46th

International Chemistry Olympiad

PREPARATORY PROBLEMS

Edited by Anton Sirota

29 theoretical problems
7 practical problems

2014

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Preparatory Problems

46th International Chemistry Olympiad (IChO - 2014)

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Preface

written by editor-in-chief, Nguyen Tien Thao (Hanoi)
(a shortened version)

These problems were prepared with reliance on fundamental topics firmly covered in high school chemistry courses along with some advanced topics for the chemistry olympiad competition. These topics are listed under “Topics of Advanced Difficulty”, and their applications are given in the problems.

We hope that these problems will be motivating for students to participate in the IChO-2014 competition. We believe that IChO-2014 will not only be a chemistry competition, but also a pleasant time for you to know about Vietnamese culture.

We look forward to seeing you in Hanoi and at Hanoi University of Science, Vietnam National University in Hanoi.

Hanoi, January 31st, 2014
Editor in Chief
Nguyen Tien Thao

Fields of Advanced Difficulty

Theoretical

Kinetics: Integrated first- and second-order rate equation; analysis of moderately complex reactions mechanisms using the steady state approximation, the use of the Arrhenius equation.

Thermodynamics: Electrochemical cells, the relationship between equilibrium constants, electromotive force and standard Gibbs energy, the variation of the equilibrium constant with temperature.

Quantum mechanics: Particle-in-a-box calculations, orbital-overlaps, spin-orbit coupling.

Spectroscopy: Interpretation of IR spectra and relatively simple ^{1}H, ^{13}C, and ^{27}Al NMR spectra: chemical shifts, multiplicities, coupling constants and integrals.

Advanced Inorganic: Trans effect; the use of simple crystal field theory to explain electronic configurations in octahedral and tetrahedral complexes; calculation of the magnetic moment using the spin-only formula, solid state structures, packing arrangement.

Advanced Organic: Stereoselective transformations; aromatic nucleophilic substitution; polycyclic aromatic compounds and heterocycles.

Practical

Basic synthesis techniques: Thin layer chromatography, Extraction, Filtration, Drying, Titration.

UV – VIS spectroscopy.

THE FORTY-SIXTH
INTERNATIONAL CHEMISTRY OLYMPIAD

20 – 29 JULY 2014, HANOI, VIETNAM

PREPARATORY PROBLEMS

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PREPARATORY THEORETICAL PROBLEMS

THEORETICAL PROBLEM 1

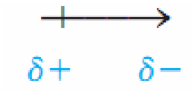
Polar and non-polar molecules

In chemistry, a molecule is considered *non-polar* when its positive charge center and negative charge center coincide, i.e. the charge distribution is symmetrical in the molecule. On the other hand, when a molecule has two distinct centers for positive and negative charges, it is considered *polar*.

This charge distribution property is measured by a quantity called the *dipole moment* which is defined as the magnitude of the charge q and the distance *l* between the charges:

$$\vec{\mu} = q\,\vec{l}$$

The dipole moment is a vector pointing from the positive charge center to the negative one.



The dipole moment is often expressed in debyes (D). The relationship between debyes (D) and coulomb meters (C·m) in SI units is as follows: 1 D = 3.33 × 10^{-30} C·m.

I. The dipole moment is closely related to the molecular geometry. In order to calculate the net dipole moment μ of multi-atomic molecules, we can add the dipole moment vectors for individual bonds. In this case, an individual bond is considered to have its own dipole moment called the bond moment. For a non-linear molecule with three atoms, ABC, the net dipole moment μ can be calculated by adding vectors in which $\vec{\mu}_1$ and $\vec{\mu}_2$ are the bond moments for AB and AC bonds, and α is the bond angle. For a non-linear molecule with three atoms, ABC, the net dipole moment μ can be calculated by adding vectors in which $\vec{\mu}_1$ and $\vec{\mu}_2$ are the bond moments for AB and AC bonds, and α is the bond angle.

1.1 Determine the general equation for calculating the net dipole moment.

II. The directions of the individual bond moments should be considered. The molecule of CO_2 is linear.

1.2 Calculate the net dipole moment μ of the molecule.

1.3 A non-linear molecule of A_2B such as H_2S has the net dipole moment $\mu \neq 0$. Determine μ for H_2S if $\mu_{SH} = 2.61 \cdot 10^{-30}$ C·m and the bond angle $\alpha = 92.0$ °.

III. The bond angle HCH in the formaldehyde molecule is determined experimentally to be approximately 120°; the bond moments for C–H and C–O bonds are $\mu_{C\text{-}H}$ = 0.4 D and $\mu_{C=O}$ = 2.3 D, respectively.

1.4 Determine the orbital hybridization of C and O atoms, and plot the overlaps of orbitals in the formaldehyde molecule.

1.5 Calculate the net dipole moment (μ) of the formaldehyde (D), given the order of the electronegativity as $\chi_O > \chi_C > \chi_H$. (<u>Hint</u>s: *Electronegativity is the ability of an atom in a molecule to attract shared electrons to itself*).

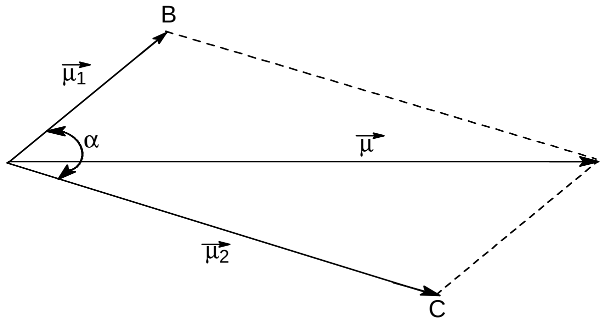
IV. The dipole moments of water and dimethylether in gaseous state are determined as 1.84 D, and 1.29 D, respectively. The bond angle formed by two bond moments of O–H in the water molecule is 105°. The bond angle formed by two bond moments of O–C in the ether molecule is 110°.

1.6 Estimate the bond angle formed by the bond moments of O–H and C–O in the methanol molecule, given that the dipole moment of methanol molecule is 1.69 D. Assume that individual bond moments are unchanged in different molecules.

SOLUTION OF PREPARATORY PROBLEM 1

I.

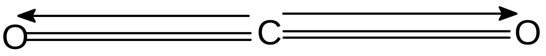
1.1 The net dipole moment μ is calculated as follows:



$$\mu^2 = \mu_1^2 + \mu_2^2 + 2\,\mu_1\,\mu_2 \cos\alpha \quad (1)$$

II.

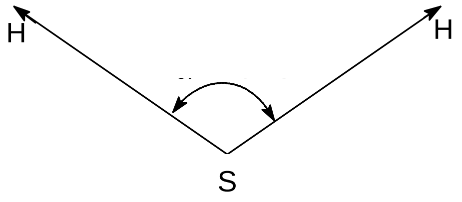
1.2 The geometry of CO_2:



Because two bond moments of μ_{CO} have opposite directions and cancel each other out, the net dipole moment for CO_2 is zero. Therefore:

$$\mu_{CO_2} = 0$$

1.3 The geometry of H_2S:



From the general equation (1),

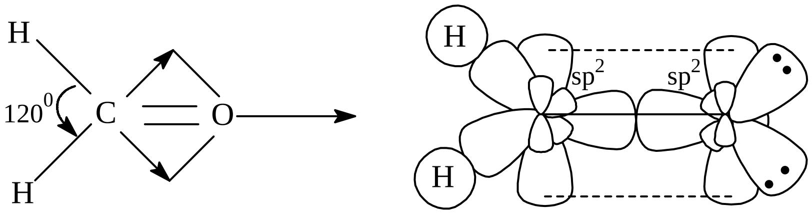
$$\mu_{H_2S}^2 = \mu_{HS}^2 + \mu_{HS}^2 + 2\,\mu_{HS}\mu_{HS}\cos\alpha = 2\mu_{HS}^2\left(1+\cos\alpha\right) = 4\,\mu_{HS}^2\cos^2\frac{\alpha}{2}$$

$$\mu_{H_2S} = 2\,\mu_{HS}\cos\frac{\alpha}{2}$$

Therefore, $\mu_{H_2S} = 2\times\dfrac{2.61\cdot 10^{-30}}{3.33\cdot 10^{-30}}\times\cos\dfrac{92}{2} = 1.09\text{ D}$

III.

1.4



1.5 Since $\chi_C > \chi_H$, $\mu_{C\text{-}H}$ has the direction showed in the above plot, and

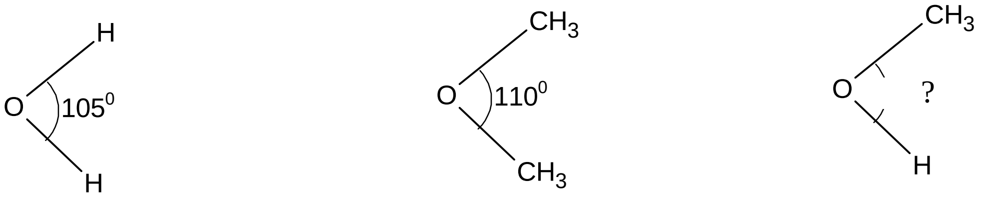
$$\mu_{H\text{-}C\text{-}H} = 2\,\mu_{C\text{-}H}\cos\frac{120}{2} = 2\times 0.4\times 0.5 = 0.4\text{ D}$$

$\mu_{C=O}$ also has the direction toward the O atom. Therefore, the net dipole moment μ of the molecule is

$\mu_{HCH} = \mu_{HCH} + \mu_{C=O}$ = 0.4 + 2.3 = 2.7 D

IV.

1.6 We can plot the geometry of the three molecules involved in this problem in the following scheme:



H_2O CH_3-O-CH_3 CH_3-O-H

- The dipole moment μ is a vector which can be calculated by adding individual bond moments μ_1 and μ_2

$$\mu^2 = \mu_1^2 + \mu_2^2 + 2\,\mu_1\,\mu_2\cos\alpha \qquad (1)$$

α is the angle formed by the individual bond moments.

- The dipole moment μ in the water molecule with the bond angle α formed by the two bond moments of O-H can be calculated as follows.
  From equation (1) we have

$$\mu = \left(2\,\mu_{OH}^2 + 2\,\mu_{OH}^2\cos\alpha\right)^{1/2}$$

$$= \left[2\,\mu_{OH}^2\left(1+\cos\alpha\right)\right]^{1/2} = \left[4\,\mu_{OH}^2\cos^2\frac{\alpha}{2}\right]^{1/2}$$

$$= 2\,\mu_{OH}\cos\frac{\alpha}{2}$$

Given α = 105^0, the bond moment μ_{OH} in water can be calculated:

$$1.84 = 2\,\mu_{OH}\cos\frac{105}{2} \;\rightarrow\; \mu_{OH} = 1.51\ \text{D}$$

Similarly, we can calculate the bond moment for O-CH_3 in dimethylether:

$$1.29 = 2\,\mu_{OCH_3}\cos\frac{110}{2} \;\rightarrow\; \mu_{OCH_3} = 1.12\ \text{D}$$

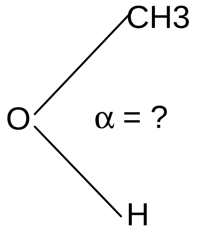
- In methanol, the individual bond moments are given as $\mu_1 = \mu_{OH}$ and $\mu_2 = \mu_{OCH_3}$ as in water and dimethylether. The bond angle *α* is formed by the two individual bond moments.

From equation (1), cos*α* is:

$$\cos\alpha = \frac{\left(\mu^2 - \mu_1^2 - \mu_2^2\right)}{2\,\mu_1\mu_2}$$

$$= \frac{\left(1.69^2 - 1.51^2 - 1.12^2\right)}{2\times1.51\times1.12} \quad \rightarrow$$

$$\alpha = 101^{o}\,57$$



Therefore, the bond angle C – O – H in methanol is of 101^{o} 57

THEORETICAL PROBLEM 2

Calculations of lattice energy of ionic compounds

I. Lithium is the lightest metal and does not exist in pure form in nature due to its high reactivity to water, moisture, oxygen... Lithium readily forms ion with a 1+ charge when reacting with nonmetals. Write down the following chemical reactions at room temperature:

2.1 Lithium reacts with water.

2.2 Lithium reacts with halogens, e.g. Cl_2.

2.3 Lithium reacts with dilute sulfuric acid and concentrated sulfuric acid.

II. The change in enthalpy of a particular reaction is the same whether it takes place in one step or in a series of steps (Hess's law). Use the following data:

Sublimation enthalpy of Li(s), $\Delta_S H = 159$ kJ mol^{-1}.

Ionization energy of Li(g), $I = 5.40$ eV.

Dissociation enthalpy of Cl_2, $\Delta_D H = 242$ kJ mol^{-1}.

Electron affinity of Cl(g), $E = -3.84$ eV.

Formation enthalpy of LiCl(s), $\Delta_f H = -402.3$ kJ mol^{-1}.

$r_{\mathrm{Li}^+} = 0.62$ Å; $r_{\mathrm{Cl}^-} = 1.83$ Å; $N_A = 6.02\times10^{23}$ mol^{-1}.

2.4 Establish the Born-Haber cycle for lithium chloride crystal.

2.5 Calculate the lattice energy U_o (kJ mol^{-1}) using the Born-Haber cycle.

III. In practice, experimental data may be employed to calculate lattice energies in addition to the Born-Haber cycle. One of the semi empirical formulae to calculate the lattice energy U_o for an ionic compound, which was proposed by Kapustinskii, is as follows:

$$U_0 = -287.2\ \frac{Z_+\ Z_-\sum\nu}{r_+ + r_-}\left(1 - \frac{0.345}{r_+ + r_-}\right)$$

where: ν is the number of ions in the empirical formula of ionic compound,

r_+ and r_- are the radii of the cation and anion, respectively, in Å,

Z_+ and Z_- are cation and anion charges, respectively,

U_0 is the lattice energy, in kcal mol^{-1}.

2.6 Use the Kapustinskii empirical formula to calculate U_o (in kJ mol^{-1}) of LiCl crystal, given that 1 cal = 4.184 J.

IV.

2.7 Based on the results of two calculation methods in sections II and III, choose the appropriate box:

According to the Born-Haber cycle and Kapustinskii empirical formula for lithium chloride crystal structure, both methods are close to the experimental value.	☐
Only the calculated result of the Born-Haber cycle is close to the experimental value.	☐
Only the calculated result of the Kapustinskii empirical formula is close to the experimental value.	☐

Data: Given the experimental value of lattice energy for LiCl is 849.04 kJ mol^{-1}.

V. In the formation of LiCl crystal, it is found out that the radius of lithium cation is smaller than that of chloride anion. Thus, the lithium ions will occupy the octahedral holes among six surrounding chloride ions. Additionally, the body edge length of LiCl cubic unit cells is 5.14 Å. Assume that Li^+ ions just fit into octahedral holes of the closest packed chloride anions.

2.8 Calculate the ionic radii for the Li^+ and Cl^- ions.

2.9 Compare the calculated (theoretical) radii with the experimental radii given below, and choose the appropriate box:

Both calculated radii of lithium and chloride ions are close to the experimental values.	☐
Only the calculated radius of lithium ion is close to the experimental value	☐
Only the calculated radius of chloride ion is close to the experimental value.	☐

The experimental radii of Li^+ and Cl^- are 0.62 Å and 1.83 Å, respectively.

SOLUTION OF PREPARATORY PROBLEM 2

I.

2.1 Lithium reacts with water:

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

2.2 Lithium reacts with chlorine:

$2\ Li(s) + Cl_2(g) \rightarrow 2\ LiCl(s)$

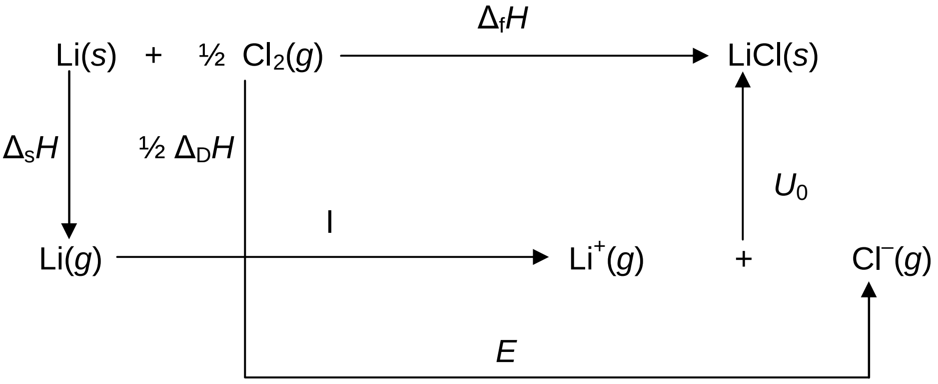
2.3 Lithium reacts with sulfuric acid:

With dilute sulfuric acid: $2\ Li(s) + H_2SO_4(aq) \rightarrow 2\ Li^+(aq) + SO_4^{2-}(aq) + H_2(g)$

With concentrated acid: $2\ Li(s) + 3\ H_2SO_4(aq) \rightarrow 2\ LiHSO_4(aq) + SO_2(g) + 2\ H_2O(l)$

II.

2.4 To calculate U_o in accordance with Born-Haber cycle, the following cycle is constructed:



2.5 Based on this cycle and Hess's law, we have:

$$\Delta_f H = \Delta_S H + \frac{1}{2}\Delta_D H + I + E + U_0$$

or $$U_0 = \Delta_f H - \left(\Delta_S H + \frac{1}{2}\Delta_D H + I + E\right)a$$

After converting all the numerical data to the same unit, we have:

$U_0 = -\ 402.3 - 159 - 121 - (5.40 - 3.84) \times 1.6 \cdot 10^{-19} \times 1 \cdot 10^{-3} \times 6.022 \cdot 10^{23}$

$U_0 = -\ 832.56$ kJ mol^{-1}.

III.

2.6 $U_0 = -287.2\,\dfrac{Z_+\,Z_-\,\sum\nu}{r_+ + r_-}\left(1-\dfrac{0.345}{r_+ + r_-}\right)$

For LiCl crystal, we have:

$$U_0 = -287.2\,\frac{1\times1\times2}{0.62+1.83}\left(1-\frac{0.345}{0.62+1.83}\right) = -201.43\ \text{kcal mol}^{-1}$$

To conveniently compare the results, we convert the obtained result to SI units:

$U_0 = -201.43\times4.184 = -842.78$ kJ/mol

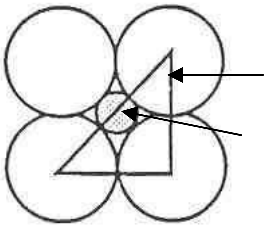
IV.

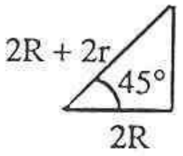
2.7 Correct answer:

According to the Born-Haber cycle and Kapustinskii empirical formula for lithium chloride crystal structure, both methods are close to the experimental value.

V.

2.8 The geometry diagram for octahedral holes is shown below.





where, R and r are the radii of Cl^- and Li^+ ions, respectively.

Based on the diagram, we have:

$$\cos 45^\circ = \frac{2R}{2R+2r} = \frac{R}{R+r}$$

$$0.707 = \frac{R}{R+r} \rightarrow \quad R = 0.707\,(R+r) \quad \rightarrow\ r = 0.414\,R$$

The body edge length of the unit cell LiCl = $2R + 2r$ = 5.14 Å

$2R + 2\,(0.414\,R) = 5.14$ Å $\rightarrow$ $R = 1.82$ Å (radius of Cl^-)

$2\,(1.82$ Å$) + 2r = 5.14$ Å $\rightarrow$ $r = 0.75$ Å (radius of Li^+)

2.9 Correct answer:

Only the calculated radius of chloride ion is close to the experimental value.

THEORETICAL PROBLEM 3

A frog in a well

The energy levels of an electron in a one-dimensional box are given by:

$$E_n = n^2 \frac{h^2}{8\,m\,L^2} \qquad n\text{: } 1, 2, 3\ldots$$

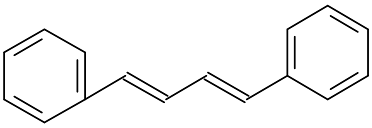
in which h is the Planck's constant, m is the mass of the electron, and L is the length of the box.

I. The π electrons in a linear conjugated neutral molecule are treated as individual particles in a one-dimensional box. Assume that the π electrons are delocalized in the molecular length with the total number of N π electrons and their arrangement is governed by the principles of quantum mechanics.

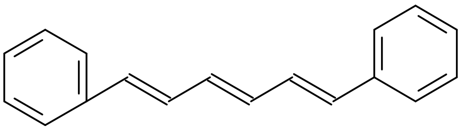
3.1 Derive the general expression for $\Delta E_{\text{LUMO – HOMO}}$ when an electron is excited from the HOMO to the LUMO.

3.2 Determine the wavelength λ of the absorption from the HOMO to the LUMO.

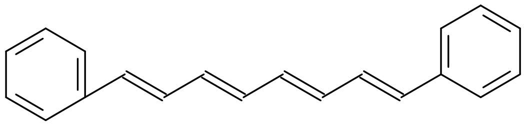
II. Apply the model of π electrons in a one-dimensional box for three dye molecules with the following structures (see the structural formula). Assume that the π electrons are delocalized in the space between the two phenyl groups with the length L is approximately equal to (2 k + 1)(0.140) nm, in which k is the number of the double bonds.



a) 1,4-diphenyl-1,3-butadiene
(denoted as **BD**)



b) 1,6-diphenyl-1,3,5-hexatriene
(denoted as **HT**)



c) 1,8-diphenyl-1,3,5,7-octatetraene
(denoted as **OT**)

3.3 Calculate the box length L (Å) for each of the dyes.

3.4 Determine the wavelength λ (nm) of the absorption for the molecules of the investigated dyes.

III.

3.5 Recalculate the box length L (Å) for the three dye molecules, assuming that the π electrons are delocalized over the linear conjugated chain which is presented as a line plotted between the two phenyl groups (see the structural formula). The bond angle C–C–C is 120° and the average length of C–C bond is 0.140 nm.

IV. The following experimental data on the wavelength λ of absorption are given:

Substance	BD	HT	OT
λ (nm)	328.5	350.9	586.1

3.6 Determine the box length L (Å) of the linear conjugated chain for each of the three investigated dyes.

3.7 Tabulate the values of the box length L for the dyes calculated above by the three different methods, denoted as **I**, **II**, and **III**.

3.8 Choose the method which is the most fit to the experimental data.

SOLUTION OF PREPARATORY PROBLEM 3

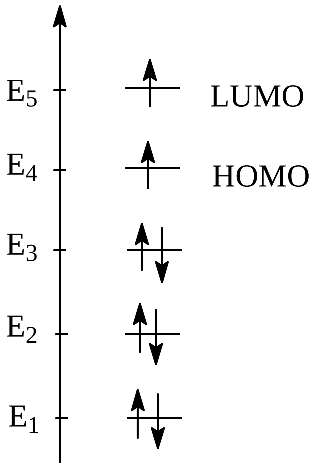
1.

3.1 The general expression is given by:

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

$$\Delta E_{\text{LUMO-HOMO}} = \frac{h^2}{8mL^2}(N+1) \qquad (1)$$

3.2



From Planck's quantum theory:

$$\Delta E = \frac{hc}{\lambda} \qquad (2)$$

λ can be given by:

$$\frac{hc}{\lambda} = \frac{h^2}{8mL^2}(N+1) \;\rightarrow\; \lambda = \frac{8mc}{h} \times \frac{L^2}{(N+1)} \qquad (3)$$

II.

3.3 For **BD:** L = (2×2 +1) 0.140 nm = 5×0.140 · 10^{-9} m = 7 · 10^{-10} m = 7.0 Å

For **HT:** L = (2×3 +1) 0.140 nm = 7×0.140 · 10^{-9} m = 9.8 · 10^{-10} m = 9.8 Å

For **OT:** L = (2×4 +1) 0.140 nm = 9×0.140 · 10^{-9} m = 12.6 · 10^{-10} m = 12.6 Å

3.4 From the general equation (3), the wavelength λ for each of the dyes are given:

$$\lambda = \frac{8mc}{h} \times \frac{L^2}{(N+1)} = \frac{8\,(9.11 \cdot 10^{-31})\,(3 \cdot 10^{8})}{6.626 \cdot 10^{-34}} \frac{L^2}{(N+1)} = 3.30 \cdot 10^{12} \frac{L^2}{(N+1)}$$

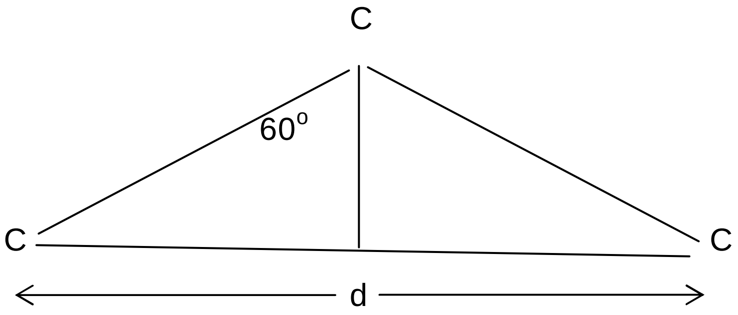
BD: $\lambda = 3.30 \cdot 10^{12} \dfrac{L^2}{(N+1)} = 3.30 \cdot 10^{12} \dfrac{(7 \cdot 10^{-10})^2}{(4+1)} = 3.234 \cdot 10^{-7}\,\text{m} = 323.4\ \text{nm}$

HT: $\lambda = 3.30 \cdot 10^{12} \dfrac{L^2}{(N+1)} = 3.30 \cdot 10^{12} \dfrac{(9.8 \cdot 10^{-10})^2}{(6+1)} = 4.528 \cdot 10^{-7}\,\text{m} = 452.7\ \text{nm}$

OT: $\lambda = 3.30 \cdot 10^{12} \dfrac{L^2}{(N+1)} = 3.30 \cdot 10^{12} \dfrac{(12.6 \cdot 10^{-10})^2}{(8+1)} = 5.82 \cdot 10^{-7}\,\text{m} = 582.0\ \text{nm}$

III.

3.5 The box length can be calculated based on the geometry of the C–C–C chain as follows:

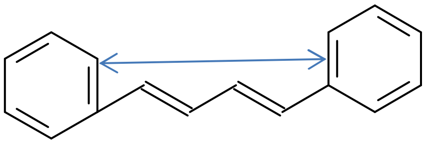


The box length is a combination of a number of the length of $\frac{d}{2}$ which is given by

$$\frac{d}{2} = l_{C\text{-}C} \times \sin 60° = (0.140 \cdot 10^{-9}) \times \sin 60° = 1.21 \cdot 10^{-10}\ \text{m}.$$

Therefore, the box length for the three dye molecules can be calculated as follows:

For BD, the box length is consisted of 5 lengths of $\frac{d}{2}$:



BD: $L = 1.21 \cdot 10^{-10}\ \text{m} \times 5 = 6.05 \cdot 10^{-10}\ \text{m} = 6.05\ \text{Å}$

Similarly, the box length for **HT** has 7 lengths of $\frac{d}{2}$:

HT: $L = 1.21 \cdot 10^{-10}\ \text{m} \times 7 = 8.47 \cdot 10^{-10}\ \text{m} = 8.47\ \text{Å}$

The box length for **OT** has 9 lengths of $\frac{d}{2}$:

OT: $L = 1.21 \cdot 10^{-10}\ \text{m} \times 9 = 10.89 \cdot 10^{-10}\ \text{m} = 10.89\ \text{Å}$

3.6 From equation (3):

$$\lambda = \frac{8mc}{h} \times \frac{L^2}{(N+1)}$$

$$L = \sqrt{\frac{\lambda \times h \times (N+1)}{8\,m\,c}}$$

For BD:

$$L = \sqrt{\frac{\lambda \times h \times (N+1)}{8\,m\,c}} = \sqrt{\frac{(328.5 \cdot 10^{-9})(6.626 \cdot 10^{-34})5}{8(9.11 \cdot 10^{-31})(3 \cdot 10^{8})}} = 7.06 \cdot 10^{-10} = 7.06\ \text{Å}$$

For HT:

$$L = \sqrt{\frac{\lambda \times h \times (N+1)}{8\,m\,c}} = \sqrt{\frac{(350.95 \cdot 10^{-9})(6.626 \cdot 10^{-34})7}{8(9.11 \cdot 10^{-31})(3 \cdot 10^{8})}} = 8.63 \cdot 10^{-10} = 8.63\ \text{Å}$$

For OT:

$$L = \sqrt{\frac{\lambda \times h \times (N+1)}{8\,m\,c}} = \sqrt{\frac{(586.1 \cdot 10^{-9})(6.626 \cdot 10^{-34})9}{8(9.11 \cdot 10^{-31})(3 \cdot 10^{8})}} = 12.64 \cdot 10^{-10} = 12.64\ \text{Å}$$

3.7 The following table shows the values of the box length for the investigated dyes calculated with different methods:

Substance	L = (2k+1)0.140 nm **(1)**	L calculated based on the bent chain **(2)**	L calculated from $\lambda_{exp.}$ **(3)**	Experimental L

BD

7.0

6.05

7.06

7.66

HT

9.8

8.47

8.63

8.64

OT

12.6

10.89

12.64

–

3.8 Method (3) is the best fit.

THEORETICAL PROBLEM 4

Particles in 2, 3 - Dimensional Box

I. In Problem 3, the energy E of particle in one- dimensional box is calculated as:

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

where h is Planck's constant; m is the mass of the particle; L is the box length; n is the quantum number, n = 1, 2, 3…

An electron in a 10 nm one-dimensional box is excited from the ground state to a higher energy level by absorbing a photon of the electromagnetic radiation with a wavelength of $1.374 \cdot 10^{-5}$ m.

4.1 What is the energy gap (ΔE) of the two mentioned states?

4.2 Determine the final energy state for this transition.

II. The treatment of a particle in a one- dimensional box can be extended to a two-dimensional box of dimensions L_x and L_y yielding the following expression for energy:

$$E = \frac{h^2}{8\,m}\left(\frac{\mathrm{n}_x^2}{\mathrm{L}_x^2} + \frac{\mathrm{n}_y^2}{\mathrm{L}_y^2}\right)$$

The two quantum numbers independently can assume only integer values. Consider an electron confined in a two-dimensional box that is L_x = 8.00 nm in the x direction and L_y = 5.00 nm in the y direction.

4.3 What are the quantum numbers for the first three allowed energy levels? Write the first three energy, E_{xy}, in order of increasing energy?

4.4 Calculate the wavelength of light necessary to move an electron from the first excited state to the second excited one.

III. Similarly, the treatment of a particle in a one-dimensional box can be extended to a rectangular box of dimensions L_x, L_y, and L_z, yielding the following expression for energy:

$$E = \frac{h^2}{8\,m}\left(\frac{\mathrm{n}_x^2}{\mathrm{L}_x^2} + \frac{\mathrm{n}_y^2}{\mathrm{L}_y^2} + \frac{\mathrm{n}_z^2}{\mathrm{L}_z^2}\right)$$

The three quantum numbers n_x, n_y, and n_z independently can assume only integer values.

An oxygen molecule is confined in a cubic box of volume 8.00 m^3. Assume that the molecule has an energy of $6.173 \cdot 10^{-21}$ J; temperature $T = 298$ K.

4.5 What is the value of $n = (n_x^2 + n_y^2 + n_z^2)^{1/2}$ for this molecule?

In a rough approximation to estimate the energy gap of this system, assume that the two closest energy levels correspond to n and n + 1.

4.6 What is the energy separation between the levels n and n + 1?

IV. In quantum mechanics, an energy level is said to be degenerate if it corresponds to two or more different measurable states of a quantum system. Consider a particle in a cubic box.

4.7 What is the degeneracy of the level that has energy 21/3 times that of the lowest level?

SOLUTION OF PREPARATORY PROBLEM 4

I.

4.1

$$\Delta E = \mathrm{n}^2 \frac{h^2}{8\,m\,\mathrm{L}^2} - 1^2 \frac{h^2}{8\,m\,\mathrm{L}^2} = \frac{h^2}{8\,m\,\mathrm{L}^2}(\mathrm{n}^2 - 1^2)$$

4.2 According to Planck's equation:

$$\Delta E = \frac{h\,c}{\lambda} = \frac{(6.626 \cdot 10^{-34}\ \mathrm{J\,s})(2.9979 \cdot 10^{8}\ \mathrm{m\,s^{-1}})}{1.374 \cdot 10^{-5}\ \mathrm{m}} = 1.446 \cdot 10^{-20}\ \mathrm{J}$$

$$\Delta E = 1.446 \cdot 10^{-20}\ \mathrm{J} = \frac{(6.626 \cdot 10^{-34}\ \mathrm{J\,s})^2}{8(9.109 \cdot 10^{-31}\ \mathrm{kg})(10.0 \cdot 10^{-9}\ \mathrm{m})^2}\left(\mathrm{n}^2 - 1\right)$$

$$1.446 \cdot 10^{-20}\ \mathrm{J} = 6.025 \cdot 10^{-22}\left(\mathrm{n}^2 - 1\right)$$

$$\rightarrow \mathrm{n}^2 - 1 = 24.00 \ \rightarrow\ \mathrm{n}^2 = 25.00 \ \rightarrow\ \mathbf{n = 5.00}$$

II.

4.3 The quantum numbers are:

Ground state (E_{11}) → $n_x = 1, n_y = 1$

First excited state (E_{21}) → $n_x = 2, n_y = 1$

Second excited state (E_{12}) → $n_x = 1, n_y = 2$

Since the energy levels, E_{xy}, are inversely proportional to L^2, then the $n_x = 2$, $n_y = 1$ energy level will be lower than the $n_x = 1$, $n_y = 2$ energy level since $L_x > L_y$.

The first three energy levels, E_{xy}, in order of increasing energy are: $E_{11} < E_{21} < E_{12}$

4.4 Calculate the wavelength of light necessary to promote an electron from the first excited state to the second excited state.

$E_{21} \rightarrow E_{12}$ is transition. $E_{xy} = \dfrac{h^2}{8\,m}\left(\dfrac{n_x^2}{L_x^2} + \dfrac{n_y^2}{L_y^2}\right)$

$$E_{12} = \frac{h^2}{8\,m}\left(\frac{1^2}{(8.00\cdot 10^{-9}\,\text{m})^2} + \frac{2^2}{(5.00\cdot 10^{-9}\,\text{m})^2}\right) = \frac{1.76\cdot 10^{17}\,h^2}{8\,m}$$

$$E_{21} = \frac{h^2}{8\,m}\left(\frac{2^2}{(8.00\cdot 10^{-9}\,\text{m})^2} + \frac{1^2}{(5.00\cdot 10^{-9}\,\text{m})^2}\right) = \frac{1.03\cdot 10^{17}\,h^2}{8\,m}$$

$$\Delta E = E_{12} - E_{21} = \frac{1.76\cdot 10^{17}\,h^2}{8\,\text{m}} - \frac{1.03\cdot 10^{17}\,h^2}{8\,\text{m}} = \frac{7.3\cdot 10^{16}\,h^2}{8\,\text{m}}$$

$$\Delta E = \frac{(7.3\cdot 10^{16}\,\text{m}^{-2})(6.626\cdot 10^{-34}\,\text{Js})^2}{8\,(9.11\cdot 10^{-31}\,\text{kg})} = 4.4\cdot 10^{-21}\,\text{J}$$

$$\lambda = \frac{h\,c}{\Delta E} = \frac{(6.626\cdot 10^{-34}\,\text{J s})\,(2.998\cdot 10^{8}\,\text{m s}^{-1})}{4.4\cdot 10^{-21}\,\text{J}} = 4.5\cdot 10^{-5}\,\text{m}$$

III.

4.5 $E = \dfrac{(n_1^2 + n_2^2 + n_3^2)\,h^2}{8\,m\,L^2} = \dfrac{n^2\,h^2}{8\,m\,L^2} = 6.173\cdot 10^{-21}\,\text{J}$

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

If $L^3 = 8.00\text{ m}^3$, then $L^2 = 4.00\text{ m}^2$

$$\frac{h^2}{8\,m\,L^2} = \frac{(6.626\cdot 10^{-34})^2}{8\left(\dfrac{0.032}{6.022\cdot 10^{23}}\right)4} = 2.582\cdot 10^{-43}\,\text{J}$$

$$n^2 = \frac{6.173\cdot 10^{-21}}{2.582\cdot 10^{-43}} = 2.39\cdot 10^{22};\quad n = 1.55\cdot 10^{11}$$

4.6 $\Delta E = E_{n+1} - E_n = E_{1.55\times10^{11}+1} - E_{1.55\times10^{11}}$

$$\Delta E = (2n+1)\frac{h^2}{8mL^2} = [2(1.55\cdot10^{11})+1]\frac{h^2}{8mL^2} = 8.00\cdot10^{-31}\,\mathrm{J}$$

IV.

4.7 The energy levels are

$$E_{n_1,n_2,n_3} = \frac{(n_1^2+n_2^2+n_3^2)h^2}{8mL^2} = E_1(n_1^2+n_2^2+n_3^2)$$

where E_1 combines all constants besides quantum numbers. The minimum value for all quantum numbers is 1, so the lowest energy is

$E_{1,1,1} = 3E_1$

The question asks about an energy 21/3 times this amount, namely $21E_1$. This energy level can be obtained by any combination of allowed quantum numbers such that

$$(n_1^2+n_2^2+n_3^2) = 21 = 4^2 + 2^2 + 1^2$$

The degeneracy, then is 6, corresponding to (n_1, n_2, n_3) = (1, 2, 4), (1, 4, 2), (2, 1, 4), (2, 4, 1), (4, 1, 2), or (4, 2, 1).

THEORETICAL PROBLEM 5

Tug of war

"Tug of war is a sport that directly pits two teams against each other in a test of strength. This is also a traditional game of Vietnamese people"

The following table gives the standard molar Gibbs energy at different temperatures for the reaction (1) below:

$$SO_3(g) \rightleftharpoons SO_2(g) + ½\, O_2(g) \qquad (1)$$

T/°C	527	552	627	680	727
Δ_rG^o /kJ·mol^{-1}	21.704	20.626	14.210	9.294	4.854

5.1 Use the Van Hoff's equation to estimate the lnK_{p1} at each temperature.

5.2 Plot ln K_{p1} against 1/T to determine the value of Δ_rH^o in kJ mol^{-1} assuming that $\Delta_{rnx}H^o$ does not vary significantly over the given temperature range.

5.3 Using the best-fit line to plot a lnK_{p1} versus 1/T, determine the K_{p2} for the following reaction (2) at 651.33 °C:

$$2\, SO_3(g) \rightleftharpoons 2\, SO_2(g) + O_2(g) \qquad (2)$$

5.4 An amount of 15.19 g of iron (II) sulfate was heated in an evacuated 1.00 dm^3 container to 651.33 °C, in which the following reactions take place:

$$FeSO_4(s) \rightleftharpoons Fe_2O_3(s) + SO_3(g) + SO_2(g) \qquad (3)$$

$$2\, SO_3(g) \rightleftharpoons 2\, SO_2(g) + O_2(g) \qquad (4)$$

When the system has reached equilibrium, the partial pressure of oxygen is of 21.28 mmHg. Calculate the equilibrium pressure of the gases and the value of K_{p3} for the reaction (3) at equilibrium.

5.5 Calculate the percentage of $FeSO_4$ decomposed?

SOLUTION OF PREPARATORY PROBLEM 5

5.1 $\Delta_{rnx} G = \Delta_{rnx}G^o + RT \ln \frac{p_{SO_2} p_{O_2}^{1/2}}{p_{SO_3}}$

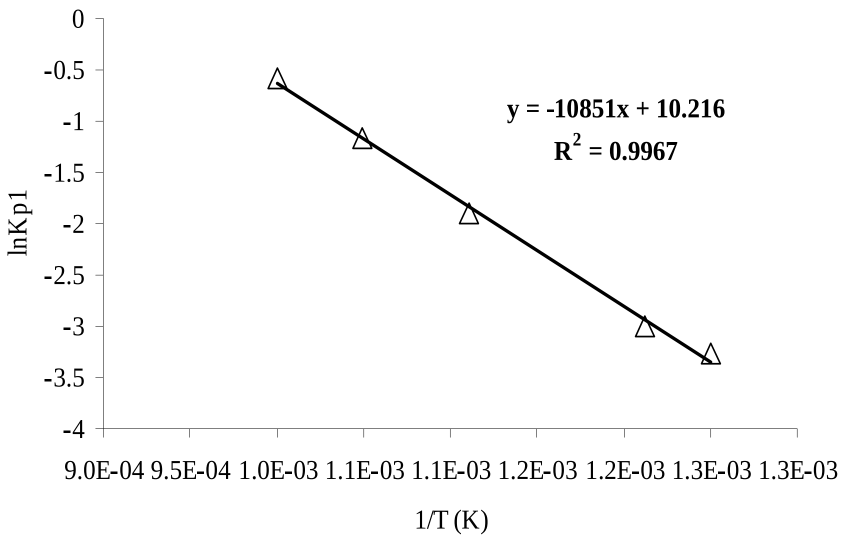
At equilibrium: $\Delta_{rnx} G = \Delta_{rnx}G^o + RT \ln \frac{p_{SO_2} p_{O_2}^{1/2}}{p_{SO_3}} = 0$

$\Delta_r G^o = -RT \ln \frac{p_{SO_2} p_{O_2}^{1/2}}{p_{SO_3}} = -RT \ln K_{p1}$

T / K = T / °C + 273;

T/ K	800	825	900	953	100
ln K_{p1}	–3.263	–3.007	–1.899	–1.173	– 0.591

5.2 Plot lnK_p against 1/T:



Assuming that $\Delta_r H^o$ is temperature independent, the slope of this plot is $-\Delta_r H^o / R$, so that $\Delta_{rnx}H^o$ = 90.2 kJ/mol.

5.3 $2\ SO_3(g) \rightleftharpoons 2\ SO_2(g) + O_2(g)$ (2)

A best-fit equation is $\ln K_{p1} = -10851(1/T) + 10.216$ with R-squared value of 0.9967. We can use this equation to estimate the K_{p1} at (651.33 + 273) = 924.33 K because $\Delta_{rnx}H^o$ is temperature independent.

$\ln K_{p1} = -10851(1/924.33) + 10.216 \rightarrow \ln K_{p1} = -1.523313881 \rightarrow K_{p1} = 0.218$

For reaction (2), the equilibrium constant is expressed as:

$$K_{p2} = \frac{p^2_{SO_2}\, p_{O_2}}{p^2_{SO_3}} = (K_{p1})^2 = (0.218)^2 = 0.047524$$

5.4 Reaction (3): $2\,FeSO_4\,(s) \rightleftharpoons Fe_2O_3\,(s) + SO_3\,(g) + SO_2\,(g)$

Reaction (3):	$2\,FeSO_4\,(s)$ $\rightleftharpoons$	$Fe_2O_3\,(s)$ +	$SO_3\,(g)$ +	$SO_2\,(g)$
Decomposition:	-	-	-	
Equilibrium:			$p - a$	$p + a$

Reaction (4):	$2\,SO_3(g)$ $\rightleftharpoons$	$2\,SO_2\,(g)$ +	$O_2\,(g)$
Initial p:	p	p	0
Change	-a	+a	+a/2
Equilibrium	$p - a$	$p + a$	a/2

At equilibrium: partial pressure of oxygen = 21.28 / 760 = 0.028 atm

a/2 = 0.028 atm → a = 0.056 atm

Equilibrium constant for (4):

$$K_{p4} = \frac{p^2_{SO_2} p_{O_2}}{p^2_{SO_3}} = (K_{p1})^2 = (0.218)^2 = 0.047524$$

$$K_{p4} = \frac{p^2_{SO_2}\, p_{O_2}}{p^2_{SO_3}} = \frac{(p+a)^2(a/2)}{(p-a)^2} = \frac{(p+0.056)^2 0.028}{(p-0.056)^2} = 0.047524$$

$$\frac{(p+0.056)^2\ 0.028}{(p-0.056)^2} = 0.047524$$

$$\rightarrow \frac{(p+0.056)^2}{(p-0.056)^2} = 1.6973$$

$$\rightarrow \frac{(p+0.056)}{(p-0.056)} = 1.303 \quad \rightarrow \quad p + 0.056 = 1.303\,p - 0.073$$

$\rightarrow 0.303\,p = 0.12896 \quad \rightarrow \quad p = 0.425$ atm

Equilibrium constant for (3) $2\,FeSO_4\,(s) \rightleftharpoons Fe_2O_3\,(s) + SO_3\,(g) + SO_2\,(g)$

$K_{p3} = p_{SO3}\ p_{SO2} = (p - a)(p + a) = (0.425 - 0.056)(0.425 + 0.056) = 0.177$

5.5 Calculate the percentage of $FeSO_4$ decomposed?

Amount of substance of SO_3 = SO_2 comes from the decomposition of $FeSO_4$:

$p\ V = n\ R\ T$, $n = pV / RT$ = (0.425)1 / (0.082 × 924.33) = $5.6 \cdot 10^{-3}$ mol

Amount of substance of $FeSO_4$ decomposed = 2 n_{SO3} = 0.0112 mol

Mass of $FeSO_4$ decomposed = 0.0112 ×151.91 = 1.70 g

Percentage of $FeSO_4$ decomposed = (1.70 / 15.19) 100 = 11.19 %.

THEORETICAL PROBLEM 6

Radiochemistry

Zircon ($ZrSiO_4$) is a mineral found abundantly in placer deposits located in the central coast of Vietnam. Besides being widely utilized in the ceramic industry, zircon is also used as a raw material for the manufacture of zircaloy which is used to build fuel rods that hold the uranium dioxide (UO_2) fuel pellets in nuclear reactors. Zircon ore contains a trace amount of uranium, and it is not a viable source of uranium in practice. However, zircon crystals make a perfect storage medium to avoid the loss of uranium and lead (Pb) isotopes because of its stable crystal structure. This allows developing uranium-lead dating method.

There are three naturally occurring decay series:

- The thorium series begins with ^{232}Th and ends up with ^{208}Pb.
- The uranium series (also referred to as the uranium-radium series) is headed by ^{238}U. The half-life ($t_{1/2}$) of ^{238}U is $4.47 \cdot 10^9$ years.
- The actinium series is headed by ^{235}U with the half-life of $7.038 \cdot 10^8$ years.

Four stable isotopes of Pb exist in nature: ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. The natural abundance of each isotope is shown in the following table.

^{204}Pb	^{206}Pb	^{207}Pb	^{208}Pb
1.4	24.1	22.1	52.4

An analysis of a zircon mineral sample gives the following mass ratios of U and Pb isotopes:

$$m(^{238}\text{U}) : m(^{235}\text{U}) : m(^{206}\text{Pb}) : m(^{204}\text{Pb}) = 99.275 : 0.721 : 14.30 : 0.277$$

6.1 Indicate the stable isotope of Pb which is not involved in the above decay series.

6.2 Determine the mass ratio of ^{238}U to ^{235}U when the zircon mineral was first formed. Assume that the mineral already contained natural Pb right at the onset of its formation.

Production of uranium from low-grade will encounter many difficulties, notably large concentration of impurities and low concentrations of uranium in leach solutions. Various technological advances have been applied to overcome the aforementioned problems; these include fractional precipitation, liquid-liquid extraction, or ion exchange methods.

In an experiment to extract uranium from sample of low uranium content using diluted H_2SO_4, in the preliminary treated leach solutions, the concentration of uranyl sulfate (UO_2SO_4) is 0.01 mol dm^{-3} and the concentration of iron(III) sulfate ($Fe_2(SO_4)_3$) goes up to 0.05 mol dm^{-3}. The separation of uranium from iron and other impurities can be carried out by the fractional precipitation method.

6.3 Calculate the pH necessary to precipitate 99% of Fe^{3+} without losing uranium ions. Assume that the adsorption of uranium onto $Fe(OH)_3$ is negligible. Under the experimental conditions, the solubility product values for $UO_2(OH)_2$ and $Fe(OH)_3$ are $1.0 \cdot 10^{-22}$ and $3.8 \cdot 10^{-38}$, respectively.

6.4 One of the proper methods to obtain a rich uranium solution is the liquid-liquid extraction with the organic phase containing the extracted agent of tributylphosphate (TBP) diluted in kerosene. When extracting uranium in the form of uranyl nitrate ($UO_2(NO_3)_2$) under appropriate conditions, the relationship between the concentrations of uranium in water and organic phases is given by:

Distribution coefficient: $D = \dfrac{c_{org.}}{c_{aq}} = 10$

where: c_{org} and c_{aq} are the equilibrium concentrations (mol dm^{-3}) of $UO_2(NO_3)_2$ in organic and aqueous phases, respectively.

Calculate the mole percentage (in comparison with the initial concentration) of $UO_2(NO_3)_2$ remaining in the aqueous phase after extracting 1.0 dm^3 of the solution (with an initial concentration of 0.01 mol dm^{-3}) with 500 cm^3 of organic solvent.

6.5 Propose a scheme to extract 96 % of $UO_2(NO_3)_2$ from 1.0 dm^3 of the aqueous phase into 500 cm^3 of the organic phase. Assume that the distribution coefficient remains constant throughout the extraction process (D = 10).

SOLUTION OF PREPARATORY PROBLEM 6

6.1

^{204}Pb	^{206}Pb	^{207}Pb	^{208}Pb
x			

6.2 Assume that the mineral initially contained $n_{1,0}$ moles of ^{238}U, $n_{2,0}$ moles of ^{206}Pb, and n_3 moles of ^{204}Pb; and at present, it contains n_1 moles of ^{238}U, n_2 moles of ^{206}Pb, and n_3 moles of ^{204}Pb (this isotope is not generated by the decay of ^{238}U and ^{235}U). The age of the zircon mineral is usually very large, and we can consider that the century equilibrium for the decay process has been reached (i.e. loss of 1 mole of ^{238}U will lead to formation of 1 mole of ^{206}Pb). By conservation of mass, we have the following equation:

$$n_1 + n_2 = n_{1,0} + n_{2,0} \qquad (1)$$

Dividing (1) by n_3:

$$n_1/n_3 + n_2/n_3 = n_{1,0}/n_3 + n_{2,0}/n_3$$

$$\rightarrow\ n_2/n_3 = n_{1,0}/n_3 - n_1/n_3 + n_{2,0}/n_3 \qquad (2)$$

In addition, we have $n_{1,0} = n_1 e^{\lambda t}$, where λ is the decay constant of ^{238}U, and t is the age of the mineral,

$$\rightarrow n_2 / n_3 = n_1 e^{\lambda t} / n_3 - n_1 / n_3 + n_{2,0} / n_3 = (n_1 / n_3)(e^{\lambda t} - 1) + n_{2,0} / n_3 \qquad (3)$$

$$\rightarrow\ e^{-\lambda t} - 1 = \frac{n_2/n_3 - n_{2,0}/n_3}{n_1/n_3}$$

$$\rightarrow\ e^{\lambda t} = 1 + \frac{n_2/n_3 - n_{2,0}/n_3}{n_1/n_3}$$

$$\rightarrow t = \frac{1}{\lambda}\ln\left(1 + \frac{n_2/n_3 - n_{2,0}/n_3}{n_1/n_3}\right) \qquad (4)$$

According to the data given:

$$\frac{n_2}{n_3} = \frac{\frac{14.30}{206}}{\frac{0.277}{204}} = 51.12; \qquad \frac{n_{2,0}}{n_3} = \frac{\frac{24.10}{206}}{\frac{1.4}{204}} = 17.05$$

$$\frac{n_1}{n_3} = \frac{\dfrac{99.275}{238}}{\dfrac{0.277}{204}} = 307.19$$

$$t = \frac{4.47 \cdot 10^9}{0.693} \ln(1 + \frac{51.12 - 17.05}{307.19}) = 6.78 \cdot 10^8 \text{ years}$$

$$m_0(^{235}U) = 0.721 \times e^{\frac{0.693}{7.038 \times 10^8} \times 6.78 \times 10^8} = 1.406 \text{ g}$$

$$m_0(^{238}U) = 99.275 \times e^{\frac{0.693}{4.47 \times 10^8} \times 6.78 \times 10^8} = 110.28 \text{ g}$$

$m_0(^{235}U)/\ m_0(^{238}U)$ = 1.406 / 110.28 = 0.0127

6.3 After 99% of Fe^{3+} precipitated, the concentration of the remaining Fe^{3+} in the solution is:

$[Fe^{3+}] = 2 \times 0.05 \cdot 10^{-2} = 1 \cdot 10^{-3}$ mol dm^{-3}

The concentration of hydroxide ions necessary to maintain a Fe^{3+} concentration of $1 \cdot 10^{-3}$ mol dm^{-3} in the solution is:

$$[OH^-] = \left(\frac{K_{s(Fe(OH)_3)}}{[Fe^{3+}]}\right)^{\frac{1}{3}} = \left(\frac{3.8 \cdot 10^{-38}}{10^{-3}}\right)^{\frac{1}{3}} = (38)^{\frac{1}{3}} \cdot 10^{-12} \text{ mol dm}^{-3}$$

Thus, the pH value of the solution can be calculated as follows:

$pH = -\log\{10^{-14} / [(38)^{1/3} \cdot 10^{-12}]\} = 2 + (1/3) \log 38 = 2.53$

At this pH, the reaction quotient of the dissociation of $UO_2(OH)_2$ in 0.01 mol dm^{-3} of solution is:

$[UO_2^{2+}][OH^-]^2 = 0.01 \times [(38)^{1/3} \cdot 10^{-12}]^2 = 1.13 \cdot 10^{-25} < 10^{-22}$

Since the ionic product is much smaller than the solubility product of $UO_2(OH)_2$, we can conclude that uranium cannot precipitate under these conditions.

6.4 Volume ratio of the two phases: V_{aq} / V_{org} = 1000 : 500 = 2

Let x represent the equilibrium concentration of $UO_2(NO_3)_2$ in the aqueous phase.

Let c_o represent the initial concentration of $UO_2(NO_3)_2$ in the organic phase.

The equilibrium concentration of $UO_2(NO_3)_2$ in the organic phase is calculated as follows:

$c_{org} = (V_{aq} / V_{org})\ (c_0 - x)$

$$D = \frac{c_{org}}{x} = \frac{2(c_o - x)}{x} = 10 \qquad (6)$$

$x : c_o = 1 : 6 = 16.67$ %.

6.5. 500 cm^3 of organic solvent may be divided into n equal portions for extraction.

Volume ratio of the two phases: $V_{aq} / V_{org} = 1000 : (500/n) = 2\,n$

- After the first extraction:

$$D = \frac{c_{org}}{x_1} = \frac{2\,n\,(c_o - x_1)}{x_1} = 10 \qquad (7)$$

$$\rightarrow \quad x_1 = \frac{2\,n\,c_o}{D + 2\,n} \qquad (8)$$

- For the second extraction, the initial concentration of the aqueous phase is x_1, while the equilibrium concentration is x_2. Using equation (8), we replace x_2 with x_1, and x_1 with C_o to obtain the following expression:

$$x_2 = \frac{2\,n\,x_1}{D + 2\,n} = \left(\frac{2\,n}{D + 2n}\right)^2 c_o \qquad (9)$$

- After n extractions, the concentration of $UO_2(NO_3)_2$ remaining in the aqueous phase is:

$$x_n = \left(\frac{2\,n}{D + 2\,n}\right)^n c_o \qquad (10)$$

% $UO_2(NO_3)_2$ remaining in the aqueous phase after n extractions is:

$$\frac{x_n}{c_0} 100\,\% = \left(\frac{2\,n}{D + 2\,n}\right)^n 100\ \%$$

$n =$	1	2	3	4	5	6
$\left(\frac{2\,n}{D + 2\,n}\right)^n$ 100 %	16.67	8.16	5.27	3.9	3.1	2.63

$$n = 5 \rightarrow \frac{x_n}{c_0} 100\% = \left(\frac{2\,n}{D + 2n}\right)^n < 4\%$$

Thus, the optimal approach is to divide 500 cm3 of solvent into 5 portions and extract 5 times.

Other schemes are acceptable, if all calculations and justifications are reasonable.

THEORETICAL PROBLEM 7

Applied thermodynamics

I. In applied thermodynamics, Gibbs free energy plays an important role and can be calculated according to the following expression:

$\Delta G^o_{298} = \Delta H^o_{298} - T\Delta S^o_{298}$

ΔG^o_{298} - standard free energy change

ΔH^o_{298} - standard enthalpy change

ΔS^o_{298} - standard entropy change

The burning of graphite is represented by two reactions:

$C(\text{graphite}) + ½\ O_2\ (g) \rightarrow CO\ (g)$ (1)

$C(\text{graphite}) + O_2\ (g) \rightarrow CO_2\ (g)$ (2)

The dependence of ΔH^o, ΔS^o on temperature is as follows:

Reaction (1): $\Delta H^o_T\ (1)\ (J\cdot mol^{-1}) = –112298.8 + 5.94T$;

$\Delta S^o_T\ (1)\ (J\cdot K^{-1}\cdot mol^{-1}) = 54.0 + 6.21\ \ln T$

Reaction (2): $\Delta H^o_T\ (2)\ (J\cdot mol^{-1}) = – 393740.1 + 0.77\ T$;

$\Delta S^o_T\ (2)\ (J\cdot K^{-1}\cdot mol^{-1}) = 1.54 – 0.77\ \ln T$

Based on the above data:

7.1 Derive the expression for the Gibbs free energy as a function of temperature, $\Delta G^o_T = f(T)$ for each reaction.

7.2 Predict the changes of ΔG^o_T with an increase in temperature.

II. Assume that at 1400 °C, during the course of reactions (1) and (2), CO gas might continue to react with O_2 to form the final product CO_2.

7.3 Write down the reaction (3) for the formation of CO_2 from CO gas.

7.4 Calculate $\Delta G^o_T\ (3)$.

7.5 Determine the equilibrium constant K_p for reaction (3) at the given temperature.

III. In an experiment, NiO powder and CO gas were placed in a closed container which was then heated up to 1400 °C. When the system reached equilibrium, there were four species present: NiO(*s*), Ni(*s*), CO(*g*) and CO_2(*g*). The mole percentages of CO and CO_2 are 1 % and 99 %, respectively, and the pressure of the system is 1.0 bar (10^5 Pa).

7.6 Write down the reactions in the above experiment.

7.7 Based on the experimental results and the above thermodynamic data, calculate the pressure of O_2 in the equilibrium with NiO and Ni at 1400 °C.

SOLUTION OF PREPARATORY PROBLEM 7

I.

7.1 Based on the above data:

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

Reaction (1): $\Delta G^o_T(1) = (-112298.8 + 5.94\,T) - T(54.0 + 6.21 \ln T)$

$\Delta G^o_T(1) = -112298.8 - 48.06\,T - 6.21\,T \ln T$

$\Delta G^o_T(1)$ decreases with an increase in temperature.

Reaction (2): $\Delta G^o_T(2) = (-393740.1 + 0.77\,T) - T(1.54 - 0.77 \ln T)$

$\Delta G^o_T(2) = -393740.1 - 0.77\,T + 0.77\,T \ln T$

7.2 $\Delta G^o_T(2)$ increases with an increase in temperature.

II.

7.3 $C(\mathit{graphite}) + ½\,O_2(g) \rightarrow CO(g)$ (1)

$\underline{C(\mathit{graphite}) + O_2(g) \rightarrow CO_2(g)}$ (2)

$(2) - (1) \rightarrow CO(g) + ½\,O_2 \rightarrow CO_2(g)$ (3)

We have, $\Delta G^o_T(3) = \Delta G^o_T(2) - \Delta G^o_T(1)$

7.4 Substitute the values in:

$\Delta G^o_T(3) = (-393740.1 - 0.77\,\mathrm{T} + 0.77\,T \ln T) - (-112298.8 - 48.06\,T - 6.21 T \ln T)$

$\Delta G^o_T(3) = -281441.3 + 47.29\,T - 6.98\,T \ln T$

At 1673 K: $\Delta G^o_T(3) = -115650$ J/mol

7.5 Since $\Delta G^o = -RT \ln K_p$, the equilibrium constant K_p for reaction (3) can be calculated as follows:

$$\ln K_{p,1673}(3) = -\frac{\Delta G^0_{1673}(3)}{RT} = \frac{115650}{8.314 \times 1673} = 8.313457$$

$\rightarrow$ $\mathrm{K}_{p,1673}(3) = 4083$

III.

7.6 $CO(g) + \frac{1}{2}\,O_2(g) \rightarrow CO_2(g)$ (3)

$\underline{NiO(s) + CO(g) \rightarrow Ni(s) + CO_2(g)}$ (4)

(4) – (3) $NiO(s) \rightarrow Ni(s) + \frac{1}{2}\,O_2(g)$ (5)

7.7 At 1673 K, we have:

For reaction (4): $K_p(4) = \dfrac{p_{CO_2}}{p_{CO}} = \dfrac{99}{1}$

For reaction (3): $K_p(3) = \dfrac{p_{CO_2}}{p_{CO}\,p_{O_2}^{1/2}} = 4083$ or $p_{O_2}^{1/2} = \dfrac{p_{CO_2}}{p_{CO}\,4083} = \dfrac{K_p(4)}{4083} = \dfrac{99}{4083}$

For reaction (5): $K_p(5) = p_{O_2}^{1/2} = \dfrac{p_{CO_2}}{p_{CO}\,K_p(3)} = \dfrac{K_p(4)}{K_p(3)}$ or

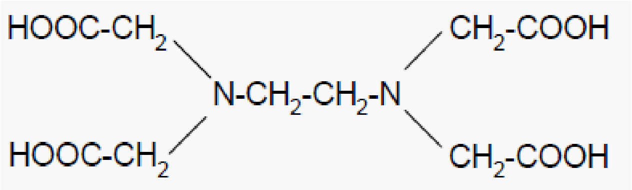
$$K_p(5) = p_{O_2}^{1/2} = \frac{K_p(4)}{K_p(3)} = \frac{99}{4083} = 0.024247 = 2.4247 \cdot 10^{-2}$$

Hence, $p_{O_2} = \left[K_p(5)\right]^2 = \left(2.4247 \cdot 10^{-2}\right)^2$ and $p_{O_2} = 5.88 \times 10^{-4}\ \text{bar} = 58.8\ \text{Pa}$

THEORETICAL PROBLEM 8

Complex compounds

Ethylenediamine tetraacetic acid (EDTA) is used as a reagent to titrate the metal ions in the complexometric titration. EDTA is a tetraprotic acid, abbreviated as H_4Y, with the structure:



As EDTA is sparingly soluble in water, a more soluble sodium form, Na_2H_2Y, is usually used and H_2Y^{2-} is commonly known as EDTA. EDTA forms strong 1:1 complexes with most metal ions M^{n+}.

I.

8.1 How many atoms of an EDTA molecule are capable of binding with the metal ion upon complexation?

Check in the appropriate box.

☐	☐	☐	☐
2	4	6	8

8.2 Draw the structure of the complex of a metal ion M^{2+} with EDTA.

II. Complexation reaction between Y^{4-} form of EDTA and metal ion M^{n+} has a large formation constant (stability constant) β:

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{(4-n)-} \qquad \beta = \frac{[MY^{(4-n)-}]}{[M^{n+}][Y^{4-}]}$$

Besides complexation reaction between Y^{4-} form of EDTA and metal ion M^{n+}, other processes in the solution also develop such as formation of hydroxo complexes of the metal ion, acid-base equilibrium of H_2Y^{2-}… To account for such processes conditional formation constant *β*' is used for the calculations. *β*' is determined from *β* as the following expression:

$$\beta' = \beta\, \alpha_{M^{n+}}\, \alpha_{Y4-}$$

where: $\alpha_{Y^{4-}}$ and $\alpha_{M^{n+}}$ are fractions of Y^{4-} ($\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[Y]'}$) and free metal ion M^{n+} ($\alpha_{M^{n+}} = \frac{[M]}{[M]'}$), with $[Y]'$ and $[M]'$ being the total concentrations of all forms of Y^{4-} and M^{n+}, excluding $MY^{(4-n)-}$. Given that: H_4Y has $pK_{a1} = 2.00$; $pK_{a2} = 2.67$; $pK_{a3} = 6.16$; and $pK_{a4} = 10.26$ *(pK$_a$ values for H_5Y^+ and H_6Y^{2+} are ignored)*.

$$pK_{s(Mg(OH)_2)} = 10.95; \quad \log\beta_{MgY^{2-}} = 8.69$$

$Mg^{2+} + H_2O \rightleftharpoons MgOH^+ + H^+$ $\quad {}^*\beta = 1.58\times10^{-13}$; $\quad$ ($pK_a = -\log K_a$; $\;pK_s = -\log K_s$)

In a typical experiment, 1.00 cm^3 of $MgCl_2$ solution (c = 0.10 mol dm^{-3}) and 1.00 cm^3 of Na_2H_2Y solution (c = 0.10 mol dm^{-3}) are mixed together. pH of the resulting solution is adjusted to 10.26 by an NH_3/NH_4^+ buffered solution.

8.3 Calculate conditional formation constant (β') of the MgY^{2-} complex at pH = 10.26 given that acid-base equilibrium of H_2Y^{2-} and formation of mononuclear hydroxo complex of Mg^{2+} occur in the solution.

8.4 Does the $Mg(OH)_2$ precipitate in this experiment? Check in the appropriate box.

☐ Precipitation

☐ No precipitation

III. In order to titrate metal ions by EDTA, the conditional formation constant (β') of the complex metal – EDTA ($MY^{(4-n)-}$) must be large enough, usually $\beta' \geq 1.00 \cdot 10^8 - 1.00 \cdot 10^9$. To determine the concentrations of Mn^{2+} and Hg^{2+} in an analytical sample, two experiments are carried out.

Experiment 1: Add 25.00 cm^3 of 0.040 mol dm^{-3} EDTA solution to 20.00 cm^3 of the analytical solution. Adjust the pH of the resulting solution to 10.50. Titrate the excess EDTA with a suitable indicator; 12.00 cm^3 of 0.025 mol dm^{-3} Mg^{2+} solution is consumed.

Experiment 2: Dissolve 1.400 g of KCN in 20.00 cm^3 of the analytical solution (assuming that the volume is unchanged upon dissolution) and then add 25.00 cm^3 of 0.040 mol dm^{-3} EDTA solution. Titrate the excess EDTA in the resulting mixture at the pH of 10.50; 20.00 cm^3 of 0.025 mol dm^{-3} Mg^{2+} solution is consumed.

8.5 Prove that: in the experiment 2, Hg^{2+} cannot be determined by titration with EDTA in the presence of KCN in solution (or Hg^{2+} is masked in the complex form of $Hg(CN)_4^{2-}$).

8.6 Write down chemical equations for the reactions in the two experiments and calculate molar concentrations of Mn^{2+} and Hg^{2+} in the analytical solution. Given that:

$$\log\beta_{HgY^{2-}} = 21.80; \quad \log\beta_{Hg(CN)_4^{2-}} = 38.97; \quad pK_{a(HCN)} = 9.35$$

(Other processes of Hg^{2+} are ignored; the pK_a values of H_4Y are provided in question 2).

IV. In the titration of polyprotic acids or bases, if the ratios of consecutive dissociation constants exceed $1.00 \cdot 10^4$, multiple titrations are possible with an error less than 1%. To ensure the allowed error, only acids or bases with equilibrium constants larger than $1.00 \cdot 10^{-9}$ can be titrated. To find the end-point, pH range of the indicator must be close to that of the equivalence point (pH_{EP}); the point at which the stoichiometric amounts of analyte and titrant has reacted. Titrate 10.00 cm^3 of 0.25 mol dm^{-3} Na_2H_2Y solution by 0.20 mol dm^{-3} NaOH solution in a typical experiment.

8.7 Write down the chemical equation for the titration reaction.

8.8 Determine the value of pH_{EP}.

8.9 Choose the most suitable indicator (check in the appropriate box) for the above titration from the following: bromothymol blue (pH = 7.60); phenol red (pH = 8.20); phenolphtalein (pH = 9.00).

☐	☐	☐
Bromothymol blue	Phenol red	Phenolphtalein

8.10 Titration error *q* defined as the difference between the titrant amount added and the titrant amount needed to reach the equivalence point is expressed as:

$$q = \frac{c_{NaOH}V_1 - c_{NaOH}V_2}{c_{NaOH}V_2} \times 100\ \% = \frac{V_1 - V_2}{V_2} \times 100\ \%$$

where c_{NaOH} is the NaOH concentration; V_1: end-point volume of NaOH; V_2: equivalence point volume of NaOH.

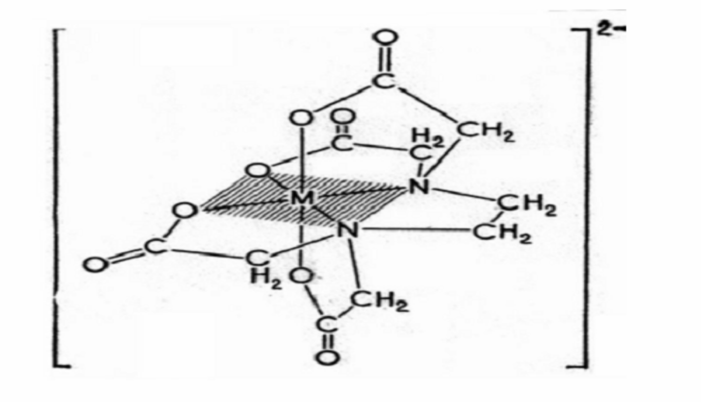
Calculate the consumed volume of NaOH solution and the titration error if the final pH is 7.60.

SOLUTION OF PREPARATORY PROBLEM 8

I. How many atoms of EDTA are capable of binding with the metal ions upon complexation?

8.1	☐	☐	☑	☐
	2	4	6	8

8.2



II.

8.3 Let [H$^+$] be h and at pH = 10.26:

$$\beta' = \beta\,\alpha_{Mg^{2+}}\alpha_{Y^{4-}}$$

$$= \beta\,\frac{1}{1+{}^{*}\beta\,h^{-1}}\,\frac{K_{a4}}{h+K_{a4}} = 10^{8.69}\,\frac{1}{1+1.58\cdot10^{-13}\times10^{10.26}}\,\frac{10^{-10.26}}{10^{-10.26}+10^{-10.26}}$$

$$\beta' = \beta\,\alpha_{Mg^{2+}}\alpha_{Y^{4-}} = 10^{8.69}\times1\times0.5 = 2.45\cdot10^{8}$$

8.4 At pH = 10.26:

$(Mg^{2+})' \ + \ (Y^{4-})' \rightarrow MgY^{2-}$

0.05 0.05

\- \- 0.05

$MgY^{2-} \rightleftharpoons (Mg^{2+})' \ + \ (Y^{4-})' \qquad (\beta')^{-1} = (2.45\cdot10^{8})^{-1}$

$0.05 - x \qquad x \qquad x$

$$c_{Mg^{2+}} = c'_{Mg^{2+}} = x = 1.43 \cdot 10^{-5} (\text{mol dm}^{-3})$$

$$c_{Mg^{2+}}[OH^-]^2 = 1.43 \cdot 10^{-5}\left(10^{-3.74}\right)^2 = 10^{-12.32} < K_{s(Mg(OH)_2} = 10^{-10.95}$$

Hence no $Mg(OH)_2$ precipitate appears

III.

8.5

$$[CN^-] = c_{CN^-}\frac{K_a}{h + K_a} = \frac{1.400 \times 1000}{65 \times 20.00}\,\frac{10^{-9.35}}{10^{-10.50} + 10^{-9.35}} = 1.00\,(M)$$

$$\alpha_{Hg^{2+}} = \frac{1}{1 + \beta_{Hg(CN)_4^{2-}}[CN^-]^4} = \frac{1}{1 + 10^{38.97} \times 1^4} = 1.00 \times 10^{-38.97}$$

$$\alpha_{Y^{4-}} » \frac{K_{a4}}{h + K_{a4}} = \frac{10^{-10.26}}{10^{-10.50} + 10^{-10.26}} = 0.635$$

$$\beta'_{HgY^{2-}} = \beta_{HgY^{2-}}\alpha_{Hg^{2+}}\alpha_{Y^{4-}} = 10^{21.80}(1.00 \times 10^{-38.97})0.635 = 4.29 \cdot 10^{-18}$$

$\beta'_{HgY^{2-}}$ is very small, Hg^{2+} is cannot be titrated in the experiment 2.

8.6 Chemical equations:

Experiment 1:
$Hg^{2+} + Y^{4-} \rightarrow HgY^{2-}$
$Mn^{2+} + Y^{4-} \rightarrow MnY^{2-}$
$Mg^{2+} + Y^{4-}(\text{excess}) \rightarrow MgY^{2-}$

$(c_{Mn^{2+}} + c_{Hg^{2+}}) \times 20.00 = 25.00 \times 0.040 - 12.00 \times 0.025$ (1)

Experiment 2:
$Hg^{2+} + 4CN^- \rightarrow Hg(CN)_4^{2-}$
$Mn^{2+} + Y^{4-} \rightarrow MnY^{2-}$
$Mg^{2+} + Y^{4-}(\text{excess}) \rightarrow MgY^{2-}$

$c_{Mn^{2+}} \times 20.00 = 25.00 \times 0.040 - 20.00 \times 0.025$ (2)

According to (1) and (2): $c_{Mn^{2+}} = 0.025$ mol dm^{-3}; $c_{Hg^{2+}} = 0.010$ mol dm^{-3}

IV.

8.7 As K_{a3} / K_{a4} > 1 · 10^4 and $K_{a4} < 10^{-9}$ only one endpoint can be determined for the titration of H_2Y^{2-}:

Titration reaction: $H_2Y^{2-} + OH^- \rightarrow HY^{3-} + H_2O$

8.8 $pH_{EP} = pH(HY^{3-}) = (pK_{a3} + pK_{a4}) / 2 = 8.21$

8.9 $pH_{EP} = pH_{(phenol\ red)}$, hence the most suitable indicator is phenol red

8.10 If the final pH is 7.60 the percentage of H_2Y^{2-} that is titrated:

$$\frac{[HY^{3-}]}{[H_2Y^{2-}]+[HY^{3-}]} = \frac{K_{a3}}{[H^+]+K_{a3}}100 = \frac{10^{-6.16}}{10^{-6.16}+10^{-7.60}}100 = 96.5\%$$

The volume of NaOH solution needed to reach pH of 7.60 is:

$V_{NaOH} = V_1 = (0.25 \times 10 \times 0.965) / 0.2 = 12.06\ (cm^3)$

$V_{EP} = V_2 = (0.25 \times 10) / 0.20 = 12.50\ (cm^3)$

$$q = \frac{12.06 - 12.50}{12.50} \times 100\% \text{ » } -3.5\,\%$$

(As 96.5% of H_2Y^{2-} is titrated, 3.5% of the analyte has not been titrated, or the error q = - 3.5%.)

THEORETICAL PROBLEM 9

Lead compounds

I. Consider the following nuclide: ^{209}Bi(I), ^{208}Pb(II), ^{207}Pb(III), ^{206}Pb(IV).

9.1 Which nuclide is the last member of the decay series for ^{238}U? Check in the appropriate box.

☐ ☐ ☐ ☐

I II III IV

II. There are three natural decay series. They begin with Th-232(I), U-238(II), U-235(III) and end with Pb-208, Pb-206, Pb-207.

9.2 In which decay chain are there 6 α-decays and 4 β-decays? Choose the correct answer by checking in the appropriate box.

☐ ☐ ☐ ☐

I II III none

(c = mol dm^{-3})

III. $Pb(NO_3)_2$ solution is slowly added into 20.00 cm^3 of a mixture consisting of Na_2SO_4 (c = 0.020 mol dm^{-3}); $Na_2C_2O_4$ ($c = 5.0 \cdot 10^{-3}$ mol dm^{-3}); KI ($c = 9.7 \cdot 10^{-3}$ mol dm^{-3}); KCl (c = 0.05 mol dm^{-3}) and KIO_3 (c = 0.0010 mol dm^{-3}). When the bright yellow precipitate of PbI_2 begins to form, 21.60 cm^3 of $Pb(NO_3)_2$ solution is consumed.

Use the following data: $pK_s(PbSO_4) = 7.66$; $pK_s(Pb(IO_3)_2) = 12.61$; $pK_s(PbI_2) = 7.86$; $pK_s(PbC_2O_4) = 10.05$; $pK_s(PbCl_2) = 4.77$. (Other processes of the ions are ignored).

9.3 Determine the order of precipitation?

9.4 Calculate the concentration of $Pb(NO_3)_2$ solution?

IV. One of the common reagents to detect Pb^{2+} species is K_2CrO_4, giving yellow precipitate $PbCrO_4$, which is soluble in excess of NaOH. The solubility of $PbCrO_4$ depends not only on pH but also on the presence of coordinating species.

9.5 Calculate the solubility product K_{sp} of $PbCrO_4$ if the solubility of $PbCrO_4$ in acetic acid solution (c = 1 mol dm^{-3}) is $s = 2.9 \cdot 10^{-5}$ mol dm^{-3}.

Use the following data:

pK_a(CH_3COOH) = 4.78; log β($Pb(CH_3COO)^+$ = 2.68;

log β($Pb(CH_3COO)_2$ = 4.08; pK_a($HCrO_4^-$) = 6.50

$Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+$ $^*\beta = 10^{-7.8}$

$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\ CrO_4^{2-} + 2\ H^+$ $K = 10^{-14,64}$

V. Lead-acid battery, commonly known as lead battery consists of two lead plates a positive electrode covered with a paste of lead dioxide and a negative electrode made of sponge lead. The electrodes are submersed in an electrolyte consisting of water and sulfuric acid H_2SO_4.

9.6 Write the chemical equations for processes on each electrode, overall reaction as the battery discharges and the cell diagram.

VI.

9.7 Calculate the values of $E^0(\mathrm{PbSO_4/Pb})$ and $E^0(\mathrm{PbO_2/PbSO_4})$

9.8 The potential V of the lead battery if $c(\mathrm{H_2SO_4}) \approx 1.8$ mol dm^{-3}.

The following data are given: $E^0(\mathrm{Pb^{2+}/Pb}) = -0.126$ V; $E^0_{\mathrm{PbO_2/Pb^{2+}}} = 1.455$ V;

$\mathrm{p}K_\mathrm{a}(\mathrm{HSO_4^-}) = 2.00$; $\mathrm{p}K_\mathrm{s}(\mathrm{PbSO_4}) = 7.66$; at 25 °C: $2.303\dfrac{RT}{F} = 0.0592$ V

SOLUTION OF PREPARATORY PROBLEM 9

I.

9.1 The correct answer is IV.

II.

9.2 The correct answer is I.

III.

9.3 Condition for precipitation of:

$$\mathrm{PbSO_4}:\ c_{\mathrm{Pb^{2+}}(1)} \geq \frac{10^{-7.66}}{0.02} = 1.09 \cdot 10^{-6}\ (\mathrm{mol\,dm^{-3}})$$

PbC_2O_4 : $c_{Pb^{2+}(2)} \geq \dfrac{10^{-10.05}}{5.0 \cdot 10^{-3}} = 1.78 \cdot 10^{-8}\ \text{mol dm}^{-3}$

PbI_2 : $c_{Pb^{2+}(3)} \geq \dfrac{10^{-7.86}}{(9.7 \cdot 10^{-3})^2} = 1.47 \cdot 10^{-4}\ \text{mol dm}^{-3}$

$Pb(IO_3)_2$: $c_{Pb^{2+}(4)} \geq \dfrac{10^{-12.61}}{(0.001)^2} = 2.45 \cdot 10^{-7}\ \text{mol dm}^{-3}$

$PbCl_2$: $c_{Pb^{2+}(5)} \geq \dfrac{10^{-4.8}}{(0.05)^2} = 6.34 \cdot 10^{-3}\ \text{mol dm}^{-3}$

$c_{Pb^{2+}(2)} < c_{Pb^{2+}(4)} < c_{Pb^{2+}(1)} < c_{Pb^{2+}(3)} < c_{Pb^{2+}(5)} \rightarrow$

The order of precipitation: PbC_2O_4, $Pb(IO_3)_2$, $PbSO_4$, PbI_2 and $PbCl_2$.

9.4 When PbI_2 begins to precipitate (assume I^- has not reacted)

$$[SO_4^{2-}] = \frac{K_{s(PbSO_4)}}{c_{Pb^{2+}(3)}} = \frac{10^{-7.66}}{1.47 \cdot 10^{-4}} = 1.49 \cdot 10^{-4}$$

$$= \sqrt{K_{s(PbSO_4)}} = 1.48 \cdot 10^{-4} = s_{PbSO_4}$$

(s is the solubility of $PbSO_4$ in saturated solution). Hence PbC_2O_4, $Pb(IO_3)_2$ and $PbSO_4$ have precipitated completely.

$\rightarrow 21.60 \times c_{Pb(NO_3)_2} = 20.00 \times (c_{C_2O_4^{2-}} + 2\ c_{IO_3^-} + c_{SO_4^{2-}})$

$= 20.00\ (5.0 \cdot 10^{-3} + 2 \times 0.0010 + 0.020)$

$\rightarrow c_{Pb(NO_3)_2} = 0.025\ \text{mol dm}^{-3}$

IV.

9.5 $PbCrO_4 \rightleftharpoons Pb^{2+} + CrO_4^{2-}$ $\qquad K_s$

$c \qquad s \qquad s$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ $\qquad K_a = 10^{-4.76}$

$Pb^{2+} + CH_3COO^- \rightleftharpoons Pb(CH_3COO)^+$ $\qquad \beta_1 = 10^{2.68}$

$Pb^{2+} + 2\ CH_3COO^- \rightleftharpoons Pb(CH_3COO)_2$ $\qquad \beta_2 = 10^{4.08}$

$Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+$ $\qquad {}^*\beta = 10^{-7.8}$

$$CrO_4^{2-} + H^+ \rightleftharpoons HCrO_4^- \qquad K_a^{-1} = 10^{6.5}$$

$$2\ CrO_4^{2-} + 2\ H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O \qquad K^{-1} = 10^{14.64}$$

Let h be $[H^{+\cdot}]$. A conservation of mass requires that:

$$s = c_{CrO_4^{2-}} = [CrO_4^{2-}] + [HCrO_4^-] + 2\,[Cr_2O_7^{2-}] =$$

$$= [CrO_4^{2-}](1 + K_a^{-1}\,h) + 2\ K^{-1}\,h^2\ [CrO_4^{2-}]^2 \qquad (1)$$

$$s = c_{Pb^{2+}} = [Pb^{2+}] + [PbOH^+] + [Pb(CH_3COO)^+] + [Pb(CH_3COO)_2]$$

$$= [Pb^{2+}](1 + {}^*\beta\,h^{-1} + \beta_1[CH_3COO^-] + \beta_2[CH_3COO^-]^2)$$

$$\rightarrow\ [Pb^{2+}] = \frac{s}{1 + {}^*\beta\,h^{-1} + \beta_1[CH_3COO^-] + \beta_2[CH_3COO^-]^2} \qquad (2)$$

Because $s = 2.9 \cdot 10^{-5}$ mol dm^{-3} << $c_{CH_3COOH} = 1$ mol dm^{-3} → pH of the solution is largely dependent on the dissociation of CH_3COOH:

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^- \qquad K_a = 10^{-4.76}$$

$$1 - h \qquad\qquad h \qquad\qquad h$$

$$\rightarrow\ [CH_3COO^-] = [H^+] = h = 1 \cdot 10^{-2.38}$$

Substitute $[CH_3COO^-] = [H^+] = h = 10^{-2.38}$ and $s = 2.9 \cdot 10^{-5}$ into (1) and (2), we have:

$[CrO_4^{2-}] = 2.194 \cdot 10^{-9}$ and $[Pb^{2+}] = 9.051 \cdot 10^{-6}$

$\rightarrow\ K_{sp} = [Pb^{2+}][CrO_4^{2-}] = 1.99 \cdot 10^{-14}$.

V.

9.6 Cathode:

$$PbO_2 + 4\ H^+ + 2\ e \rightleftharpoons Pb^{2+} + 2\ H_2O \qquad 10^{\frac{2(1.455)}{0.0592}}$$

$$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+ \qquad 10^{-2}$$

$$Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4 \qquad 10^{7.66}$$

Cathode reaction:

$$PbO_2 + HSO_4^- + 3\ H^+ + 2\ e \rightleftharpoons PbSO_4 + 2\ H_2O \qquad K_1 \qquad (*)$$

Anode:

$$Pb \rightleftharpoons Pb^{2+} + 2e \qquad 10^{\frac{-2(-0.126)}{0.0592}}$$

$$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+ \qquad 10^{-2}$$

$$Pb^{2+} + SO_4^{2-} \rightleftharpoons PbSO_4 \qquad 10^{7.66}$$

Anode reaction:

$$Pb + HSO_4^- \rightleftharpoons PbSO_4 + H^+ + 2\ e \qquad K_2 \qquad (**)$$

Overall reaction as the battery discharges:

PbO_2 + Pb + 2 HSO_4^- + 2 H^+ $\rightleftharpoons$ 2 $PbSO_4$ + 2 H_2O (***)

Cell diagram:

(a) Pb | $PbSO_4$, H^+, HSO_4^- | PbO_2 (Pb) (**c**)

VI.

9.7 According to (*): $10^{\frac{2E^0_{PbO_2/PbSO_4}}{0.0592}} = K_1 = 10^{\frac{2(1.455)}{0.0592}}\,10^{-2}\,10^{7.66}$

$\rightarrow E^0_{PbO_2/PbSO_4} = 1.62\ \text{V}$

According to (**):

$10^{\frac{-2E^0_{PbSO_4/Pb}}{0.0592}} = K_2 = 10^{\frac{-2(-0.126)}{0.0592}}\,10^{-2}\,10^{7.66} \rightarrow E^0_{PbSO_4/Pb} = -0.29\ \text{V}$

9.8 According to (***):

$$V = E_{(c)} - E_{(a)} = E^0_{PbO_2/PbSO_4} - E^0_{PbSO_4/Pb} + \frac{0.0592}{2}\log[HSO_4^-]^2[H^+]^2$$

In which $[HSO_4^-]$, $[H^+]$ are calculated as follows:

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ $K_a = 10^{-2}$

1.8 – x 1.8 + x x

$[SO_4^{2-}] = x = 9.89 \cdot 10^{-3} \rightarrow [H^+] = 1.81$; $[HSO_4^-] = 1.79$

$$V = 1.62 + 0.29 + \frac{0.0592}{2}\log(1.79)^2(1.81)^2 = 1.94\ \text{V}$$

THEORETICAL PROBLEM 10

Applied electrochemistry

I. Reduction-oxidation reactions have played an important role in chemistry due to their potential to be valuable sources of energy for technology and life.

10.1 Write down chemical equation for the oxidation of glucose ($C_6H_{12}O_6$) with $KMnO_4$ solution in the presence of sulfuric acid to form gaseous CO_2.

10.2 Write down chemical equation for the oxidation of $FeSO_4$ with $KMnO_4$ in an acidic medium (sulfuric acid) to form $Fe_2(SO_4)_3$.

10.3 Based on the reaction in 10.2 determine the anodic reaction and cathodic reaction and the relevant cell diagram.

10.4 Derive the expression for electromotive force E of the cell.

II. In the thermodynamics point of view, Gibbs free energy ΔG at constant *p*, *T* condition is closely related to electromotive force *E* of a redox reaction according to below expression:

$$\Delta G = -\,n\,F\,E \;\rightarrow\; E = -\frac{\Delta G}{n\,F}$$

where: n – number of electrons transferred,

F – Faraday constant.

The correlation of the standard reduction potential between Mn ions in acidic medium is:

$$\begin{tikzcd}
MnO_4^- \arrow[r, "+0.56V"] \arrow[rr, bend right, "+1.7V"'] & MnO_4^{2-} \arrow[r, "E_3^0?"] & MnO_2 \arrow[r, "E_4^0?"] \arrow[rr, bend right, "+1.23V"'] & Mn^{3+} \arrow[r, "+1.51V"] & Mn^{2+}
\end{tikzcd}$$

10.5 Determine the standard reduction potential of the pair MnO_4^{2-} / MnO_2

10.6 Determine the standard reduction potential of the pair MnO_2/ Mn^{3+}

III. A process is spontaneous if Gibbs free energy is negative. Based on the thermodynamic data:

10.7 Determine Gibbs free energy of the following reaction:

10.8

$$3\,MnO_4^{2-} + 4\,H^+ \rightleftharpoons 2\,MnO_4^- + MnO_2 + 2\,H_2O$$

10.8 Is the reaction spontaneous?

10.9 Calculate K_c for the reaction.

SOLUTION OF PREPARATORY PROBLEM 10

I.

10.1 $5\,C_6H_{12}O_6 + 24\,KMnO_4 + 36\,H_2SO_4 \rightarrow 12\,K_2SO_4 + 24\,MnSO_4 + 30\,CO_2 + 66\,H_2O$

10.2 $2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 \rightarrow 2\,MnSO_4 + 5\,Fe_2(SO_4)_3 + 8\,H_2O$

10.3 Anode: $2\,Fe^{2+} \rightleftarrows 2\,Fe^{3+} + 2\,e^-$

Cathode: $MnO_4^- + 8\,H^+ + 5\,e^- \rightleftarrows Mn^{2+} + 4\,H_2O$

The cell diagram:

$$Pt\left|Fe^{3+},Fe^{2+}\right\|\,MnO_4^-,Mn^{2+},H^+\left|Pt\right.$$

10.4 Electromotive force E of the cell can be calculated as follows:

$$E = E^0 - \frac{0.059}{5}\log\frac{\left[Mn^{2+}\right]\left[Fe^{3+}\right]^5\left[H_2O\right]^4}{\left[MnO_4^-\right]\left[Fe^{2+}\right]^5\left[H^+\right]^8}$$

II.

10.5 In order to determine the reduction potential of the pair MnO_4^{2-}/MnO_2 we need to use the below diagram:

$$\begin{tikzcd}
MnO_4^- \arrow[rr, "\Delta G_2"] \arrow[dr, "\Delta G_1"'] & & MnO_2 \\
& MnO_4^{2-} \arrow[ur, "\Delta G_3"'] &
\end{tikzcd}$$

According to Hess' Law:

$\Delta G^0_2 = \Delta G^0_1 + \Delta G^0_3$

$\Delta G^0_3 = \Delta G^0_2 - \Delta G^0_1$

We have $\Delta G_3^0 = -\mathrm{n} F E^0 \rightarrow E_3^0 = 2.27\,\mathrm{V} = E^0_{\mathrm{MnO_4^{2-}}/\mathrm{MnO_2}}$

10.6 Similarly, we have:

$$\begin{tikzcd}
\mathrm{MnO_2} \arrow[rr, "\Delta G_4"] \arrow[dr, "\Delta G_5"'] & & \mathrm{Mn^{3+}} \\
& \mathrm{Mn^{2+}} \arrow[ur, "\Delta G_6"'] &
\end{tikzcd}$$

$\Delta G^0{}_4 = \Delta G^0{}_5 + \Delta G^0{}_6$

We have $\Delta G^0 = -\mathrm{n}\, F E^0$.

$\Delta\ E_{\mathrm{MnO_2}/\mathrm{Mn^{3+}}} = 0.95\,\mathrm{V} = E_4^0$

III.

10.7 According to the standard reduction potential diagram, we have:

$\mathrm{MnO_4^{2-}} + 4\,\mathrm{H^+} + 2\,\mathrm{e} \rightleftharpoons \mathrm{MnO_2} + 2\,\mathrm{H_2O}$ (3) $\Delta G^0{}_3$ ($E^0{}_3 = 2.27$ V)

$2\,\mathrm{MnO_4^-} + 2\,\mathrm{e} \rightleftharpoons 2\,\mathrm{MnO_4^{2-}}$ (1) $\Delta G^0{}_1$ ($E^0{}_1 = 0.56$ V)

$3\,\mathrm{MnO_4^{2-}} + 4\,\mathrm{H^+} \rightleftharpoons 2\,\mathrm{MnO_4^-} + \mathrm{MnO_2} + 2\,\mathrm{H_2O}$ $\Delta_r G^0$

10.8 In order to know if the reaction is spontaneous, ΔG must be considered.

The reaction that is considered can be obtained by subtracting (1) from (3):

$\Delta_r G^0 = \Delta G^0{}_3 - \Delta G^0{}_1$. We have $\Delta G^0 = -\,n\,F\,E^0$ where $\Delta E^0{}_{\mathrm{reaction}} = 1.71$ V, or $\Delta G_3 < 0$ and the reaction is spontaneous.

10.9 The equilibrium constant can also be calculated:

$$\log K_3 = \frac{n\,\Delta E^0}{0.059} \rightarrow \log K_3 = \frac{2 \times 1.71}{0.059} \rightarrow K_3 = 9.25 \times 10^{57}$$

The large value of K confirms the reaction to be spontaneous.

THEORETICAL PROBLEM 11

Phosphoric acid

A is a solution of H_3PO_4 with pH of 1.46.

11.1 Calculate the molar concentrations of all species in solution **A**. Given that K_a values for H_3PO_4 are $7.2 \cdot 10^{-3}$; $6.3 \cdot 10^{-8}$ and $4.2 \cdot 10^{-13}$, respectively.

11.2 Mixing of 50 cm^3 of solution **A** and 50 cm^3 of NH_3 solution (c = 0.4 mol dm^{-3}) results in 100 cm^3 of solution **B**. Calculate pH of solution **B** ($pK_{NH_4^+} = 9.24$).

11.3 100 cm^3 of solution **B** is mixed with 100 cm^3 of $Mg(NO_3)_2$ solution (c = 0.2 mol dm^{-3}). Determine if precipitate of NH_4MgPO_4 forms. The hydrolysis of Mg^{2+} is ignored and precipitation of NH_4MgPO_4 is assumed to be the only reaction. $K_s(NH_4MgPO_4) = 2.5 \cdot 10^{-13}$.

11.4 Calculate the solubility (mol·dm^{-3}) of $Ca_3(PO_4)_2$ if $K_s(Ca_3(PO_4)_2) = 2.22 \cdot 10^{-25}$.
(Hint: The hydrolysis of Ca^{2+} is ignored).

SOLUTION OF PREPARATORY PROBLEM 11

11.1 H^+ is used instead of H_3O^+ for clarity. The activities of the ions are ignored. $[H^+]$ is abbreviated as h in all calculations and acid constants for H_3PO_4 are written as K_1, K_2 and K_3.

As $K_1 >> K_2 >> K_3$, only first dissociation step is considered.

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$

As

$$K_1 = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{h^2}{c_o - h} = 10^{-2.14} = \frac{(10^{-1.14})^2}{c_o - 10^{-1.46}}$$

Solving for c_o gives c_o = 0.200

The concentrations of the forms:

$$[H_3PO_4] = \frac{h^3 c_o}{h^3 + h^2 K_1 + h K_1 K_2 + K_1 K_2 K_3} (h K_1 K_2 + K_1 K_2 K_3 \text{ is ignored})$$

$$= \frac{h^3 c_o}{h^3 + h^2 K_1} = \frac{h c_o}{h + K_1} = \frac{10^{-1.46} \times 0.2}{10^{-1.46} + 10^{-2.14}} = 0.1653$$

Similarly, we have:

$$[H_2PO_4^-] = \frac{h^2 K_1 c_o}{h^3 + h^2 K_1} = \frac{K_1 c_o}{h + K_1} = \frac{10^{-2.14} \times 0.2}{10^{-1.46} + 10^{-2.14}} = 0.0346$$

$$[HPO_4^{2-}] = \frac{h K_1 K_2 c_o}{h^3 + h^2 K_1} = \frac{K_1 K_2 c_o}{h^2 + h K_1} = \frac{10^{-2.14} \times 10^{-7.20} \times 0.2}{(10^{-1.46})^2 + 10^{-1.46} \times 10^{-2.14}} = 6.29 \times 10^{-8}$$

$$[PO_4^{3-}] = \frac{K_1 K_2 K_3 c_o}{h^3 + h^2 K_1} = \frac{10^{-2.14} \times 10^{-7.20} \times 10^{-12.38} \times 0.2}{(10^{-1.46})^3 + (10^{-1.46})^2 \times 10^{-2.14}} = 7.56 \times 10^{-19}$$

11.2 We have:

$n_{H_3PO_4} = 0.2 \times 0.050 = 0.010 \text{ mol}$

$n_{NH_3} = 0.4 \times 0.050 = 0.020 \text{ mol}$

Hence the following reaction occurs: $H_3PO_4 + 2\ NH_3 \rightarrow (NH_4)_2HPO_4$

And $[(NH_4)_2HPO_4] = \frac{0.010}{0.100} = 0.1$

In solution **B**: $(NH_4)_2HPO_4 \rightarrow 2\ NH_4^+ + HPO_4^{2-}$

0.2 M 0.1 M

We have the following equilibria:

$NH_4^+ \rightleftharpoons NH_3 + H^+$

$HPO_4^{2-} + H^+ \rightleftharpoons H_2PO_4^-$

$H_2PO_4^- + H^+ \rightleftharpoons H_3PO_4$

$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$

A conservation of protons requires:

$[H^+] + 2\ [H_3PO_4] + [H_2PO_4^-] = [OH^-] + [PO_4^{3-}] + [NH_3]$ (1)

In which $[NH_3] + [NH_4^+] = 0.2$

$[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] = 0.1$

We also have:

$$[NH_3]=\frac{K_{NH_4^+}\times 0.2}{h+K_{NH_4^+}}$$

$$[H_3PO_4]=\frac{h^3\times 0.1}{h^3+h^2K_1+hK_1K_2+K_1K_2K_3}$$

$$[H_2PO_4^-]=\frac{h^2K_1\times 0.1}{h^3+h^2K_1+hK_1K_2+K_1K_2K_3}$$

$$[HPO_4^{2-}]=\frac{hK_1K_2\times 0.1}{h^3+h^2K_1+hK_1K_2+K_1K_2K_3}$$

$$[PO_4^{3-}]=\frac{K_1K_2K_3\times 0.1}{h^3+h^2K_1+hK_1K_2+K_1K_2K_3}$$

As pH of the solution is of about 7 – 9 so we can ignore the $[H^+]$, $[OH^-]$, $[H_3PO_4]$ and $[PO_4^{3-}]$ in the equation (1):

$$[H_2PO_4^-] = [NH_3]$$

$$\frac{h^2K_1\times 0.1}{h^3+h^2K_1+hK_1K_2+K_1K_2K_3}=\frac{K_{NH_4^+}\times 0.2}{h+K_{NH_4^+}}$$

$$\frac{h\times 0.1}{h+K_2}=\frac{h\times 0.1}{h+10^{-7.20}}=\frac{10^{-9.24}\times 0.2}{h+10^{-9.24}}\ (h^3+K_1K_2K_3\text{ is ignored})$$

Solving for h gives $h = 8.81 \times 10^{-9}$ and pH = 8.06.

11.3 Mixing of **B** and $Mg(NO_3)_2$ solution leads to precipitation reaction:

$$NH_4^+(aq) + Mg^{2+}(aq) + PO_4^{3-}(aq) \rightarrow NH_4MgPO_4(s)$$

$[Mg^{2+}] = 0.2 / 2 = 0.1\ mol\ dm^{-3}$

As **B** is a buffer solution when it is diluted to twice the original volume, pH is virtually unchanged and is 8.06.

$$[NH_4^+]=\frac{hc}{h+K_{NH_4^+}}=\frac{10^{-8.06}\times 0.1}{10^{-8.06}+10^{-9.24}}=0.094\ \text{mol dm}^{-3}$$

$$[PO_4^{3-}]=\frac{K_1K_2K_3\times c_o}{h^2K_1+hK_1K_2}=\frac{K_2K_3c_o}{h^2+hK_2}=\frac{10^{-7.20}\times 10^{-12.38}\times 0.05}{(10^{-8.06})^2+10^{-8.06}\times 10^{-7.20}}=2.06\cdot 10^{-8}\ \text{mol dm}^{-3}$$

The solubility product:

$[NH_4^+][Mg^{2+}][PO_4^{3-}] = 0.1 \times 0.094 \times 2.06 \cdot 10^{-6} = 1.93 \cdot 10^{-8} > 2.5 \cdot 10^{-13}$

Therefore, the precipitation occurs.

11.4 We have: $Ca_3(PO_4)_2 \rightleftarrows 3\ Ca^{2+} + 2\ PO_4^{3-}$

Assume that the hydrolysis of PO_4^{3-} can be ignored, the solubility s_o of $Ca_3(PO_4)_2$ can be calculated as follows:

$K_s = [Ca^{2+}]^3[PO_4^{3-}]^2 = (3\ s_o)^3(2\ s_o)^2 = 108\ s_o^5 = 2.22 \cdot 10^{-25}$

Solving for s_o gives $s_o = 4.6 \cdot 10^{-6}$ mol dm^{-3}

However, the hydrolysis of PO_4^{3-} cannot be ignored due to its rather strong basicity ($pK_b = 14 - pK_a = 14 - 12.38 = 1.62$)

$$PO_4^{3-} + H_2O \rightleftarrows HPO_4^{2-} + OH^- \qquad (1)$$

We can ignore the hydrolysis of HPO_4^{2-} ($pK_b = 14 - 7.20 = 6.80$) and $H_2PO_4^-$ ($pK_b = 14 - 2.14 = 11.86$).

According to (1): $[HPO_4^{2-}] + [PO_4^{3-}] = 2\ s \qquad (2)$

As $[PO_4^{3-}]$ is very small (the calculation above), it can be ignored in (2). It can alternatively be calculated as follows:

Let x is the concentrations of HPO_4^{2-} and OH^-, $[HPO_4^{2-}] = [OH^-] = x$

We have: $$\frac{x^2}{2 \times 4.6 \cdot 10^{-6} - x} = 10^{-1.62} = 0.024$$

Solving for x gives $x = 9.19 \cdot 10^{-6} \rightarrow [PO_4^{3-}] = 0.01 \cdot 10^{-6}$ mol dm^{-3}

Therefore we can assume that $[HPO_4^{2-}] = [OH^-] = 2s$ and $[PO_4^{3-}]$ is determined based on K_3:

$$K_3 = 10^{-12.38} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = \frac{10^{-14}}{[OH^-]} \times \frac{[PO_4^{3-}]}{[HPO_4^{2-}]}$$

$$\Rightarrow \quad [PO_4^{3-}] = \frac{10^{-12.38} \times 2s \times 2s}{10^{-14}} = 167\, s^2$$

The solubility s of $Ca_3(PO_4)_2$: $K_s = 2.25 \cdot 10^{-25} = (3\ s)^3\ (2 \times 167\ s^2)^2 = 3012012\ s^7$

$\Rightarrow \quad s = 3.6 \cdot 10^{-5}$

We can see that solubility of $Ca_3(PO_4)_2$ increases about 10 times due to the hydrolysis of PO_4^{3-}.

Note: Students may use logarithmic concentration diagram to get the relationship $[HPO_4^{2-}] = [OH^-] = 2\ s$.

THEORETICAL PROBLEM 12

Chemical kinetics

Thermal decomposition of dinitrogen pentoxide (N_2O_5) in the gas phase has time-independent stoichiometry.

$$2\ N_2O_5\ (g) \rightarrow 4\ NO_2\ (g) + O_2\ (g) \qquad (1)$$

A kinetic measurement for N_2O_5 at 63.3 °C is shown in Figure 1 below.

Time (s)	$[N_2O_5]$/ mol dm^{-3}
0	$3.80 \cdot 10^{-3}$
50	$3.24 \cdot 10^{-3}$
100	$2.63 \cdot 10^{-3}$
150	$2.13 \cdot 10^{-3}$
225	$1.55 \cdot 10^{-3}$
350	$9.20 \cdot 10^{-4}$
510	$4.70 \cdot 10^{-4}$
650	$2.61 \cdot 10^{-4}$
800	$1.39 \cdot 10^{-4}$

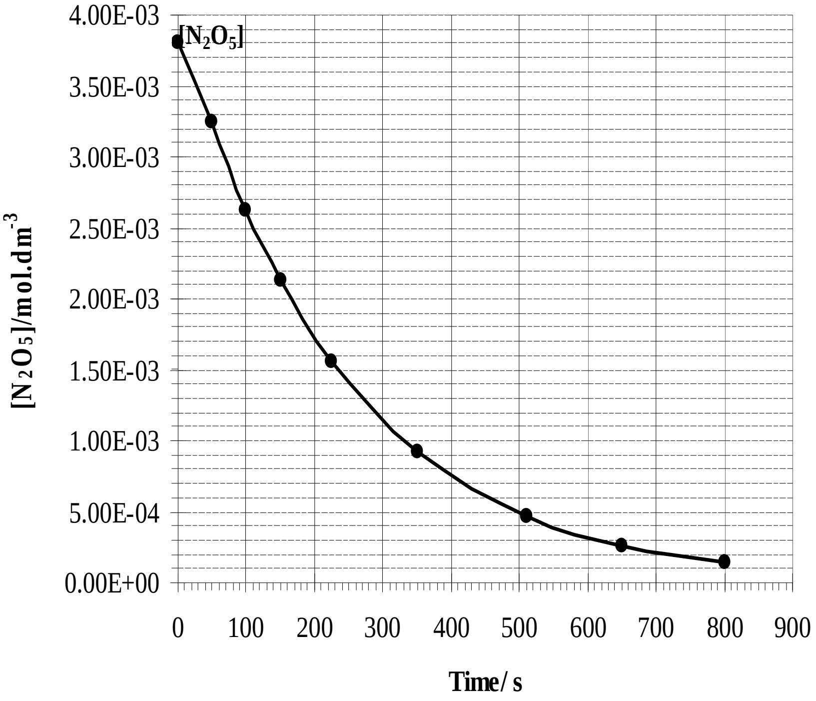


Figure 1. Concentration of N_2O_5 versus time.

12.1 What is the half-life ($t_{1/2}$) for the decomposition of N_2O_5 at 63.3 °C?

The reaction order for the reaction (1) can be determined by plotting of:
ln $[N_2O_5]_0 / [N_2O_5]_t$ *versus* time or $\{[N_2O_5]_0 / [N_2O_5]_t - 1\}$ *versus* time.

12.2 Plot the graphs to determine the reaction order?

12.2 Write down the rate law and integrated rate equation.

12.3 Determine the rate constant for the reaction (1).

12.4 The rate constant *k* for (1) at 45 °C is $5.02 \cdot 10^{-4}\ s^{-1}$. Calculate the activation energy (E_a) and pre-exponential factor (*A*) for the reaction (1) assuming that the activation energy and pre-exponential factor are temperature independent.

12.5 The following mechanism is proposed for the reaction (1):

$$N_2O_5 \xrightleftharpoons[k_{-1}]{k_1} NO_2 + NO_3 \qquad (2)$$

$$NO_2 + NO_3 \xrightarrow{k_2} NO_2 + O_2 + NO \qquad (3)$$

$$NO + NO_3 \xrightarrow{k_3} 2\ NO_2 \qquad (4)$$

Using this mechanism, derive the rate law for $-d[N_2O_5] / dt$ assuming that the intermediate concentrations can be treated by the steady-state approximation.

SOLUTION OF PREPARATORY PROBLEM 12

12.1 To determine $t_{1/2}$, the time taken from the initial concentration of N_2O_5 ($3.80 \cdot 10^{-3}$ mol.dm^{-3}) to fall to one-half of its value:

$t_{1/2} \approx 180$ s corresponding to $[N_2O_5]t_{1/2} = 1.90 \cdot 10^{-3}$ mol dm^{-3}

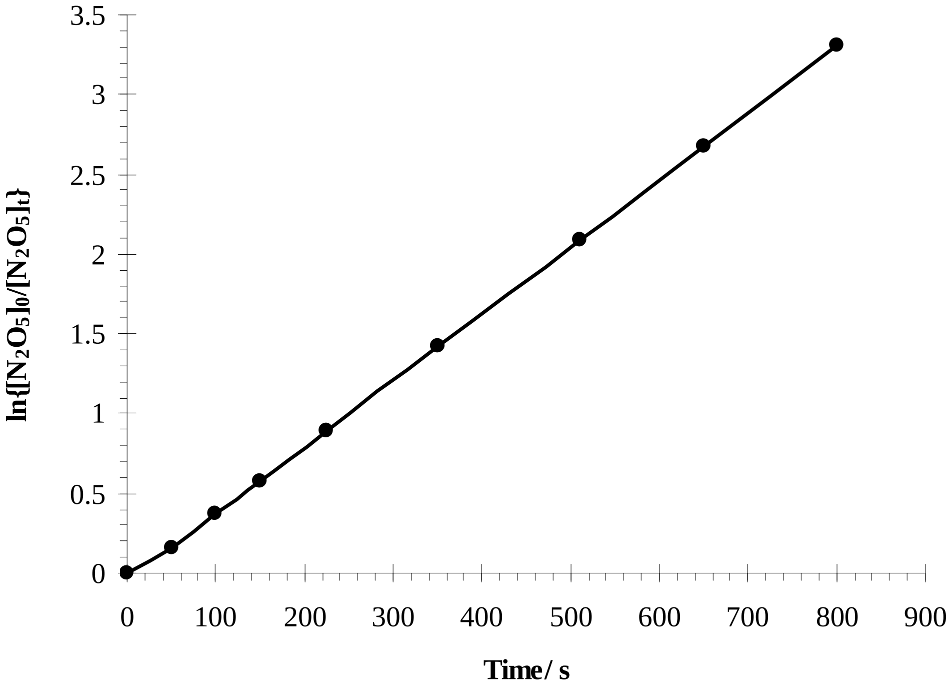


Figure 2. A re-plot of the data in Figure 1 as function of ln $\{[N_2O_5]_0/[N_2O_5]t\}$ vs. time

The plot of ln {$[N_2O_5]_0$ / $[N_2O_5]$t} versus time is linear for a first order reaction.

$r = k\,[N_2O_5]$

The form of integrated rate equation:

$$\ln\frac{[N_2O_5]_0}{[N_2O_5]_t} = k\,t \qquad \text{or} \qquad [N_2O_5]_t = [N_2O_5]_0\,e^{-kt}$$

12.3 The 1st order reaction:

$k = \ln 2 / t_{1/2} = \ln 2 / 180\text{ s} = 3.85 \cdot 10^{-3}\text{ s}^{-1}$

12.4 E_a is independent of temperature:

$$\ln\frac{k_{336.6\text{K}}}{k_{318\text{K}}} = \frac{E_a}{R}\left[\frac{1}{318} - \frac{1}{336.6}\right] \Rightarrow \ln\frac{3.85\cdot 10^{-3}}{5.02\cdot 10^{-4}} =$$

$$= \frac{E_a}{8.314\text{J mol}^{-1}\ \text{K}^{-1}}\left[3.145\cdot 10^{-3} - 2.97\cdot 10^{-3}\right]$$

E_a = 97.46 kJ

Pre-exponential factor (A):

$k = A.\ e^{-Ea/RT}$ at 336.3 K, $\boldsymbol{A} = k.\ e^{Ea/RT} = 3.85 \cdot 10^{-3}\ e^{97460/8.3145\times 336.3} = 5.28 \cdot 10^{12}\text{ s}^{-1}$.

12.5 The intermediate concentrations can be treated by the steady-state approximation:

$$r_{NO} = \frac{d[NO]}{dt} = k_2[NO_2][NO_3] - k_3[NO][NO_3] = 0 \;\rightarrow\; [NO] = \frac{k_2[NO_2]}{k_3} \qquad \text{(Eq.1)}$$

Substituting this equation into the below equation:

$$r_{NO_3} = \frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_2][NO_3] - k_3[NO][NO_3] = 0 \quad \text{(Eq. 2)}$$

$$\rightarrow k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO_2][NO_3] - k_3\frac{k_2[NO_2]}{k_3}[NO_3] = 0$$

$$\rightarrow k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - 2\,k_2[NO_2][NO_3] = 0$$

$$\rightarrow \frac{k_1[N_2O_5]}{k_{-1} + 2\,k_2} = [NO_2][NO_3] \qquad \text{(Eq.3)}$$

The reaction rate:

$$r_2 = r_{N_2O_5} = -\frac{d[N_2O_5]}{dt} = k_1[N_2O_5] - k_{-1}[NO_2][NO_3]$$

$$= k_1[N_2O_5] - k_{-1}\frac{k_1[N_2O_5]}{k_{-1} + 2\,k_2}$$

$$= \frac{2\,k_1\,k_2}{k_{-1} + 2\,k_2}[N_2O_5]$$

$$= k\,[N_2O_5]$$

THEORETICAL PROBLEM 13

Kinetics of the decomposition of hydrogen peroxide

In order to decompose hydrogen peroxide (H_2O_2) with iodide ion as catalyst in neutral solution, the 3 % H_2O_2 solution (which approximately corresponds to 30 g of H_2O_2 in 1 dm^3 of solution) is mixed with a KI solution (0.1 mol dm^{-3}) and water at different volumetric ratios; and the volume of the oxygen gas released $V_{O_2}(cm^3)$ is measured.

Experiment	$V_{H_2O_2}(cm^3)$	$V_{KI}(cm^3)$	$V_{H_2O}(cm^3)$	$V_{O_2}(cm^3/min)$ at 298 K and 1 atm
1	25	50	75	4.4
2	50	50	50	8.5
3	100	50	0	17.5
4	50	25	75	4.25
5	50	100	0	16.5

13.1 Determine the reaction order with respect to H_2O_2, and I^-, respectively.

13.2 Write down the chemical reaction, and determine the rate law.

13.3 Calculate the molarity of H_2O_2 at the beginning of the experiment 4 and after 4 min.

13.4 The reaction mechanism involves a series of the following steps:

$H_2O_2 + I^- \xrightarrow{k_1} H_2O + IO^-$ (1) −

$IO^- + H_2O_2 \xrightarrow{k_2} O_2 + I^- + H_2O$ (2)

Do the two above steps have the same rate or different rates? Which step determines the overall rate of the oxygen release? Justify your answer.

SOLUTION OF PREPARATORY PROBLEM 13

13.1 Chemical reaction: $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$

The reaction rate is proportional to the volume of oxygen gas released in a unit of time.

In experiments 1, 2, and 3 when the volume of H_2O_2 solution doubles while keeping the same volume of KI solution, the reaction rate also doubles. Therefore, the rate is directly proportional to the concentration of H_2O_2. Hence, the reaction is the first-order with the respect to H_2O_2.

Similarly, from experiments 2, 4, and 5 the rate is directly proportional to the concentration of I^-. Hence, the reaction is the first-order with the respect to I^-.

13.2 Chemical reaction: $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$

The rate law: $v = k\, c_{H_2O_2} c_{I^-}$

13.3 In the experiment #4, the solution of H_2O_2 is diluted three times; therefore, the concentration of H_2O_2 was reduced three times.

c_0 = 10 g H_2O_2 / 1 dm^3 = 10 / 34 = 0.294 mol dm^{-3}.

Because the reaction proceeds slowly, the reaction rate (or the rate of releasing oxygen gas) is considered to be unchanged after of short period of time (4 min).

The volume of oxygen released after 4 min is equal to 4.25 × 4 = 17 cm^3 O_2.

Hence, $n_{O_2} = \dfrac{pV}{RT} = \dfrac{(1)(17 \cdot 10^{-3})}{(0.082)(298)} = 0.695 \cdot 10^{-3}$ mol

At the beginning, $n_{H_2O_2}$ = (0.294)(0.15) = 44.1 · 10^{-3} mol

After 4 min, $n_{H_2O_2}$ = 44.1 · 10^{-3} – 2 (0.695 · 10^{-3}) = 42.71 · 10^{-3} mol

Therefore, after 4 min $c_{H_2O_2} = \dfrac{0.04271}{0.15} = 0.285$ mol dm^{-3}.

13.4 The overall reaction: $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$ (*)

$$v = -\frac{1}{2}\frac{d[H_2O_2]}{dt}$$

Consider three different cases:

i) If step (1) is slow and determines the overall rate, the rate of the overall reaction (*) will be the same as the rate of step (1):

$$v = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = k_1[H_2O_2]\,[I^-]$$

which corresponds to the overall rate law as determined in section 2.

ii) If step (2) is slow, hence

$$v = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = k_2[H_2O_2][IO^-] \qquad (a)$$

Assume that the steady-state approximation is applied for IO^-, we have

$$\frac{d[IO^-]}{dt} = k_1[H_2O_2][I^-] - k_2[IO^-][H_2O_2] = 0 \;\rightarrow\; [IO^-] = \frac{k_1}{k_2}[I^-] \qquad (b)$$

Replace $[IO^-]$ from (b) in (a), we have:

$$v = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = k_1[H_2O_2][I^-]$$

which is also appropriate to the overall rate law.

iii) If the two steps have similar rates:

$$v = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = \frac{1}{2}\left(k_1[H_2O_2][I^-] + k_2[H_2O_2][IO^-]\right)$$

Let us assume that the concentration of IO^- is in steady-state condition. Similar to the case b), we have:

$$v = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = k_1[H_2O_2][I^-]$$

which corresponds to the overall rate law.

Among the three cases, case a) is the most appropriate to the overall rate law because no assumption is made. Besides, in the case b) the assumption of the steady-state IO^- is not valid since the step (2) is considered slow.

THEORETICAL PROBLEM 14

Magnetism of transition metal complexes

A transition metal complex containing diamagnetic ligands can be overall *diamagnetic* (all electrons are paired) or *paramagnetic* (having unpaired electron(s)) depending on the electronic configuration of the central metal ion, the nature of the ligand, and geometry of the ligand sphere. The magnitude of paramagnetism of a metal complex is commonly reported in terms of the effective magnetic moment (μ_{eff}) which can be obtained from the experimental measurement of molar magnetic susceptibility (χ_{m}) and is commonly expressed in Bohr magneton (BM).

Theoretically, the magnetic moment is contributed by two components, the spin angular momentum and the orbital angular momentum. For many complexes of first row d-block metal ions, however, the contribution of the second component can be ignored. Thus, the so-called spin only magnetic moment can be determined by the number of unpaired electrons, n:

$$\mu(\text{spin only}) = \sqrt{n(n+2)} \quad \text{(B.M.)}$$

I. The observed effective magnetic moment of two octahedral complexes $K_4[Mn(CN)_6]$. 3 H_2O and $K_4[Mn(SCN)_6]$ are 2.18 B.M. and 6.06 B.M., respectively.

14.1 Calculate number of unpaired electrons in each complex. Which complex is low spin? Which complex is high spin?

14.2 Rationalize your answers by applying crystal field theory.

14.3 Calculate the μ (spin only) of complex $[Ni(H_2O)_6]Cl_2$.

II. In practice, the experimentally observed μ_{eff} value of $[Ni(H_2O)_6]Cl_2$ is 3.25 BM. This is not surprising due to the fact that magnetic moment of octahedral complexes of Ni^{2+} (d^8) usually does not obey the spin only formula. In these cases, the contribution of orbital angular momentum should be taken into account. The simplification of spin-orbit coupling model can be applied to calculate their magnetic moment:

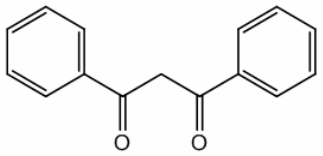
$$\mu_{\text{eff}} = \mu(\text{spin only}) \times \left(1 - \frac{4\lambda}{\Delta_{\text{oct}}}\right)$$

where λ is spin-orbit coupling constant of Ni^{2+} and has the value of -315 cm^{-1}

Δ_{oct} is the crystal-field splitting parameter

14.4 Calculate the effective magnetic moment of $[Ni(H_2O)_6]Cl_2$ taking into account spin–orbit coupling. Δ_{oct} of $[Ni(H_2O)_6]^{2+}$ is 8500 cm^{-1}.

III. Dibenzoylmethane (DBM) is a well known chelating κ-O,O-ligand which can form stable complexes with many transition metal ions.



DBM

Reaction of $Ni(CH_3COO)_2 \cdot 4\ H_2O$ with DBM in EtOH–H_2O solution gives light green crystalline complex **A** which loses 6.8 % of mass on heating at 210 °C in the air to form green solid **B**. The substance **B** is quantitatively converted to brown prismatic crystals **C** by re-crystallization in dry toluene. **B** and **C** are two polymorphic forms and their inter-conversion is reversible. The X-ray single crystal structure of **C** shows a square planar geometry with the chemical composition of $[Ni(DBM)_2]$. While **B** is paramagnetic with effective magnetic moment of 3.27 BM, the complex **C** is diamagnetic. When **B** and **C** are kept in the air, they slowly convert to **A.** This happens much faster in the presence of some organic solvents (*Inorg. Chem., 2001, 40, 1626-1636*).

14.5 Draw the splitting diagram of the d orbitals of Ni^{2+} in **C** and confirm its diamagnetic property.

14.6 What is the molecular formula of **A**? Assume that **A** is a mononuclear complex.

14.7 The effective magnetic moment of **A** is 3.11 BM (*Synth. React. Inorg. Met. Org. Chem., 2009, 39, 694-703)*. What is the most suitable molecular geometry of **A**? (Assuming that A is an octahedral complex, Δ_{oct} of **A** is similar to that of $[Ni(H_2O)_6]^{2+}$).

14.8 Draw all possible isomers of **A.**

14.9 What do you expect for the molecular geometry of **B**?

SOLUTION OF PREPARATORY PROBLEM 14

I.

14.1 Two compounds are octahedral complexes of Mn^{2+} (d^5).

$K_4[Mn(CN)_6] \cdot 3\ H_2O$ is low spin, 1 unpaired electron.

$K_4[Mn(SCN)_6]$ is high spin, 5 unpaired electrons.

14.2 CN^- is strong field ligand, electronic configuration is $(t_{2g})^5(e_g)^0$

SCN^- is weak filed ligand, electronic configuration is $(t_{2g})^3(e_g)^2$

14.3 Ni^{2+} (d^8) in octahedral field has electronic configuration of $(t_{2g})^6(e_g)^2$ with two unpaired electrons. The spin only χ_{eff} is 2.83 MB.

II.

14.4 $$\mu_{eff} = 2.83 \times \left(1 - \frac{4(-315)}{8500}\right)(BM)$$

Thus, μ_{eff} is 3.25 MB

III.

14.5 d^8 in square planar field is diamagnetic.

14.6 **C** is neutral, DBM is monoanionic form. $M_c = 504$ g mol^{-1}. **A** should be hydrate form of **C**, $M_A = M_B / 0.932 = 540.8$ g mol^{-1}, corresponding to two molecules of H_2O per $[Ni(DBM)_2]$. Thus, the formula is $[Ni(DBM)_2] \cdot .2\ H_2O$

14.7 Water should coordinate to Ni center due to the change of color and magnetic property. μ_{eff} value of **A** is close to that of $[Ni(H_2O)_6]Cl_2$. Thus, an octahedral complex is expected for **A**.

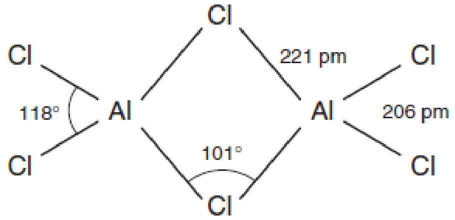
14.7 There are three isomers, the *trans* isomer and two optical *cis* isomers.

14.8 **B** should be an octahedral complex, due to the color and magnetic moment are similar to those of **A**. Octahedral geometry can be formed by oligomerization / polymerization of **B** on heating, the DBM may play as bridging ligand.

THEORETICAL PROBLEM 15

Structure and synthesis of Al-Keggin ion

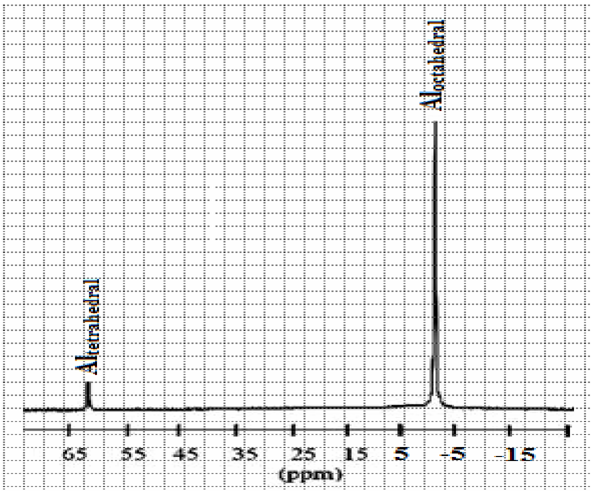
I. A molecular dimer of aluminum chloride in gas phase has the structure:



15.1 What is the hybridization of the Al atoms in a dimer?

15.2 Determine the distance between two Al atoms.

II. Aluminum chloride dissociates in basic solution yielding several Al-polycations. A typical Al-Keggin ion with the molecular formula of $[Al_{13}O_{28}H_{24}.12H_2O]Cl_n$ was formed at a hydrolysis ratio $[OH^-] / [Al^{3+}]$ of 1.5 to 2.5. It is only composed of tetrahedral and octahedral Al cations. The ^{27}Al NMR spectrum of an Al_{13} ion is shown below. The sharp signal at 64 ppm is due to the very symmetrical environment of the corresponding Al atom(s) in the Keggin cation.



15.3 Determine the absolute value of (n) in the Al_{13} Keggin ion.

15.4 Assign ^{27}Al NMR signals in the spectrum to the appropriate Al cation(s) in the right figure.

15.5 In an Al_{13}-Keggin ion, Al tetrahedron(s) is(are) only linked with other Al atoms by the oxygen bridge. Propose the structural formula for the Al_{13}-Keggin ion.

15.6 Determine the number of oxygen atoms bridging adjacent octahedra.

15.7 Write down the overall equation to prepare Al-Keggin ions from the reaction between NaOH and $AlCl_3$ solution.

III. Al_{13}-Keggin ions have recently been prepared by solid - solid interaction referred to as mechanochemical synthesis [*J. Catal. 245 (2007) 346*; *Inorg. Chem. Commun. 11 (2008) 1125*]. A mixture of $(NH_4)_2CO_3/[Al(H_2O)_6]Cl_3$ was blended together in a silicon carbide crucible (with the inner volume of 17 cm^3) in the presence of three hardened silicon carbide balls (with the radius of 0.542 cm) in atmospheric condition (25 °C, 1 atm). The milling was kept for a period of time at 25 °C until the pressure gauge remains at constant value of 2.50 atm *(Hint: The volume of solids is negligible).*

15.8 Write down the overall reaction between aluminum hexahydrate chloride and ammonium carbonate to yield the Al_{13} -Keggin ions.

15.9 Determine the number of molecular Al_{13}-Keggin cations in the crucible.

SOLUTION OF PREPARATORY PROBLEM 15

1.

15.1 Al_2Cl_6 has sp^3 hybridization

15.2 $\mathrm{Al-Al} = \frac{2\times(\mathrm{Al-Al})}{2} = 2(\mathrm{Al-Cl})\cos(39.5^{\circ}) = 2\times 221\,\mathrm{pm}\times 772 = 325.63\,\mathrm{pm}$

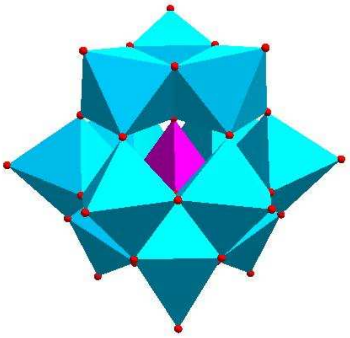
II.

15.3 n = 7+

15.4 The $Al_{octahedral}$ / $Al_{tetrahedral}$ is estimated ~ 12/1. The center Al atom at number 7 is tetrahedral; the other atoms are octahedral.

15.5 and **15.6**

The Al-Keggin cation structure is composed of one $Al_{tetrahedral}$ cation surrounded by four oxygens. This Al atom is located centrally and caged by 12 octahedral AlO_6-units linked to one another by the neighboring oxygen atoms. There are a total of 24 bridging oxygen atoms that link the 12 adjacent atoms. The cations centered in the 12 octahedra are arranged on a sphere almost equidistant from each other. The formula can be expressed as $(AlO_4Al_{12}(OH)_{24}(H_2O)_{12})^{7+}$.



15.7 $13\ AlCl_3 + 32\ NaOH + 8\ H_2O = [(AlO_4Al_{12}(OH)_{24}(H_2O)_{12})^{7+}]Cl_7 + 32\ NaCl$

III.

15.8 $13\ Al\ [(H_2O)_6]Cl_3 + 16\ (NH_4)_2CO_3 + 24\ H_2O =$

$[(AlO_4Al_{12}(OH)_{24}(H_2O)_{12})]Cl_7 + 32\ NH_4Cl + 16\ CO_2 \uparrow + 54\ H_2O$

15.9 Volume of a ball = $(4/3)\ \pi\ r^3 = (4/3) \times 3.14 \times (0.542)^3 = 0.667\ cm^3$.

Volume of 3 balls = $3 \times 0.667 = 2.00\ cm^3$.

Inner volume of crucible = $15\ cm^3$

Volume of gas = $13 - 2 = 13\ cm^3$.

$P\ V = n\ R\ T \rightarrow n = 1 \times 13 \times 10^{-3} /\ 0.082 \times 298 = 5.32 \times 10^{-4}$ mol.

After reaction:

$$\sum n_{\text{gases}} = n_{\text{before}} + n_{CO_2}$$

$P\ V = n_{\text{gases}}\ R\ T \ \rightarrow n = (2.50\ \text{atm}) \times (13.10^{-3}\ \text{L}) / (0.082\ \text{L.atm.mol}^{-1}.\text{K}^{-1}) \times (298\ \text{K}) =$
$= 1.33 \times 10^{-3}$ mol

$$n_{CO_2} = n_{\text{after}} - n_{\text{before}} = 1.33 \cdot 10^{-3} - 5.23 \cdot 10^{-4} = 8 \cdot 10^{-4}\,\text{mol}$$

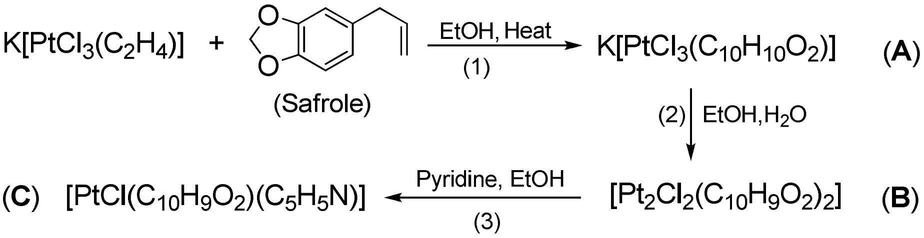
Amount of substance of Al_{13}-Keggin cation = $8 \cdot 10^{-4} / 16 = 5 \cdot 10^{-5}$ mol.

Number of Al_{13}-Keggin cations = $5 \cdot 10^{-5}$ mol × $6.023 \cdot 10^{23} = 3 \cdot 10^{19}$ ionic molecules

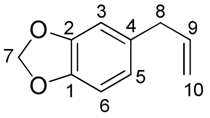
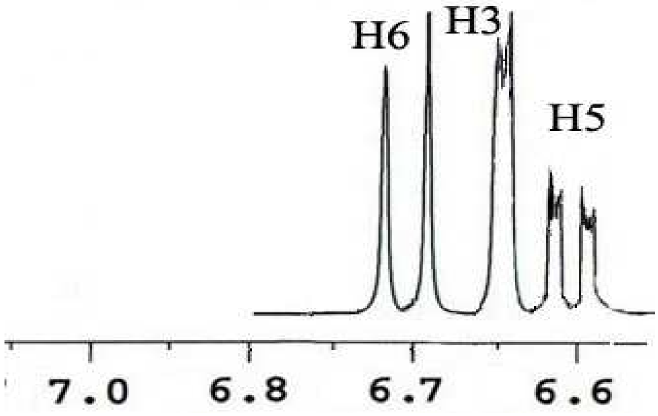
THEORETICAL PROBLEM 16

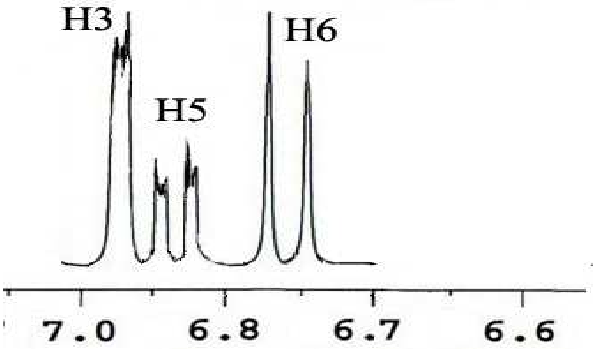
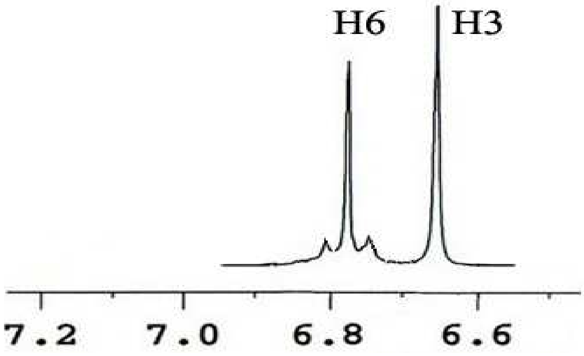
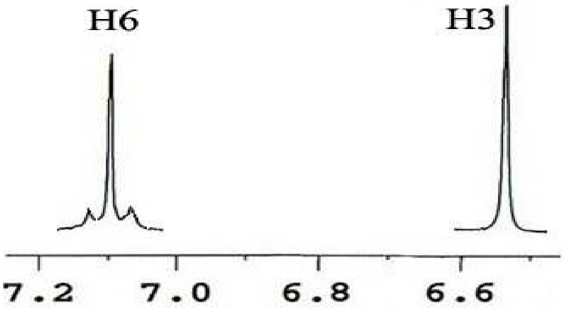
Safrole

Safrole (4-allyl-1,2-methylendioxybenzene) is obtained from oil extracted from sassafras, an evergreen tree growing in the central and northern regions of Vietnam. Safrole has interesting functionality and chemical reactivity suggesting its use as an efficient and versatile natural synthon in the synthesis of numerous biologically active compounds. [PtCl(Safrole-1H)(Pyridine)] is a complex with a similar activity to the anticancer drug Cisplatin. [PtCl(Safrole-1H)(Pyridine)] has been synthesized for the first time by chemists at the Department of Chemistry, Hanoi National University of Education. The reaction scheme is given below.



Some spectral signals of uncoordinated safrole and coordinated safrole in **A**, **B** and **C** are given below.

	**IR** absorption, ν_{C9-C10} , cm^{-1}	^{1}H NMR signals of aromatic protons, δ (ppm)
Uncoordinated	1630	

Coordinated in **A**	1510	
Coordinated in **B**	1495	
Coordinated in **C**	1500	

16.1 Write balanced equations for the three reactions in the above scheme.

16.2 What information about the coordination of safrole with Pt in **A**, **B** and **C** can be obtained from the IR and ^{1}H NMR data?

16.3 Draw the structures of **A**, **B** and **C**, given that in **C** pyridine is in the *cis*-position with respect to the allyl group of safrole.

16.4 What is the driving force of each of the reactions (1), (2) and (3)?

16.5 Why does reaction 3 not seem to obey the *trans effect*?

SOLUTION OF PREPARATORY PROBLEM 16

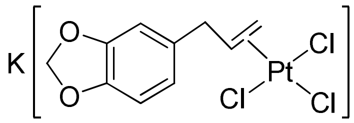
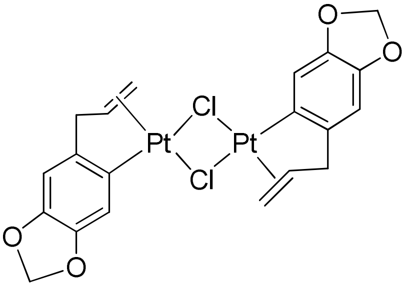
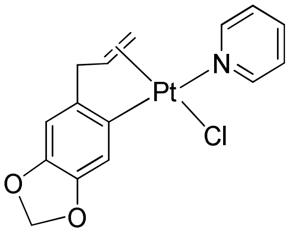
16.1

Reaction	Balanced equation
1	$K[PtCl_3C_2H_4] + C_{10}H_{10}O_2 \rightarrow K[PtCl_3(C_{10}H_{10}O_2)] + C_2H_4$
2	$2\ K[PtCl_3(C_{10}H_{10}O_2)] \rightarrow [Pt_2Cl_2(C_{10}H_9O_2)_2] + 2\ KCl + 2\ HCl$
3	$[Pt_2Cl_2(C_{10}H_9O_2)_2] + 2\ C_5H_5N \rightarrow 2\ [PtCl(C_{10}H_9O_2)(C_5H_5N)]$

16.2

	in **A**	in **B**	in **C**
From the IR data	C9 and C10 bond with Pt	C9 and C10 bond with Pt	C9 and C10 bond with Pt
From the ^1H NMR data	safrole coordinated with Pt	safrole lost H5, C5 bonds with Pt	safrole lost H5, C5 bonds with Pt

16.3

A	**B**	**C**
		

16.4

Reaction	Driving force
1	$K[PtCl_3C_2H_4] + C_{10}H_{10}O_2 \rightarrow K[PtCl_3(C_{10}H_{10}O_2)] + C_2H_4\uparrow$ Ethylene (C_2H_4, gas) is more volatile than safrole ($C_{10}H_{10}O_2$, liquid).
2	$2\ K[PtCl_3(C_{10}H_{10}O_2)] \rightarrow [Pt_2Cl_2(C_{10}H_9O_2)_2] + 2\ KCl + 2\ HCl$ The chelate complex $[Pt_2Cl_2(C_{10}H_9O_2)_2]$ is more stable.
3	$[Pt_2Cl_2(C_{10}H_9O_2)_2] + 2\ C_5H_5N \rightarrow 2\ [PtCl(C_{10}H_9O_2)(C_5H_5N)]$ In the dinuclear complex $[Pt_2Cl_2(C_{10}H_9O_2)_2]$, two bridging Cl weakly bond with Pt but in $[PtCl(C_{10}H_9O_2)(C_5H_5N)]$ the ligand C_5H_5N strongly bonds with Pt.

16.5 This reaction was controlled by steric effects rather than the *trans* effect.

THEORETICAL PROBLEM 17

Imidazole

Heterocyclic chemistry is one of the most important fields of organic chemistry and biochemistry. Approximately 55 % of publications in organic chemistry are related to the field, and the number of heterocyclic compounds recently found is far more than that of homocyclic compounds. The five-membered ring compounds with two heteroatoms are often present in many substances that are important for life. For example, imidazole ring is present in the essential amino acid, histidine, and its decarboxylation product, histamine. Histidine residues are found at the active sites of ribonuclease and of several other enzymes and play a vital part in the structure and binding functions of hemoglobin. Several drugs are based on the imidazole ring such as nitroimidazole, cimetidine, azomycin, metronidazole, midazolam.

17.1 Draw the structures of 1,3-diazole (imidazole, $C_3H_4N_2$), imidazol-1-ide anion, imidazolium cation, 1,3-oxazole (oxazole, C_3H_3NO) and 1,3-thiazole (thiazole, C_3H_3NS). Which structure(s) can be considered aromatic?

17.2 Arrange imidazole, 1,3-oxazole and 1,3-thiazole in decreasing order of melting and boiling points and justify your order.

17.3 Using structural formulae, write down equations for the ionization of imidazole, oxazole, and thiazole in water. Arrange the substances in decreasing order of base strength and justify your answer.

17.4 Propose a reaction mechanism showing the catalytic behavior of imidazole in hydrolyzing RCOOR' without a participation of OH^-. Justify this behavior based on the structure of imidazole.

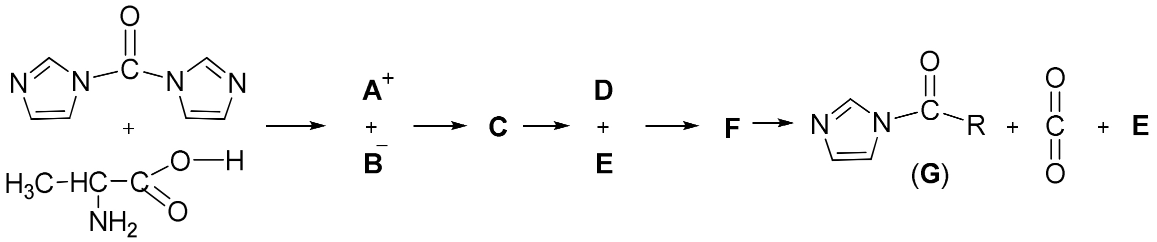
17.5 Propose a reaction mechanism for the formation of 1,1'-carbonyldiimidazole ($C_7H_6N_4O$, CDI) from imidazole and phosgen ($COCl_2$).

17.6 Explain why the C=O IR stretching frequency in 1,1'-carbonyldiimidazole is 100 cm^{-1} higher than that of 1,1'-carbonyldipyrrolidine ($CO(C_4H_8N)_2$).

17.7 Write down reaction equations for the preparation of CDI (a) using a mixture of 4 mol imidazole and 1 mol phosgene and (b) using a mixture of 2 mol imidazole, 1 mol phosgene, and 2 mol NaOH. Explain why reaction (a) is preferable.

CDI is often used for the activation of carbonyl group for the coupling of amino acids in peptide synthesis.

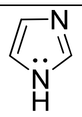
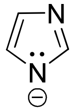
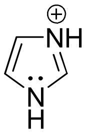
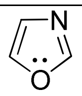
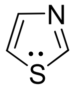
17.8 Use curly arrow mechanisms to complete the scheme below, showing the formation of the active compound **G** from CDI and Alanine.



17.9 Propose a reaction mechanism for the formation of dipeptide Ala-Gly from **G** and Glycine.

SOLUTION OF PREPARATORY PROBLEM 17

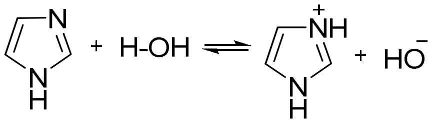
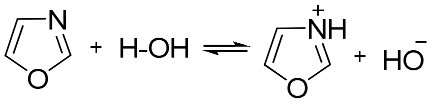
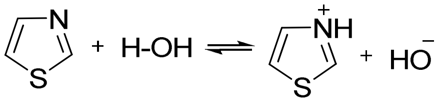
17.1

	Structure	aromatic or not
Imidazole ($C_3H_4N_2$)		aromatic
Imidazol-1-ide anion ($C_3H_3N_2$)		aromatic
Imidazolium cation ($C_3H_5N_2$)		aromatic
Oxazole (C_3H_3NO)		aromatic
Thiazole (C_3H_3NS)		aromatic

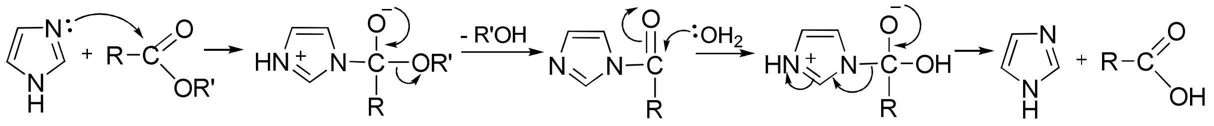
17.2

Melting point	Imidazole > Thiazole > Oxazole
Justification	Imidazole is the first because of intermolecular hydrogen bonding. Thiazole is placed before oxazole because thiazole's molecular mass and polarizability are lager than those of oxazole.
Boiling point	Imidazole > Thiazole > Oxazole
Justification	Imidazole is the first because of intermolecular hydrogen bonding. Thiazole is placed before oxazole because thiazole's molecular mass and polarizability are lager than those of oxazole.

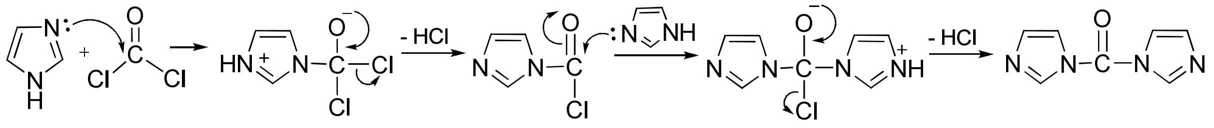
17.3

Equation for the ionization	  
K_b	Imidazole > Thiazole > Oxazole
Justification	Conjugate acid of imidazole is symmetrical delocalized, forms stronger hydrogen bonding with water, i.e. more stable, thus imidazole more basic than oxadiazole and thiazole. Atom O is more electronegative than N and S, it decreased electron density at N of oxazole, decreased stability of oxazole's conjugate acid making oxazole less basic than thiazole.

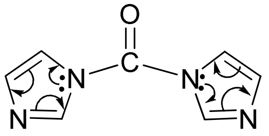
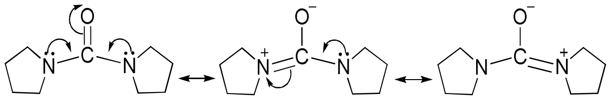
17.4

Reaction mechanism: 
Explanation: Atom N-3 (N at 3-position) is strong nucleophile; The positive charge is delocalized; The imidazole is good leaving group.

17.5



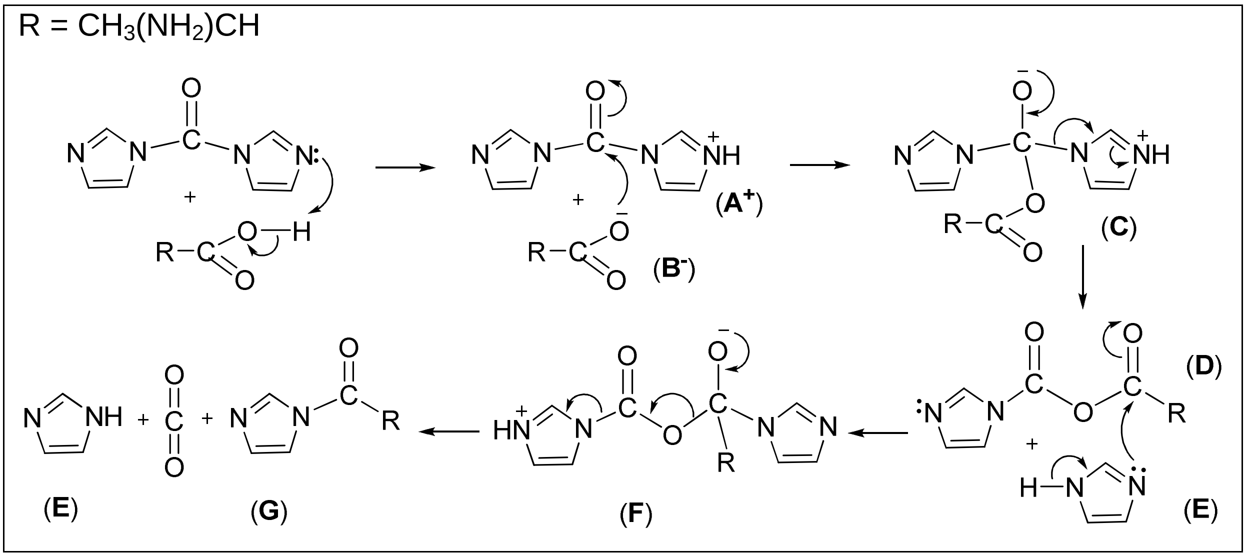
17.6

	
The pair of electrons from N-1 and four electrons of the remaining four atoms form a sextet of π-electron of aromatic system. They do not conjugate with C=O, thus do not affect the bond order of C=O.	The pair of electrons from N-1 conjugate with C=O decreasing the bond order of C=O, hence decrease its IR stretching frequency.

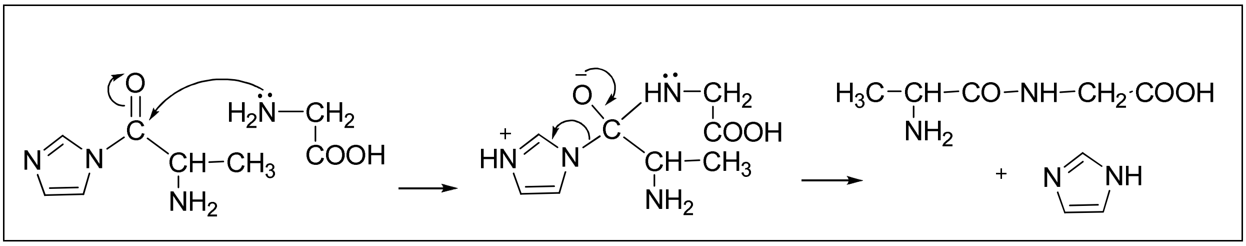
17.7

$4\ C_3H_4N_2 + COCl_2 \rightarrow (C_3H_3N_2)_2CO + 2\ [C_3H_5N_2]Cl$ (1) 2 mol of imidazole react with 1 mol of phosgene to form 1 mol of CDI and 2 mol of HCl; the other 2 mol of imidazole are used to react with the HCl.
$2\ C_3H_4N_2 + COCl_2 + 2\ NaOH \rightarrow (C_3H_3N_2)_2CO + 2\ NaCl + 2\ H_2O$ (2) In imidazolyl groups of CDI the pair of electrons from N-1 and four electrons of the remaining four atoms form a sextet of π-electron of aromatic system. They do not conjugate with C=O. Two electron-withdrawing imidazolyl groups make C=O more active, the imidazole is good leaving group, hence CDI readily reacts with water from reaction (2): $(C_3H_3N_2)_2CO + H_2O \rightarrow 2\ C_3H_4N_2 + CO_2$ (3)

17.8



17.9



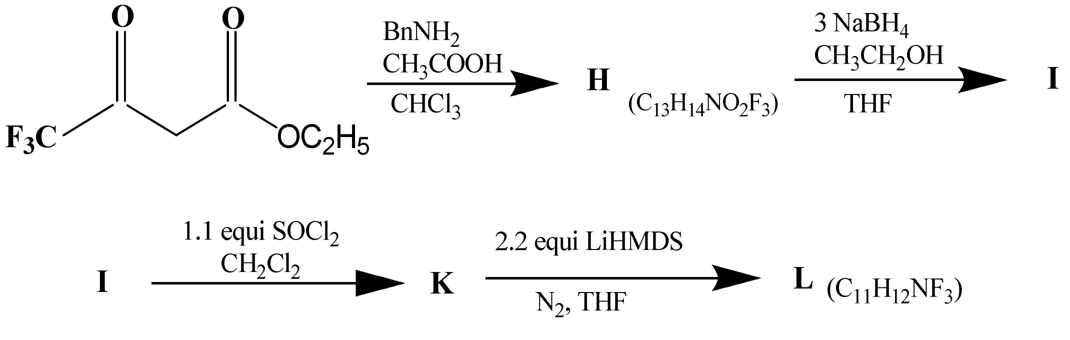
THEORETICAL PROBLEM 18

Small heterocycles

Heterocyclic compounds containing the CF_3 group are interesting targets of advanced researches to generate biologically active compounds. It is quite difficult to bring the trifluoromethyl group into saturated heterocyclic structures, especially heterocycles containing nitrogen. However, these heterocycles bearing CF_3 groups have several promising applications. Therefore, studies of such compounds have been carried out by many chemists.

Trifluoroacetaldehyde (**A**) was treated with ethanol and then refluxed with benzylamine in toluene to afford compound **B** ($C_9H_8NF_3$). The reaction of compound **B** with ethyl diazoacetate in diethyl ether with boron trifluoride etherate ($BF_3.Et_2O$) as a catalyst at -78 ^oC for 4 hours provided compound **C** ($C_{13}H_{14}NO_2F_3$). The reduction of compound **C** by $LiAlH_4$ in THF at room temperature for 2 hours formed compound **D**. Then, **D** reacts with hydrogen in the presence of $Pd(OH)_2$ as a catalyst in CH_2Cl_2 at room temperature for 60 hours to obtain **E** ($C_4H_6NOF_3$). Compound **E** was then allowed to react with 2 equivalents of tosyl chloride (TsCl) in dicloethane with Et_3N and an amount of 4-dimethylaminopyridine (DMAP) as catalyst. The reaction was carried out at room temperature for 2 hours, then 3 hours of reflux, to furnish compound **F**. **F** reacted with 1.2 equivalents of phenol in the presence of K_2CO_3 in DMF to form compound **G** ($C_{17}H_{16}NSO_3F_3$).

A derivative of **G** can be synthesized according to the following diagram:



18.1 Complete schemes of syntheses from **B** to **L**.

18.2 Write reaction mechanisms from **B** to **C**.

18.3 Write reaction mechanisms from **F** to **G**.

Note:

$BnNH_2$ = benzylamine, $C_6H_5CH_2NH_2$;

Bn = Benzyl, $C_6H_5CH_2$-,

THF = tetrahydrofuran

LiHMDS = Lithium bis(trimethylsilyl)amide,

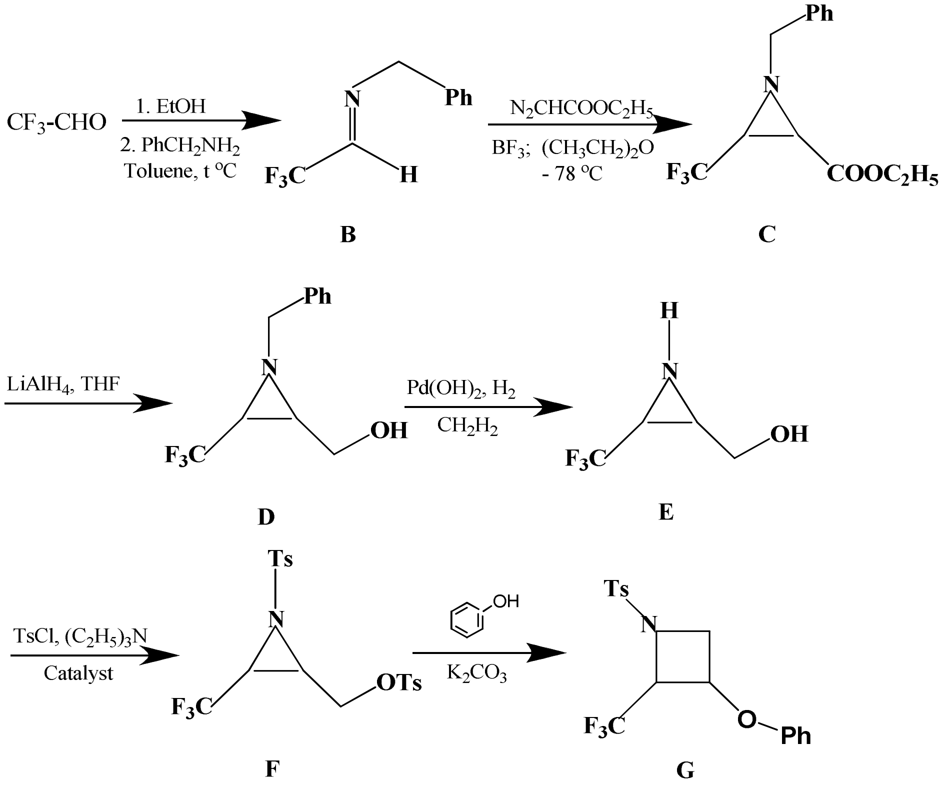
Et = C_2H_5-;

Equi = equimolarity

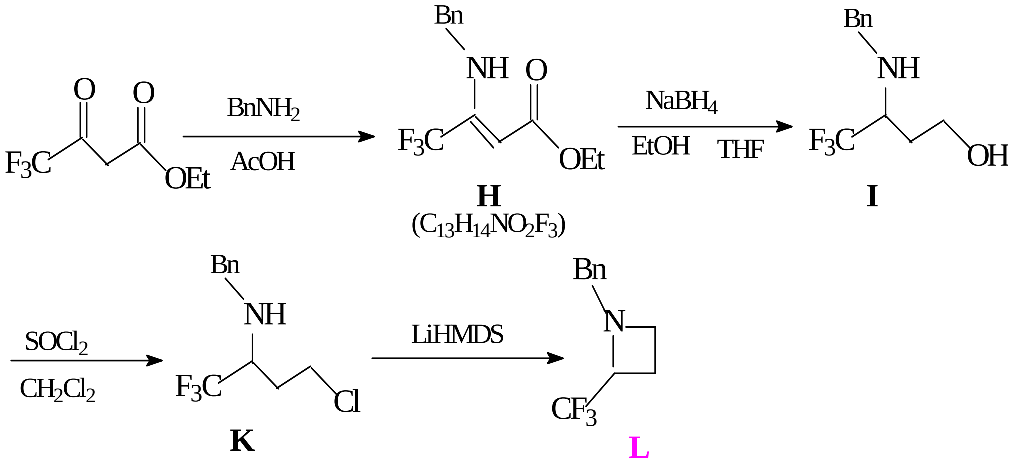
SOLUTION OF PREPARATORY PROBLEM 18

18.1

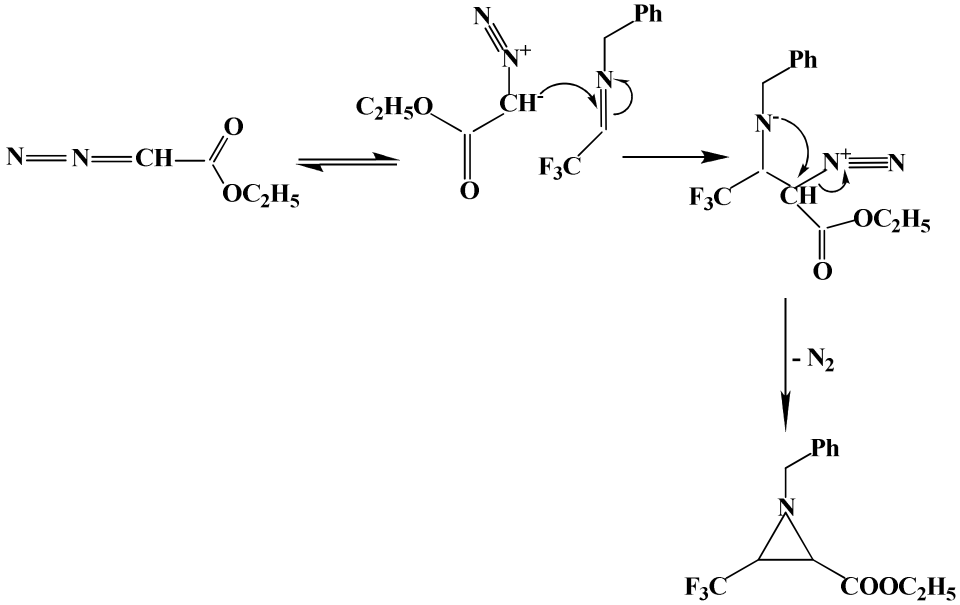
Scheme 1:



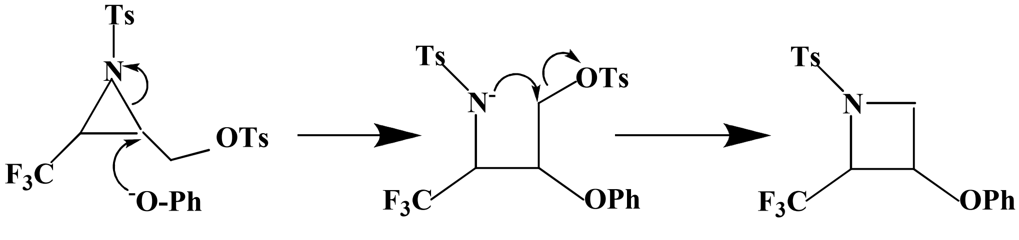
Scheme 2:



18.2 Reaction mechanism for the transformation from **B** to **C**:



18.3 Reaction mechanism for the transformation from **F** to **G**:

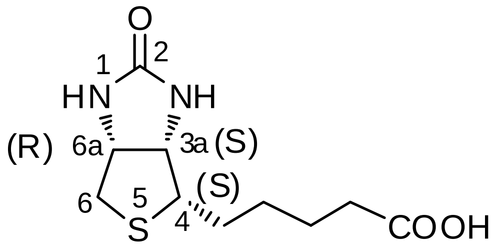


THEORETICAL PROBLEM 19

Vitamin H

Vitamin H or biotin is a highly effective growth promoter which plays an important role in many organisms, for instance baker's yeast (*Saccharomyces corevisiae*). Human beings have different demand in biotin depending on age. Lack of biotin can lead to diseases such as dermatitis, absence of appetite, fatigue, muscular pain and nerve perturbance.

Biotin was first found in 1901 by Wildiers as a growth-promoting vitamin of yeasts. Thereafter, it was found in egg yolk (by Kögl, 1936) and in liver (by Szent-Györgyi, 1936). The absolute configurations of chiral carbons of biotin were established by Trotter and Hamilton in 1966 by the single-crystal X-Ray diffraction. The molecule of biotin has three chiral carbons. Hence, there are theoretically eight diastereomers. Only the (*3aS, 4S, 6aR*)-*(D)*-(+)-biotin, however, shows the high bioactivity.

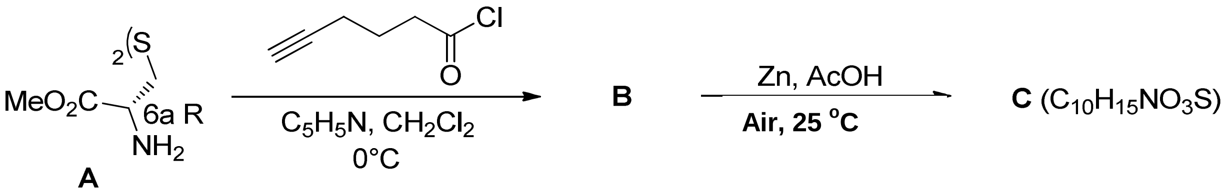


(D)-(+)-Biotin

In 1982, researchers from Hoffmann-La Roche published an elegant synthesis procedure for (*D*)-(+)-Biotin from the methyl ester of the amino acid L-Cysteine with the following steps.

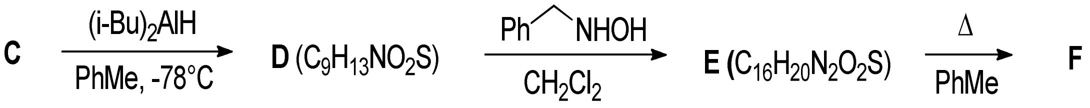
The thiol group of the methyl ester of L-cysteine was transformed into a disulfide S-S bond (compound **A**) in an oxidation reaction. **A** was then treated with hex-5-inoyl chloride to give compound **B** which was subsequently reduced by Zn / CH_3COOH to afford a thiol. This compound was cyclized by the addition of the –SH group to the terminal alkyne under atmospheric condition, resulting in the formation of **C** with a ten-membered ring containing a (*Z*) C=C double bond.

19.1 Write down the structural formulae of **A**, **B** and **C** in the hereunder scheme.



The reduction of **C** by diisobutylaluminium hydride ((*i*-Bu)$_2$AlH, DIBAL) resulted in the formation of (**D**). The condensation reaction between **D** and benzylhydroxylamine in dichloromethane produced nitrone **E** (a nitrone is an organic compound which contains a > C=N$^+$-O$^-$ group). **E** underwent a 1,3-dipolar intramolecular cyclization reaction to afford polycyclic compound **F** of which the two heterocycles, isoxazolidine (1,2-oxazolidine) and tetrahydrothiophene, shared a common bond. The cyclization reaction resulted in the (*S*) configurations of the two carbons at the common bond and the (*R*) configuration of the carbon connected to the oxygen.

19.2 Write down the structural formulae of **D**, **E** and **F.**



When **F** was reduced with Zn powder in acetic acid, the N-O bond of the heterocycle isoxazolidine was broken to give compound **G**. The reaction between **G** and chloroformate in the presence of Na$_2$CO$_3$ in THF resulted in the formation of compound **H**. The treatment of **H** in a hot solution of Ba(OH)$_2$ in dioxane, followed by an acidic work-up yielded the bicyclic δ-hydroxy acid **I** containing all the chiral centers of (*D*)-(+)-Biotin but with an "excessive" -OH group.

19.3 Draw the structures of **G**, **H** and **I** and explain the formation of **I** from **H**.

$$\mathbf{F} \xrightarrow[70^\circ\text{C}]{\text{Zn, AcOH, H}_2\text{O}} \mathbf{G}\ (C_{16}H_{22}N_2O_2S) \xrightarrow[\text{Na}_2\text{CO}_3\text{, THF}]{\text{ClCO}_2\text{Me}} \mathbf{H}\ (C_{18}H_{24}N_2O_4S) \xrightarrow[\text{2) H}_3\text{O}^{\oplus}]{\substack{\text{1) Ba(OH)}_2\\ \text{Dioxan, H}_2\text{O}}} \mathbf{I}\ (C_{17}H_{22}N_2O_4S)$$

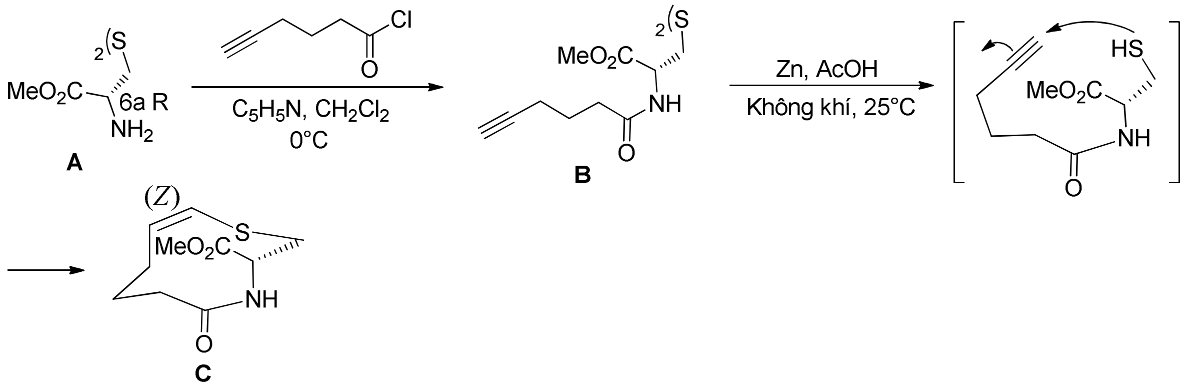
Compound **I** was treated with SOCl$_2$ to yield the corresponding chloride acid **K**, given that the configuration of the carbon attached to the "excessive" -OH is maintained in **K**.

Ester **L** was formed when **K** was reacted with methanol. **L** was reduced with $NaBH_4$ in dimethylformamide at 80°C to give ester **M** which was hydrolyzed in aqueous acidic solution of HBr to give optically pure (*D*)-(+)-Biotin.

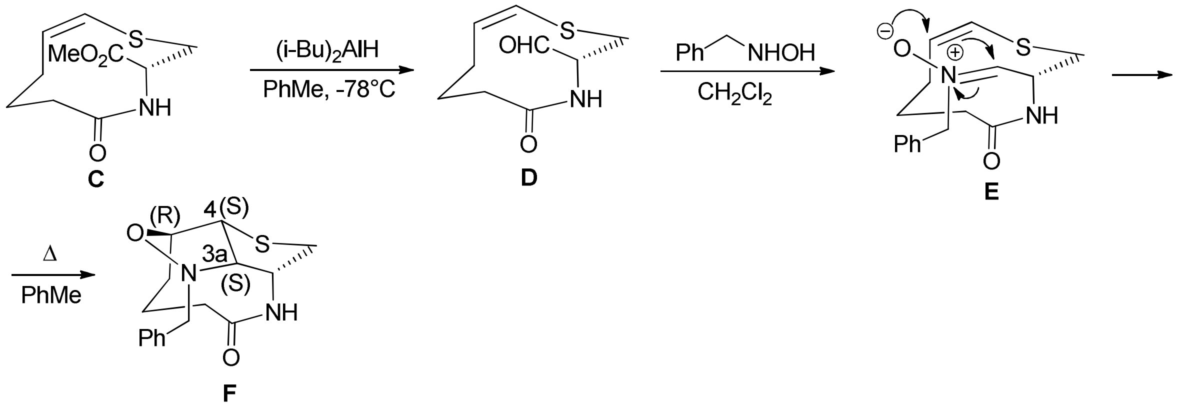
19.4 Draw the structures of **I**, **K**, **L** and **M** and the intermediates to explain the influence of the sulfur atom on the stereochemical outcome of **K**.

SOLUTION OF PREPARATORY PROBLEM 19

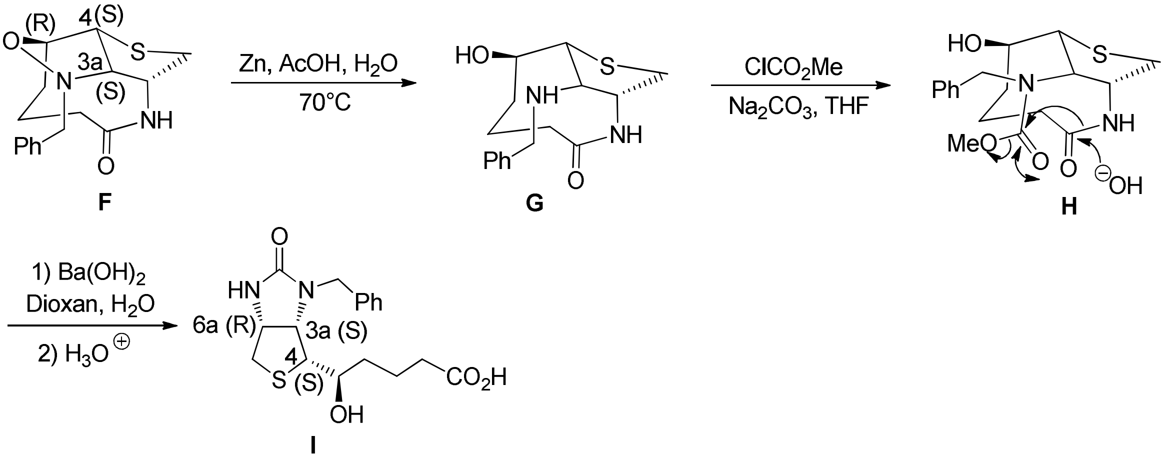
19.1 The chloride acid was reacted with the amino group of the "bis(L-cystein)" (**A**) to give amide (**B**). Zn powder in acetic acid solution reduced the S-S bond of (**B**) to give an intermediate containing a thiol (-SH) group. Under normal condition, the -SH group added spontaneously to the terminal alkyne group to yield (**C**) with a ten-membered ring, of which the newly formed C=C double bonds had (Z) configuration.



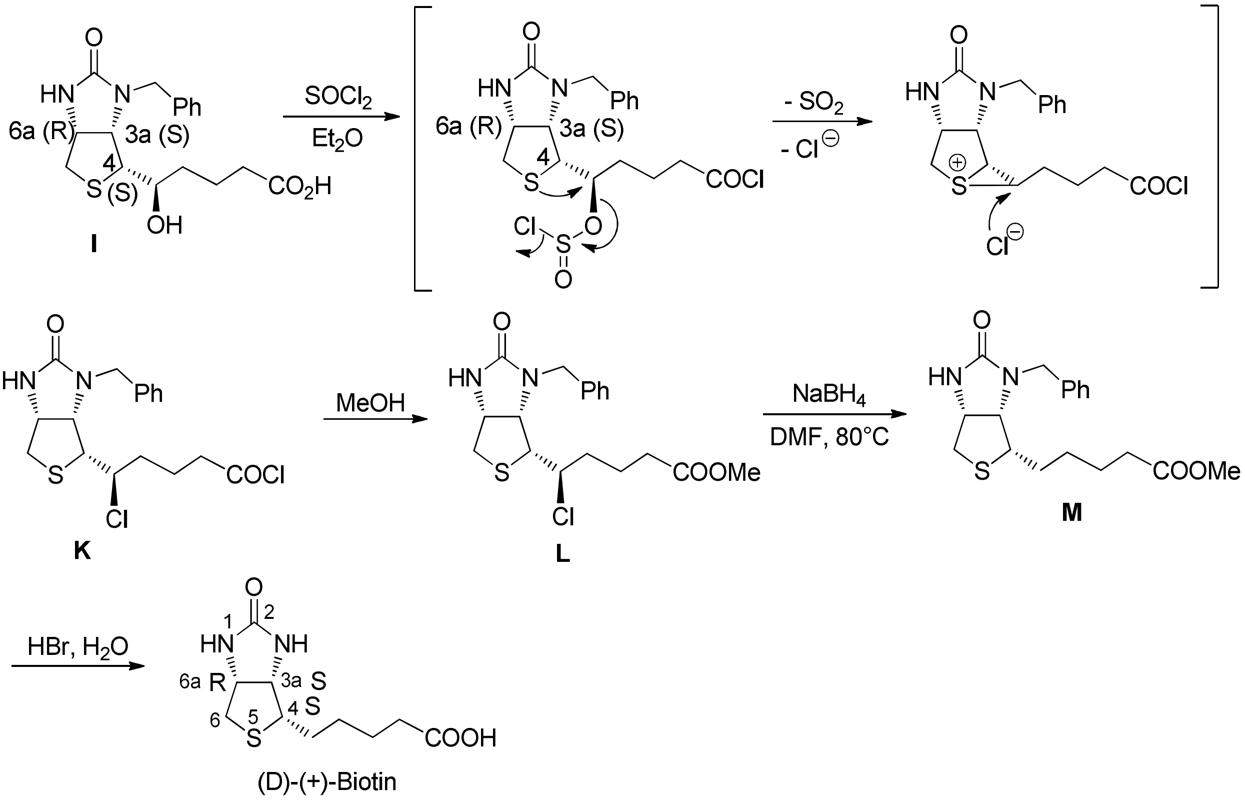
19.2 Diisobutyl aluminium hidride (DIBAL) partially reduced ester (**C**) into aldehyde (**D**) which was condensed with benzylhydroxylamine to give nitrone (**E**) with (*E*) configuration. In the intramolecular [4+2] cyclization reaction of (**E)** (*note that '4' and '2' are the numbers of π electron of the nitrone and the double bond involved in the cyclization, respectively*), the configuration of the double bonds C=C and C=N remained unchanged. The resulting compound (**F**) had three new chiral centers, two of which were (3a*S*, 4*R*). They were the configurations of the corresponding C3 and C4 in the skeleton of (*D*)-(+)-Biotin. The third chiral carbon which was attached to the oxygen atom had an (*R*) configuration.



19.3 (**F**) was reduced by Zn in acetic acid to give (**G**) containing one –OH group and a second-order amino group. The amino group was reacted with chlorofomate in the presence of Na_2CO_3 in THF solution produce (**H)**. Under basic condition, the ten-membered ring of (**H)** was opened to give δ-hydroxy acid (I). The configuration (6a*R*) of (**I**) resulted from the (*R*) configuration of the chiral carbon in L-cysteine. Therefore, L-cystein is chosen as the starting material for the synthesis.



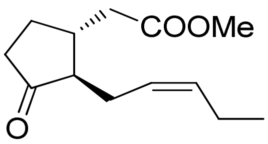
19.4 The sulfur atom caused an anchimeric effect by which the configuration of the carbon attached to the –OH in compound (□) remained unchanged as this –OH group was replaced by the halogen atom to yield (**K**). The halogen atom was then replaced when (**K**) was reduced with $NaBH_4$ in which the "pentanoic acid" branch of (*D*)-(+)-biotin was formed. The hydrolysis of ester (**M**) in the aqueous solution of HBr, followed by the removal of the benzyl group resulted in the formation of the target molecule, (*D*)-(+)-Biotin.


I
SOCl2
Et2O
6a (R)
3a (S)
4
(S)
- SO2
- Cl⊖
K
MeOH
L
NaBH4
DMF, 80°C
M
HBr, H2O
(D)-(+)-Biotin

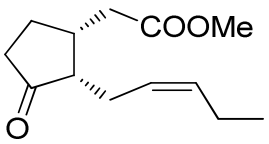
THEORETICAL PROBLEM 20

No perfume without jasmine

The Spanish jasmine originated from the valleys of Himalaya. This so called *Jasminum grandiflorum* L., which was grafted on the wild *Jaminum officinale* L, has the possibility to resist against the cold of the mountain climate. In 1962, E. Demole and E. Lederer successfully isolated and clearly determined the structures of the important flavor component of the essential oil of jasmine. It was actually a mixture of two diastereomers (*Z*)-(*3R,7R*) methyl jasmonate and (*Z*)-(*3R,7S*) methyl jasmonate with the structures shown below.



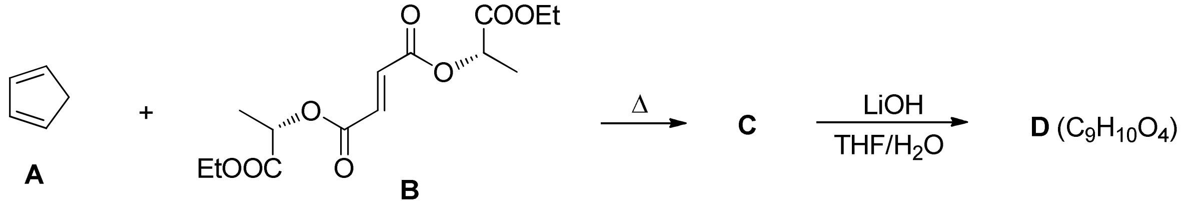
(*Z*)-(*3R,7R*) methyl jasmonate



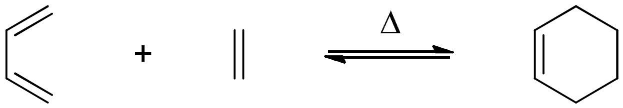
(*Z*)-(*3R,7S*) methyl jasmonate

Due to its important role in perfume industry as well as its limited natural resource, the synthesis of jasmonates has attracted interest of many chemists. The first synthesis of optically pure (*Z*)-(*3R,7S*)-methyl jasmonate was carried out in 1990 by Helmchen with the following steps:

I. The first step in the synthesis is a Diels-Alder reaction between cyclopentadiene **A** and ester **B** of fumaric acid with (*S*)-ethyl lactate to yield **C**.



A cyclo-addition reaction, a kind of pericyclic reaction, involves bonding between the termini of two π systems to produce a new ring (scheme below). The product has two more σ bonds and two less π bonds than the reactants. The Diels-Alder reaction, or so called [4+2], is a common thermally activated cycloaddition whose stereoselectivity is *syn* addition. In this concerted *syn* addition, the stereochemical relationships among the substituents are retained in the product(s).



The hydrolysis of **C** in basic solution followed by an acidification step resulted in the formation of **D**.

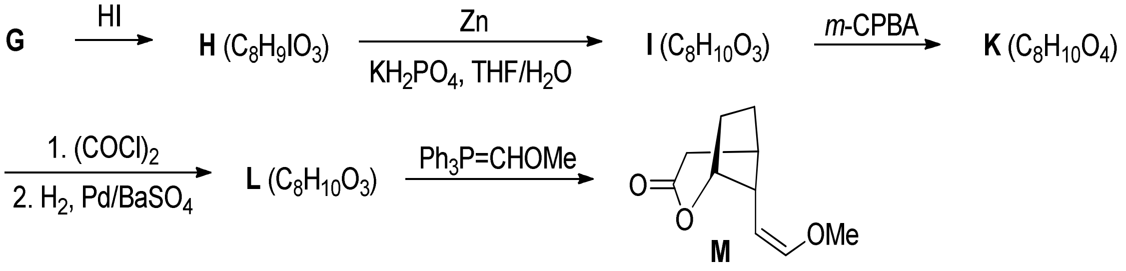
20.1 Draw the structures of **C** and **D**.

II. The reaction between **D** and I_2 in KI solution gave rise to the formation of the five-membered ring lactone of the *endo* –COOH group. When heated under basic condition, **E** underwent a decarboxylation-cyclization reaction to produce compound **F**. The hydrolysis in basic medium followed by oxidation with $NaIO_4/RuO_4$ transformed **F** into γ-keto acid **G**.

$$\mathbf{D} \xrightarrow{KI_3} \mathbf{E} \xrightarrow[\substack{DMSO,\ 175°C \\ -CO_2}]{KOH} \mathbf{F} \xrightarrow[2.\ NaIO_4,\ RuO_4]{1.\ NaOH} \mathbf{G}$$

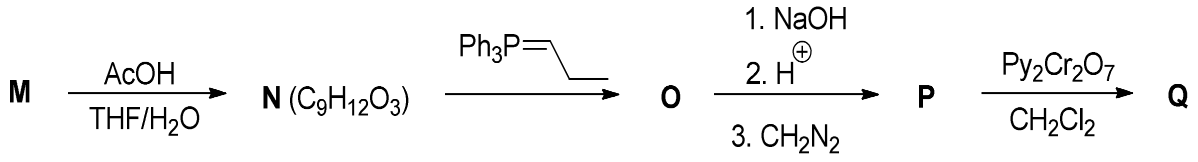
20.2 Write down the structures of **E** to **G**.

III. **G** was reacted with HI to yield compound **H** containing only five-membered rings. When **H** was reduced by Zn/KH_2PO_4 in tetrahydrofuran, it transformed into carboxylic acid **I** which was then oxidized in a Bayer-Villiger rearrangement with *meta*-chloroperoxybenzoic acid (*m*-CPBA) to give the major product **K**. **K** was treated with oxaloyl chloride, followed by a $Pd/BaSO_4$ catalyzed reduction with H_2 (Rosenmund reduction) to give **L**. Compound **M** was separated from the Wittig reaction mixture between **L** and the yield Ph_3P $=CHOCH_3$.



20.3 Draw the structures of the compounds from **G** to **L**.

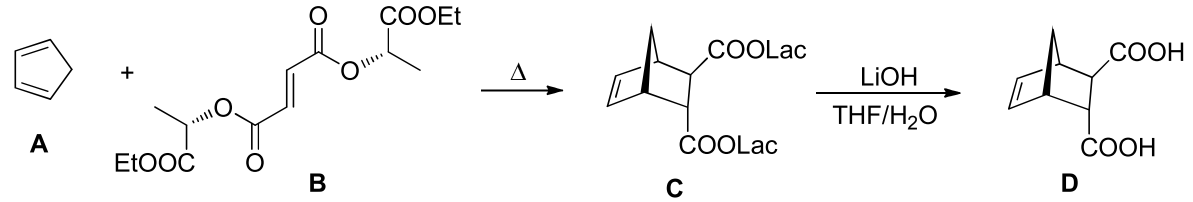
IV. Hydrolysis of **M** in THF/H_2O solution of acetic acid produced **N** which underwent a Wittig reaction with the ylide $Ph_3P = CHCH_2CH_3$ to form **O**. The hydrolysis of **O** in basic solution, followed by a neutralization step and then treatment with diazomethane resulted in the formation of **P**. In the last step, the target molecule, (*Z*)-(*3R,7S*)-methyl jasmonate **Q**, was obtained in the oxidation reaction of **P** with pyridinium dichromate.



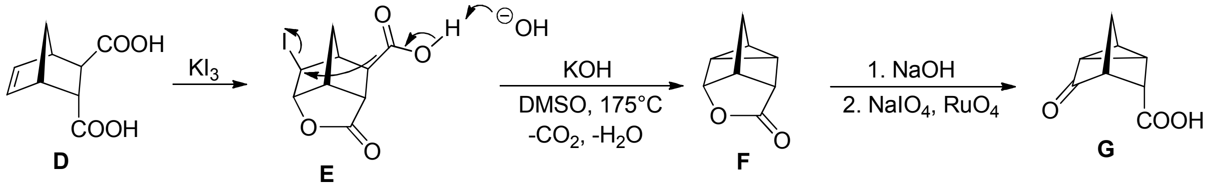
20.1 Draw the structures of compounds from **N** to **P**.

SOLUTION OF PREPARATORY PROBLEM 20

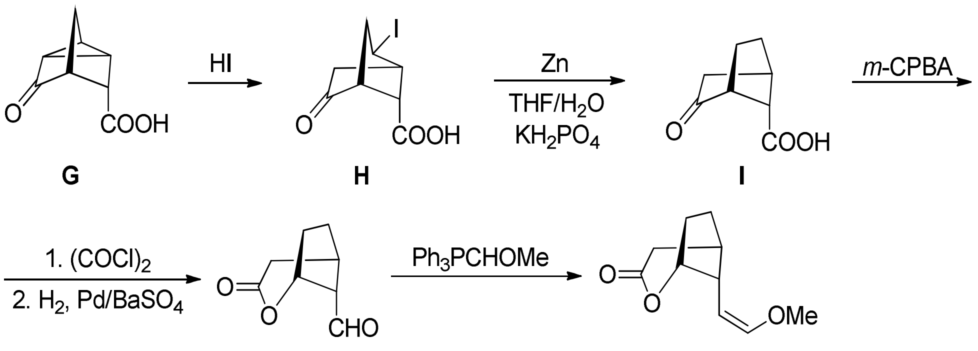
20.1 In a [4+2] cycloaddition reaction (Diels-Alder reaction), the configuration of the dienophine (**B**) remained unchanged: the two ester groups –COOLac of compound (**C**) were placed in different sites in comparison to the six-membered ring. The hydrolysis of these two ester groups in LiOH solution gave the two corresponding *trans* carboxyl groups.



20.2 When dicarboxylic acid (**D**) was treated with I_2/KI, it was transformed into γ-iodolactone (**E**) of the *endo* –COOH. This lactone then underwent a decarboxylation-cyclization in basic solution step to give lactone (**F**) containing a three-membered ring. The secondary –OH group which resulted from the hydrolysis of (**F**) was oxidized by $NaIO_4$ to form a carbonyl group.



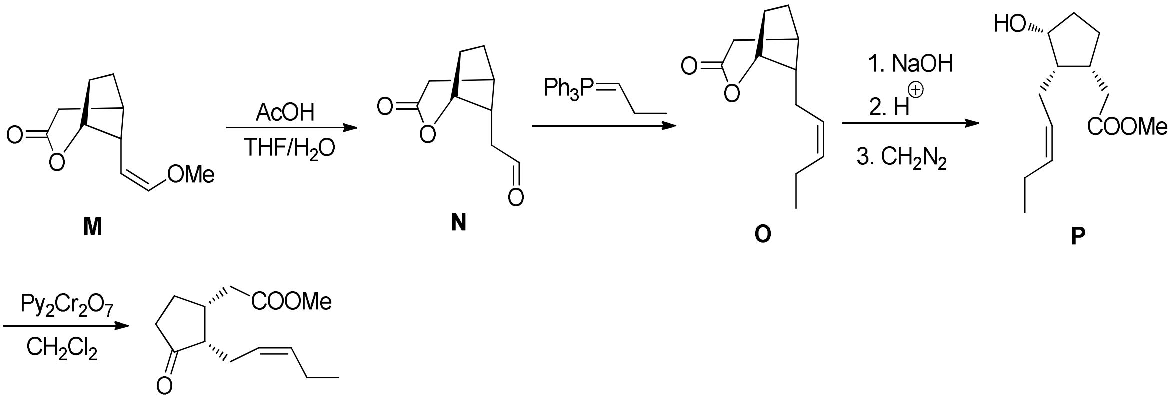
20.3 The addition-ring opening step of the cyclopropane ring with HI oriented by the (-C) conjugation effect of the carbonyl resulted in the formation of γ-iodo acid (**H**) containing only five-membered rings. The reductive elimination of the iodine atom by Zn in acetic acid produced ketoacid (**I**) which underwent a Bayer-Viiliger oxidation to yield lactone (**K**) (the main product) with one carboxyl group. The carboxyl group was treated under Rosenmund reduction condition in which lactone (**L**) with an aldehyde functional group was obtained. Vinyl ether (**M**) was separated from the Wittig reaction between the aldehyde and the ylide $Ph_3P=CHOMe$.



G **H** **I** **K**

L **M**

20.4 Methyl vinyl ether (**M**) was hydrolyzed in acidic medium to give lactone (**N**) containing an aldehyde functional group. From the Wittig reaction between (**N**) and the ylide $Ph_3P=CHCH_2CH_3$, lactone (**O**) with a *cis* carbon-carbon double bond was separated. The hydrolysis of the lactone (**O**) followed by treatment with diazomethane produced ester (**P**) which was oxidized with pyridine dichromate to give the target compound (*Z*)-(*3R,7S*)-methyl jasmonate.



M **N** **O** **P**

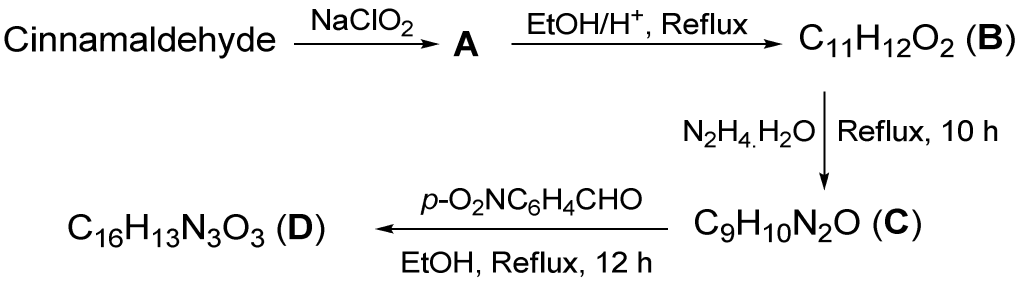
(*Z*)-(*3R,7S*)

THEORETICAL PROBLEM 21

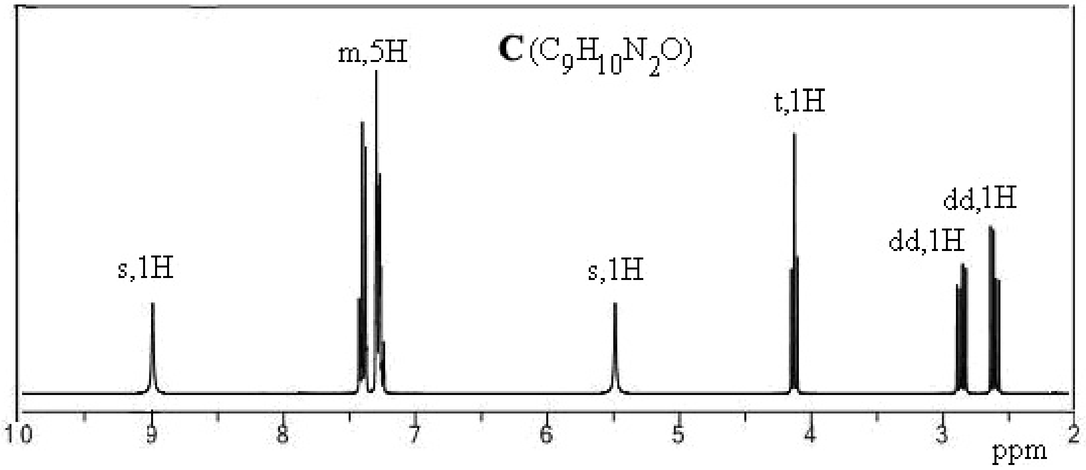
Vietnamese cinnamon

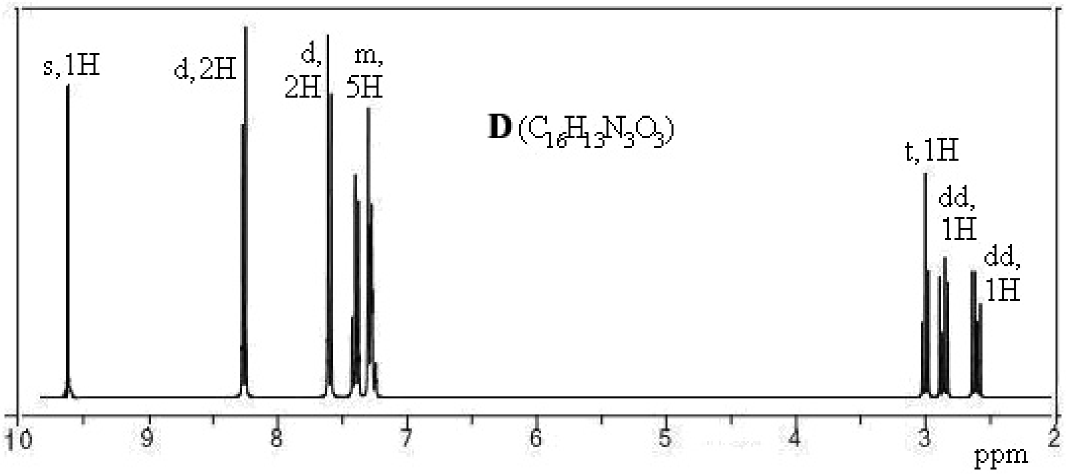
Cinnamomum loureiroi, also known as Vietnamese cinnamon, is an evergreen tree grown in the central and northern regions of Vietnam. Aromatic bark of the tree has medicinal and culinary value. Essential oil of the bark contains cinnamaldehyde ((2*E*)-3-phenylprop-2-enal) as the main component.

Mild oxidation of cinnamaldehyde with $NaClO_2$ affords an acid **A**. **A** undergoes subsequent esterification with ethanol to form ethyl cinnamate (**B**). Refluxing ethyl cinnamate and 80% hydrazine hydrate solution for 10 h gives **C** ($C_9H_{10}N_2O$). Refluxing **C** and *p*-nitrobenzaldehyde in ethanol for 12 h affords **D** ($C_{16}H_{13}N_3O_3$).



^{1}H NMR spectra of **C** and **D** are given below (the multiplicity and relative intensity is shown for each signal).



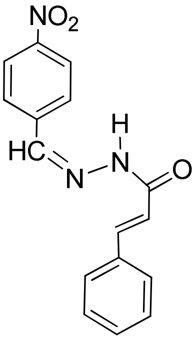


21.1 Give the structures for **A**, **B**, **C.**

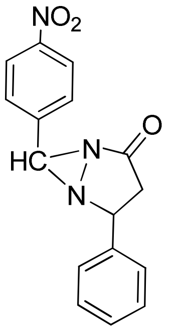
21.2 Assign ^{1}H NMR signals in the first spectrum to appropriate proton groups of **C**.

21.3 Propose a reaction mechanism for the formation of **C** from **B**.

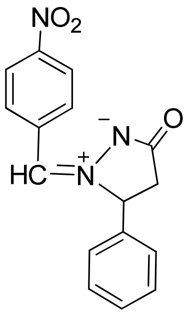
21.4 Among four given below structures, select one for **D** and give the reasons for your selection.



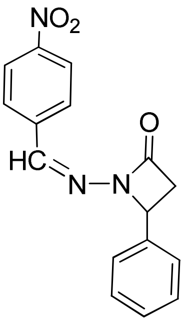
(**D1**)



(**D2**)



(**D3**)

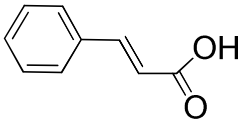
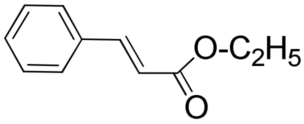
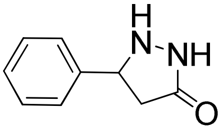


(**D4**)

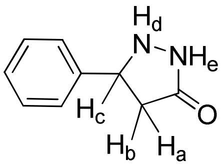
21.5 Assign ^{1}H NMR signals in the second spectrum to appropriate proton groups of **D**.

SOLUTION OF PREPARATORY PROBLEM 21

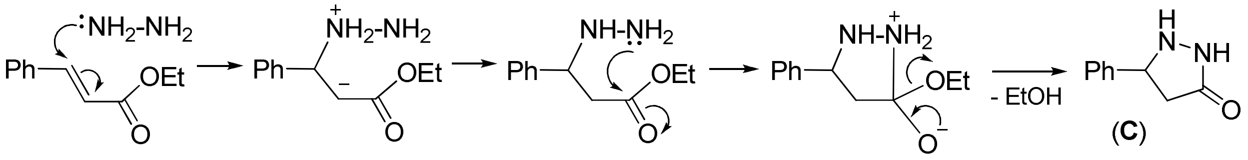
21.1

A	**B**	**C**
		

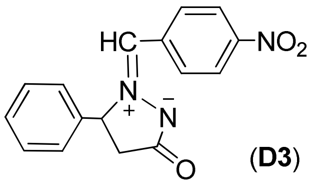
21.2

C	9.0 ppm, s	7.4-7.3 ppm, m	5.5 ppm, s	4.2 ppm, t	2.8 ppm, dd	2.6 ppm, dd
	**H_e**	**C_6H_5**	**H_d**	**H_c**	**H_a**	**H_b**

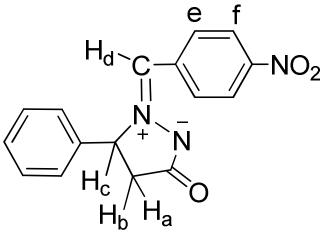
21.3



21.4

The structure for **D**	Reasons for your selection.
	**D3** derives from **C** and corresponds with the given ^{1}H NMR spectrum. **D1** and **D4** do not derive from **C**. **D1** does not correspond with second ^{1}H NMR spectrum (For example in the spectrum there are not two ethylenic protons). **D2** and **D4** seem corresponding to the given ^{1}H NMR spectrum, but **D2** contains three members and **D4** contains four members cycles, which cannot exist after reflux for 12 h.

21.5 Assignment of ^{1}H NMR signals in second spectrum to appropriate proton groups of **D**.

D	9.6 ppm, s	8.3 ppm, d	7.6 ppm, d	7.4-7.3 ppm, m	3.0 ppm, t	2.9 ppm, dd	2.6 ppm, dd
	**H_d**	**2 H_f**	**2 H_e**	**C_6H_5**	**H_c**	**H_a**	**H_b**

THEORETICAL PROBLEM 22

Cinnamic acid

I. Ultraviolet irradiation of *trans*-cinnamic acid ((*E*)-3-phenylprop-2-enoic acid) in solution yielded a mixture of *cis*-cinnamic and *trans*-cinnamic acids. *trans*-Cinnamic acid can be crystallized in two forms: α-form or β-form. Ultraviolet irradiation of crystalline *trans*-cinnamic acid in the α-form yielded α-truxillic acid (2,4-diphenylcyclobutane-1,3-dicarboxylic acid). Ultraviolet irradiation of crystalline *trans*-cinnamic acid in the β-form yielded β-truxinic acid (2,3-diphenylcyclobutane-1,4-dicarboxylic acid). α-Truxillic acid possesses a symmetric center. In β-truxinic acid, the two phenyl groups are on the same side of the cyclobutane ring, and the two carboxyl groups are on the opposite sides.

22.1 Propose a reaction mechanism for the isomerization of *trans*-cinnamic acid.

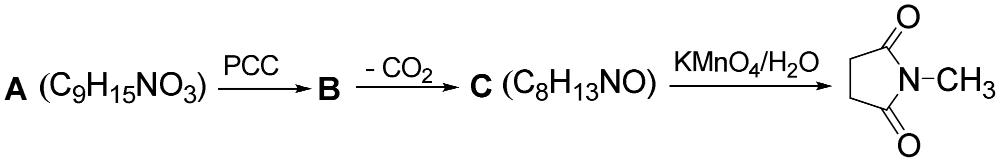
22.2 Draw the structure of α-truxillic acid and all its diastereoisomers.

22.3 Draw the structure of β-truxinic acid and all its diastereoisomers. Show the structures which have enantiomers.

22.4 Suggest how the different packing arrangements of trans-cinnamic acid in the α- and β- crystal forms leads to the different structures of α-truxillic and β-truxinic acid.

22.5 Why does cinnamic acid not dimerize in solution upon ultraviolet irradiation?

II. Hydrolysis of α-truxilline ($C_{38}H_{46}N_2O_8$, an alkaloid obtained from Truxillo coca) gives α-truxillic acid, methanol and an acid **A** ($C_9H_{15}NO_3$). Oxidation of **A** with pyridinium chlorochromate (PCC) leads to **B**, which is readily decarboxylated to form optically inactive ketone **C** ($C_8H_{13}NO$). Oxidation of **C** with potassium permanganate gives N-methylsuccinimide.



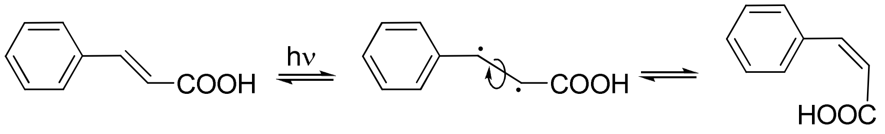
22.6 Propose the structures of **A**, **B**, **C**. Are **A**, **B** optically active or not? Explain. Why **C** is optically inactive?

22.7 Propose the structure of α-truxilline. Is α-truxilline optically active or not? Explain.

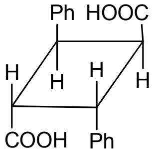
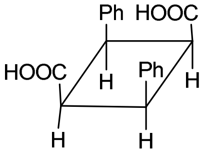
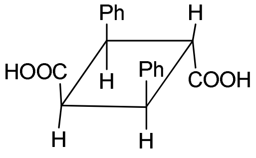
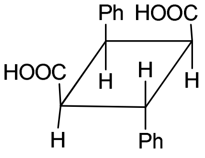
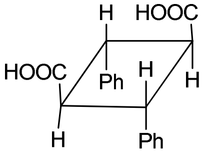
SOLUTION OF PREPARATORY PROBLEM 22

I.

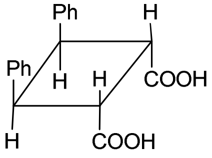
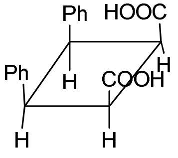
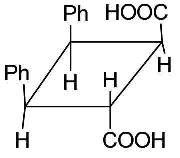
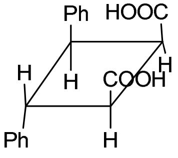
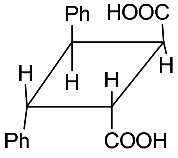
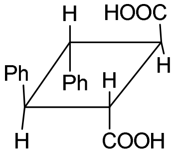
22.1

Reaction mechanism for the isomerization


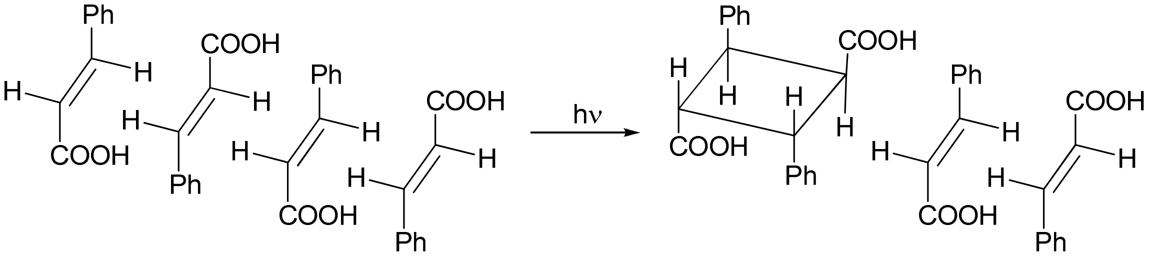
22.2

 α-truxillic acid			
			

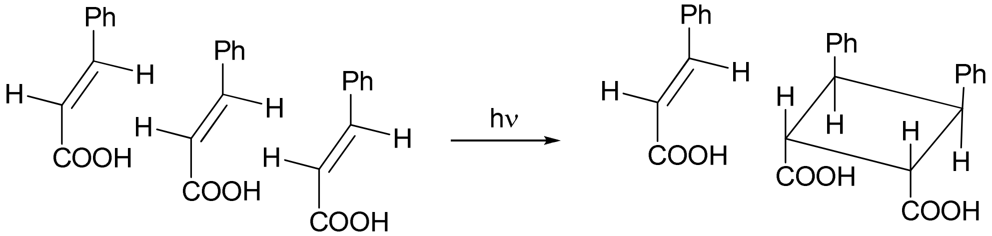
22.3

			
β-truxinic acid		Has an enantiomer	Has an enantiomer
			
Has an enantiomer	Has an enantiomer		

22.4 The packing arrangement of α-type of *trans*-cinnamic acid which leaded to the formation of α-truxillic acid

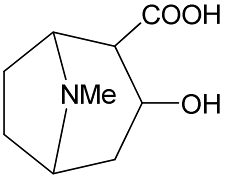
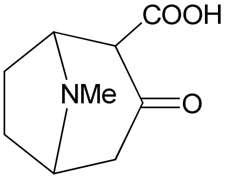
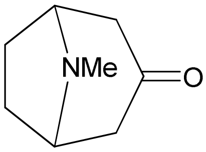


The packing arrangement of β-type of *trans*-cinnamic acid which leaded to the formation of β-truxinic acid.

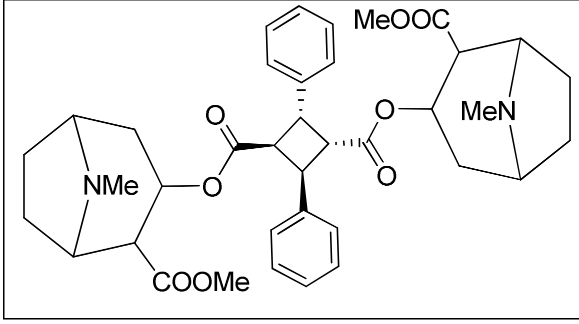


22.5 In solution all molecules of cinnamic acid were solvated and randomly arranged.

II.**22.6**

A	B	C
		
Optically active since A has four asymmetric carbons and has no symmetrical plane and no symmetrical center.	Optically active since B has three asymmetric carbons and has no symmetrical plane and no symmetrical center.	Optically inactive since C has symmetrical plane although has two asymmetric carbons.

22.7

	Optical active since each bicyclooctane moiety has four asymmetric carbons and their configurations are exactly the same as in A thus *α*-truxilline has no symmetrical plane and no symmetrical center.

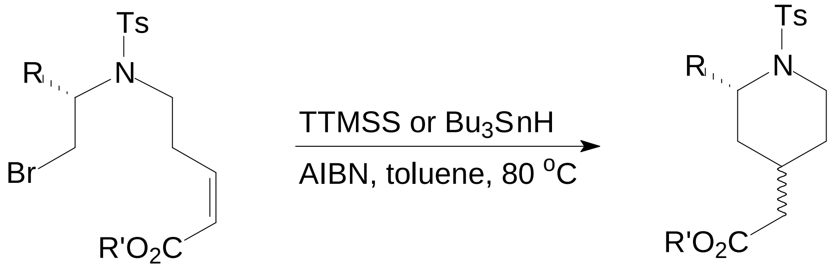
THEORETICAL PROBLEM 23

Tris(trimethylsilyl)silane and azobisisobutyronitrile

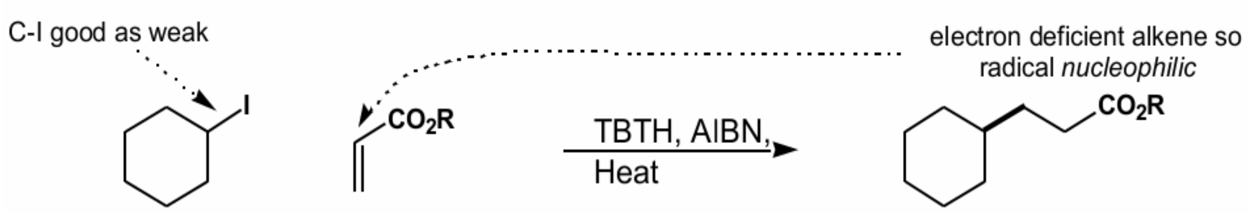
In the late eighties, Chatgilialoglu and coworkers introduced tris(trimethylsilyl)silane, (TTMSS or $(TMS)_3SiH$) as a radical-based reducing agent for functional group modifications and a mediator for sequential radical reactions. The use of $(TMS)_3SiH$ allows reactions to be carried out under mild conditions with excellent yields of products and remarkable chemo-, regio-, and stereoselectivity. $(TMS)_3SiH$ is an effective reducing agent for the removal of a variety of functional groups. Examples of dehalogenation (Cl, Br and I) and reductive removal of chalcogen groups (SR and SeR) are well known. The most popular thermal initiator is azobisisobutyronitrile, {AIBN, $[(CH_3)_2C(CN)]_2N_2$} under heating conditions in toluene.

I. Reactions using TTMSS and AIBN are given in the hereunder examples.

1. Radical cyclisation was studied using two different reducing agents: tributyltin hydride (TBTH, Bu_3SnH) and tris(trimethylsilyl)silane (TTMSS).

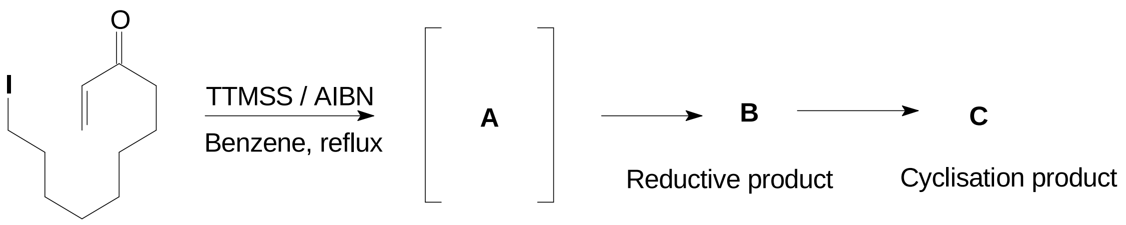


2. Radical introduction of a side chain (alkylation)



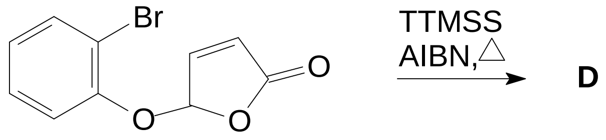
II. TMSS has found multiple applications in the organic synthesis described in the below reactions:

3. The compound (**I**) was converted to **B** and **C** *via* the radical intermediate **A**.



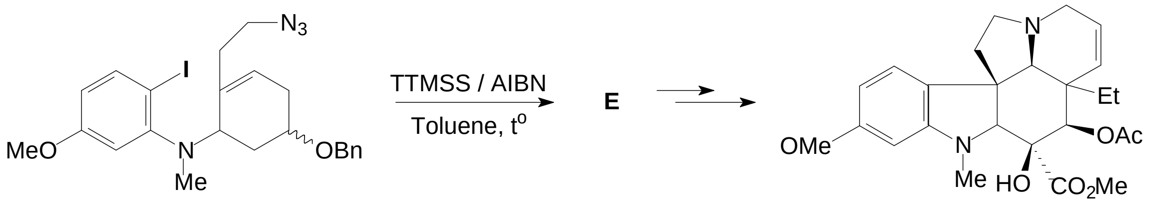
(I)

4. The compound (**II**) was converted to **D.**



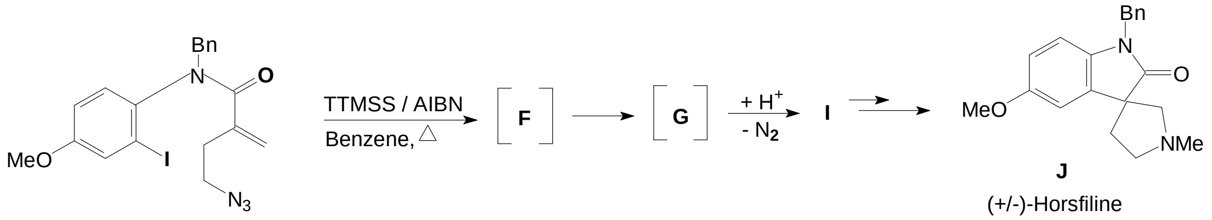
(II)

5. The compound (**III**) was converted to **E,** and then through several steps to afford (±) - vindoline



(III)

6. Horsfiline (**J**) is an oxindole alkaloid found in the plant *Horsfieldia superba*, which has analgesic effects. The method for horsfiline synthesis from the compound (**IV**) was described below:



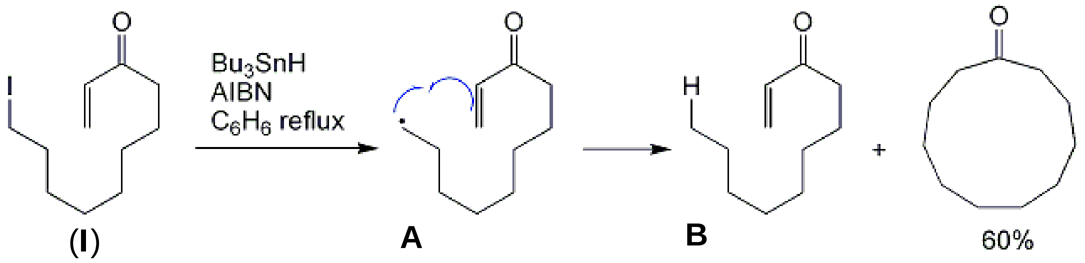
(IV)

23.1 Write down the structural formulae of all compounds **A** to **I** in the above reactions.

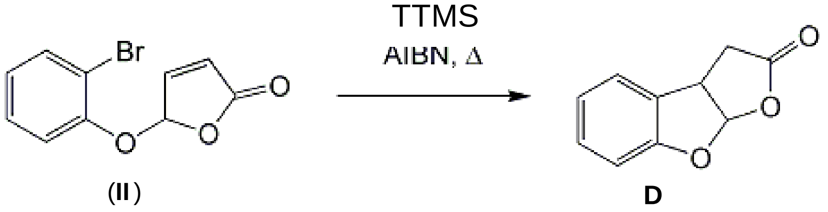
SOLUTION OF PREPARATORY PROBLEM 23

The products from the each reaction:

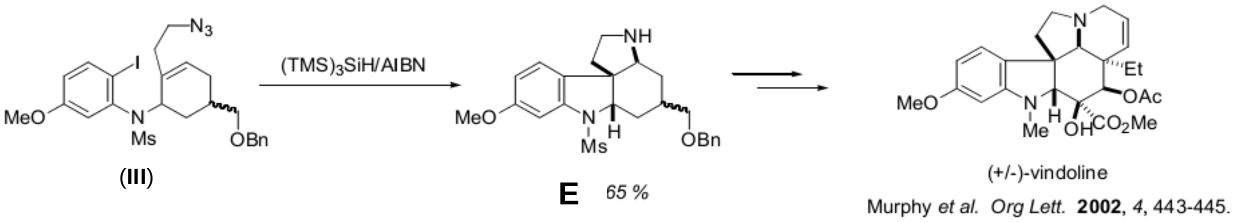
23.1 **A**, **B** and **C** from the compound (**I**):



From the compound (**II**):

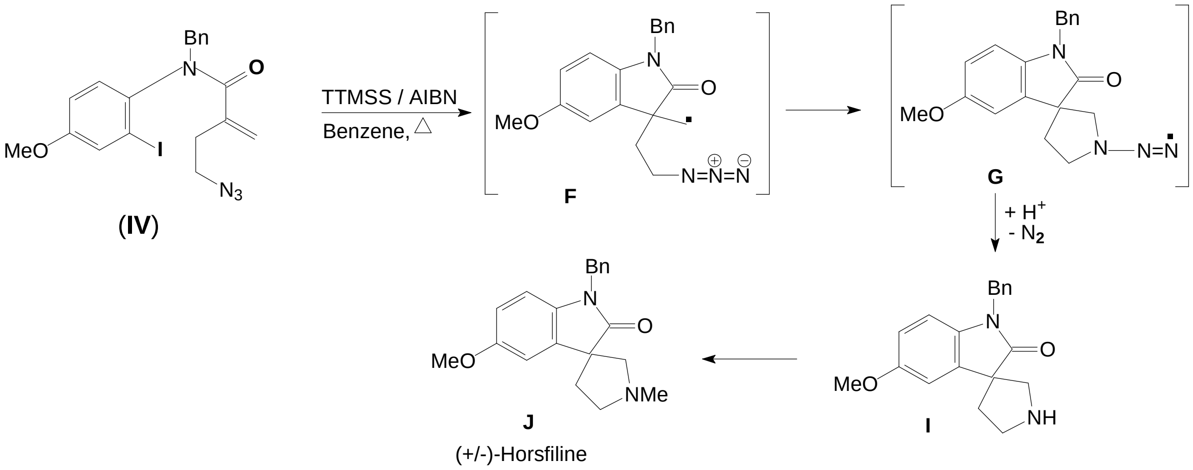


E from the compound (**III**):



Murphy *et al.* *Org Lett.* **2002**, *4*, 443-445.

I from the compound (**IV**) through radicals **F** and **G**:

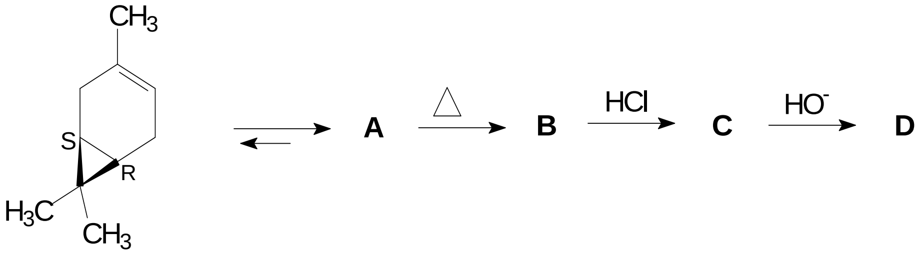


THEORETICAL PROBLEM 24

(–)-Menthol from (+)-δ-3-Carene

Carene, or δ-3-carene, is a bicyclic monoterpene which occurs naturally as a constituent of turpentine. (+)-δ-3-Carene has the required structural features to serve as a starting material for (-)-menthol.

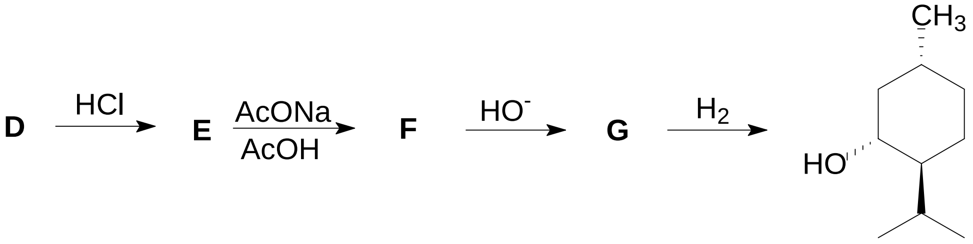
The procedure of preparation of (-)-menthol from (+)-δ-3-carene was described as follows. Catalytic isomerization of δ-3-carene provides the needed (+)-δ-2-carene (**A**) which then was pyrolysed to cleave the cyclopropane ring. The resultant 2,8-menthaldien (**B**) had the right stereochemistry at C1 and C4 of (–)-menthol. Treatment of the unconjugated diene **B** with 1 equivalent mole of HCl gives **C** and then, dehydrochlorination leads to a conjugated diene (**D**).



1S, 6R-(+)-delta-3-Carene

Treatment of **D** with hydrogen chloride affords 8-chloro-3-*p*-menthene (**E**) which then reacted with sodium acetate and acetic acid to give mixed (*cis/trans*) pulegol esters (**F**) via allylic displacements. Hydrolysis of **F** affords (-)-cis and (+)-*trans*-pulegol (**G**).

Because the absolute configuration of C-1 is fixed in this system, reduction of either pulegol isomer provides menthol isomers which can be readily equilibrated to predominently (-)-menthol.

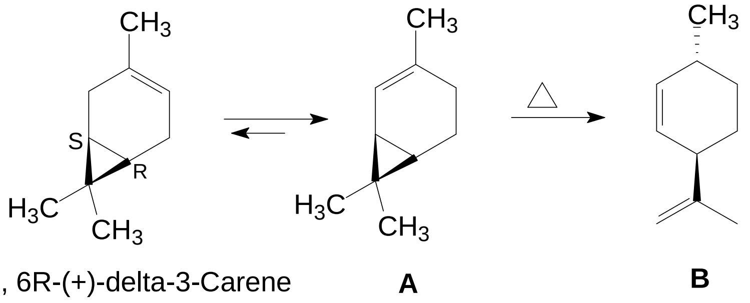


(-)-Menthol

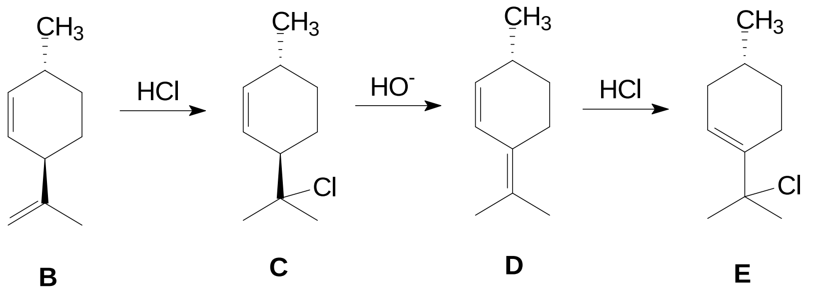
24.1 Write down the structural formulae of the compounds **A** to **G**.

SOLUTION OF PREPARATORY PROBLEM 24

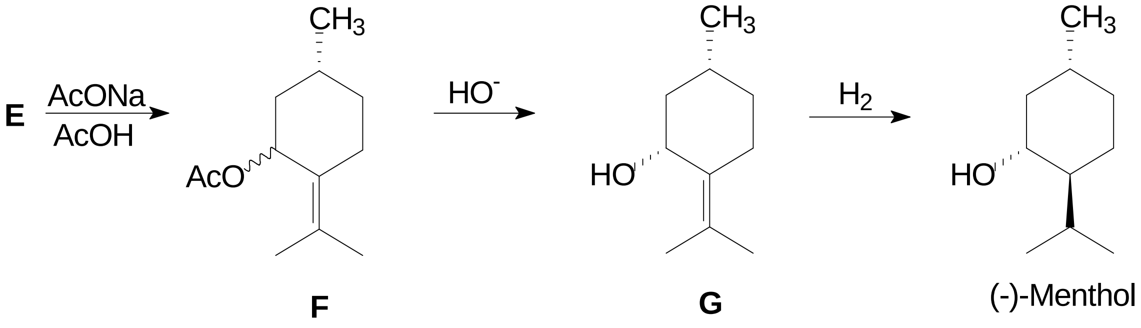
Catalytic isomerisation of δ-3-Carene provides (+)-δ-2-Carene (**A**) which then was pyrolysed to cleave the cyclopropane ring forming diene (**B**):



Treatment of the unconjugated diene (2,8-menthadiene, **B**) with HCl to give **C** and then, dehydrochlorination led to a conjugated diene ((+)-2,4(8)-*p*-menthadiene, **D**). Treatment of (+)-2,4(8)-*p*-menthadiene with hydrogen chloride affords 8-chloro-3-*p*-menthene (**E**):



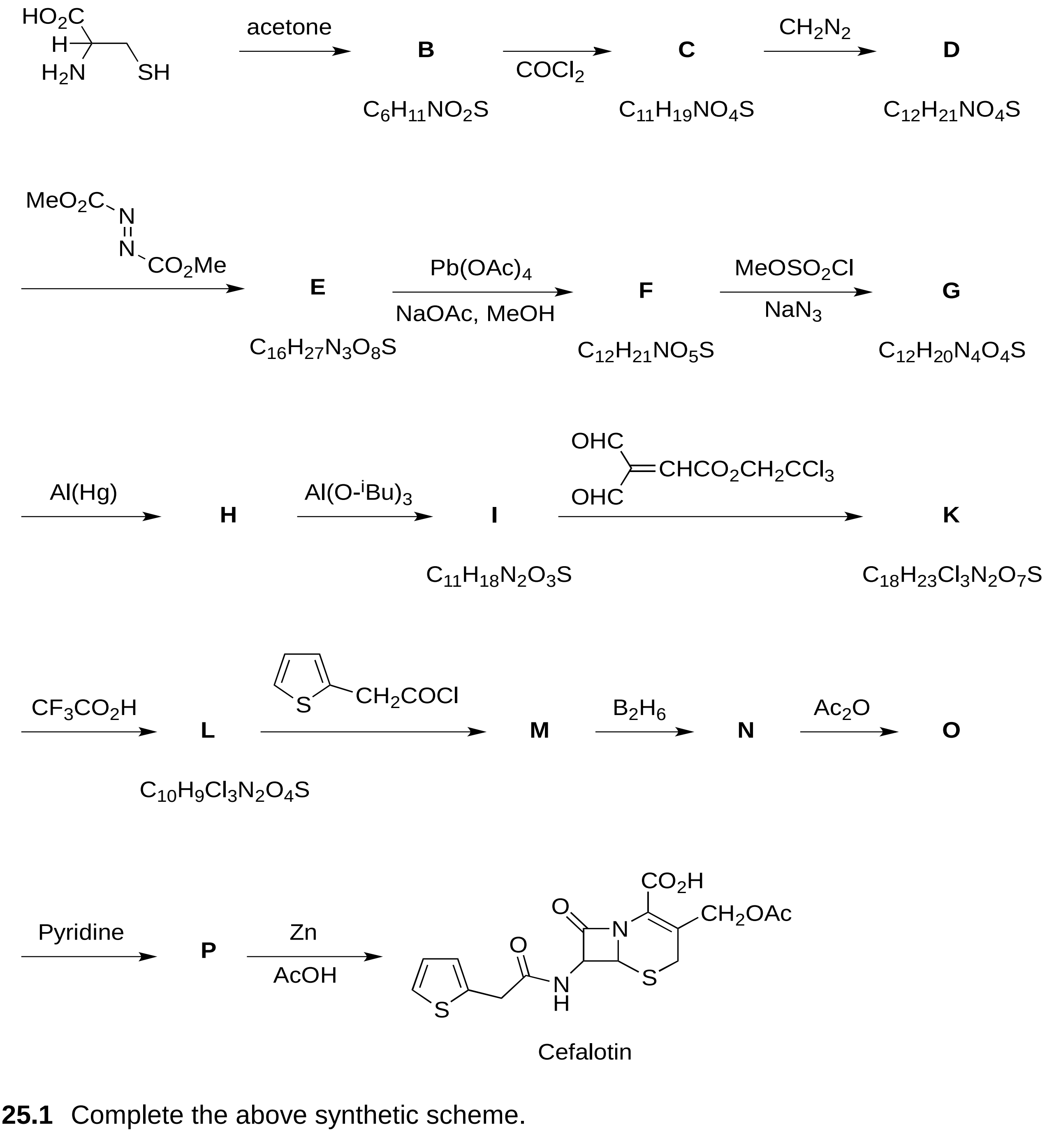
E reacted with sodium acetate and acetic acid to give mixed (*cis/trans*) pulegol esters (**F**) via allylic displacements. Hydrolysis **F** affords (-)-cis and (+)-trans-pulegol (**G**). Reduction of either pulegol isomer provides menthol isomers which can be readily equilibrated to predominently (-)-menthol.



THEORETICAL PROBLEM 25

Cefalotin

Cefalosporin is a β-lactam group antibiotic. Cefalotin, a derivative of cefalosporin, has stronger activities on gram (-) and gram (+) bateria, but lower toxicity. Therefore, it has been studied and applied into medical treatment. Cefalotin has been synthesized from L-cisteine according to the following diagram:



Cefalotin

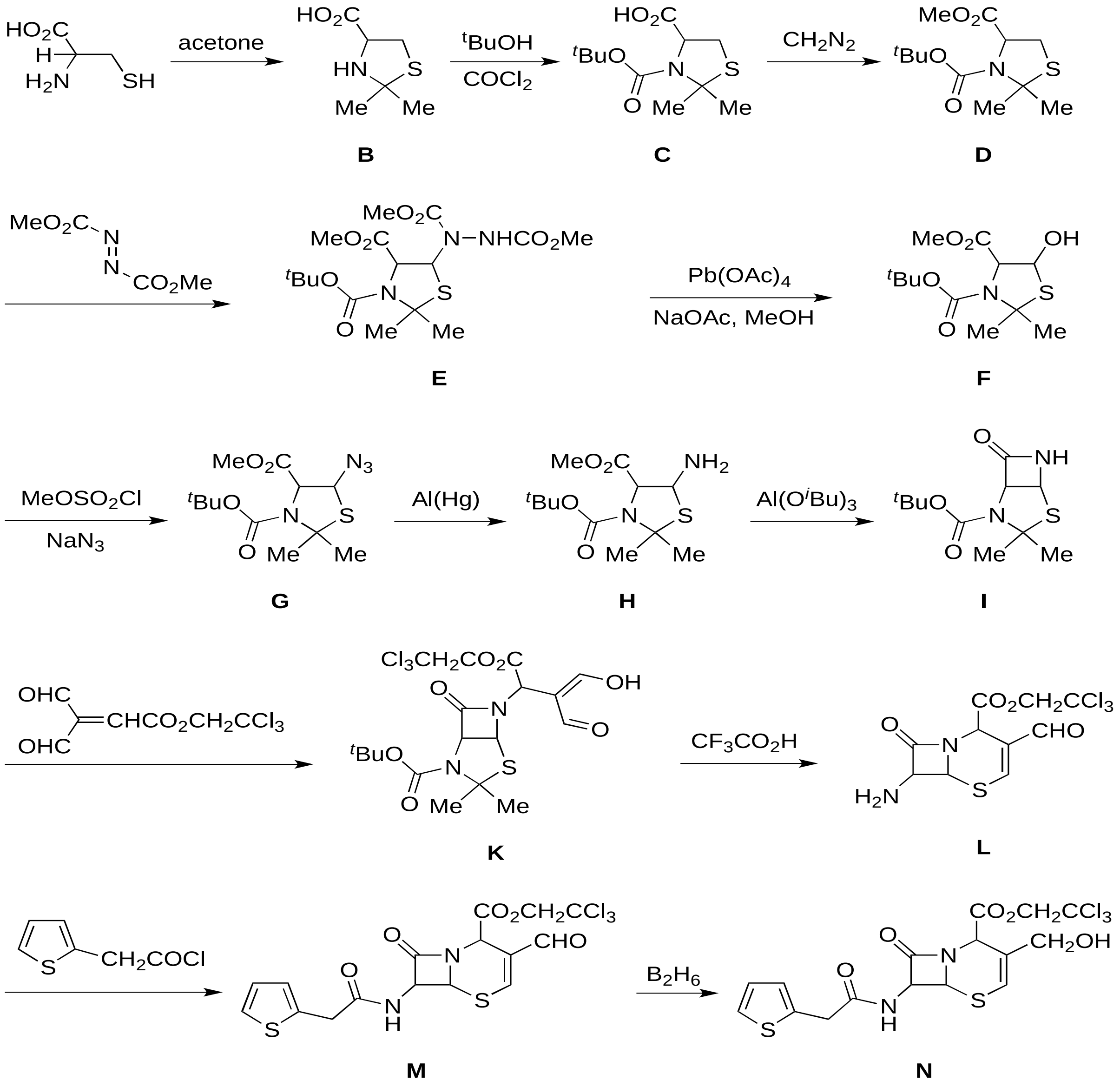
25.1 Complete the above synthetic scheme.

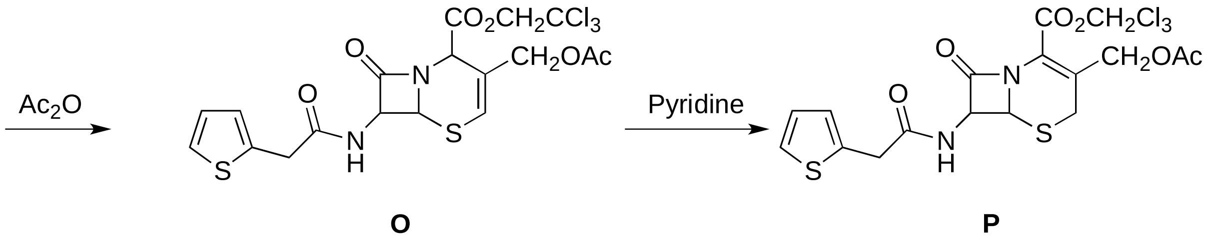
25.2 Write down a reaction mechanism from **K** to **L.**

25.3 How many optical isomers of cefalotin should be expected?

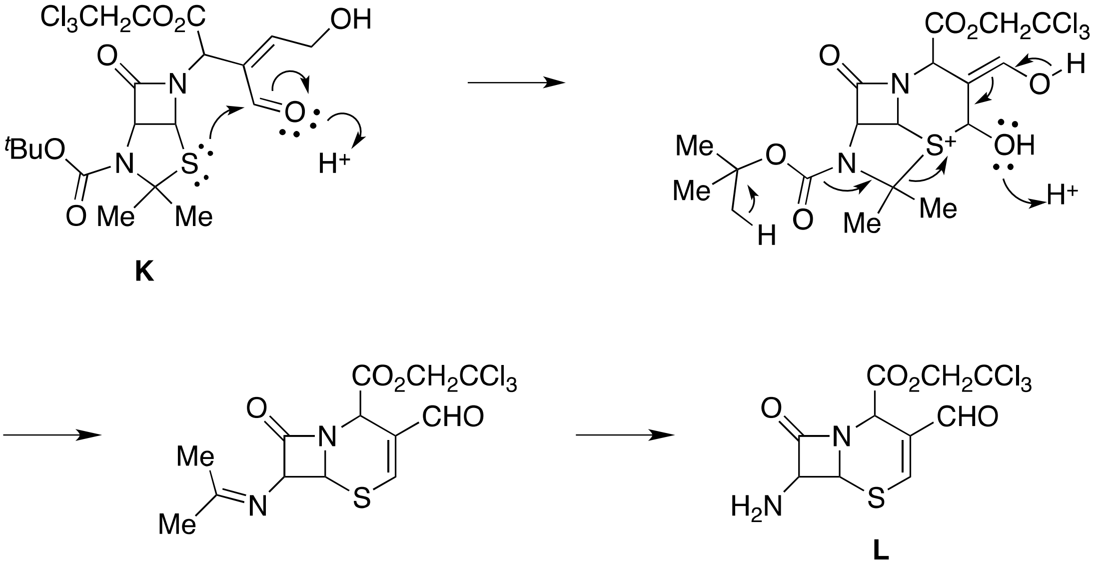
SOLUTION OF PREPARATORY PROBLEM 25

25.1 Synthetic scheme:

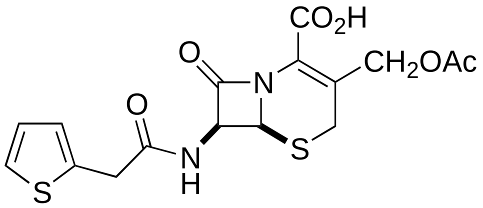


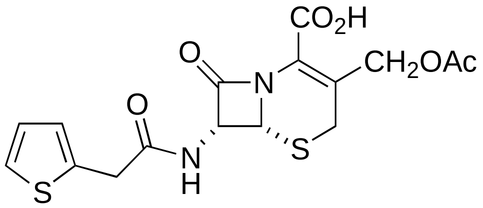


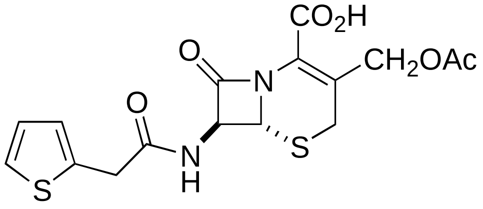
25.2 Reaction mechanism for the transformation from **K** to **L**:

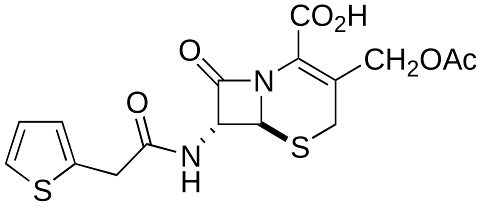


25.3 There are two asymmetric carbon atoms on cefalotin, so we should expect to have four optical isomers.





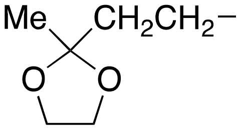
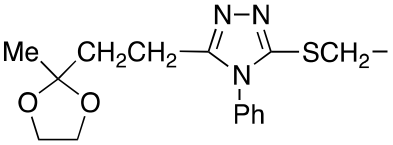
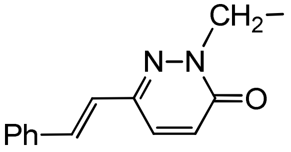




THEORETICAL PROBLEM 26

Heterocyclic compounds

Recently, several transformations of levulic acid (4-oxopentanoic acid) have been reported in the Journal of Chemistry (Vietnam). One of them is the synthesis of three hydrazides ($RCONHNH_2$) from levulic acid in which R is one of the followings:

 Compound **A**	 Compound **B**	 Compound **C**

Assuming that you have: inorganic chemicals, levulic acid, other acyclic organic compounds, benzene derivatives (PhCHO, PhNCS, $3\text{-}NO_2C_6H_4SO_3Na$), catalysts (piperidine, TsOH), and solvents.

26.1 Provide the synthetic scheme to obtain **A**. What is the purpose of 1,3-dioxolane ring formation? Write down the reaction equation to prepare TsOH from toluene.

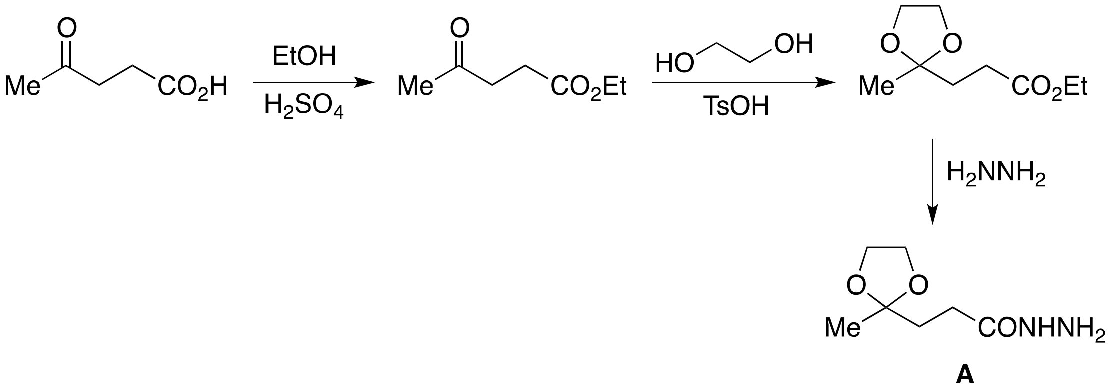
26.2 Provide the synthetic scheme to obtain **B**. What is the reation mechanism using PhNCS? Write down the reaction equation to synthesize PhNCS from aniline?

26.3 Provide the synthetic scheme to obtain **C**. What is the role of $3\text{-}O_2NC_6H_4SO_3Na$? Write down the reaction equation to prepare $3\text{-}O_2NC_6H_4SO_3Na$ from benzene. Using signals from proton nuclear magnetic resonance spectroscopy to prove that the reaction with $3\text{-}O_2NC_6H_4SO_3Na$ has occurred?

26.4 The three hydrazides (**A**, **B**, and **C**) are reacted with PhCHO to generate corresponding products (**E, F**, and **G**). Draw a common reaction mechanism for these transformations. If $4\text{-}NO_2C_6H_4CHO$ or $4\text{-}Me_2NC_6H_4CHO$ was used instead of PhCHO, would the reactions be more difficult or easier to proceed?

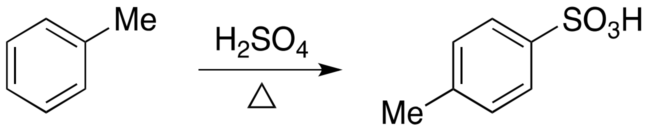
SOLUTION OF PREPARATORY PROBLEM 26

26.1 Synthesis of **A** from levulic acid:

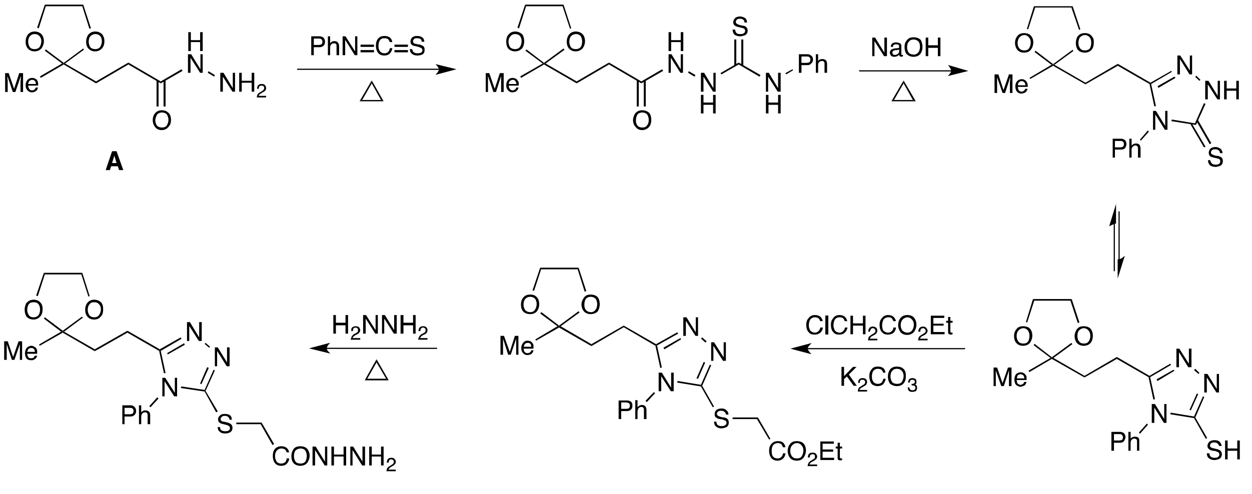


The purpose of 1.3-dioxolane formation was to protect the carbonyl group from the reaction with NH_2NH_2.

TsOH preparation from toluene:

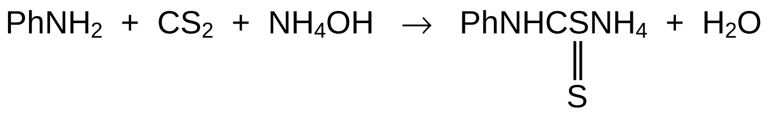


26.2 Synthesis of **B** from **A**:



The reaction of **A** and PhNCS is nucleophilic addition of the –$NHNH_2$ group to the –NCS group.

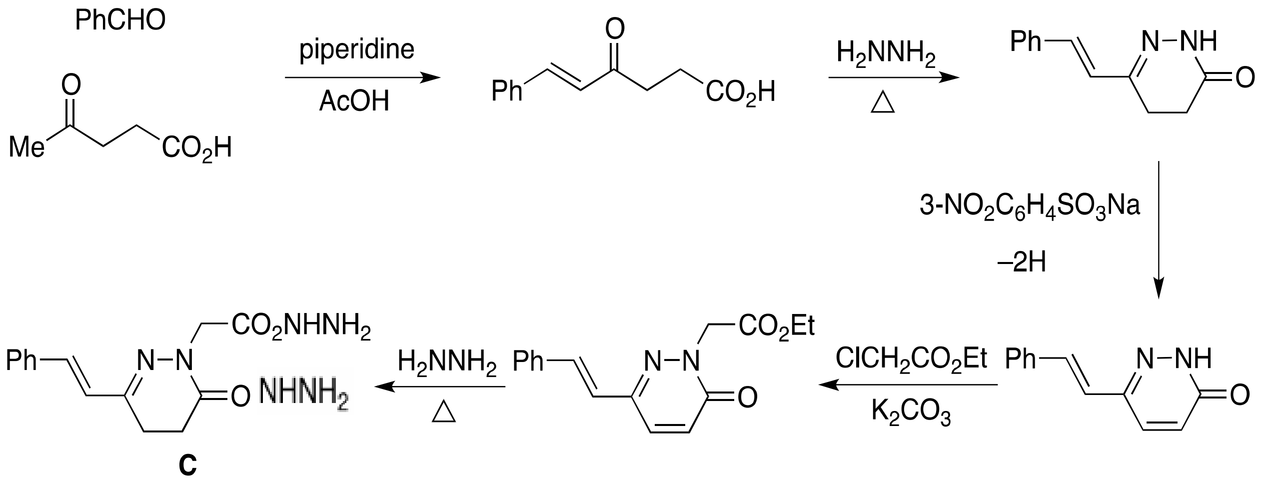
PhNCS preparation from aniline:



$$PhNH_2 + CS_2 + NH_4OH \rightarrow PhNH\underset{\underset{S}{\|}}{C}SNH_4 + H_2O$$

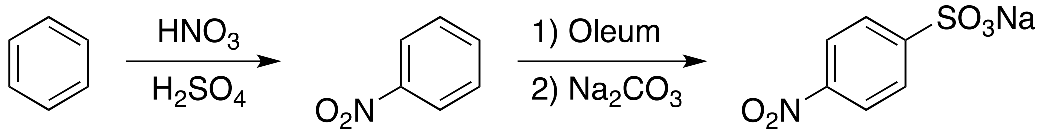
$PhNHCS_2NH4 + (Pb(NO_3)_2 \rightarrow PhNCS + NH_4NO_3 + HNO_3 + PbS$

26.3 Synthesis of **C** from levulic acid:



$3-O_2NC_6H_4SO_3Na$ is a dehydrogenation (or oxidation) reagent to convert dihydropyridazine into pyridazine ring.

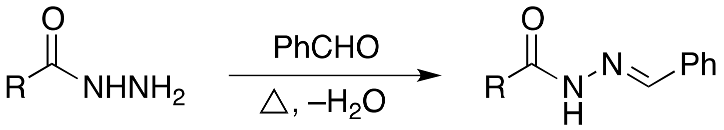
$3-O_2NC_6H_4SO_3Na$ preparation from benzene:



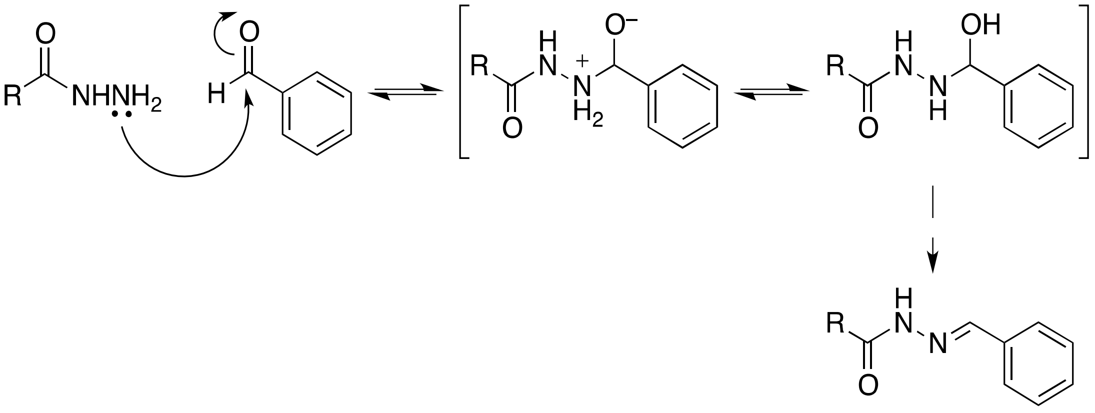
^{1}H-NMR spectrum:

Before the reaction, the heterocyclic should provide 2 resonance signals with 2H intensity in the strong field of the two CH_2 groups (experimental: 2.57 ppm and 2.83 ppm). After the reaction, these 2 signals should disappear, and two new signals in with 1H intensity the weak field of the two CH groups should appear (experimental: 7.01 ppm and 7.64 ppm).

26.4 Reaction mechanism of $R-CONHNH_2$ with PhCHO:



First, the hydrazide $-CONHNH_2$ group performed nucleophilic addition to the C=O group of benzaldehyde, then the dehydration step occurred:



The electron-withdrawing group –NO_2 facilitates the reaction, while the electron-donating group –NMe_2 retards the reaction.

$4\text{-}Me_2NC_6H_4CH{=}O \; < \; C_6H_5CH{=}O \; < \; 4\text{-}NO_2C_6H_4CH{=}O$

THEORETICAL PROBLEM 27

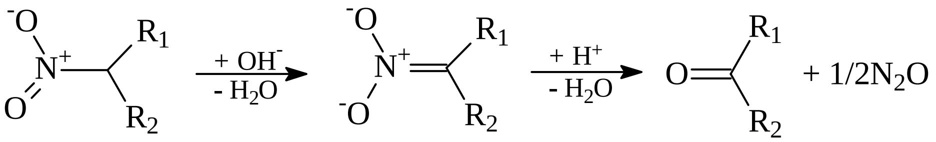
Lotus

Lotus is known as the scientific name of *Nelumbo nucifera*. Recently, Vietnamese researchers collaborating with Canadian scientists discovered the ability to promote the production of insuline in β cells of nuciferine, which may be used to treat the **Hypoglycemia**. (K. Hoa Nguyen, H.Dien Pham, B.L. Gregoire Nyomba et al. *J. of Ethnopharmacology, 2012, 142, 488-495*). There are some ways to synthesize nuciferine from different reactants, but the synthetic procedures are almost very complicated and the reaction yield is very low. Chia-Fu Chang et al. at Changhua National University (Taiwan) reported a procedure to synthesize the nuciferine through 3 steps using a benzaldehyde derivative in Nef reaction, Pictet-Spengler reaction and radical cyclization (*Synth. Commun., 2010, 40, 3452-3466,*).

Nef ‘s reaction (John Ulric Nef, 1894):

$$R_2CHNO_2 \xrightarrow[2.H_2SO_4]{1.NaOH} R_2CO + 1/2N_2O$$

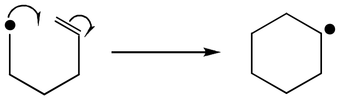
The mechanism of Nef’s reaction:



Example:

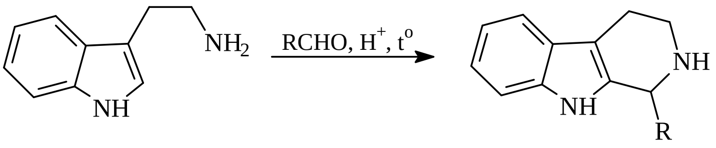
$$CH_3CH_2NO_2 \xrightarrow[2.H_2SO_4]{1.NaOH} CH_3CHO \ + 1/2\ N_2O$$

The radical cyclization reaction:



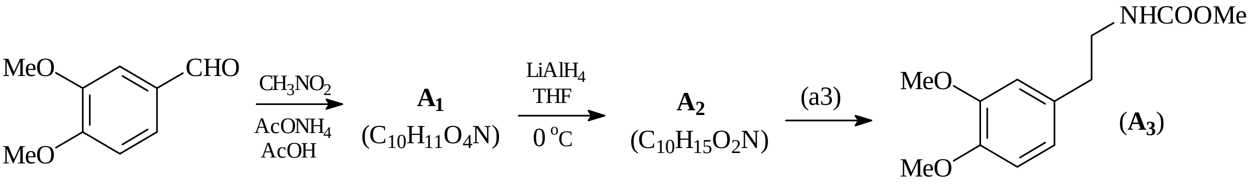
Radical initiator: AIBN [azobisisobutyronitrile, $Me_2C(CN)N=NC(CN)Me_2$]

The Pictet-Spengler addition-cyclization (Amé Pictet, Theodor Spengler, 1911): is the condensation reaction and then cyclization between *β*-arylethylamine and aldehyde or ketone in the presence of acid catalyst with heating. Example:

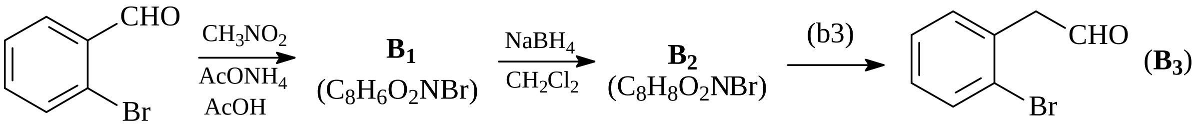


The reaction scheme for the synthesis of nuciferine is:

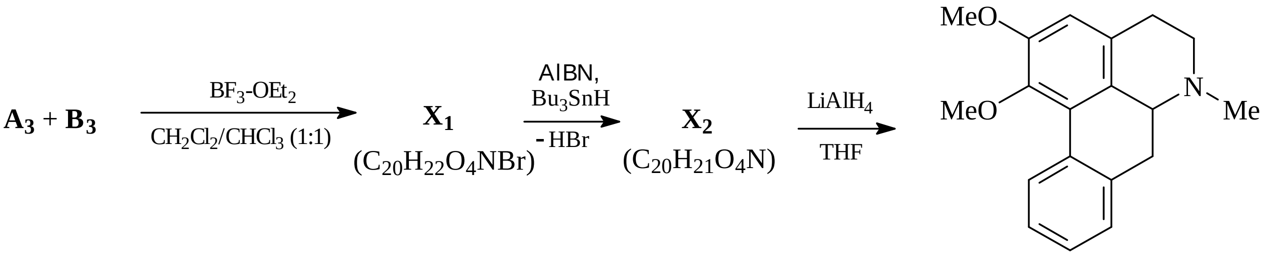
Step 1: Synthesis of *N*-methoxycarbonyl amine.



Step 2: Synthesis of arylacetaldehyde.



Step 3: Synthesis of nuciferine



Nuciferine

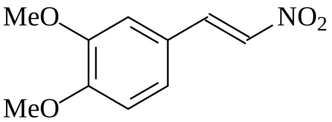
27.1 Determine the structural formulae for **A$_1$**, **A$_2$**, **B$_1$**, **B$_2$**, **X$_1$**, **X$_2$**, reaction conditions for (a3), (b3).

27.2 Indicate the reaction mechanism for the formation of **A$_1$** from 3,4-dimethoxybenzaldehyde (step 1); **X$_1$** from **A$_3$** + **B$_3$** (step 3).

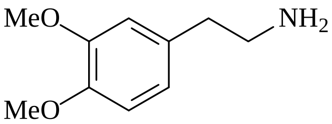
27.3 Determine the structural formulae for two isomers of **Y_{1a}**, **Y_{1b}** and compound **Y_2** based on the schematic conversion below:

SOLUTION OF PREPARATORY PROBLEM 27

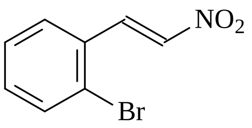
27.1 Structural formulae and the reaction conditions for (a3) and (b3):



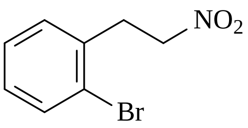
A_1



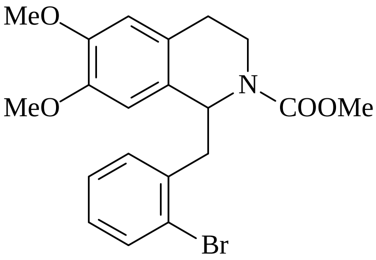
A_2



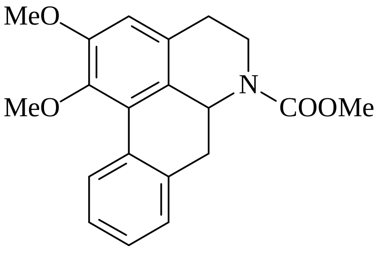
B_1



B_2



X_1



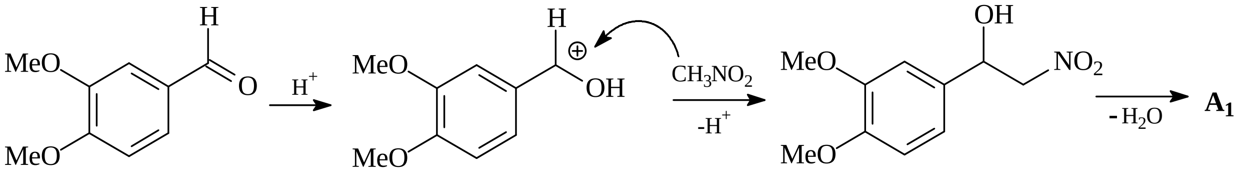
X_2

(a3) MeOCOCl, THF

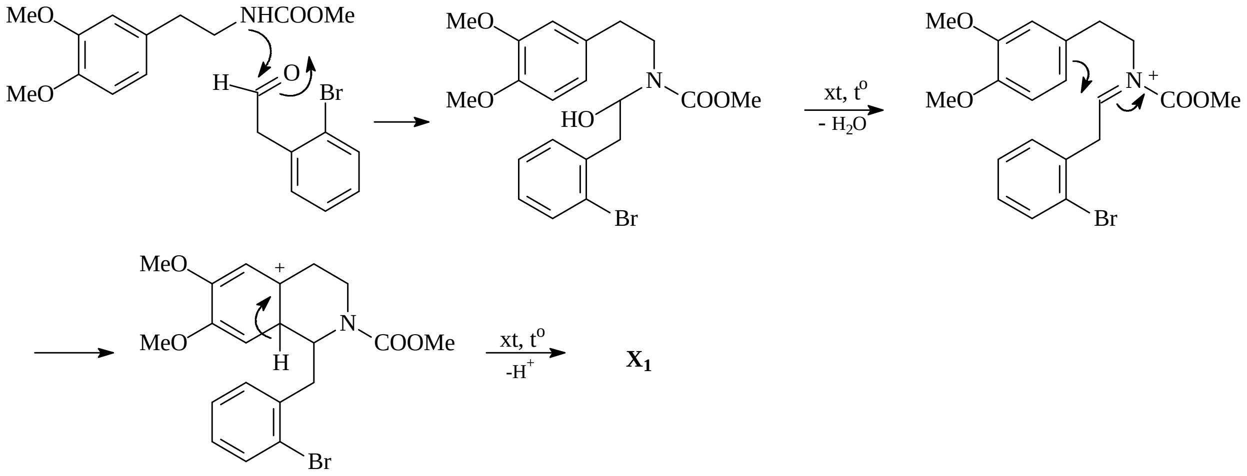
(b3) 1. NaOH/EtOH 2. H_2SO_4

27.2 Reaction mechanism:

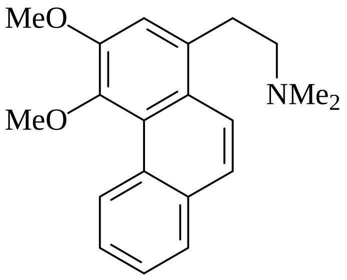
a. **A_1** from 3,4-dimethoxibenzaldehyde: aldol condensation, the water elimination, (crotonation).



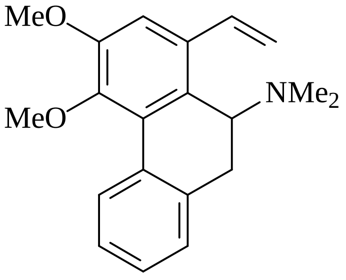
b. Reaction mechanism for the formation of $\mathbf{X_1}$: Addition-cyclization as Pictet-Spengler reaction mechanism.



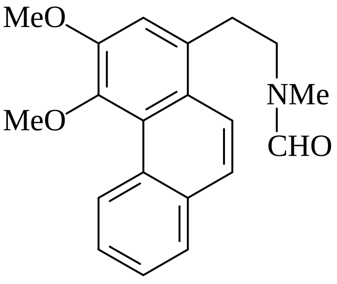
27.3 Structural formule for $\mathbf{Y_{1a}}$, $\mathbf{Y_{1b}}$, $\mathbf{Y_2}$:



Y_{1a}



Y_{1b}

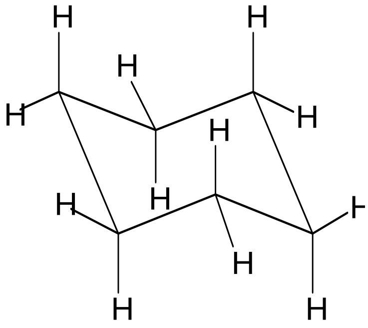


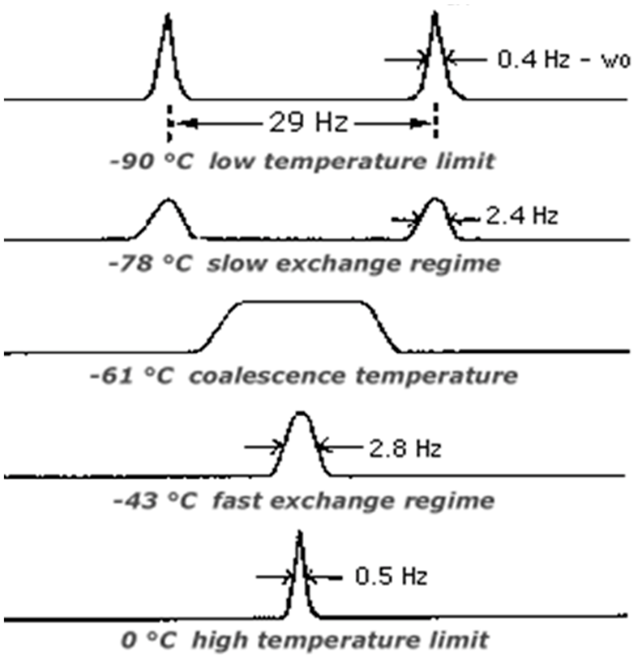
Y_2

THEORETICAL PROBLEM 28

NMR Spectra

28.1 At room temperature, the NMR spectrum of cyclohexane shows only a single resonance signal. As the temperature of the sample is lowered, the sharp single signal broadens until at -61.0 ℃ it begins to split into two broaden signals. As the temperature is lowered further to -90 ℃, each of the two signals begins to give a splitting pattern of its own. Explain the origin of these two families of signals.



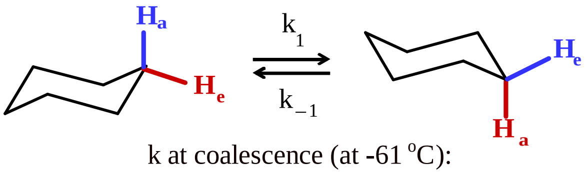


28.2 In *cis*-1-bromo-4-*tert*-butylcyclohexane, the proton on carbon-1 is found to give resonance at 4.33 ppm. In the *trans* isomer, the resonance of the C_1 hydrogen is at 3.63 ppm. Why do these compounds have different chemical shift values for the C1 hydrogen? Justify why this difference cannot be observed in the 4-bromomethylcyclohexanes except at very low temperatures.

SOLUTION OF PREPARATORY PROBLEM 28

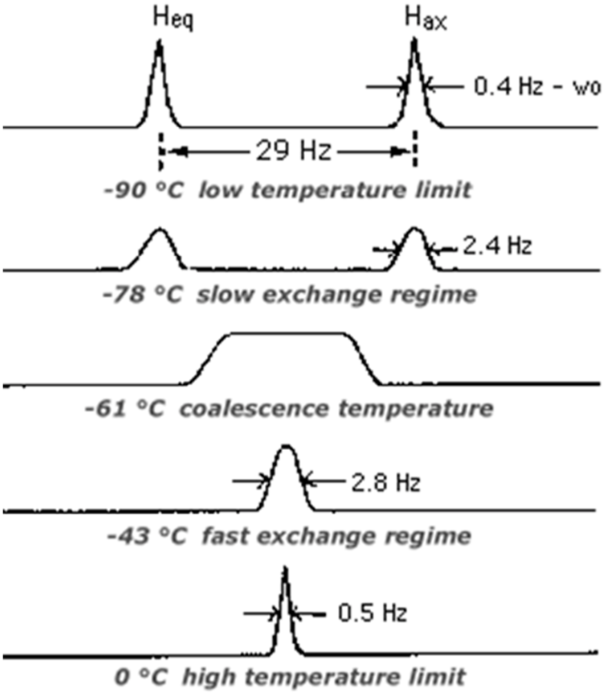
28.1 A molecule can undergo fluxional process by interchanging two or more sites. If the rate of exchange is faster than the NMR time scale, the two different groups will appear at an average shift. As temperature decreases the rate becomes lower and separate shift can be obtained.

Rapid equilibration at room temperature between chair conformations leads to one peak. As one lowers the temperature, the interconversion is slowed down until, at temperatures below -66.7 ℃, peaks due to the axial and equatorial hydrogens are observed. Axial and equatorial hydrogens have different chemical shifts under these conditions.



k at coalescence (at -61 °C):

$$k_c = \pi\Delta\nu/\sqrt{2}$$



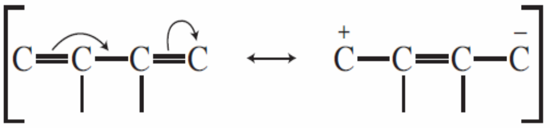
28.2 The *t*-butyl-substituted rings are conformationally locked. The hydrogen at C1 has different chemical shifts, depending upon whether it is axial or equatorial. 4-Bromocyclohexanes are conformationally mobile. No difference between axial and equatorial hydrogens is observed until the rate of chair–chair interconversion is decreased by lowering the temperature.

THEORETICAL PROBLEM 29

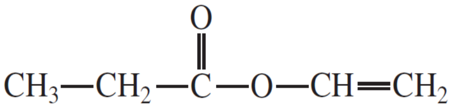
Infrared Spectroscopy (IR)

29.1 Substitution of an amino group on the *para* position of acetophenone shifts the C=O frequency from about 1685 to 1652 cm^{-1}, whereas a nitro group attached to the *para* position yields a C=O frequency of 1693 cm^{-1}. Explain the shift for each substituent from the 1685 cm^{-1} base value for acetophenone.

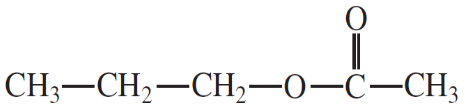
29.2 Conjugation of a C=C double bond with either a carbonyl group or another double bond provides the multiple bond with more single-bond character (through resonance, as the following example shows), a lower force constant *K*, and thus a lower frequency of vibration. For example, the vinyl double bond in styrene gives an absorption band at 1630 cm^{-1}. Esters show a very strong band for the C=O group that appears in the range of 1750–1735 cm^{-1} for simple aliphatic esters. The C=O band is shifted to lower frequencies when it is conjugated to a C=C or phenyl group (*Hint:* $\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$, *μ, reduced mass; c, speed of light).*



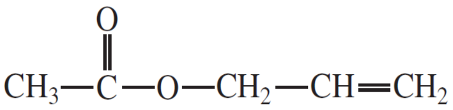
Assign a structure to each of the spectra shown. Choose from the following 5-carbon esters.



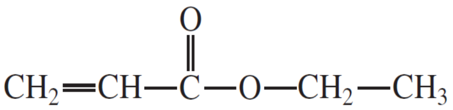
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-O-CH=CH_2$



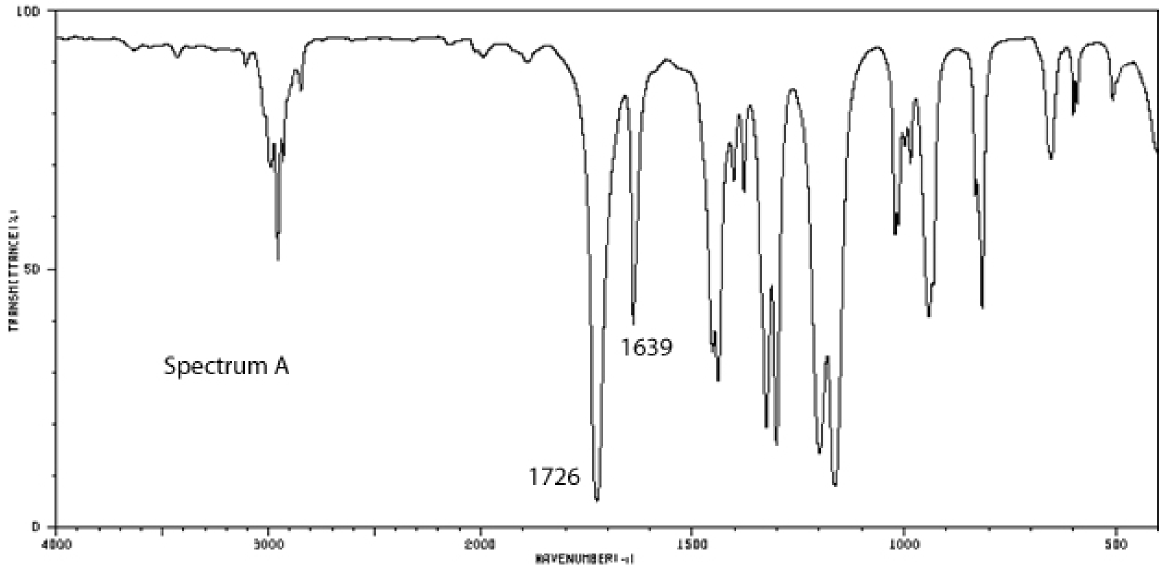
$CH_3-CH_2-CH_2-O-\overset{\overset{O}{\|}}{C}-CH_3$

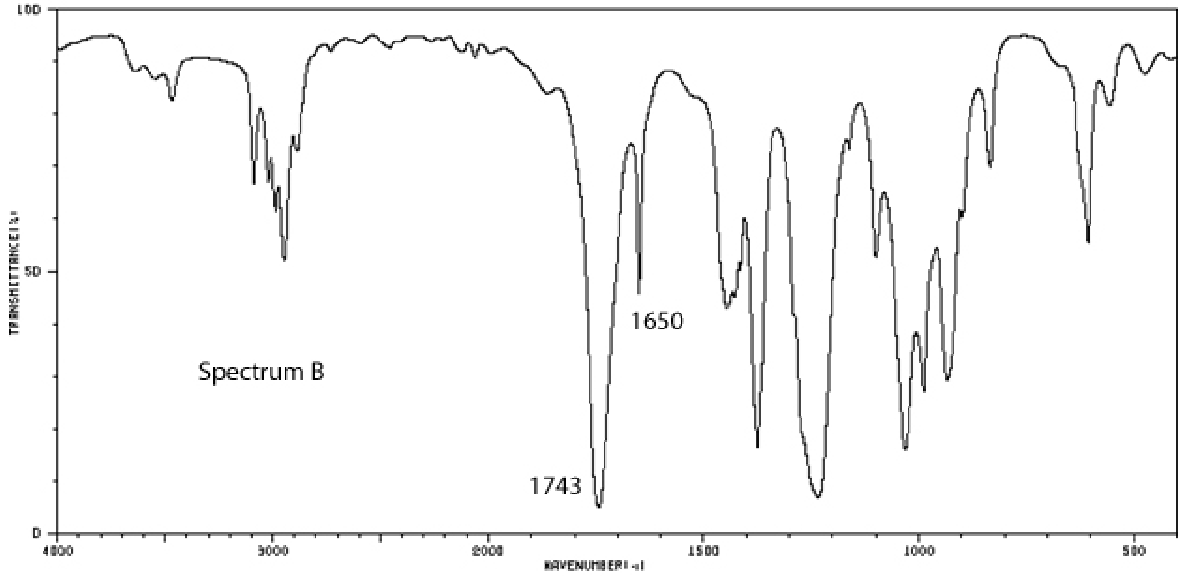


$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH=CH_2$



$CH_2=CH-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$

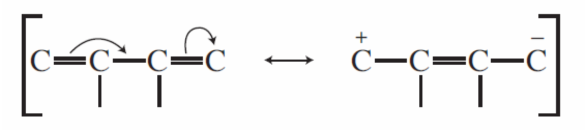




SOLUTION OF PREPARATORY PROBLEM 29

29.1 Resonance (conjugation) effect: the amino group pushes electron density into the ring and into the carbonyl group resulting in a lower frequency carbonyl group (more single bond character). A nitro group withdraws electrons resulting in higher frequency carbonyl absorption (more double bond character).

29.2 Conjugation of a C=C double bond with either a carbonyl group or another double bond provides the multiple bond with more single-bond character (through resonance, as the following example shows), a lower force constant *K*, and thus a lower frequency of vibration. For example, the vinyl double bond in styrene gives absorption band at 1630 cm^{-1}. Esters show a very strong band for the C=O group that appears in the range of 1750–1735 cm^{-1} for simple aliphatic esters. The C=O band is shifted to lower frequencies when it is conjugated to a C=C or phenyl group.



(*Hint:* $\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$, *μ: reduced mas* $\mu = m_1m_2/(m_1+m_2)$*, c: speed of light*).

Therefore,

Spectrum A: Methyl acrylate. The absorption band appears at 1726 cm^{-1} belong to the C=O group that conjugates to double carbon-carbon double bond. Similarly, the C=C bond in this molecule has the absorption bond at 1639 cm^{-1} due to the stretching vibration.

Spectrum B: Allyl acetate. The stretching vibrations of C=O and C=C double bonds appear at the normal positions for these vabrations, at 1743 and 1650 cm^{-1}, respectively.

There are only the separated C=C and C=O double bonds in vinyl propionate and allyl acetate, so the stretching bands appear at the normal positions.

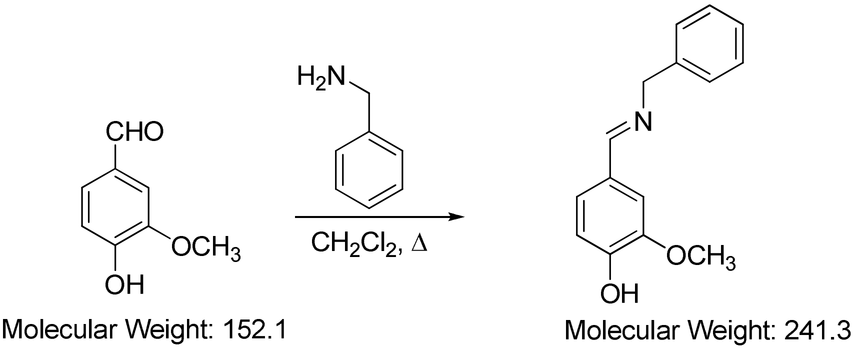
PRACTICAL PROBLEMS

PREPARATORY PROBLEM 30 (PRACTICAL)

Condensation between vanillin and benzylamine

Introduction

Vanillin is a phenolic aldehyde with the molecular formula $C_8H_8O_3$. Thus, it has three types of functional groups including aldehyde, ether, and phenol. This compound is often used as a flavoring agent in foods, beverages, and pharmaceuticals. Vanillin is the primary component of the extract of the *Vanilla planifolia*. It is known that the aldehyde functional group in vanillin can be easily converted into enamine derivatives or imides through the condensation reaction between vanillin and amines. The products are synthones which are widely applied in the synthetic organic chemistry and pharmaceuticals.



Chemicals and Reagents

- Vanillin: 1-2 g
- Benzylamine
- Dichloromethane: 20 cm^3
- Sodium sulfate, Na_2SO_4

Equipment and Glassware

- Erlenmeyer flasks, 250 cm^3
- Graduated cylinders, 10, 25, 50 cm^3
- Beral pipets

- Beakers, 50 cm^3
- Hot plate
- Spatulas
- Büchner funnel with filter flask and filter paper, separating funnel
- Melting point apparatus and capillary tubes
- Small vials with caps
- Vials with caps, 20 cm^3
- Thin layered chromatography (TLC) spotters
- TLC plates (silica with fluorescent indicator A254)
- Chamber for TLC development
- Magnetic stirrer,Ice water bath

Experimental procedure

1. Add 1.0 g of vanillin into a dry 50 cm^3 flask then add 10 cm^3 of dichloromethane solvent into the flask. The mixture is stirred for 10 min at room temperature, and then 0.7 g of benzylamine and 2.0 g of Na_2SO_4 are simultaneously added into the flask.

2. The reaction mixture is further stirred at reflux condition (65 – 67 ^oC) for 90 min. Cool the flask to room temperature.

3. Dilute the resultant mixture with 40 cm^3 and swirl the flask.

4. Transfer the mixture into a separating funnel and then extract with 30 cm^3 of dichloromethane. Extract the organic phase 2 times more with 30 cm^3 of dichloromethane.

5. Dry the extracting organic fraction with $MgSO_4$. Filter the organic fraction through a Buchner funnel. Discard the solid and collect the filtrate.

6. Remove the solvent in the filtrate by rotary evaporation to obtain the product(s).

7. Determine the purity of the crude product by thin layer chromatography method. Use precoated silica gel plates (Silica Gel PF-254) and visualize the spots by UV-light. Use ethyl acetate: heptane 15:85 mixture as an eluent.

Note: *It is recommended to carry out the experiment under a hood.*

Questions and Data analysis

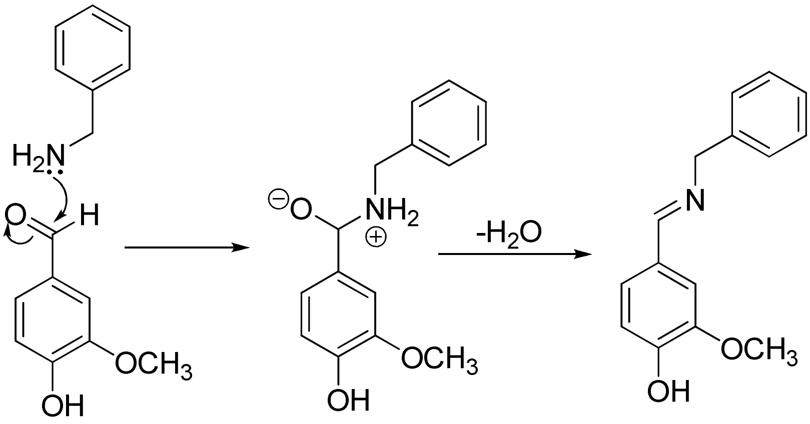
30.1 Weight the obtained product.

30.2 Draw the mechanism of imine formation.

30.3 What is the role of Na_2SO_4 in the present experiment?

SOLUTION OF PREPARATORY PROBLEM 30

30.2 Mechanism



30.3 Na_2SO_4 is a water-adsorbing substance. It removes water preventing H_2O attack to the product (imine).

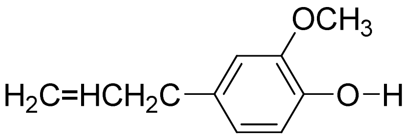
PREPARATORY PROBLEM 31 (PRACTICAL)

Synthesis of eugenoxy acetic acid

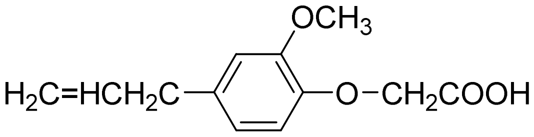
Introduction

Eugenoxyacetic acid (IUPAC name: 2-methoxy-4-(2-propenyl)phenoxyacetic) is an odorless, colorless and non-cytotoxic compound. It has shown anti-viral and anti-bacteria properties and is therefore used as antioxidant food preservative in food industry. Recently, eugenoxyactetic acid and its ester derivatives such as methyl and ethyl esters have been found to be the ability to inhibit lipid increasing which leads to their potential application in the treatment of human hyperlipidaemia. In addition, eugenoxyacetic acid acts as a promising plant growth promoter due to their auxin (aryloxyacetic) structural characteristics.

The nature and living organism friendly properties of eugenoxyacetic are the result of the combination of acetic moiety which is present in vinegar and eugenol moiety which is the main constituent of the essential oil obtained from clove oil.



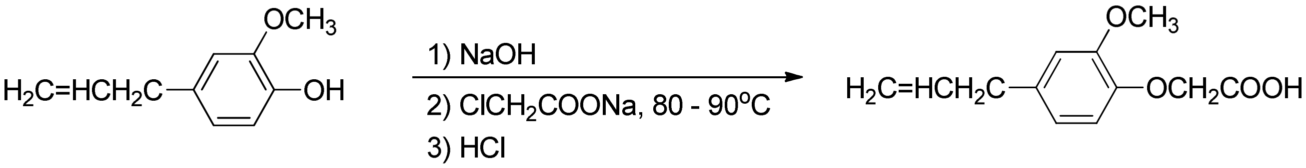
Eugenol



Eugenoxyacetic acid

Clove is an aromatic plant in the family Lamiaceae which is native to tropical areas and widespread as a cultivated plant. In Vietnam, there are two species of clove, *Ocimum sanctum* L. and *Ocimum gratissimum* L., which have been used in many tradtional medicinal purposes without adverse effects.

In this practical problem, eugenoxyacetic acid will be synthesized from eugenol as shown in the scheme below:



Chemicals and apparatus

- Clove essential oil
- Monochloroacetic acid
- NaOH
- Na_2CO_3
- Aqueous HCl solution
- Distilled water.

Apparatus and glassware

- Erlenmayer flask, 50 cm^3
- Magnetic stirrer with heater
- Magnetic bar
- Beaker, 100 cm^3
- Beaker, 250 cm^3
- Glass filter, 25 cm^3
- Glass filter. 50 cm^3
- Vacuum filter set (vacuum pump, Filter flask)
- Dropping funnel
- Spatula
- Glass rode

Experimental procedure

Step 1

1. Dissolve 0.6 g NaOH in 3.0 cm^3 distilled water in a 50 cm^3 Erlenmayer flask and then add 2.0 cm^3 clove essential oil. Keep the flask in the water bath at 80 – 90 ^oC while stirring with the magnetic stirrer.
2. Dissolve carefully 1.0 g monochloroacetic acid in 5.0 cm^3 distilled water in a 25 cm^3 beaker and stir the solution with the spatula. Add Na_2CO_3 slowly just to the alkaline reaction (Solution **A**).

Step 2

1. Add slowly solution **A** to an Erlenmayer flask and keep stirring the mixture at 90 – 95 °C for 60 min. Cool the reaction mixture with water to room temperature, and then acidify with HCl solution (1 : 1) to the acidic reaction (*test by litmus paper*) (Solution **B**).
2. Add a small amount of crushed ice (5 –10 g) to the solution B and stir until the yellow oil turns to the solid. Isolate the solid by filtration with suction in to a sintered glass crucible. Wash the solid with water to obtain the crude product as pale yellow solid.

Step 3

1. Purify the product as follows: Transfer the crude product to a 250 cm^3 beaker, add 80 - 100 cm^3 of hot water (about 90 °C) to the beaker and continue boiling for 5 – 10 min. Cool the solution with water and ice-cold water.
2. Isolate the product by filtering with suction into a sintered glass crucible and wash the solid product several times to obtain white needles. Dry the product in the drying oven for 60 min. Weigh the dried product.

Questions and data analysis

31.1 Write down the reactions occurring in steps 1 and 2.

31.2 Calculate the reaction yield.

31.3 Propose a mechanism for the reaction in step 2.

31.4 Explain why the reaction must be conducted in alkaline medium? Should an excess amount of alkaline be used in the reaction?

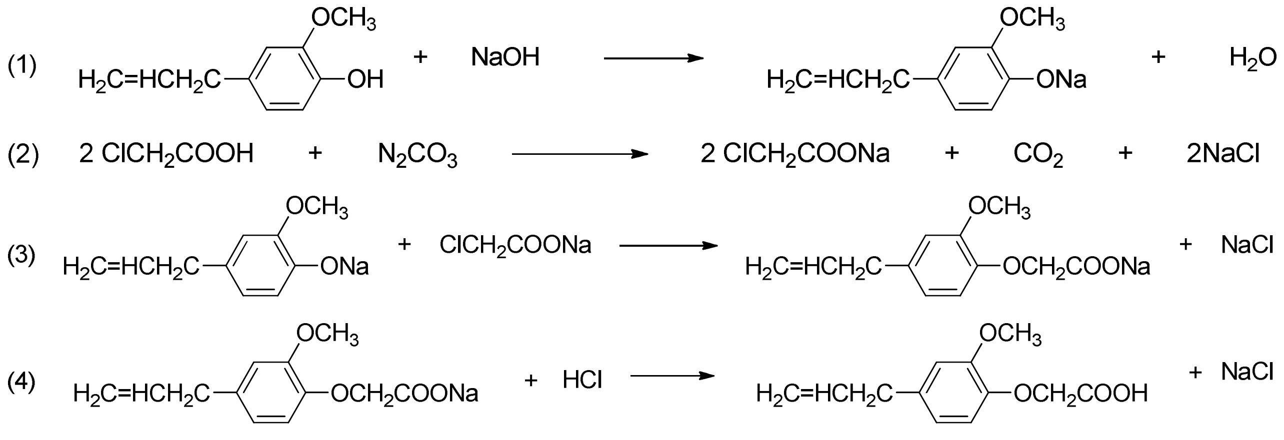
31.5 Compare the possibilities of the chlorine atom in monochloroacetic acid and those in alkyl chlorides to be substituted.

31.6 If the pure product obtained in the experiment above (m. p. 72 °C) is recrystallized in benzene, its m. p. will rise to 100.5 °C. Suggest an explanation for this observation and propose method to test your explanation.

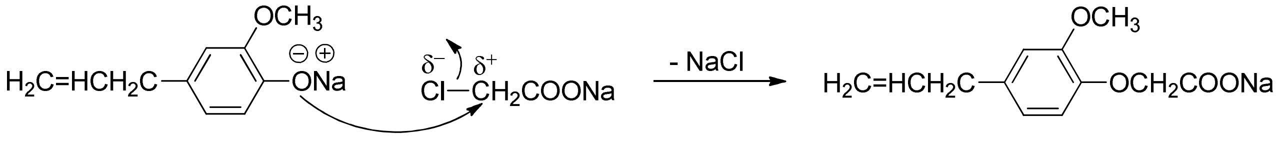
31.7 When eugenoxyacetic acid is refluxed in KOH solution, and acidified with HCl solution (1 : 1), an isomer of eugenoxyacetic acid, isoeugenoxyacetic acid can be obtained in the form of two stereoisomers. Determine the structures of these two isomers and explain the formation of isoeugenoxyacetic acid with a suitable reaction mechanism.

SOLUTION OF PREPARATORY PROBLEM 31

31.1 Reactions in steps 1 and 2:

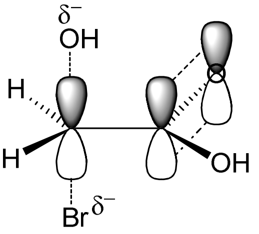


31.3 The reaction in step 2 follows a S_N2 substitution:



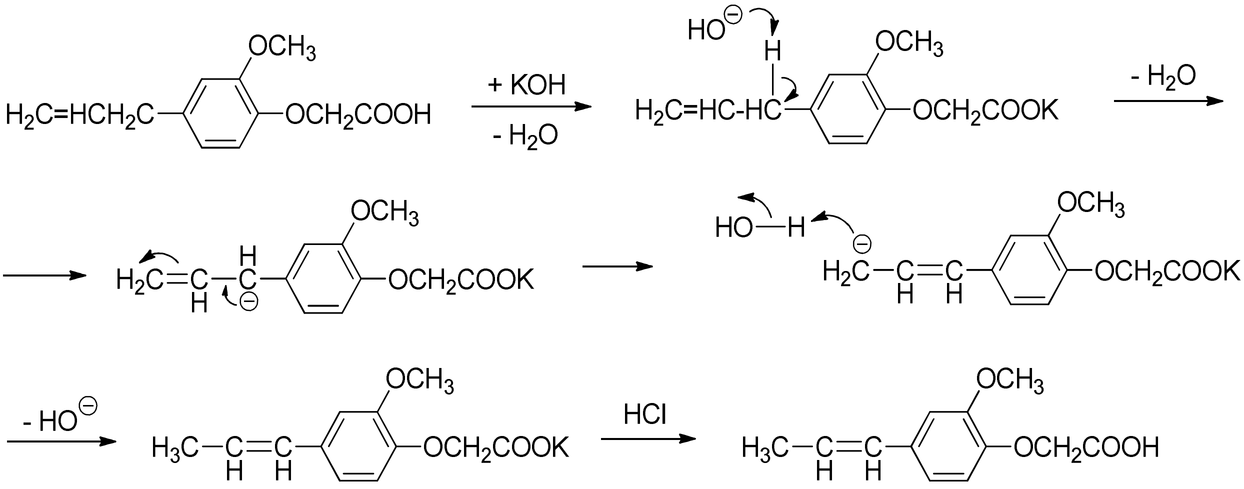
31.4 In alkaline media, eugenol is transformed into eugenolate which has adequate nucleophilicity to replace the chlorine atom of monochloroacetic acid. An excess amount of alkaline, however, should not be used as the hydroxide ions can compete with the eugenolate ions to form the hydroxide derivative of acetic acid.

31.5 The carboxyl group, on the one hand, provides for an (-I) effect to increase the positive charge density at the alpha carbon, facilitating the attack of nucleophiles. On the other hand, the carboxyl can delocalize the negative charges appearing in the transition state of the S_N2 reaction.

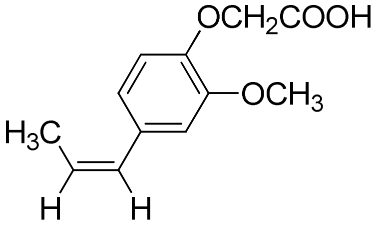


31.6 Crystallized water in the product re-crystallized from hot water lowers down its melting point. Re-crystallization of the product from dry benzene helps eliminate water and increase the melting point. Titration or TGA can be used to determine the amount of water crystallized in the product

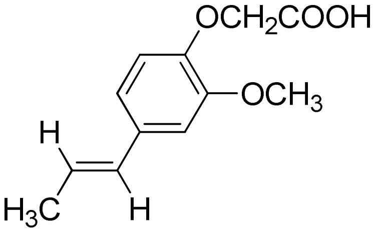
31.7 In basic condition, eugenoxyacetic acid is subjected to isomerization in which the terminal C=C double bond is moved in and conjugated with the benzene ring to yield isoeugenoxyacetic acid as shown in the scheme below:



Isoeugenoxyacetic can exist in form of two configuration isomers (*Z*) and (*E*):



(Z)



(E)

PREPARATORY PROBLEM 32 (PRACTICAL)

Complexometric titration of iron, aluminum, and magnetism in the aqueous solution

Introduction

Complexometric titration is one of the most common methods of volumetric analysis in chemical laboratories. In this method, the most widely used complexing agent is disodium salt of ethylenediaminetetraacetic acid (EDTA). EDTA is a polyprotic acid (H_4Y). The solution Na_2H_2Y is used as a standard solution for titration of metal ions (M^{n+}):

$$M^{n+} + H_2Y^{2-} + 2\ H_2O \rightarrow MY^{n-4} + 2\ H_3O^+$$

The formation constant (K_f) of MY^{n-4} depends on the nature of metal ions. For example:

Metal ions	K_f	Titrated at pH
Fe^{3+}	$10^{25.1}$	2.0
Al^{3+}, Pb^{2+}, Zn^{2+}	$10^{16.13}$	4.0 – 5.0
Mg^{2+}	$10^{8.69}$	9.0 – 10.0

Metal ions can be titrated separately due to the formation of MY^{n-4} complex with conditional formation constant at a suitable pH condition. In practical, the metallochromic indicators are usually used for the detection of the end point. These indicators are the color complexing agents for the metal ions. The color of the indicator differs from that of the metal-ion-complex and metal indicator complex (MInd) is much less stable than metal-EDTA-complex. Therefore, the titration of a metal ion solution is carried out with a given indicator at suitable pH of the solution:

$$MInd + H_2Y^{2-} \rightarrow MY^{n-4} + Ind$$

This task is to help participants to use techniques of the volumetric analysis for the determination of metal cations.

Chemicals and reagents

- Standard solutions of 0.050 mol dm^{-3} EDTA (prepared from $Na_2H_2Y.\ 2\ H_2O$)
- $Zn(NO_3)_2$, solution (c = 0.050 mol dm^{-3})
- Buffer solutions of 1 mol dm^{-3} CH_3COOH and 1 mol dm^{-3} $NaCH_3COO$ (pH = 4.7)
- Solution of 2 mol dm^{-3} NH_3 and 2 mol dm^{-3} NH_4Cl (pH = 9.2)
- Solution of HCl (c = 1 mol dm^{-3})
- Solution of NaOH (c = 1 mol dm^{-3})

- Distilled water
- Indicators: xylenol orange (1% in KCl)
- Eriochrome black T (ET – 00) (1% in KCl); The congo red (pH indicator); universal pH indicator paper; 5% solution of sulfosalicylic acid

Apparatus and glassware

- Burette, 50 cm^3
- Volumetric pipette, 25 cm^3
- Erlenmeyer flask, 250 cm^3
- Graduated cylinder, 10 cm^3
- Glass beaker, 250 cm^3
- Funnels and filter papers (the red tape)
- Droppers
- Hot plate.

Experimental procedure

Step 1. Sample preparation

Prepare a sample solution containing three ions of Fe^{3+}, Al^{3+}, and Mg^{2+} within concentration range of 0.01 mol dm^{-3} to 0.1 mol dm^{-3}.

Step 2. Titration of iron, aluminum, and magnesium ions

1. Titration of Fe^{3+}

Add 5.00 cm^3 of the sample solution into an Elenmeyer flask. Adjust the pH of the solution to 2 using NaOH or HCl solution with the Congo red paper. Heat the solution to 80 – 90 °C on a hot plate and then add 0.5 cm^3 of sulfosalicylic acid as indicator. The solution is titrated with EDTA solution from a colorless to yellow end point. Record the volume of the standard solution (V_1 cm^3).

2. Titration of the total amount of $Fe^{3+}$and Al^{3+}

Add 25.00 cm^3 of the sample solution into an Elenmeyer flask. Add 50 cm^3 of EDTA standard solution into the flask. Heat the solution to 80 – 90 °C and add 10 – 15 cm^3 of the buffer solution CH_3COOH/ $NaCH_3COO$ and a small amount of xylenol orange. Titrate the remaining amount of EDTA with the Zn^{2+} standard solution until the solution changes from red to yellow at the end-point. Record the volume of the standard solution (V_2, cm^3).

3. Titration of Mg^{2+}

Measure 25.00 cm^3 of the sample solution to a glass beaker. Add slowly the NH_3 + NH_4Cl buffer solution while stirring the mixture. After the precipitation reaction is complete, add 5 cm^3 of buffer solution and swirl the mixture. Filter the solution to an Elenmeyer flask through filter paper in a funnel. Wash the precipitate (3 – 4 times) with warm water. Finally, titrate Mg^{2+} with standard EDTA solution using ET – 00 until the solution changes from pale red to blue. Record the volume of the standard solution (V_3, cm^3).

Questions and Data analysis

32.1. Write down the chemical reactions in each individual step of the titration.

32.2 Derive the formulae for calculating the concentrations of Fe^{3+}, $Al^{3+}$and Mg^{2+} in the sample solution.

32.3 Calculate the concentrations of each ion in the sample solution.

SOLUTION OF PREPARATORY PROBLEM 32

32.1 The chemical equations of the reactions used in the titration:

Titration of Fe^{3+}:

The stability constant of FeY^- is much larger (= $10^{25.1}$) than the constants of complex of Al^{3+} ($10^{16.13}$) and that of Mg^{2+} ($10^{8.7}$) and therefore, in the solution with pH = 2 only ions Fe^{3+} are totally titrated:

$Fe^{3+} + Na_2H_2Y \rightarrow FeY^- + 2\ Na^+ + 2\ H^+$

In the solution with pH of 4.7 only ions Fe^{3+} and Al^{3+} are totally titrated:

$Fe^{3+} + Na_2H_2Y\ (\text{extra}) \rightarrow FeY^- + Na_2H_2Y$

$Al^{3+} + Na_2H_2Y\ (\text{extra}) \rightarrow AlY^- + Na_2H_2Y$

32.2 Separation and titration of Mg^{2+}:

In the buffer $NH_3 + NH_4^+$ (pH = 9.2) only $Al(OH)_3$ and $Fe(OH)_3$ are precipitated and all Mg^{2+} ions are present in the solution. After the filtration of $Al(OH)_3$ and $Fe(OH)_3$ we can titrate Mg^{2+} in the filtrate:

$Mg^{2+} + Na_2H_2Y \rightarrow MgY^{2-} + 2\,Na^+ + 2\,H^+$

32.3 The formulae for calculation of ion concentrations (in mol dm^{-3})

$c(\text{Fe(III)}) = V_1\ 0.05 / 25.0$

$c(\text{Al(III)}) = [(50.0 - V_2 - V_1)\ 0.05] / 25.0$

$c(\text{Mg(II)}) = V_3\ 0.05 / 25.0$

PREPARATORY PROBLEM 33 (PRACTICAL)

Determination of zinc and lead in zinc oxide powder

Introduction

Zinc oxide ZnO, a soft, white or faintly yellowish-white is used in the vulcanization of rubber, ceramics, paints, and many other products.

Zinc oxide is produced by burning zinc metal in air as follows:

$$Zn(s) \rightarrow Zn(l) \rightarrow Zn(g)$$

$$2\ Zn(g) + O_2(g) \rightarrow 2\ ZnO(s)$$

Purity of the given zinc has an influence on the quality of zinc oxide powder. There is a very wide range of commercial grades of zinc oxide depending on content of impurities. For example, zinc oxide powder -Grade 2 (having greater than 60 wt.% of Zn) produced by electro-thermal process contains less than 4 % of Ca; 0.4 % of Fe; and 8 % of Pb.

This task is to determine the contents of zinc and lead (in %) in a commercial zinc oxide powder by EDTA and dichromate solution.

Materials and reagents

- Zinc oxide powder
- Sulfuric acid solution, H_2SO_4 (aq), 4 mol dm^{-3}
- Nitric acid solution, HNO_3 (aq), 6 mol dm^{-3}
- 0.025 mol dm^{-3} EDTA standard solution (from $Na_2H_2Y \cdot 2\ H_2O$)
- Sodium thiosulfate, 0.02 mol dm^{-3} solution (from $Na_2S_2O_3 \cdot 5\ H_2O$)
- Fe(II) sulphate, solution, c = 0.025 mol dm^{-3} (from $FeSO_4 \cdot 7\ H_2O$)
- Mixture of HCl and NaCl: Dissolve 320 g of NaCl in 200 cm^3 of distilled water, add 100 cm^3 of concentrated HCl (37 %) and dilute to 1.0 dm^3 with distilled water
- Solution of 5 % (w/v) $K_2Cr_2O_7$
- Mixture of potassium iodide and thiocyanate, KI+ KSCN, 10 % w/v
- Mixture of CH_3COOH (2 mol dm^{-3}) and NH_4CH_3COO (1 mol dm^{-3})
- NH_3, solution, (c = 6 mol dm^{-3})
- 200 cm^3 of buffer solution, NH_3 / NH_4Cl, pH = 10
- Eriochrome Black T (ET-00) indicator, 1% (w/w) in NaCl(s)

- Diphenylamine sulfonate indicator, 0.2% (w/w) in water
- Starch indicator, 1% in water. This solution is prepared daily by mixing 0.5 g soluble of starch with 2 – 3 cm^3 distilled water and then pouring the starch into 50 cm^3 boiling distilled water with stirring. Continue heating the solution until the solution is nearly transparent. Cool solution to room temperature before use.

Apparatus and glassware

- Analytical balance (± 0.0001 g)
- Hotplate
- Erlenmeyer flask, 250 cm^3
- Volumetric flask, 100 cm$^{3;}$
- Volumetric pipette, 10.00 cm^3
- Burette, 25 cm^3
- Glass beaker, 250 cm^3
- Whatman Filter paper, Grade 2V, 110 mm.

Experimental procedure

Step 1

1. Place 0.50 g of a powder sample in a 100 cm^3 glass beaker. Add 10 cm^3 of H_2SO_4 solution H_2SO_4 (4 mol dm^{-3}) into the beaker. Place the beaker on a hot plate and begin heating the mixture in the hood. Set the hot plate at medium heat. As a portion of solid dissolves, the yellowish residue still remains in the beaker. Add slowly 3 cm^3 of HNO_3 solution into the beaker and keep heating the solution until white precipitate appears. Evaporate the solution in the beaker until white fumes of SO_3 forms, and then stop heating. Cool the solution to the room temperature (*Hint: in hood)*.

   Filter the cooled solution by using filter paper to a 100 cm^3 volumetric flask; rinse the beaker and filter paper with 1 % H_2SO_4 several times; make up the filtrate to the mark with distilled water and shake well (solution **A**).
2. Place the funnel together with the filter paper on a 250 cm^3 Erlenmeyer flask. Pour slowly a hot mixture of 20 cm^3 of CH_3COOH + NH_4CH_3COO through the white precipitate on the filter paper until it is dissolved. Wash the filter paper with distilled water to get solution **B**.

Step 2

1. Add 10.00 cm^3 of solution (**A**) and 5 cm^3 of NH_3 solution into a 250 cm^3 Erlenmeyer flask using pipettes and swirl to mix. Then, add 10 cm^3 of NH_3/NH_4Cl buffer solution (pH = 10) to the mixture.

   Add ET-00 indicator and about 10 cm^3 of deionized water. Titrate carefully with the EDTA standard solution until the color changes from wine red to blue. Record the volume of EDTA used for this titration.

   (Hint: Adjust the size of the aliquot on Zn^{2+} as necessary to stay within titration range).

2. Add the solution **B** and 5 cm^3 of 10 % $NaCH_3COO$ into a 250 cm^3 beaker. Heat the mixture slowly (at least 10 minutes) to 90 °C and then add gently 10 cm^3 of $K_2Cr_2O_7$ solution. Cool the mixture to room temperature and keep at this condition for 1 hour. Filter the precipitate through a Whatman filter paper. Wash the precipitate with warm distilled water until the filtrate is almost colorless.

   Transport the funnel with filter paper to a 250 cm^3 Erlenmeyer flask. Dissolve the yellow precipitate with 15 cm^3 of warm mixture HCl +NaCl. Rinse the filter paper with distilled water to get the solution **C**.

   Add about 5 cm^3 of 4 mol dm^{-3} H_2SO_4, 5 cm^3 of 4 mol dm^{-3} H_3PO_4, and 10 cm^3 of distilled water to the solution C. Drop 8 droplets of diphenylamine sulfonate indicator in the solution C. Titrate carefully with the standard ferrous solution until the color changes from violet to green. Record the volume of ferrous solution used.

   (Hint: Solution C can also be titrated using the iodometric titration).

Questions and Data Analysis

33.1 Give balanced chemical equations for the reactions when:

- **i.** zinc oxide powder dissolves in sulfuric acid and nitric acid to form a white solid,
- **ii.** the white precipitate is dissolved in a mixture of 2 mol dm^{-3} CH_3COOH and 1 mol dm^{-3} NH_4CH_3COO to form the complex **X,**
- **iii.** the product **X** reacts with $K_2Cr_2O_7$(aq) to form a yellow precipitate,
- **iv.** the yellow precipitate dissolves in the mixture of HCl and NaCl,
- **v.** the solution **C** is titrated with Fe^{2+} and/or iodometric titration.

33.2 Calculate the mass percentage of Zn and Pb in the powder.

33.3 In iodometric titration, $S_2O_3^{2-}$ is used to titrate I_2 produced in the reduction of $H_2Cr_2O_7$ by I^-. Why do we not use $S_2O_3^{2-}$ for titration of the $H_2Cr_2O_7$?

33.4 $PbCrO_4$ is completely precipitated in the medium with pH of at least 5 (acetic acid-acetate buffer).

vi. Does the addition of 100 cm^3 of 1.0×10^{-4} mol dm^{-3} $Pb(OAc)_2$ to 20 cm^3 of 1.0×10^{-3} mol dm^{-3} K_2CrO_4 lead to a precipitate formation, given that K_{sp} for $PbCrO_4$ is 1.8×10^{-14}?

vii. Find the equilibrium concentration of Pb^{2+} remaining in solution after the $PbCrO_4$ precipitates.

SOLUTION OF PREPARATORY PROBLEM 33

33.1

i. $ZnO(s) + H_2SO_4\,(aq) \rightarrow ZnSO_4(aq) + H_2O(l)$

$PbO(s) + 2\,HNO_3(aq) \rightarrow Pb(NO_3)_2\,(aq) + H_2O(l)$

$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4\,(s)$ (white precipitate)

ii. $PbSO_4(s) + 4\,NH_4CH_3COO(aq) \rightarrow Pb(CH_3COO)_4(NH_4)_2(aq) + (NH_4)_2SO_4(aq)$

iii. $2\,Pb(CH_3COO)_4(NH_4)_2(aq) + K_2Cr_2O_7(aq) + H_2O(l) \rightarrow 2\,PbCrO_4(\textit{yellow ppt.}) + {}$

$+ 2\,KCH_3COO(aq) + 4\,NH_4CH_3COO(aq) + 2\,CH_3COOH(aq)$

iv. $2\,PbCrO_4(s) + 4\,NaCl(aq) + 4\,HCl(aq) \rightarrow 2\,Na_2PbCl_4\,(aq) + H_2Cr_2O_7(aq) + H_2O(l)$

v. $Cr_2O_7^{2-} + 6\,Fe^{2+} + 14\,H^+ \rightarrow 2\,Cr^{3+} + 6\,Fe^{3+} + 7\,H_2O$

$H_2Cr_2O_7 + I^- + 12\,H^+ \rightarrow 2\,Cr^{3+} + 3\,I_2 + 7\,H_2O$

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

33.2 Mass of zinc oxide powder = a (g). The volume of standard solution is recorded in cm^3.

$$\% \text{ Zn} = (V_{\text{EDTA}} \times c_{\text{EDTA}}) \times 10 \times 100$$

$$\% \text{ Pb} = \frac{1}{3} \times 207.02 \times (V_{\text{Fe}^{2+}} \times c_{\text{Fe}^{2+}}) \times 100$$

33.3 The half reactions:

$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O$ $E° = 1.33$ V

$I_2 + 2\ e \rightarrow 2\ I^-$ $E^0(I_2 / 2I^-) = +0.54$ V;

$S_4O_6^{2-} + 2\ e \rightarrow 2\ S_2O_3^{2-}$ $E^0(S_4O_6^{2-} / S_2O_3^{2-}) = +0.08$ V

As $K_2Cr_2O_7$ is a strong oxidant, it can oxidize $S_2O_3^{2-}$ to $S_4O_6^{2-}$ and SO_4^{2-}. The reactions proceeds not stoichiometrically.

33.4

vi. $Pb(OAc)_2(aq) + K_2CrO_4(aq) \rightarrow PbCrO_4(s) + 2\ KOAc(aq)$

Then $PbCrO_4(s) \Leftrightarrow Pb^{2+} + CrO_4^{2-}$

$[Pb^{2+}] = 0.1 \times 10^{-5} / 0.12 = 8.3 \cdot 10^{-6}$ mol dm^{-3}

$[CrO_4^{2-}] = 0.02 \times 1.0 \cdot 10^{-3} / 0.12 = 1.7 \cdot 10^{-4}$ mol dm^{-3}

Therefore $Q = 8.3 \cdot 10^{-6} \times 1.7 \cdot 10^{-4} = 1.4 \cdot 10^{-9} > K_{sp}$.

Thus, a precipitate will occur.

vii. Since $[Pb^{2+}] = 8.3 \cdot 10^{-6}$ and $[CrO_4^{2-}] = 1.7 \cdot 10^{-4}$ and there is a 1 : 1 stoichiometry, Pb^{2+} is completely reacted.

$PbCrO_4(s) \Leftrightarrow$	Pb^{2+}	+ CrO_4^{2-}
I. (after ppt.)	$8.3 \cdot 10^{-6}$	$7 \cdot 10^{-4} - 8.3 \cdot 10^{-6} = 1.7 \cdot 10^{-4}$
C.	x	x
E.	x	$1.7 \cdot 10^{-4} + x$

$K_{sp} = [x]\,[1.7 \cdot 10^{-4} + x] = 1.8 \cdot 10^{-14}$

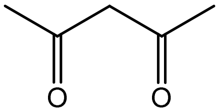
Solving for x gives $x = 1.1 \cdot 10^{-10}$, so the concentration of Pb^{2+} remaining in solution is very small.

PREPARATORY PROBLEM 34 (PRACTICAL)

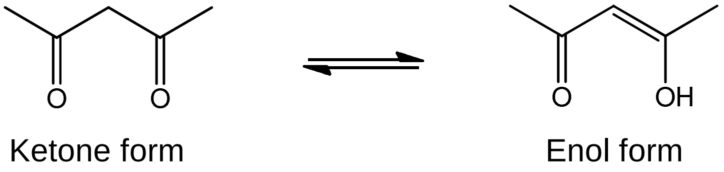
Preparation of copper(II) acetylacetonate

Introduction

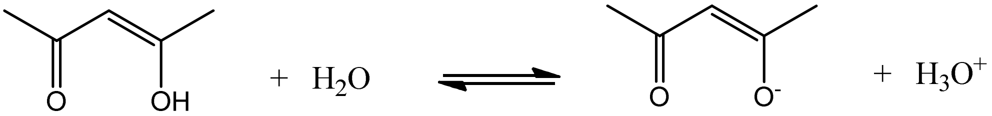
Acetylacetone (Hacac) is the simplest of the beta-diketones.



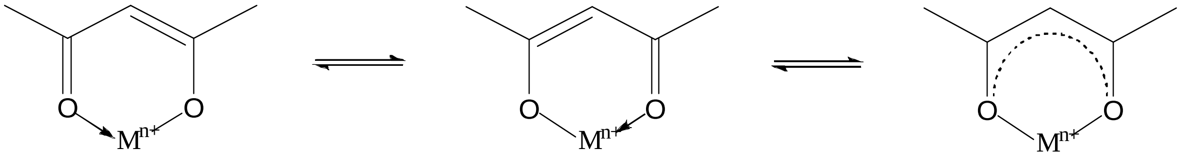
Hacac commonly exists in two tautomeric forms, ketone and enol, which can rapidly interconvert in solution as well as in the gas phase.



In aqueous solutions, Hacac is in equilibrium with hydrogen ions (H^+) and with acetylacetonate (enolate) ions ($acac^-$). The dissociation constant K_a is $1.51 \cdot 10^{-9}$.



Acetylacetone can form stable complexes with many transition metal ions. In most of the structurally characterized complexes, Hacac that is singly deprotonated acts as a bidentate ligand, and binds to the metal via both two oxygen donor atoms to form six-membered chelate ring.



Acetylacetone is known to form neutral complexes with about 60 metals and is among the most versatile and most used chelating ligand in coordination chemistry.

Copper (II) acetylacetonate can be synthesized in a ligand exchange reaction:

$$2\ acac^- + [Cu(H_2O)_6]^{2+} \rightleftharpoons [Cu(acac)_2].\ n\ H_2O + (6 - n)\ H_2O$$

Chemicals and Reagents

- Acetylacetone
- 0.2 mol dm^{-3} $CuSO_4$ aqueous solution
- 25 % NH_3 solution
- Diluted HCl solution
- Diluted NH_3 solution
- Universal indicator papers
- Chemicals for determination of Cu content.

Apparatuses and Glassware

- Glass beakers, 100 cm^3, 50 cm^3
- Pipette, 5 cm^3
- Graduated cylinder, 50 cm^3
- Rubber bulb
- Watch glass
- Glass rod
- Magnetic stirrer
- Sintered glass funnel
- Vacuum pump
- Wash bottle
- Analytical balance with readability of 0.001 g.

Experimental procedure

Step 1. Preparation of copper (II) acetylacetonate

1. Use 25 cm^3 of 0.2 mol dm^{-3} $CuSO_4$ aqueous solution to calculate the quantities of chemicals required for synthesis of the complex.
2. Prepare the ammonium acetylacetonate (NH_4acac) solution: Add slowly 25% NH_3 aqueous solution (ρ = 0.90 g cm^{-3}) into liquid acetylacetone in a 50 cm^3 glass beaker with a molar ratio Hacac : NH_3 of 1.0 : 0.9. A white solid appears for seconds and then dissolves completely to obtain a clear solution.
3. Prepare the copper(II) acetylacetonate: Add the freshly prepared NH_4acac solution (with a 50% excess) into a 100 cm^3 glass beaker in which 25 cm^3 of 0.2 mol dm^{-3} $CuSO_4$ aqueous solution and a stirring bar are placed. Start stirring the solution on a

magnetic stirrer and adjust the pH of the mixture to 3-4 by the addition of dilute solutions of HCl and NH_3. The pale blue solid of copper (II) acetylacetonate is precipitated. The reaction mixture is stirred for additional 30 min to complete the precipitation. The formed solids are collected on sintered glass funnel by a vacuum filtration, washed 3 times with small portions of distilled water and then transported to a watch glass and dried at 120°C for 30 min. Weigh the product on the analytical balance with the readability of 0.001 g.

Step 2. Determination of the Cu content in the complex

1. Students propose an appropriate procedure to determine the Cu content in the product. *(Hints: The* Cu^{2+} *concentrations can be determined by iodometric titration, complexometric titration with EDTA…)*.

Questions and Data analysis

34.1 Calculate the copper content in the complex. Suggest an appropriate molecular formula of copper (II) acetylacetonate and then calculate the percentage yield of the synthesis of the complex.

34.2 In the Step 1(3), why is the excess of NH_4acac used? Why does the pH need to be adjusted to 3 - 4?

34.3 Propose the molecular structure of copper (II) acetylacetonate.

SOLUTION OF PREPARATORY PROBLEM 34

34.1 Cu(acac)$_2$

34.2 There are four main equilibria involved the complex formation:

$$\text{Hacac}(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + \text{acac}^-(aq)$$

$$H_3O^+(aq) + OH^-(aq) \rightleftarrows 2\,H_2O(l)$$

$$Cu^{2+}(aq) + 2\,\text{acac}^-(aq) \rightleftarrows [Cu(\text{acac})_2](s)$$

$$Cu^{2+}(aq) + 2\,OH^-(aq) \rightleftarrows Cu(OH)_2(s)$$

At a low pH, $acac^-$ is not sufficiently concentrated to precipitate complex or to form the complex with a high yield. On the contrary, at high pH regions, $Cu(OH)_2$ can be competitively precipitated and an impure product can be obtained.

34.3 Square planar complex with two six-membered chelate rings.

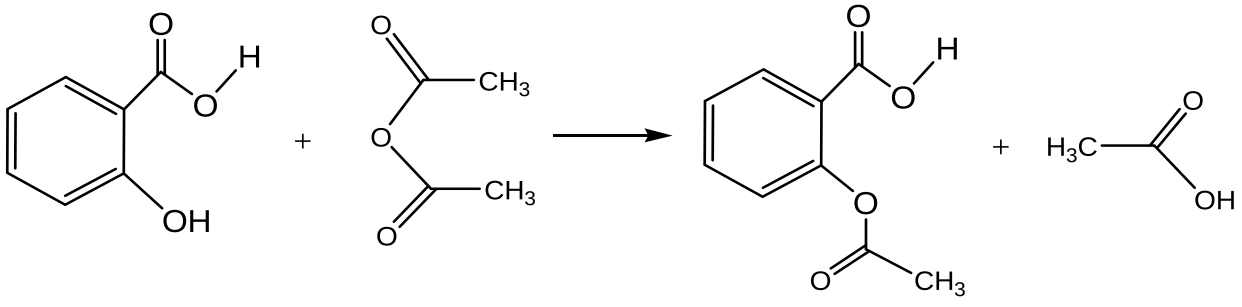
PREPARATORY PROBLEM 35 (PRACTICAL)

Kinetic analysis of the hydrolysis of aspirin

Introduction

Aspirin (acetylsalicylic acid) is an ester of salicylic acid. It has been widely used in medicinal treatment. It is an effective analgesic (pain killer) that can reduce the mild pain of headache, toothache, neuralgia (nerve pain), muscle pain and joint pain (from arthritis and rheumatism). Aspirin behaves as an antipyretic drug (it reduces fever), and an anti-inflammatory agent capable of reducing the swelling and redness associated with inflammation. It is an effective agent in preventing strokes and heart attacks due to its ability to act as an anti-coagulant.

Aspirin can be easily synthesized in laboratory by the esterification reaction between salicylic acid and acetic anhydride as shown in the reaction below:



Salicylic acid Acetic anhydride Acetylsalicylic acid Acetic acid

In acidic or basic media, aspirin is hydrolyzed to give its active form – salicylic acid. The hydrolysis reaction of aspirin, however, takes place in basic condition much faster than in acidic condition. This illustrates a very important principle: the stability of drugs and their mechanisms strongly depend on the pH condition of the body.

In general, the hydrolysis of esters may be catalyzed by either acid or base. The detailed mechanism of hydrolysis reactions has been the subject of an enormous research effort, since they are of such fundamental importance. The generally accepted mechanism of acid-base-catalyzed hydrolysis is known; however many researchers particularly in biotechnology are applying this fundamental knowledge in new and more complicated systems.

This experiment deals with both the synthesis of aspirin and kinetic study of the hydrolysis of aspirin under a basic condition. Working with synthesis of aspirin, the preparative method uses acetic anhydride and an acid catalyst, concentrated sulfuric acid, to speed up the reaction with salicylic acid. Then the hydrolysis of aspirin will be studied under pseudo-order conditions. This will allow the order with respect to aspirin concentration to be determined. The order with respect to the concentration of hydroxide ions will be given and from this data you will be asked to draw conclusions about the mechanism.

Chemicals and Reagents

- Salicylic acid $CH_3CO_2C_6H_4CO_2H$
- Acetic anhydride $CH_3C_2O_3CH_3$
- Concentrated sulfuric acid H_2SO_4
- Absolute ethanol C_2H_5OH
- Standard NaOH solution.

Apparatus and glassware

- Vis Spectrophotometer
- Thermostat
- Stirrer hotplate
- Analytical balance (± 0.0001 g)
- Beaker glass, 100 cm^3
- Erlenmeyer flask, 100 cm^3
- Pipette, 5 cm^3
- Büchner flask (Filter flask)
- Büchner filter
- Filter paper
- Glass rod
- Stopwatch

Experimental procedure

Step 1. Synthesis of acetyl salicylic acid

1. Prepare a bath using a 400 cm^3 beaker filled about half-way with water. Heat to boil.

2. Weigh 2.0 g salicylic acid using an analytical balance and place it in a 100 cm^3 Erlenmeyer flask. Use this quantity of salicylic acid to calculate the theoretical or expected yield of aspirin.
3. Carefully add 5.0 cm^3 of acetic anhydride by pipette to the Erlenmeyer flask containing the acid.
4. Add about 5 – 6 drops of concentrated sulfuric acid as catalyst.

   Caution! *Acetic anhydride could irritate your eyes. Sulfuric acid could cause burns to the skill. Handle both chemicals with care.*
5. Mix the reagents and then place the Erlenmeyer flask in boiling water bath. Heat for 15 min. The solid will completely dissolve. Swirl the solution occasionally.
6. Add 10.0 cm^3 water to the Erlenmeyer flask, shake the flask thoroughly, and then place it in an ice bath for 10 – 15 min to crystallize out the entire product, acetylsalicylic acid. Collect the crystals by filtration under vacuum. If the crystallization takes place slowly, scratch gently inside the flask with a glass rod.
7. Re-crystalize the crude product as follow: Dissolve the crude product in 10.0 cm^3 ethanol, then pour the ethanol solution into 60.0 cm^3 warm water and place the obtained solution in the ice water for 10-15 min. Filter off the product.
8. Dry the product in an oven at 100 ^{o}C for 30 min. Weigh the dried product.

Step 2. Hydrolysis of acetylsalicylic acid

1. Prepare 50.0 cm^3 of a $5 \cdot 10^{-3}$ mol dm^{-3} solution of salicylic acid in 20% ethanol and approx. NaOH $5 \cdot 10^{-3}$ mol dm^{-3} solution as follows:
   i) Weigh out the required amount of salicylic acid (M = 138.1 g mol^{-1}) in small beaker on an analytical balance.
   ii) Dissolve the weighed acid in 10.0 cm^3 of ethanol.
   iii) Transfer this quantitatively into a 50 cm^3 volumetric flask already containing 5.0 cm^3 $5 \cdot 10^{-2}$ mol dm^{-3} NaOH, wash the vial several times and add water to the mark.
2. Prepare 50.0 cm^3 of a $5 \cdot 10^{-4}$ mol dm^{-3} solution of salicylic acid as follows:
   i) Place 10.0 cm^3 of ethanol in a 50 cm^3 volumetric flask, add by pipette to this flask 5 cm^3 solution prepared in step 1.
   ii) Add a required amount of $5 \cdot 10^{-3}$ mol dm^{-3} NaOH solution to fill up to the mark. Place the flask in a heated bath at 37 ^{o}C.

3. Measure the absorbance at 295 nm. This will be the A_∞ in the subsequent calculation (*Note*: Before measuring the absorbance of salicylic acid, the UV-Vis spectrophotometer should be zeroed with standard sample. Standard sample is a $5 \cdot 10^{-3}$ mol dm^{-3} NaOH solution containing 20% ethanol).
4. Prepare 50 cm^3 of a $5 \cdot 10^{-4}$ mol dm^{-3} solution of acetylsalicylic acid ($2\text{-}CH_3CO_2C_6H_4CO_2H$) as described in parts 1 and 2 above.
5. Place the reaction bottle in a thermostated bath at 37 °C. Start counting the reaction time as soon as the solution is placed in the bath.
6. Five minutes after the start of the reaction, transfer a sufficient amount of the reaction solution into 1 cm UV-Vis absorption cuvette and measure the absorbance at 295 nm. Continue recording the absorbance and write down the obtained experimental data in the table below:

Time/min	5	10	20	30	40	50	60	∞
Absorbance A								

Questions and data analysis

35.1 Calculate the yield of the reaction.

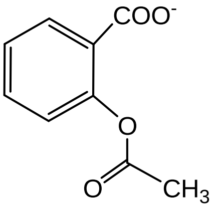
35.2 Aspirin can irritate the stomach. What is usually done in the preparation of the drug that reduces this side effect?

35.3 Calculate the concentration of NaOH in $5 \cdot 10^{-4}$ mol dm^{-3} solution of aspirin.

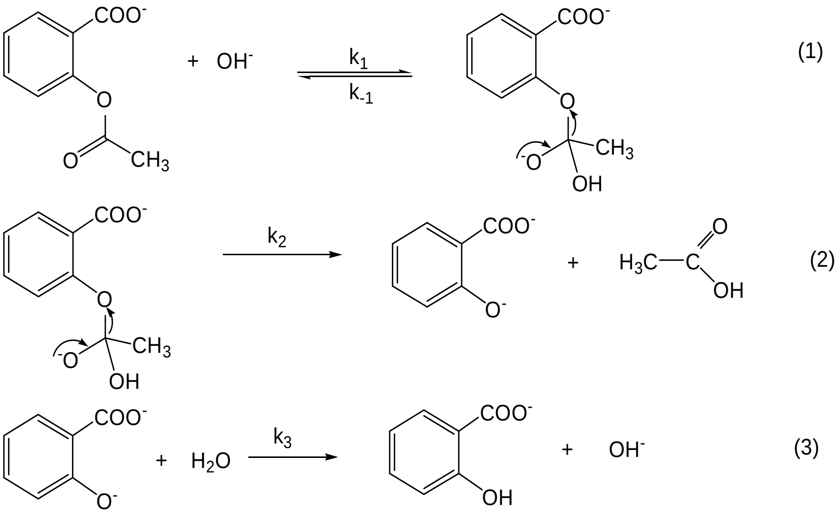
35.4 Plot $(A_\infty - A)$ vs. time *t*, $\ln(A_\infty - A)$ vs. *t*, and $\left(\frac{1}{A_\infty - A} - \frac{1}{A_\infty}\right)$ vs. *t* on three separate charts. From these plots determine the order with respect to acetylsalicylic acid.

35.5 Determine the value of the pseudo-order rate constant, k_{obs}. Calculate the half-life of the hydrolysis under the reaction condition used. For how many half-lives was the reaction allowed to run?

35.6 In basic solution, acetylsalicylic acid exists as an anion.



The following mechanism has been proposed to account for the base catalyzed hydrolysis of aspirin. Based on the order with respect to aspirin, and given the order with respect to [OH$^-$] = 1, derive the rate law and indicate which of the following reactions is the rate - determining step.



SOLUTION OF PREPARATORY PROBLEM 35

35.1 The theoretically obtained amount of aspirin is:

n(salicylic acid) = 2.00g / 138.1 = 0.0145 mol

m(aspirin) = 0.0145 mol × 180.2 g mol^{-1} = 2.6129 g

For example, the amount of aspirin obtained experimentally is 2.0132 g

$\rightarrow$ The yield of the reaction is: (2.0132 g / 2.6129 g) ×100 = 77.04 %

35.2 Magnesium hydroxide, magnesium carbonate and aluminum glycinate, when mixed into the formulation of the aspirin will reduce the irritation.

35.3 Ignoring the volume change upon mixing and supposing that aspirin occupies only negligible volume:

In the 5 $\cdot 10^{-4}$ mol dm^{-3} solution of acetylsalicylic acid, the concentration of NaOH = (5.0 $\cdot$ 10^{-3} mol dm^{-3} × 40 cm^3) / 50 cm^3 – 5.0 $\cdot$ 10^{-4} mol dm^{-3} = 3.5 $\cdot$ 10^{-3} mol dm^{-3}

35.4 Determine the order with respect to the concentration of aspirin and the pseudo -order rate constant of the reaction.

The UV-Vis absorption obtained in the experiments is given below:

Time/minute	5	10	20	30	40	50	60	∞
Absorbance A	0.549	0.829	1.178	1.389	1.506	1.569	1.602	1.653

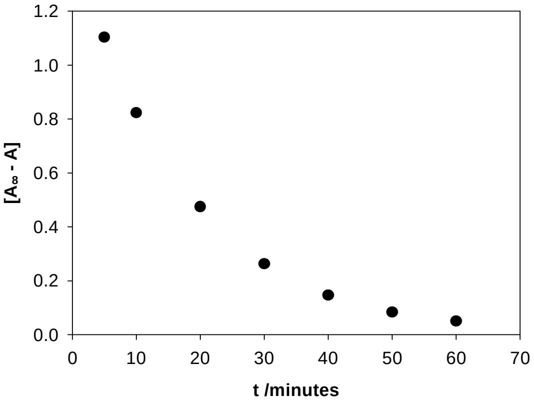


Figure 1. Plot of (A_∞ - A) versus time

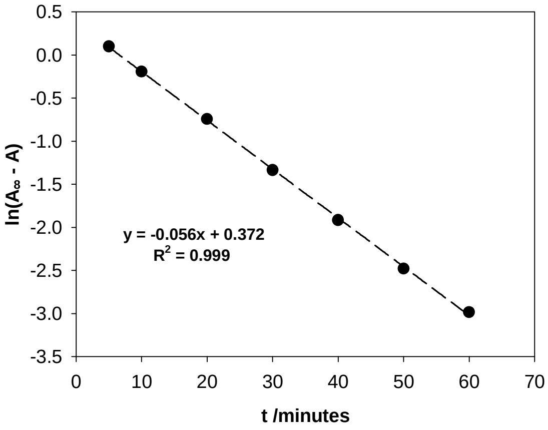


Figure 2. Plot of ln(A_∞ - A) vs. t

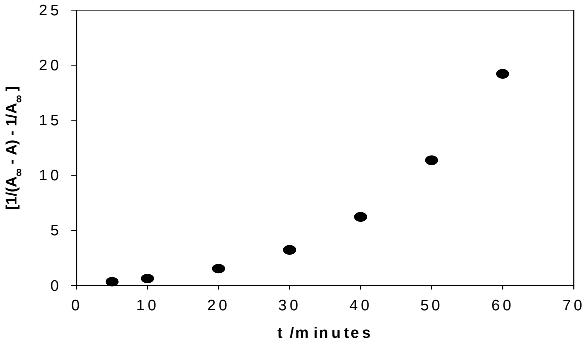


Figure 3. Plot of $\left(\frac{1}{A_\infty - A} - \frac{1}{A_\infty}\right)$ vs. t

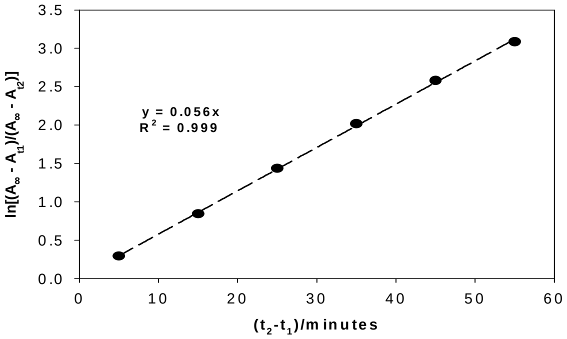


Figure 4. Plot of $\ln\frac{A_\infty - A_{t_1}}{A_\infty - A_{t_2}}$ vs. $(t_2 - t_1)$

35.5 Experimental results showed that the reaction obeyed the pseudo-first-order rate law (figure 2 and 4), but not the second-order (figure 3). Based on the equation $\ln\frac{A_\infty - A_{t_1}}{A_\infty - A_{t_2}} = kt$ and the results in figure 4, as well as in figure 2, we can easily calculate k_{obs} = 0.056 min^{-1}. Hence, the half-life is 17.85 minutes and the reaction time is 3.36 times greater than the half-life.

35.6 From the obtained experimental results the reaction is first order with respect to both [asp] and [OH$^-$], therefore the rate law may be given as

Rate = k [asp]^1[OH$^-$]^1.

According to this mechanism, in step 1, the hydroxide nucleophile attacks at the electrophilic **C** of the ester **C=O**, breaking the σ bond and creating the **tetrahedral intermediate**. In step 2, the intermediate collapses, reforming the C=O and, the last step (step 3) is an acid-base reaction which takes place very fast, a very rapid equilibrium. Hence, it is not the rate-determining step of the reaction.

Let denote the **tetrahedral intermediate** as **I** and (2-$HOC_6H_4COO^-$), a product in step (2) as **P**. The rate of formation of product may be given as

$$Rate = \frac{d[P]}{dt} = k_2[I]$$

With regard to the stability of the intermediate I, the two possibilities, which may be considered, are

i) If $k_{-1} \gg k_2$, means the rate of reconversion of **I** into asp and OH$^-$ is significantly greater than the rate with which it undergoes to give the **P**, the concentration of intermediate **I**, [I] can be calculated by considering equilibrium (1) alone

[I] = K [asp] [OH$^-$]

Where equilibrium constant $K = k_1/k_{-1}$ and, therefore

Rate of the reaction = k_2K [asp] [OH$^-$]

which is matching well with experimental results.

ii) If intermediate complex **I** is much less stable species, means the rate of its conversion to product (step 2) is not small compared with the reverse rate in step 1. In this case, the concentration of **I** must be calculated by using steady-state treatment.

By applying the steady state with respect to [I], we get

$$k_1[\text{asp}][\text{OH}^-] = k_{-1}[\text{I}] + k_2[\text{I}]$$

or

$$[\text{I}] = \frac{k_1[\text{asp}][\text{OH}^-]}{k_{-1} + k_2}$$

and, therefore

$$\text{Rate of reaction} = \frac{k_1 k_2[\text{asp}][\text{OH}^-]}{k_{-1} + k_2}$$

However, when $k_{-1} \gg k_2$, the rate law becomes the same as in case 1. Thus, the steady state treatment is the general one, and reduces to the equilibrium treatment when $k_{-1} \gg k_2$.

Conclusion: if the equilibrium in step 1 is controlled throughout the reaction process (step 1 is very fast and represents rapid pre-equilibrium to the rate), the given mechanism agrees with the rate law and in this case the step 2 is rate-determining step of the reaction.

The obtained rate laws clearly show the rate is dependent on the NaOH concentration. For a given concentration of NaOH, we may write

where $k_{\text{obs}} = \dfrac{k_1 k_2[\text{OH}^-]}{k_{-1} + k_2}$ or k_2K [OH$^-$] (when $k_{-1} \gg k_2$)

Constant k_{obs} is proportional to [OH$^-$] and is known as catalytic coefficient for the catalyst.

PREPARATORY PROBLEM 36 (PRACTICAL)

Complex formation of ferric ion and salicylic acid

Introduction

In this simple experiment we will study the complex formation of Fe^{3+} and salicylic acid in the aqueous solution. The empirical formula of the complex will be determined and also its stability constant can be estimated.

Several stable complexes between ferric ion and salicylic acid H_2Sal have been known. Their structures and compositions are much dependent on pH. In acidic solution, a violet complex is formed. At neutral pH, a different dark-red complex forms, and in basic solution the complex that forms is orange. This experiment will be carried out at pH of about 2. Under this condition, the hydrolysis of ferric ion is largely suppressed. To simplify the calculations, we will not consider to the dissociation of H_2Sal during the complex formation. Thus, regardless of the structure of the complex, we can present the complex formation equilibrium as:

$$Fe^{3+} + n\ H_2Sal \rightleftharpoons Fe^{3+}(H_2Sal)_n$$

Thus, the stability constant K_f is defined as

$$K_f = \frac{[Fe^{3+}(H_2Sal)_n]}{[Fe^{3+}]\,[H_2Sal]^n} \qquad (1)$$

where the $[Fe^{3+}]$ and $[H_2Sal]$ refer to the concentrations of the free species.

The complex $Fe^{3+}(H_2Sal)_n$ absorbs most strongly at 528 nm (neither Fe^{3+} nor H_2Sal absorb at this wavelength). Its concentration is related to the optical absorbance through Beer's law, which is:

$$A = \varepsilon\, l\ [Fe^{3+}(H_2Sal)_n]$$

where ε is the molar extinction coefficient for the complex and l is the optical path length.

Job's method can be used to find the empirical formula of the complex. Following this method, equimolar solutions of Fe^{3+} and H_2Sal are prepared, and then mixed in ratios of 1:9; 2:8 … 9:1. The total reagent concentrations therefore are the same in each solution. Maximum amount of equilibrium complex will be formed when the proportions of reagents employed correspond to the empirical formula of the complex and can be deduced through the measurement of optical absorbance.

Chemicals and Reagents

- A solution of 0.0025 mol dm^{-3} Fe^{3+} made by dissolving the appropriate amount of ferric ammonium sulfate in 500 cm^3 of 0.0025 mol dm^{-3} sulfuric acid.
- A solution of 0.0025 mol dm^{-3} salicylic acid made by dissolving the appropriate amount of salicylic acid in 500 cm^3 0.0025 mol dm^{-3} sulfuric acid.
- Saturated solution of salicylic acid (about 50 cm^3) in 0.0025 mol dm^{-3} sulfuric acid.

Apparatuses and Glassware

- Glass beaker: 100 cm^3, 50 cm^3
- Burette: 25 cm^3
- Volumetric flask: 500 cm^3
- Wash bottle
- Electronic balance with readability of 0.0001 g
- UV-vis spectrophotometer
- Glass cuvettes.

Experimental procedure

Step 1. Determine the empirical formula of the complex by Job's-method

1. Prepare in 100 cm^3 beakers (should be **dry** and **clean**) a series of nine mixtures of the 0.0025 mol dm^{-3} iron(III) and the 0.0025 mol dm^{-3} salicylic acid solutions, plus 10.0 cm^3 0.0025 mol dm^{-3}:

Mixture	1	2	3	4	5	6	7	8	9
V_{cm3} Iron(III)	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00
V_{cm3} salicylic acid	9.00	8.00	7.00	6.00	5.00	4.00	3.0	2.00	1.0
V_{cm3} 0.0025 mol dm^{-3} HCl	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00

(Note: *Use burette to measure the volumes of the solution.*)

2. Measure the absorbance of each mixture.
3. Plot absorbance *versus* volume of Fe^{3+}. Absorbance should be highest for the stoichiometric mixture.

Step 2. Determine the molar extinction coefficient *ε* of the complex

1. Pipette out 1.00, 2.00, 3.00, 4.00, 5.00, 6.00 cm^3 of 0.0025 mol dm^{-3} iron(III) solution into 5 beakers (100 cm^3). To each beaker add 10.00 cm^3 of saturated salicylic acid solution and enough HCl solution (0.0025 mol dm^{-3}) to reach the total volume to 20.00 cm^3.
2. Measure the absorbance of each solution.
3. Plot absorbance *versus* [Fe^{3+}] (Because the salicylic acid is in excess, it is assumed that the concentration of iron equals the concentration of the complex).
4. Calculate *ε* from the linear plot.

Step 3. Determine the stability constant K_f

1. Prepare (in 100 cm^3 beakers) three mixtures of the same volumes of 0.0025 mol dm^{-3} Iron(III) and the 0.0025 mol dm^{-3} salicylic acid solutions and plus 0.0025 mol dm^{-3} HCl solution to total volume of 20 cm^3:

Mixture	1	2	3
V_{cm3} 0.0025 mol dm^{-3} Iron(III)	5.00	4.00	3.00
V_{cm3} 0.0025 mol dm^{-3} salicylic acid	5.00	4.00	3.00
V_{cm3} 0.0025 mol dm^{-3} HCl	10.00	12.00	14.00

2. Measure the absorbance of each solution.
3. Calculate the initial concentration of Fe(III) and H_2Sal in each solution.
4. From the measured absorbance and observed ε value determined in step 2(4)). Calculate the concentration of the complex in each solution.
5. Calculate the equilibrium concentration of Fe(III) and H_2Sal. Assume that:
$[Fe^{3+}]_{eq} = [Fe^{3+}]_{initial} – [Fe^{3+}(H_2Sal)_n]$
$[H_2Sal]_{eq} = [H_2Sal]_{initial} – n × [Fe^{3+}(H_2Sal)_n]$
6. Calculate the equilibrium constants K_{eq} for each solution (using equation 1) and determine an average value.

Questions and Analysis

36.1 What is the empirical formula of the complex?

36.2 The above complex is normally reported as $[Fe(Sal)]^+$ in which the salicylic ligand is doubly deprotonated.

i. Write the chemical equation in the ionic form to the formation of $[Fe(Sal)]^+$.

ii. Let formulate the stability constant of the ion complex $[Fe(Sal)]^+$ from observed K_{eq}, $[H^+]$, K_{a1} and K_{a2} of H_2Sal.

iii. pK_{a1} and pK_{a2} values of H_2Sal are 2.98 and 13.60, respectively (*CRC Handbook of Chemistry and Physics, CRC Press, 2003, pp. 1247).* Calculate the stability constant (K_f) of the ion complex $[Fe(Sal)]^+$ for each solution (in section 2.3) and determine an average value. Assume that the dissociation of H_2Sal can be ignored. *(Hint: $[H^+]_{eq} = 0.0025 + 2 \times n \times [Fe^{3+}(H_2Sal)_n]$).*

iv. Comment on your K_f value and explain the probable errors?

SOLUTION OF PREPARATORY PROBLEM 36

36.1 $n = 1$, thus the empirical formula is $Fe^{3+}(H_2Sal)$

36.2 **i.** The chemical equation:

$$H_2Sal + Fe^{3+} \rightarrow [Fe(Sal)]^+ + 2\,H^+ \qquad (1)$$

ii. $$K_{(1)} = K_f\,K_{a1}K_{a2} = \frac{[Fe(Sal)]\,[H^+]^2}{[H_2Sal]\,[Fe^{3+}]} \quad \text{or} \quad K_f = \frac{K_{eq}\,[H^+]^2}{K_{a1}\,K_{a2}}$$

$[H^+]$ need be calculated from initial concentration 0.0025 M and dissociation concentration during complex formation:

$$[H^+]_{eq} = 0.0025 + 2 \times [Fe(Sal)]^+$$

iii. The average value is about $1.4 \cdot 10^{16}$

iv. The average K_f value is not the same with literature values which vary from $2.2 \cdot 10^{16}$ to $2.7 \cdot 10^{16}$ (ref. 2) due to the simplifications of the equilibrium as mentioned, and also using concentrations instead of activities in the K_f equation.

[1]. D. R. Lide. CRC Handbook of Chemistry and Physics (84th Ed). CRC Press, 2003, pp. 1247.

[2] *Z. L. Ernst; J. Menashi.* Complex formation between the Fe^{3+} ion and some substituted phenols. Part 1. Spectrophotometric determination of the stability constant of ferric salicylate. Trans. Faraday Soc., 1963, 59, 1794-1802.