentration c (g cm^{-3}) is defined as follows:

$$\eta_{\text{red}} = \frac{t - t_0}{t_0 c} \quad \left[\text{cm}^3\ \text{g}^{-1}\right],$$

where t and t_0 are the flow times of the solution and pure solvent, respectively.

Reduced viscosity for dilute polymer solutions depends on concentration as follows:

$$\eta_{red}(c) = [\eta] + kc\ ,$$

with k, a parameter and $[\eta]$, intrinsic viscosity (cm^3 g^{-1}). The intrinsic viscosity $[\eta]$ is determined by extrapolation of the reduced viscosity to zero polymer concentration. In general, the intrinsic viscosity is related to the molecular mass M of the polymer according to the Mark-Kuhn-Houwink equation:

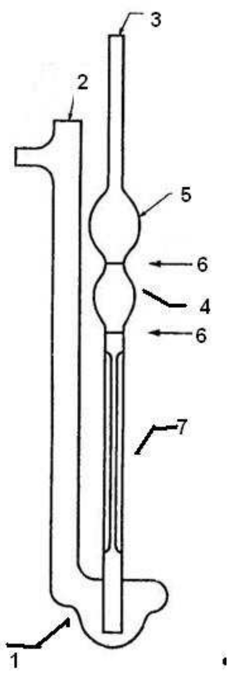
$$[\eta] = K\,M^{\alpha}\ ,$$

where K and α are the constants for a particular solvent–polymer pair at a certain temperature. Thus, M can be derived from the Mark-Kuhn-Houwink equation using experimentally determined $[\eta]$ and reference data for K and α.

How to work with viscometer

a) Mount the viscometer (see the picture below) attached so that its tubing (3) is vertical, and the collection vessel (1) stands on the lab stand basement. Adjust the fixing clamp as low as possible.

b) Put 10 cm^3 of the liquid to be analyzed into the collection vessel (1) through the tubing (2) using a pipette.



1 – collection vessel
2 – supplementary tubing
3 – supplementary tubing
4 – measurement vessel
5 – collection vessel
6 – the match marks
7 - capillary

c) Place the pipette filler or rubber bulb on top of the tubing (3) and suck the liquid into the measurement vessel (4) so that the liquid is drawn into the collection vessel (5). When sucking the liquid, avoid the air bubbles in the capillary (7) and the vessels (4, 5), as these can cause significant experimental errors. The liquid meniscus should be about 10 mm above the upper mark (6).

d) Zero the stopwatch, and remove the pipette filler or bulb out of the tube (3). The liquid starts flowing down to the collection vessel (1).

e) Measure the flow time: start the stopwatch when the liquid meniscus passes the upper match mark (6) and stop the stopwatch when the liquid meniscus passes the lower match mark (6).

ATTENTION: Handle the viscometer with great care!
There will be no replacement if you have broken your viscometer!
If you break your viscometer tell the lab assistant. You may then attempt to do the experiment using the 25 mL pipette and beaker in place of viscometer.

Clean the viscometer three times with tap water and once with distilled water before you pass over to a new polymer sample. To do this, first wash it with tap water, and then rinse with distilled water. There is no need to wash it with the polymer solution, the error can occur but it is negligible.

You are NOT requested to fill in all table cells in the Answer Boxes. Perform as many measurements as you prefer for accurate averaging.

Chemicals

- Poly(vinyl) alcohol, 40 cm^3 each, 5 vials

Procedure

You are provided with a set of aqueous solutions of polymers (0.01 g cm^{-3}, stock solutions). Three of P1-P4 are solutions of poly(vinyl alcohol), whereas the fourth one is that of a partially hydrolyzed poly(vinyl acetate) containing *ca*. 10 % of non-hydrolyzed units. It is unknown which of the P1 – P4 solutions is partially hydrolyzed poly(vinyl acetate). Molecular masses of the polymers P1 – P4 are given in the Table.

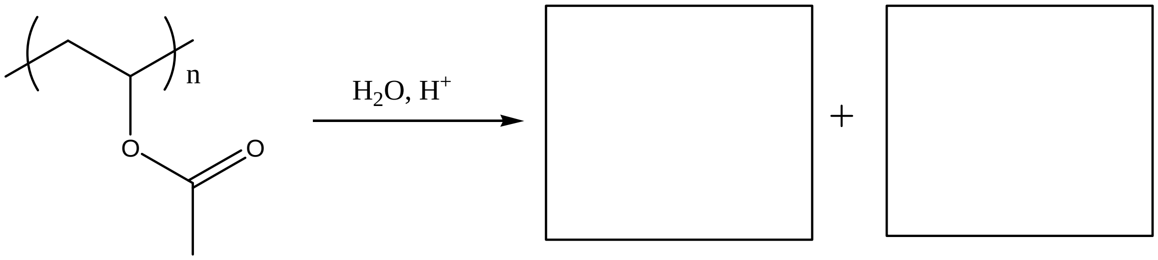
Approximate molecular mass	Sample code
26650	P2
50850	P1
65300	P4
91900	P3

Sample X is poly(vinyl alcohol) of an unknown molecular mass.

In this task you will have to identify which of P1 – P4 is the solution of partially hydrolyzed poly(vinyl acetate) and determine the molecular mass of polymer X.

3.1 Write down the reaction scheme of poly(vinyl alcohol) preparation by hydrolysis of poly(vinyl acetate).

Reaction scheme:



3.2 Choose (tick appropriate box) which polymer shows the stronger interaction with water and compare the viscosities of aqueous solutions of fully and partially hydrolyzed poly(vinyl acetates). Assume that the concentration of the solutions and the molecular masses of the polymers are the same.

Poly(vinyl alcohol) ☐

Partially hydrolyzed poly(vinyl acetate) ☐

Compare the viscosities:

η (poly(vinyl alcohol) _____ η (partially hydrolyzed poly(vinyl acetate)

(put either <. >, or ≈)

3.3 Measure the flow time of the pure solvent (distilled water). You are not requested to fill all the boxes in the answer sheet.

3.4 Measure the flow times of the stock solutions of P1 – P4, and that of X. Calculate the reduced viscosities. You are NOT requested to fill in all table cells in the Answer Boxes. Perform as many measurements as you prefer for accurate averaging.

3.5 Encircle the solution out of P1, P2, P3, P4 which is the sample of partially hydrolyzed poly(vinyl acetate). Hint: Take into account the given molecular masses of the polymers P1 – P4.

Do not use this polymer in the next part of the experiment.

3.6 To determine the parameters of the Mark-Kuhn-Houwink equation and calculate the unknown molecular mass of X choose and encircle two most appropriate solutions of poly(vinyl alcohol) with different molecular masses. Assume that the absolute error of intrinsic viscosity determination does not depend on the sample molar mass.

3.7 Using appropriate measuring glassware to prepare the solutions, measure the flow time of a number of diluted solutions of three poly(vinyl alcohol) samples: that of an unknown molecular mass (X), and the pair of poly(vinyl alcohols) chosen in 3.6, and calculate the corresponding reduced viscosities. When calculating the diluted solutions concentration, assume that density of the polymer solutions is equal to that of water. Determine the intrinsic viscosities for each of the examined samples. Submit the graph paper with your plots together with the booklet. **Note:** if you would like to plot the data referring to different samples on the same plot, make sure you use clearly distinguishable symbols for each dataset. You are NOT requested to fill in all table cells in the answer booklet.

Summary of experimental results (only fill in the measured values)

Sample	P__	P__	X
Concentration (c), g cm$^{–3}$:	0.01	0.01	0.01
Reduced viscosity (η_{red}), cm^3 g$^{–1}$			
c (1st dilution), g cm$^{–3}$:			
η_{red}, cm^3 g$^{–1}$			
c (2nd dilution), g cm$^{–3}$:			
η_{red}, cm^3 g$^{–1}$			
c (3rd dilution), g cm$^{–3}$:			
η_{red}, cm^3 g$^{–1}$			
c (4th dilution), g cm$^{–3}$:			
η_{red}, cm^3 g$^{–1}$			
c (5th dilution), g cm$^{–3}$:			
η_{red}, cm^3 g$^{–1}$			

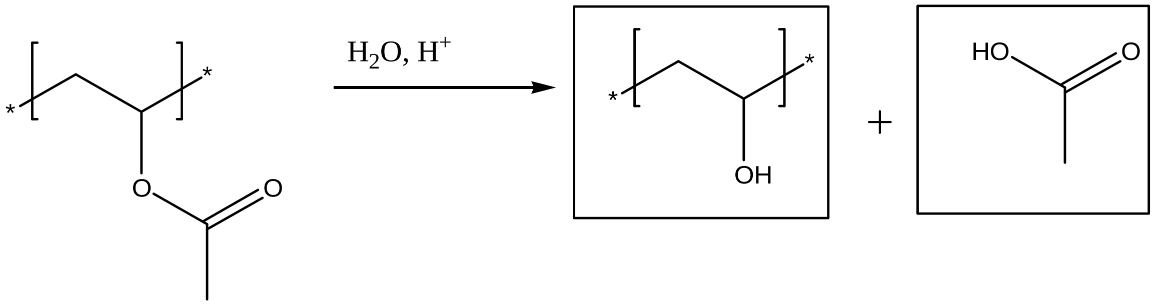
3.8 Write down the form of equation you would use to determine K and α.

Derive the K and α values for the aqueous solution of poly(vinyl alcohol).

3.9 By using the obtained K and α values, as well as the intrinsic viscosity of the X solution, calculate the molecular mass of the polymer X. If you have failed to determine K and α, use K = 0.1 cm^3 g^{-1} and α = 0.5.

SOLUTION

3.1



3.2

Poly(vinyl alcohol) ☑

η (poly(vinyl alcohol) > η (partially hydrolyzed poly(vinyl acetate)

3.8 $\log[\eta] = \log K + \alpha \log M$

3.9 Sample calculation:

$$23.7 = 0.1 \times M^{0.5} \Rightarrow 237 = M^{0.5}$$

$$M = 237^2 = 56169 \approx 56200$$

QUANTITIES AND THEIR UNITS USED IN THIS PUBLICATION

SI Basic Units

Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Temperature	T	kelvin	K
Amount of substance	n	mole	mol

Special names and symbols for certain derived SI Units

Force	F	Newton	N
Pressure	p	pascal	Pa
Energy	E	joule	J
Power	P	watt	W
Electric charge	Q	coulomb	C
Electric potential difference	U	volt	V
Electric resistance	R	ohm	Ω

Other derived SI Units used in chemistry

Area	S	square metre	m^2
Volume	V	cubic metre	m^3
Density	ρ	kilogram per cubic metre	$kg\ m^{-3}$
Concentration	c	mole per cubic metre	$mol\ m^{-3}$ $(mol\ dm^{-3})$
Molar mass	M	kilogram per mole	$kg\ mol^{-1}$ $(g\ mol^{-1})$

Some other quantities and constants

Relative atomic mass of an element	A_r
Relative molecular mass of a compound	M_r
Molar fraction	x
Mass fraction	w
Volume fraction	φ
Enthalpy	H
Entropy	S
Gibbs energy	G
Temperature in Celsius scale	℃

Elementary charge, e	$1.6021892 \times 10^{-19}$ C
Planck constant, h	6.626176×10^{-34} J s
Avogadro constant, A	6.022045×10^{23} mol^{-1}
Faraday constant, F	9.648456×10^{4} C mol^{-1}
Gas constant, R	8.31441 J mol^{-1} K^{-1}
Zero of Celsius scale, T_0	273.15 K (exactly)
Normal pressure, p_0	1.01325×10^{5} Pa (exactly)
Standard molar volume of ideal gas, V_0	2.241383×10^{-2} m^3 mol^{-1}