Problem 14: Lead iodide

Lead nitrate (Pb(NO3)$_2$) and potassium iodide (KI) react in aqueous solution to form a yellow precipitate of lead iodide (PbI$_2$). In one series of experiments the masses of the two reactants were varied, but the *total* mass of the two was held constant at 5.000 g. The lead iodide formed was filtered from solution, washed and dried. Data for a series of reactions are given below, together with a blank graph.

Experiment	Mass of lead nitrate (g)	Mass of lead iodide (g)
1	0.500	0.692
2	1.000	1.388
3	1.500	2.093
4	3.000	2.778
5	4.000	1.391

Mass of Pb(NO$_3$)$_2$(aq) in g
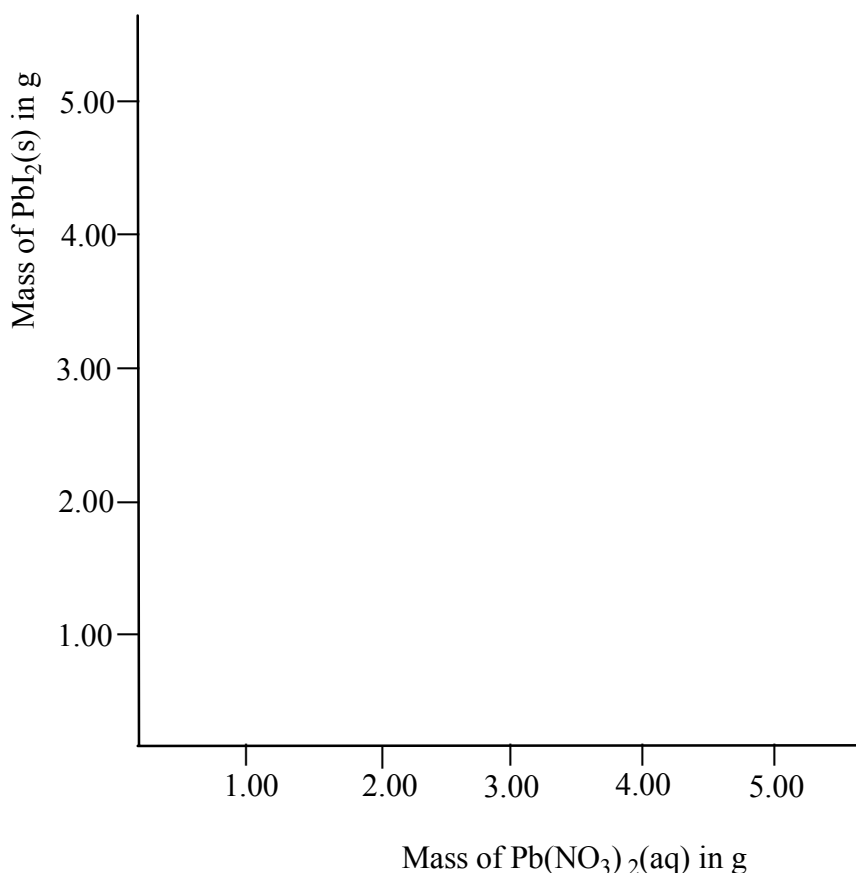
1. Complete the graph; that is, plot the data and draw the approximate curve(s) connecting the data points. Determine graphically what the maximum mass of precipitate is that can be obtained?

2. Write the balanced equation for the reaction and use it to calculate the maximum mass of PbI$_2$ and the corresponding amount of Pb(NO$_3$)$_2$.
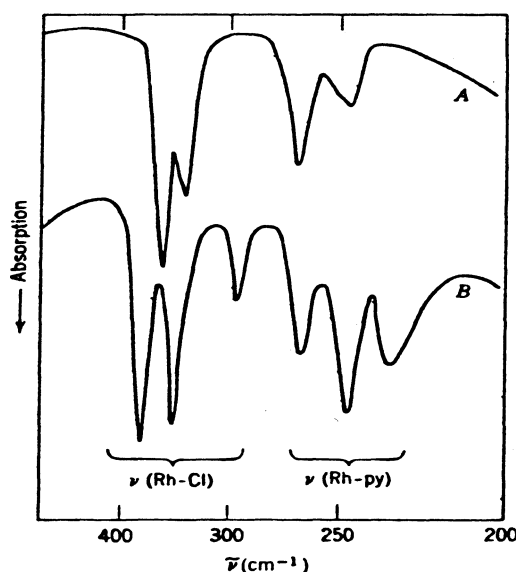
Problem 15: Octahedral complexes

The doubly charged metal ions of the first row transition elements with the configuration d^1, d^2, ... d^9 form mainly octahedral complexes of the general formula ML$_6^{2+}$ (L = neutral monodentate ligand). From the magnetic behavior point of view these complexes are of two types. Those with the same number of unpaired electrons with the M$_{(g)}^{2+}$, the so called "high spin" complexes, and those in which this number is smaller or even zero, the "low spin" ones. If the separation between the energy levels t$_{2g}$ and e$_g$ is Δ and the pairing energy (the energy necessary for two electrons to

be coupled into a singlet) is P, predict the ground state electron configuration for these complexes. Hint: The Aufbau principle and the Pauli exclusion principle must be obeyed.

Problem 16: Isomerism in Inorganic Chemistry

Isomerism is traditionally introduced in Organic chemistry courses. However, Inorganic Chemistry also offers many different types of isomerism, especially structural. The modern study of coordination compounds began with Alfred Werner[1] and Sophus Mads Jorgensen, more than one hundred years ago. It was their experiments that established the octahedron as the premier structural entity for coordination number six (6) rather than the planar hexagon or the trigonal prism, for example in the complex ion $Co(NH_3)_6^{3+}$. Thus, there are two isomers corresponding to the chemical formula $CoCl_3·4NH_3$, the *praseo* and *violeo* complexes. There are also two structural isomers for the complex $Rh(py)_3Cl_3$ (py: pyridine – only its N-atom need be considered). The far infrared spectra in the 450–200 cm^{-1} region of these two complexes are shown in the figure below.

Rotation of plane polarized light is not limited to organic molecules with a chiral carbon atom. The general condition for optical activity is that the molecule or ion should not possess an improper axis of rotation, and because $S_2 \equiv i$ and $S_1 \equiv \sigma$ the molecule may not possess a center or plane of symmetry. Thus, although there is only one *cis*–$[Co(NH_3)_4Cl_2]Cl$ complex, there are two *cis*–$[Co(en)_2Cl_2]Cl$ complexes (en: ethylene diamine or 1,2 diamino ethane, a symmetric bidentate ligand) which are enantiomers.

[1] Nobel prize in Chemistry 1913

Questions:

1. What is the electronic configuration of Co in $Co(NH_3)_6^{3+}$?
2. What is the type of bonding of NH_3 in $Co(NH_3)_6^{3+}$, which is a low spin complex, and of fluoride ion in CoF_6^{3-}, which is a high spin complex? Place electrons from the ligands in appropriate metal orbitals according to Valence Bond Theory.
3. Write the stereochemical formulae and structures for the *praseo* and *violeo* complexes.
4. Write the stereochemical formulae and structures for the two $Rh(py)_3Cl_3$ complexes. Assign the spectra to each of the two complexes.
5. How many isomers does the complex with the formula $[Co(en)_3]I_3$ exibit ?

Problem 17: Tetrahedral and square complexes

Four coordination is much less common than six coordination in first row d-block elements, mainly due to energy stabilization by the ligands. The most symmetric spatial location of ligands about a central ion is the tetrahedron, but square planar complexes are also well known. In tetrahedral geometry only one MA_2B_2 complex is possible, whereas two isomers are possible in square planar geometry. The hybridization of metal atomic orbitals for tetrahedral geometry is **sp^3** or **sd^3** and for square planar geometry **dsp^2**.

Ni^{2+} is $[Ar]3d^8$. With chloride ion a paramagnetic $NiCl_4^{2-}$ complex ion is formed, whereas with cyanide (CN^-) ion a diamagnetic $Ni(CN)_4^{2-}$ complex ion is formed.

Show the distribution of metal ion valence electrons and ligand electrons in the 3d, 4s and 4p subshells for both complexes.

Problem 18: Copper enzyme

Life on our planet is based on the conversion of solar to chemical energy during photosynthesis. Plastocyanin (PC), is a Cu-containing protein that mediates electron transfer in the photosynthetic electron transfer chain. The active site of PC consists of a Cu ion coordinated by the N atoms of the side chains of two histidines and the sulfur atoms of one cysteine and one methionine residue. Electron transfer by PC involves interconversion of the Cu ion between the Cu(I) and Cu(II) oxidation states. The three-dimensional structure of PC can be found at http://www.rcsb.org/, Protein Data Bank file for poplar PC: 1PNC.
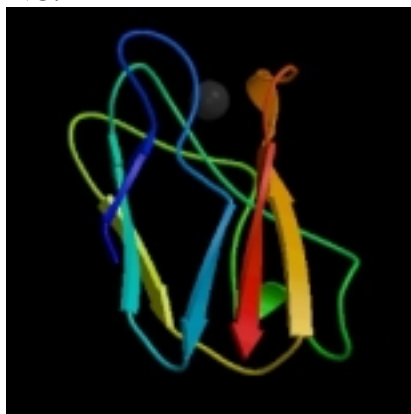

1. What is the full electron configuration of Cu, Cu(I), Cu(II) ?
2. Which oxidation state of PC is EPR active ?
3. Based on the amino-acid sequence of PC (the "primary structure" of the protein), the molar mass of PC is 10500. An aqueous solution of oxidized PC has an intense blue color (PC belongs to the family of "Blue Copper Proteins"), since it absorbs strongly at 597 nm (molar absorption coefficient 4500 $mol^{-1}dm^3 cm^{-1}$). A sample of oxidized PC in a 1cm UV-Vis cell has an absorption of 0,700. Calculate the amount (mg) of PC and the number of Cu(II) ions that are present in 5 cm^3 of this PC solution.
4. The Cu ions of certain Blue Copper proteins can be removed to give the corresponding metal-free proteins, known as apo-proteins. These forms can bind various metal ions such as Co(II), Ni(II), Zn(II) and Cd(II), and the metal sites adopt similar structures with the "native" Cu protein. Which reconstituted Blue Copper Proteins are expected to be redox inactive?

Problem 19: Palladium nanoclusters

Nanoclusters -near monodispersed metal particles that are generally less than 10 nm (100Å) in diameter- have attracted intense interest over the past decade. One reason for this is the belief that nanoclusters will have unique properties, derived in part from the fact that these particles and their properties lie somewhere between those of the bulk and single-particle species. These strange "morsels of matter" have fascinating potential uses; nanoclusters have significant potential especially for catalysis as new types of higher activity and selectivity catalysts.

There are four general synthetic methods for transition metal nanoclusters. These four methods are: (i) transition metal salts reduction (ii) thermal decomposition and photochemical methods (iii) ligand reduction and displacement from organometallics, and (iv) metal vapor synthesis. Furthermore, nanoclusters must be stabilized against aggregation into larger particles. Stabilization can be achieved by electrostatic (charge

or "inorganic") stabilization, steric ("organic") stabilization or a combination of both. Electrostatic stabilization occurs by the adsorption of ions to the often electrophilic metal surface. This adsorption creates an electrical double (real multi-) layer, which results in a Coulombic repulsion force between individual particles (Fig. 1a). Steric stabilization is achieved by surrounding the metal center by layers of material that are sterically bulky, such as polymers or surfactants. These large adsorbates provide a steric barrier, which prevents close contact of the metal particles centers (Fig. 1b).
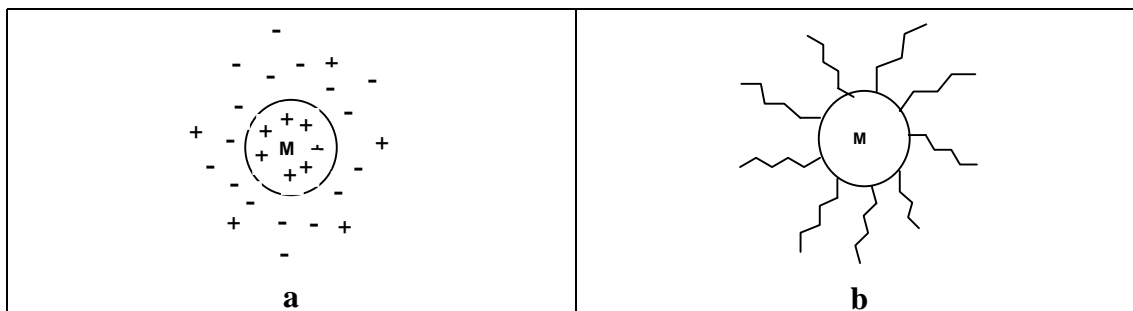

Figure 1. *A schematic illustration for (a) an electrostatically stabilized metal (M) particle and (b) a sterically stabilized metal particle.*

Metal clusters are constructed by successively packing layers- or shells- of metal atoms around a single metal atom. Metal clusters that have a complete, regular outer geometry are designated full-shell or "magic number" clusters. The total number of metal atoms, y, per n**th** shell is given by the equation $y = 10n^2 + 2$ (n = 1, 2, 3, …) (Fig. 2.)

| Full-Shell or "Magic Number" Clusters					
Number of Shells	1	2	3	4	5

Figure 2. *Idealized representation of hexagonal close-packed full-shell "magic number" clusters. Each metal atom has the maximum number of nearest neighbors, which impart some degree of extra stability to full-shell clusters.*

The most widely used technique for characterizing nanoclusters is transmission electron microscopy (TEM) or high resolution TEM (HR-TEM), techniques which provide direct visual information on the size, shape, dispersity, structure and morphology of nanoclusters.
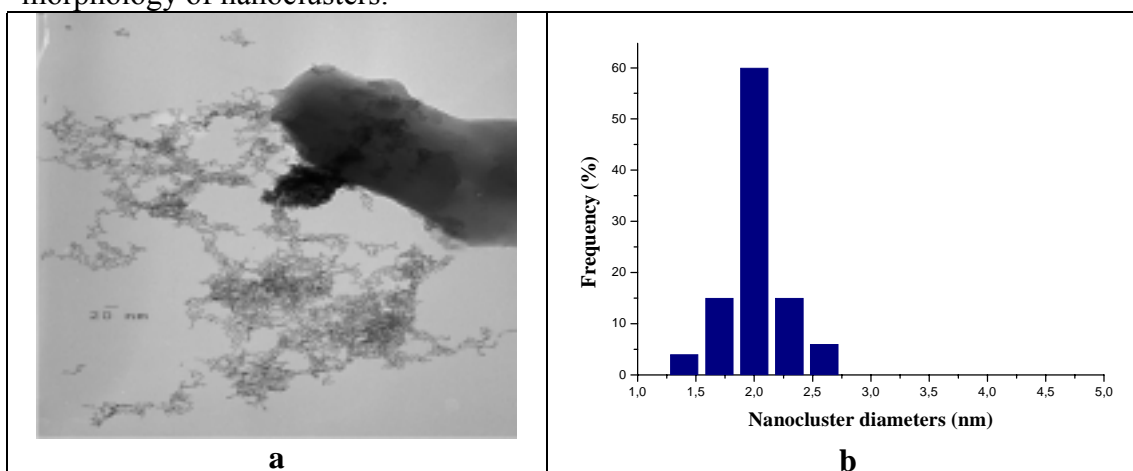
Figure 3. *(a) Transmission electron microscopy image of Pd(0) nanoclusters stabilized by a polymer. (b) Histogram of the Pd(0) nanocluster diameters.*

1 By direct reaction of Pd(II)-polymer complex (1 mM in water solution) with gas H_2, Pd(0) nanoclusters are prepared, as following:

$$nPd(II) + nH_2 \rightarrow Pd(0)_n + 2nH^+$$
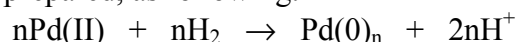
A transmission electron micrograph of the isolated $Pd(0)_n$ nanoclusters shows spherical Pd(0) nanoclusters, protected by the polymer, with an average diameter of 2.05 nm.

Calculate the number (N) of Pd atoms per cluster. Are these nanoclusters full-shell nanoclusters? Calculate the number of shells (n) in the above Pd(0) nanoclusters. Density of Pd, $\rho = 12.02$ g/cm^3.

2 The catalytic activity of the polymer stabilized $Pd(0)_n$ nanoclusters is detected by a catalytic olefin hydrogenation reaction, such as the cyclohexene plus H_2 reaction:
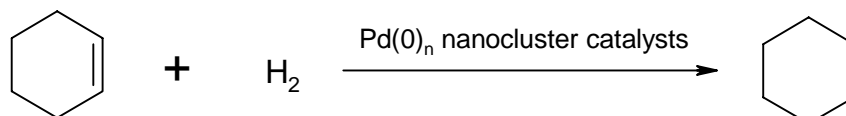
In a 400 cm^{-3} high pressure reactor, an amount of the above polymer-protected $Pd(0)_n$ nanoclusters containing a total of 50 μmol of Pd(0) was dissolved in 50 cm^{-3} of acetone, followed by the addition of 5 cm^{-3} of cyclohexene. The reactor was then sealed, purged several times with prepurified H_2 (dry and O_2 free) and the H_2 pressure was set to the desired value, approximately 4 atm. The solution was stirred continuously during the reaction and the temperature was kept constant at 30°C. H_2 pressure vs. time until the end of the reaction is presented in Fig. 4.
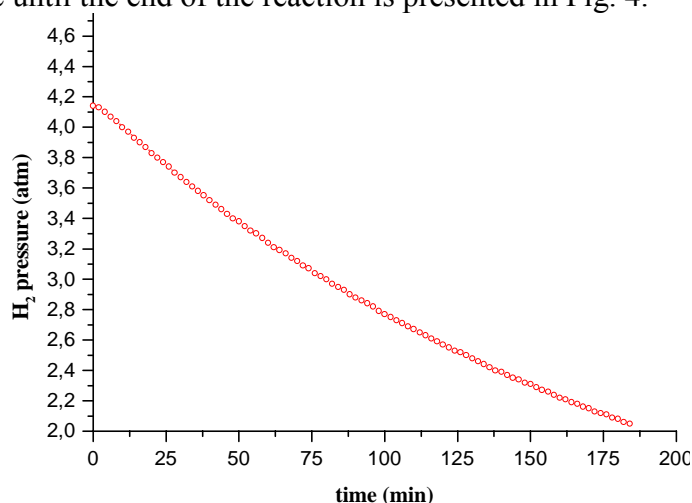

Figure 4. *Hydrogen uptake curve. Temperature 30°C, 0.5 μmol of Pd(0), 5 cm^{-3} of cyclohexene.*

(i) Calculate the % conversion of the cyclohexene.

(ii) Taking under consideration that only the surface Pd(0) atoms of the nanoclusters are catalytically active, calculate the turnover number, TON, where *TON = moles H_2 consumed / moles of catalytically active Pd(0)* and the turnover frequency, TOF, where *TOF = moles H_2 consumed / moles of catalytically active Pd(0)/ time (min) of the consumption*. Density of cyclohexene, $\rho = 0.81$ g cm^{-3}.

3 The polymer-protected $Pd(0)_n$ nanocluster catalyst are also used for the catalytic hydrogenation of hex-1-ene by H_2. The experiment was performed under the conditions cited above, exept that the solvent was chloroform. It was found that $Pd(0)_n$ nanoclusters are an efficient catalyst for the hydrogenation of hex-1-ene.
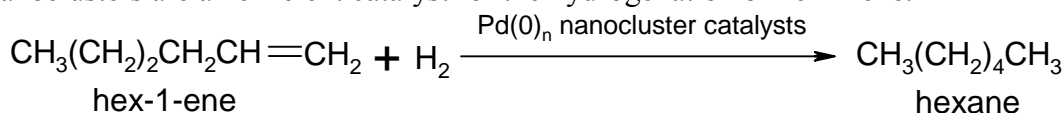
The ^{1}H-NMR spectra of the hex-1-ene and the reaction mixture after 30 min of reaction and after the removal of the catalyst are shown in the Fig. 5.
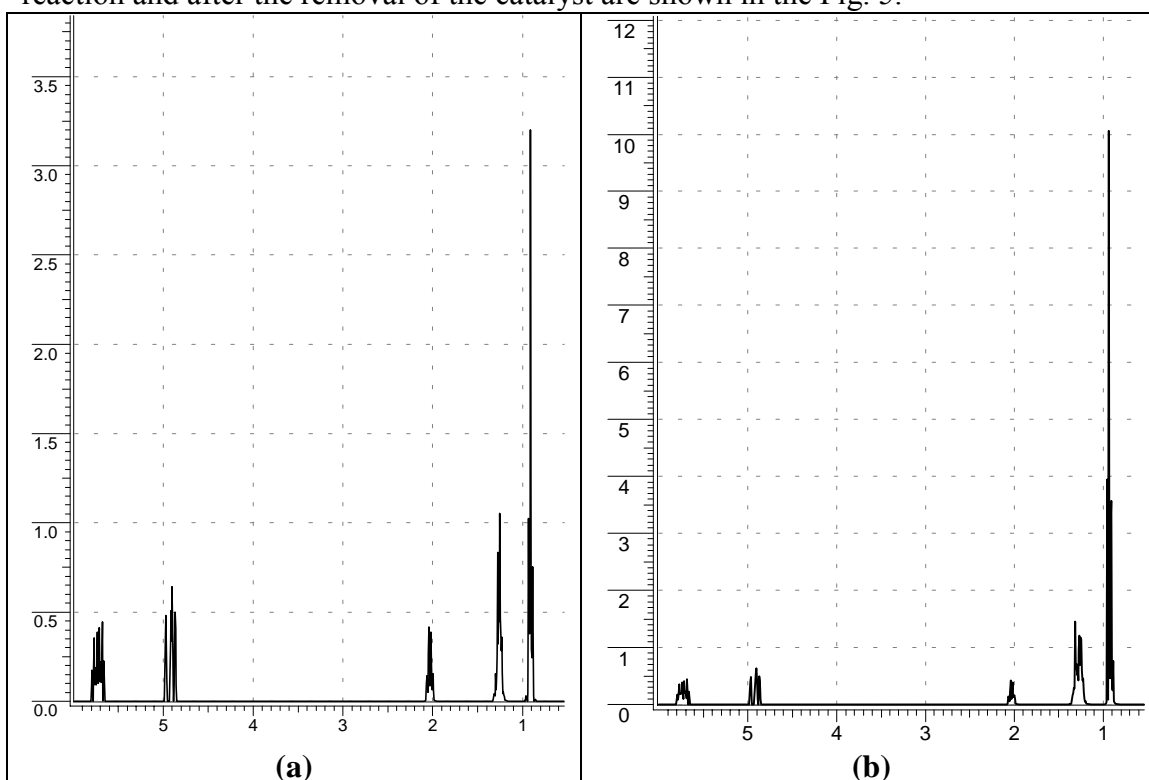
Figure 5. *300 MHz ^{1}H-NMR spectra of (a) hex-1-ene and (b) the solution of the reaction after 30 min of reaction and after the elimination of the catalyst and the solvent.*

The relative integrals of the ^{1}H-NMR spectra are given in the table below:

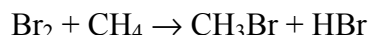|	δ / ppm	relative integral
Hex-1-ene (Fig. 5a)	0.88-0.96	3
	1.15-1.32	4
	1.99-2.08	2
	4.85-4.98	2
	5.65-5.79	1
Solution of the reaction (Fig. 5b)	0,88-0.96	9
	1.12-1.37	12
	1.99-2.08	2
	4.85-4.98	2
	5.65-5.79	1

Calculate the % conversion of hex-1-ene to hexane after 30 min.
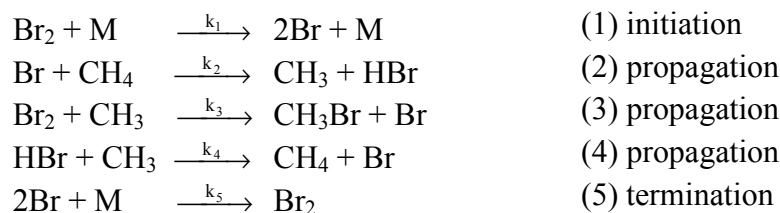
Problem 20: Drug kinetics

The absorption of a drug by an organism often follows simple kinetics though the mechanism is very complicated. Consider a drug delivered orally in a common capsule. Let $[A]_s$ be its concentration in the stomach and assume that the rate of its introduction into the blood stream is first order with respect to this $[A]_s$. Also assume that the rate by which the drug is metabolized or removed from the blood stream is proportional to its concentration in the blood, $[A]_b$. Give the plot of $[A]_s$ as a function of time and write the equation representing $d[A]_b/dt$. After one hour 75% of $[A]_s$ have been removed from the stomach. What percentage of the initial $[A]_s$ will remain in the stomach two hours after taking the drug?

Problem 21: Br_2 + CH_4 reaction mechanism

The reaction of bromine with methane is represented by the following chemical equation:

$$Br_2 + CH_4 \rightarrow CH_3Br + HBr$$

The proposed mechanism for this reaction is as follows:

$Br_2 + M \xrightarrow{k_1} 2Br + M$	(1) initiation
$Br + CH_4 \xrightarrow{k_2} CH_3 + HBr$	(2) propagation
$Br_2 + CH_3 \xrightarrow{k_3} CH_3Br + Br$	(3) propagation
$HBr + CH_3 \xrightarrow{k_4} CH_4 + Br$	(4) propagation
$2Br + M \xrightarrow{k_5} Br_2$	(5) termination

M stands for some molecular species. k_3 and k_4 are of the same order of magnitude.

1. In the proposed mechanism of this reaction some very unstable species are involved, such as the radicals CH_3 and Br. These very active species react as soon as they are formed, so their concentrations are very small compared to the other species. Shortly after the beginning of the reaction their concentrations remain approximately constant, so: $\dfrac{d[CH_3]}{dt} = 0$ and $\dfrac{d[Br]}{dt} = 0$. This is called the "steady state" condition or approximation for the CH_3 and Br radicals. Find the expression for the rate of formation of CH_3Br as a function of the concentration of the stable species that are involved in the reaction and the reaction rate constants, k_1, k_2, k_3, k_4, and k_5.

2. The rate law you found may be simplified when we consider the reaction progress. The three expressions below refer to the form of the rate law at the start, the steady state condition of the CH_3 and Br radicals and near the end of the reaction:

$v = \dfrac{k_1^{1/2} k_2}{k_5^{1/2}} \cdot \dfrac{[Br_2]^{1/2}[CH_4]}{\dfrac{k_4[HBr]}{k_3[Br_2]} + 1}$	**(I)**
$v' = \dfrac{k_1^{1/2} k_2}{k_5^{1/2}} \cdot [Br_2]^{1/2}[CH_4]$	**(II)**
$v'' = \dfrac{k_1^{1/2} k_2 k_3}{k_5^{1/2} k_4} \cdot \dfrac{[Br_2]^{3/2}[CH_4]}{[HBr]}$	**(III)**

Enter a numeral (I, II, III) next to each stage of the reaction to indicate which expression corresponds to which stage.

Start of the reaction	
Steady state condition	
Near the end of the reaction	

3. State the assumptions you need to make at each stage in order to simplify the rate law.

Problem 22: Buffer solutions

Buffer solutions are solutions which resist to changes in pH. Usually, buffer solutions consist of a weak acid and its conjugate base (for example CH_3COOH/CH_3COO^-) or a weak base and its conjugate acid (for example NH_3/NH_4^+). A buffer solution is formed by partial neutralization of a weak acid with a strong base or of a weak base with a strong acid. Alternatively, buffer solutions can be prepared by mixing the precalculated concentrations of each of the constituents.

The pH of a buffer solution, which is composed of a weak acid HA and its conjugate base A^- is calculated by the Henderson-Hasselbalch equation:

$$pH = pK_a + log\frac{[A^-]}{[HA]}$$

where K_a is the acid dissociation constant of the weak acid HA and [HA] and $[A^-]$ are the concentrations of HA and A^- in the buffer solution, respectively.

Questions

1. Calculate the pH of a buffer solution, which contains 0.200 M formic acid ($K_a = 2.1\times10^{-4}$) and 0.150 M sodium formate.

2. Calculate the change in pH of the buffer solution in Question 1 when 0.01000 M of sodium hydroxide is added to the solution.

3. Calculate the volume of 0.200 M of sodium hydroxide which must be added to 100.0 cm^3 of 0.150 M of acetic acid (CH_3COOH, $K_a = 1.8\times10^{-5}$) in order to prepare a buffer solution with pH = 5.00.

4. The pH of a buffer solution containing 0.0100 M benzoic acid (C_6H_5COOH, $K_a = 6.6\times10^{-5}$) and 0.0100 M sodium benzoate is: a. 5.00, b. 4.18, c. 9.82, d. 9.00

In the problems below equal volumes of the following solutions A and B are mixed:

5. A: 0.100 M CH_3COOH ($K_a = 1.8\times10^{-5}$), B: 0.0500 M NaOH
(i) The final solution: a. contains a weak acid, b. contains a strong base, c. is a buffer solution, d. none of the above
(ii) The pH of the final solution is: a. 3.02, b. 4.74, c. 3.17, d. 7.00

6 A: 0.100 M CH_3COOH ($K_a = 1.8\times10^{-5}$), B: 0.150 M NaOH
(i) The final solution: a. contains a weak acid, b. contains a strong base, c. is a buffer solution, d. none of the above
(ii) The pH of the final solution is: a. 12.00, b. 12.70, c. 13.18, d. 12.40

7. A: 0.150 M CH_3COOH, B: 0.100 M NaOH
(i) The final solution: a. contains a weak acid, b. contains a strong base, c. is a buffer solution, d. none of the above
(ii) The pH of the final solution is: a. 3.17, b. 7.00, c. 5.05, d. 13.00

8. A: 0.100 M CH_3COOH, B: 0.100 M NaOH
(i) The final solution: a. contains a weak acid, b. contains a strong base, c. is a buffer solution, d. none of the above
(ii) The pH of the final solution is:
a. 7.00, b. 13.00, c. 8.72, d. 3.02

Problem 23: Titration of weak acids

Weak acids are titrated with solutions of strong bases of known concentration (standard solutions). The solution of weak acid (**analyte**) is transferred into a 250-cm^3 conical flask and the solution of strong base (**titrant**) is delivered from a burette. The equivalence point of the titration is reached when the amount of added titrant is

chemically equivalent to the amount of analyte titrated. The graph, which shows the change of pH as a function of volume of titrant added, is called **titration curve**.

The **equivalence point** of a titration is the theoretical point, which cannot be determined experimentally. It can only be estimated by observing some physical change associated with the process of the titration. In acid-base titrations, the **end point** is detected by using acid/base indicators.
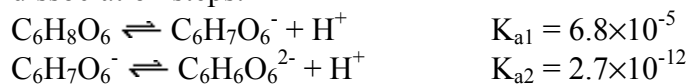
Questions

1. Construct the titration curve by calculating a few characteristic points and select indicator for the titration of 50.00 cm^3 of 0.1000 M of acetic acid (CH$_3$COOH, K_a = 1.8×10^{-5}) with 0.1000 M of sodium hydroxide; you may consult Table 1.

Table 1: Some common acid/base indicators

Common name	Transition range, pH	Color change
Methyl orange	3.2 - 4.4	red-orange
Methyl red	4.2 - 6.2	red-yellow
Bromothymol blue	6.0 - 7.6	yellow-blue
Phenol red	6.8 - 8.2	yellow-red
Phenolphthalein	8.0 - 9.8	colorless-red
Thymolphthalein	9.3 - 10.5	colorless-blue

2. Ascorbic acid (vitamin C, C$_6$H$_8$O$_6$) is a weak acid and undergoes the following dissociation steps:

C$_6$H$_8$O$_6$ ⇌ C$_6$H$_7$O$_6^-$ + H$^+$ $\qquad$ K$_{a1}$ = 6.8×10^{-5}
C$_6$H$_7$O$_6^-$ ⇌ C$_6$H$_6$O$_6^{2-}$ + H$^+$ $\qquad$ K$_{a2}$ = 2.7×10^{-12}

Hence, ascorbic acid can be titrated with sodium hydroxide according to the first acid dissociation constant.

50.00 cm^3 of 0.1000 M of ascorbic acid are titrated with 0.2000 M of sodium hydroxide. In the following calculations you can ignore the second dissociation step.

(i) The initial pH of the solution is:

a. 7.00, b. 2.58, c. 4.17, d. 1.00

(ii) The volume of titrant required for the equivalence point is:

a. 50.00 cm^3, b. 35.00 cm^3, c. 25.00 cm^3, d. 20.00 cm^3

(iii) The pH of the solution after the addition of 12.5 cm^3 of titrant is equal to:

a. 4.17, b. 2.58, c. 7.00, d. 4.58

(iv). The pH at the equivalence point is:

a. 7.00, b. 8.50, c. 8.43, d. 8.58

(v) The indicator, which must be chosen for the titration is: The appropriate indicator for the titration is (refer to Table 1):

a. bromothymol blue, b. phenol red, c. phenolphthalein, d. thymolphthalein

(vi) The pH of the solution after the addition of 26.00 cm^3 of titrant is:

a. 13.30, b. 11.30, c. 11.00, d. 11.42

Problem 24: Separation by Extraction

Extraction is one the most common separation methods and it is based on the distribution equilibria of a substance between two immiscible liquids whose densities differ appreciably so that they are separated easily after mixing.

The more usual case is the extraction of an aqueous solution with an organic solvent, whereupon the inorganic ions and the polar organic compounds are found mainly in the aqueous phase and the polar organic compounds distribute in the organic phase. Inorganic ions may be reacted with an appropriate reagent to yield a non-polar compound that distributes in the organic phase

When a species S (solute) is distributed between two solvents 1 and, then we have the following equilibrium

$$(S)_1 \overset{K_D}{\rightleftharpoons} (S)_2$$
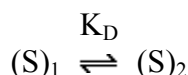
where K_D is the ***distribution coefficient*** given by

$$K_D = \frac{(a_s)_2}{(a_s)_1} \qquad (1)$$

where $(a_S)_1$ and $(a_S)_2$ are the activities of S in phases 1 and 2. For a given system of solvents and species S, K_D depends practically solely on temperature.

Separations by extraction are commonly performed with a ***separatory funnel*** (Fig. 1), a common and easy to use glass apparatus found in any chemical laboratory.

Equation 1.1 is valid only if the solute S is present in both phases in the same form. Otherwise, if any dissociation, dimerization, complexation of the solute takes place, the ***distribution ratio***, D, is used instead, which is given by

$$D = (C_S)_2 / (C_S)_1 \qquad (1.2)$$

where $(C_S)_1$ and $(C_S)_2$ are the analytical concentrations of S in phases 1 and 2 (rather than equilibrium concentrations of given species).

By convention, when one of the two solvents is water, Equation 1.2 is written with the aqueous concentration in the denominator and the organic solvent concentration in the numerator.

Figure 1. A typical separatory funnel.

D is a conditional constant dependent on a variety of experimental parameters like the concentration of S and of any other species involved in any equilibria with S in either phase and most likely on the pH of the aqueous phase (e.g. if S participates in any acid-base type equilibrium).

If W_0 g of S is initially present in V_1 mL of solvent 1 and S is extracted successively with equal fractions of V_2 mL of solvent 2, the quantity W_n of S that remains in phase 1 after n such extractions is given by

$$W_n = \left(\frac{V_1}{DV_2 + V_1}\right)^n W_0 \qquad (3)$$

or

$$f_n = \frac{W_n}{W_0} = \left(\frac{V_1}{DV_2 + V_1}\right)^n \qquad (4)$$

where f_n is the fraction of S that remains in solvent 1 after n extractions.

One can derive from Equations 1.3 and 1.4 that for a given volume of extractant, successive extractions with smaller individual volumes of extractant are more efficient than with all the volume of the extractant.
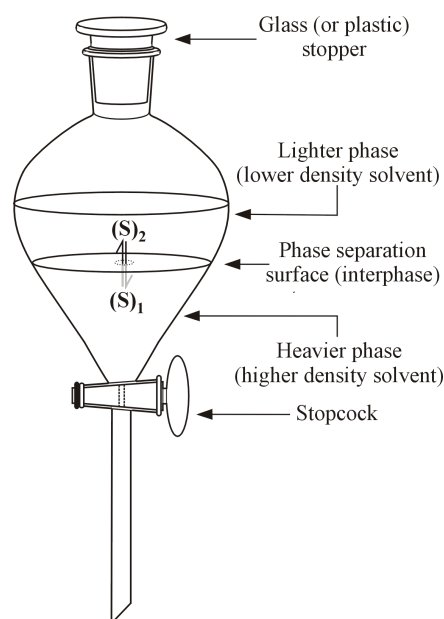
1   Prove Equation (3).
2   Substance S is distributed between chloroform and water with a distribution ratio D = 3.2. If 50 cm^3 of an aqueous solution of S is extracted with (a) one

100-cm^3, and (b) four 25-cm^3 portions of chloroform, calculated the percentage of S which is finally extracted in each case.

3   What is the minimum number of extractions required for the removal of at least 99% of substance X from 100 cm^3 of an aqueous solution containing 0.500 g of X, if each extraction is carried out with 25.0 cm^3 of hexane and the distribution coefficient is 9.5?

4   The weak organic acid HA with dissociation constant K_a (in water) is distributed between an organic solvent and water. If the only extractable species is the undissociated species HA with a distribution coefficient K_D and this is the only existing form of the acid in the organic phase, derive an expression showing the dependence of the distribution ratio D on $[H^+]$ of the aqueous phase and draw conclusions from the expression.

5   Benzoic acid and phenol are weak monoprotic organic acids with dissociation consntants 6.6×10^{-5} and 1×10^{-10}, respectively. Only the undissociated form of both compounds can be extracted from an aqueous solution with diethylether. (a) Draw a plot showing how the ratio D/K_D depends on pH for each compound, and (b) based on these plots propose a method for the separation of a mixture of these two compounds.

6   8-Hydroxyquinoline, $C_9H_6(OH)N$ (symbolized as: OxH), known also as "oxine", forms in acidic solutions the cation $C_9H_6(OH)NH^+$ (OxH_2^+) and in alkaline solutions the anion $C_9H_6(O^-)N$ (Ox^-). If chloroform extracts only the neutral molecule of oxine with a distribution coefficient $K_D = 720$,
(a) derive an expression showing the dependence of the distribution ratio, D, of 8-hydroxyquinoline on $[H^+]$ of the aqueous phase,
(b) draw a plot showing the dependence of D on pH of the aqueous phase, and
(c) calculate the pH at which D is maximized.
The consecutive dissociation constants of the cationic acid $C_9H_6(OH)NH^+$ are: $K_1 = 1\times10^{-5}$, and $K_2 = 2\times10^{-10}$ (see equilibrium reactions below).
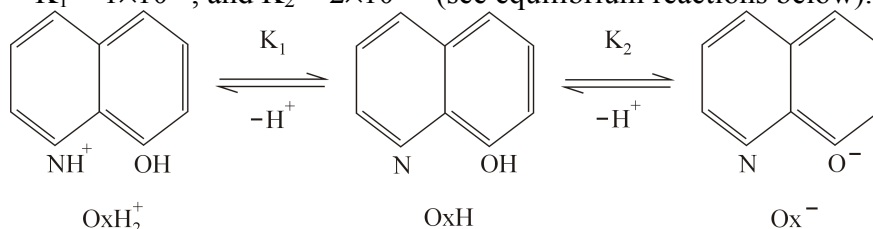
Problem 25: Mass Spectroscopy

Mass spectrometry is based on the formation of a beam of ionic fragments by bombardment of test molecules usually with energetic electrons. The generated fragments are then separated by application of electrostatic or magnetic fields or by a combination of both. This separation depends on the *mass-to-charge ratio* (m/z) of each ionic fragment. In most cases fragments are singly charged (z=1), therefore the separation depends on the mass of each ion.

The capability of a mass spectrometer to differentiate between masses is usually expressed in terms of its *resolution*, which is defined as $R = m/\Delta m$, where Δm is the mass difference between two adjacent peaks that are just resolved and m is the nominal mass of the first peak. For example, in order to discriminate the ionic species $C_2H_4^+$ and CH_2N^+, which have the same *nominal mass* (m = 28), but different *exact masses* (28.0313 and 28.0187, respectively), an instrument with a resolution of at least $R = 28/(28.0313-28.0187) \approx 2200$ is required. Less expensive low resolution mass

spectrometers (R ≈ 300-1000) can readily differentiate simple ions (of relatively low relative mass) of different nominal masses.

Isotope peaks in Mass Spectrometry

Even with the low resolution mass spectrometers, the same ionic fragment can generate multiple adjacent peaks of different nominal mass attributable to ions having the same chemical formula but different isotopic compositions. For example, the ion CH_3^+ consists of fragments of nominal mass ranging from 15 (fragment $^{12}C^1H_3^+$) up to 19 (fragment $^{13}C^2H_3^+$).

The relative intensity of isotope peaks depends on the natural isotopic composition of each element. For C the per cent natural *isotopic abundance* is 98.90% ^{12}C and 1.10% ^{13}C, and for H 99.985% ^1H and 0.015% ^2H. Therefore, the more intense peak (M=15) is attributed to the more abundant $^{12}C^1H_3^+$, the next in intensity but much smaller than peak M (M+1=16) is attributed to both $^{13}C^1H_3^+$ and $^{12}C^1H_2^2H^+$, whereas peak M+4, attributed to $^{13}C^2H_3^+$, has practically zero intensity due to the extremely low probability of occurrence.

Below is shown how the relative intensities of mass peaks for the ionic fragment CH_2Cl^+ can be exactly (without approximations) calculated, taking into consideration the isotopic abundance for C, H and Cl (75.77% ^{35}Cl and 24.23% ^{37}Cl).

Fragment M = 49	$^{12}C^1H_2^{35}Cl$:	$0.989 \times (0.99985)^2 \times 0.7577 =$	0.7491
Fragments M+1 = 50	$^{13}C^1H_2^{35}Cl$:	$0.011 \times (0.99985)^2 \times 0.7577 =$	0.00833
	$^{12}C^2H^1H^{35}Cl$:	$0.989 \times 0.00015 \times 0.99985 \times 0.7577 =$	0.00011
	$^{12}C^1H^2H^{35}Cl$:	$0.989 \times 0.99985 \times 0.00015 \times 0.7577 =$	0.00011
			0.00855
Fragments M+2 = 51	$^{13}C^2H^1H^{35}Cl$:	$0.011 \times 0.00015 \times 0.99985 \times 0.7577 =$	1.25×10^{-6}
	$^{13}C^1H^2H^{35}Cl$:	$0.011 \times 0.99985 \times 0.00015 \times 0.7577 =$	1.25×10^{-6}
	$^{12}C^1H_2^{37}Cl$:	$0.989 \times (0.99985)^2 \times 0.2423 =$	0.240
			0.240
Fragments M+3 = 52	$^{13}C^2H_2^{35}Cl$:	$0.011 \times (0.00015)^2 \times 0.7577 =$	1.9×10^{-10}
	$^{13}C^1H_2^{37}Cl$:	$0.011 \times (0.99985)^2 \times 0.2423 =$	0.00266
	$^{12}C^1H^2H^{37}Cl$:	$0.989 \times 0.99985 \times 0.00015 \times 0.2423 =$	3.59×10^{-5}
	$^{12}C^2H^1H^{37}Cl$:	$0.989 \times 0.00015 \times 0.99985 \times 0.2423 =$	3.59×10^{-5}
			0.0027
Fragments M+4 = 53	$^{13}C^2H^1H^{37}Cl$:	$0.011 \times 0.00015 \times 0.99985 \times 0.2423 =$	4.0×10^{-7}
	$^{13}C^1H^2H^{37}Cl$:	$0.011 \times 0.99985 \times 0.00015 \times 0.2423 =$	4.0×10^{-7}
	$^{12}C^2H_2^{37}Cl$:	$0.989 \times (0.00015)^2 \times 0.2423 =$	5.4×10^{-9}
			8.1×10^{-7}
Fragment M+5 = 54	$^{13}C^2H_2^{37}Cl$:	$0.011 \times (0.00015)^2 \times 0.2423 =$	6×10^{-11}

The intensity of each peak (from M to M+5) is proportional to the relative population of each fragment and the calculation of the probability is based on the summation of the probabilities of occurrence of all combinations resulting into the same nominal mass. The most intense peak is called *base peak* and the *relative intensities* of the other peaks are commonly reported as % of base peak.

Obviously, for the example above (ionic fragment CH_2Cl^+), the fragment M = 49 constitutes the base peak (relative intensity 100%). The relative intensities of the other fragments can be easily calculated, and we have:

Relative intensity for M   = 49:   100%
Relative intensity for M+1 = 50: $(0.00855/0.7491) \times 100$ =   1.14%

Relative intensity for M+2 $= 51$: $(0.240/0.7491)\times100$ $=$ 31.98%
Relative intensity for M+3 $= 52$: $(0.0027/0.7491)\times100$ $=$ 0.36%
Relative intensity for M+4 $= 53$: $(8.1\times10^{-7}/0.7491)\times100$ $=$ 1×10^{-4}%
Relative intensity for M+5 $= 54$: $(6\times10^{-11}/0.7491)\times100$ $=$ 8×10^{-9}%
[A Java applet demonstrating the isotopic peaks encountered in mass spectrometry principles can be found at the Internet site
http://www.chem.uoa.gr/applets/appletMS/appl_MS2.html.]

1. Natural silicon consists of the following 3 stable isotopes: ^{28}Si, ^{29}Si, ^{30}Si, whereas natural chlorine consists of the following 2 stable isotopes: ^{35}Cl, ^{37}Cl. How many isotopic lines are expected for the ionic fragment $SiCl_2^+$?

2. The isotopic abundance for boron is: ^{10}B 19.9%, ^{11}B 80.1%, and for chlorine is: ^{35}Cl 75.77%, ^{37}Cl 24.23%. Which one of the following mass spectra patterns (A-E) corresponds to the ionic fragment BCl^+?
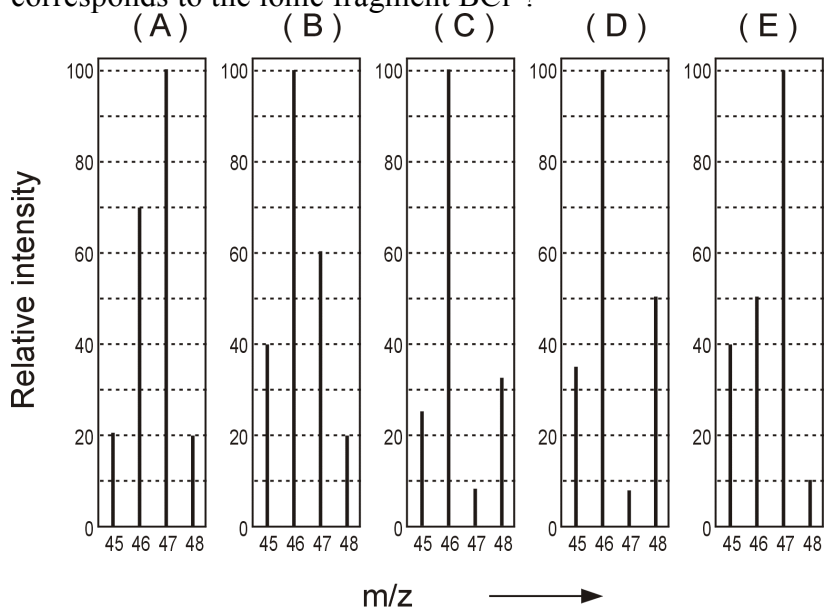
3. All the following ionic fragments: (a) N_2^+, (b) CO^+, (c) CH_2N^+, (d) $C_2H_4^+$ have nominal mass M = 28 and they cannot be resolved with a low resolution mass spectrometer. However, based on the relative intensity of the M+1 peak, identification still can be achieved. Identify the ionic fragment whose the relative intensity of the M+1 peak is 1.15. The following isotopic abundances are given:
H: ^1H: 99.985% ^2H: 0.015%
C: ^{12}C: 98.9% ^{13}C: 1.1%
N: ^{14}N: 99.634% ^{15}N: 0.366%
O: ^{16}O: 99.762% ^{17}O: 0.038% ^{18}O: 0.20%

Problem 26: Chemical Structure and Absolute Stereochemistry of Coniine

Coniine is a toxic compound found in the plant hemlock (*conium maculatum*), with which the ancient Greek philosopher Socrates was poisoned. Coniine is a nitrogenous compound belonging to the alkaloid family.

Find the chemical structure and absolute stereochemistry of coniine by completing the following series of reactions. Also, draw the structures of the intermediates A, B, and C.

Coniine $\xrightarrow[\text{2. Ag}_2\text{O ,H}_2\text{O, }\Delta]{\text{1. CH}_3\text{I (Hofmann exhaustive methylation)}}$ A ($C_{10}H_{21}N$) optically active

A $\xrightarrow[\text{2. Ag}_2\text{O ,H}_2\text{O, }\Delta]{\text{1. CH}_3\text{I (Hofmann exhaustive methylation)}}$ 1, 4 -octadiene + 1, 5-octadiene

Coniine $\xrightarrow[\text{NaOH, 0}^0\text{C}]{\text{C}_6\text{H}_5\text{CH}_2\text{OCOCl}}$ B $\xrightarrow[\Delta]{\text{KMnO}_4}$ C $\xrightarrow{\text{H}_2 \text{/Pd/C}}$ (S) -5-aminooctanoic acid
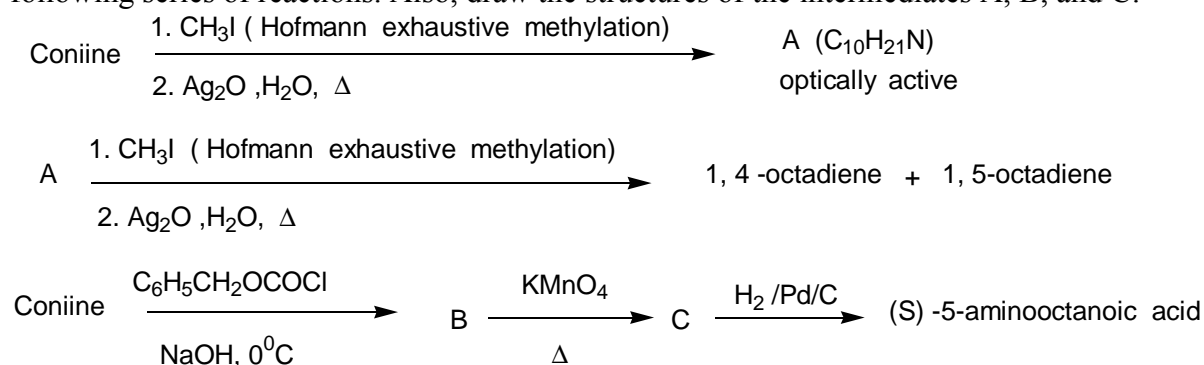
Problem 27: The Chemistry and Identification of Flavonoids

Cistus L is an aromatic, erect branched shrub and is a significant element of Greek flora. It can be found in stony slopes and hills and it can also be found in pinewoods. In folk medicine the flower branches of *cistus monospeliensis* have been used for asthma, while the leaves may replace tea. Flavonoids are widely distributed in plants as glycosides or as free aglycons. They are known to exhibit a broad spectrum of pharmacological properties including antimicrobial, antitumor, antiviral, as well as enzyme inhibition and central vascular system activity.

Apigenin is a very widely distributed flavonoid. Its structure is shown below:
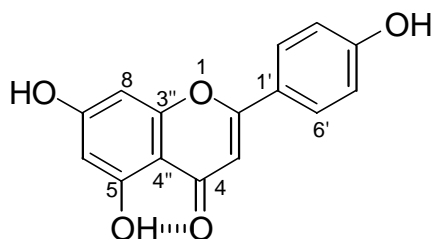
Apigenin

1. In the following reactions draw the structures of products B and C.

• Apigenin $\xrightarrow[\text{2. excess MeI}]{\text{1. NaH/DMF}}$ B

• Apigenin $\xrightarrow[\text{pyridine}]{\text{acetic anhydride(excess)}}$ C
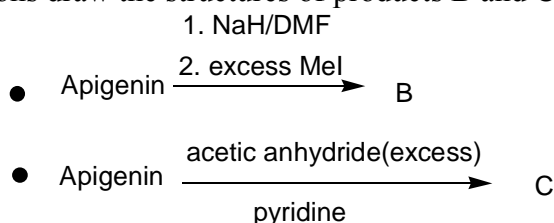
2. Apigenin can form a hydrogen bond between the phenolic hydroxyl group attached to C-5 and the carbonyl group at C-4. The ^{1}H-NMR resonance of the phenolic proton at C-5 will be shifted relative to the phenolic protons at C-7 and C-4':

a) down field, b) up field, c) not shifted

3. When treated with 2 M aqueous NaOH, **apigenin** gives among others products D and E

$$\text{Apigenin} \xrightarrow{\text{NaOH 2M}} \text{D+E}$$
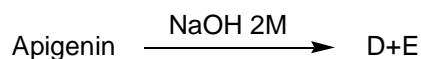
Compound D ($C_6H_6O_3$) gives a positive test with $FeCl_3$ and its ^1H NMR spectrum consists of only one aromatic singlet peak (spectrum I). Compound E ($C_9H_{12}O_2$) also gives a positive test with $FeCl_3$. In the ^1H-NMR spectrum the aliphatic region shows one multiplet and two triplet peaks, while the aromatic region consists of two doublets (spectrum II). Draw the structure of compounds D and E.
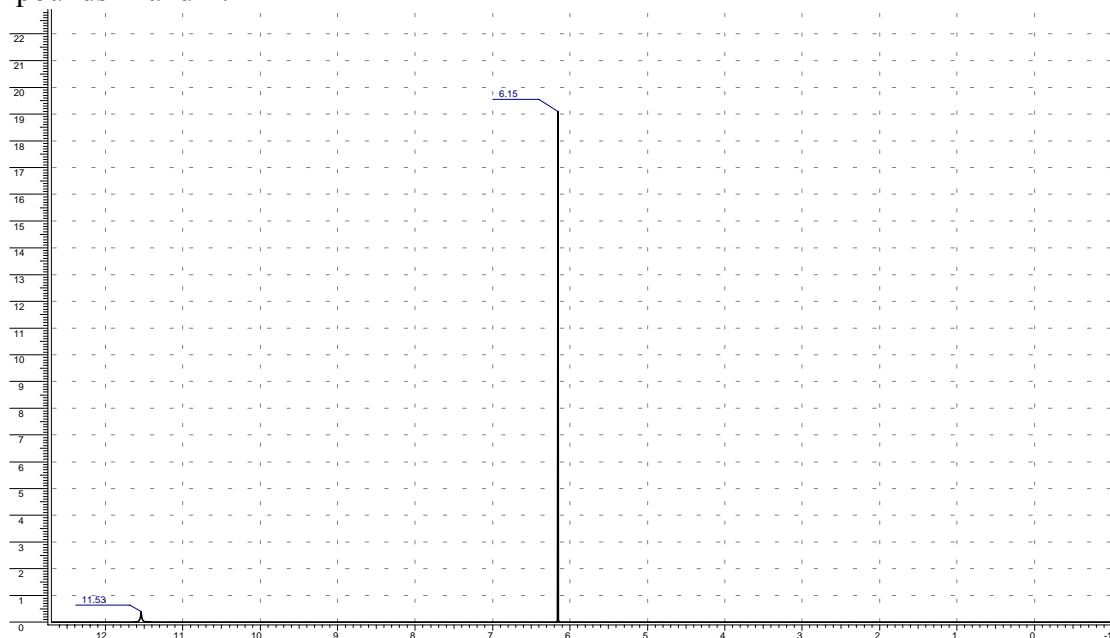
Spectrum I, Compound D ($C_6H_6O_3$)
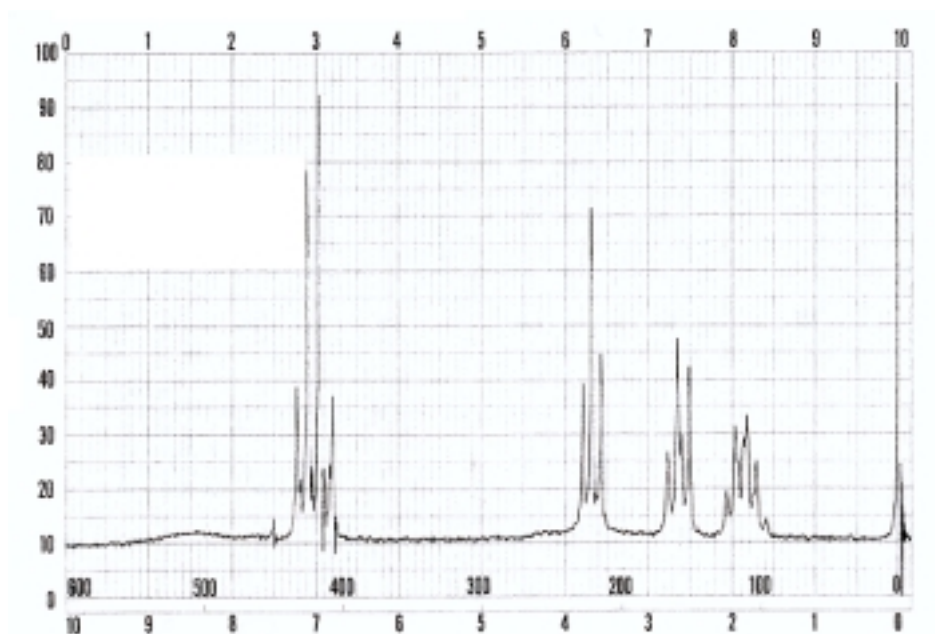
Spectrum II, Compound E ($C_9H_{12}O_2$)

4. Indicate with arrows the three carbon atoms in structure C that will give rise to characteristic peaks in ^{13}C-NMR which distinguish structure C from B.

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Problem 28: Synthesis of peptides

Peptides are linear polyamides formed by end to end linkage of α-aminoacids most frequently of the L- (or S) configuration.

1. Which dipeptides could result from condensing L- alanine and L-phenylalanine? Use stereo representations in your answer.

2. The stepwise elongation of the peptide chain almost invariably starts from the C terminal aminoacid of the desired sequence (employed in the form of ester) to which each successive aminoacid unit (employed in the form of *N*-protected aminoacid derivative) is linked, followed by removal of the *N*-substituent (protecting group) before the next unit is added. The substituent most often employed is an alkoxycarbonyl group ROCO- and the derivatives are then called carbamates.
Why does the presence of such a substituent on the amine nitrogen impede that amine from forming an amide linkage with a carboxyl group?
    1- Because the nitrogen has only one H
    2- Because the group lowers the electron density on nitrogen
    3- Because the group hinders the approach of the carboxyl
    4- Because of electrostatic repulsion
    5- Because it is already an amide

3. Draw the resonance structures for an amide moiety. Use stereo representations and curved arrows to show the flow of electron density.

4. Which of the following reagents would you use to prepare the benzyl carbamate of an amine (Bergmann-Zervas protecting group)? Write the reaction

1. $C_6H_5CH_2OCONH_2$, 2. $C_6H_5CH_2OCO_2CH_3$, 3. $C_6H_5CH_2OCO_2C(CH_3)_3$,
4. $C_6H_5CH_2OCOCl$, 5. C_6H_5OCOCl

5. The removal of an alkoxycarbonyl protecting group is often accomplished by the action of acid that triggers a fragmentation represented schematically below:

$$R\text{-}OCO\,NH \text{~~~peptide} \xrightarrow{H^+} [R^+] + CO_2 + H_2N\text{~~~peptide}$$
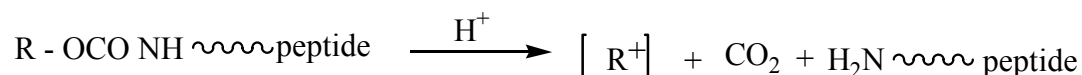
Rank the following carbamates according to increasing lability under acidic conditions:

A.

B.

C.

D.
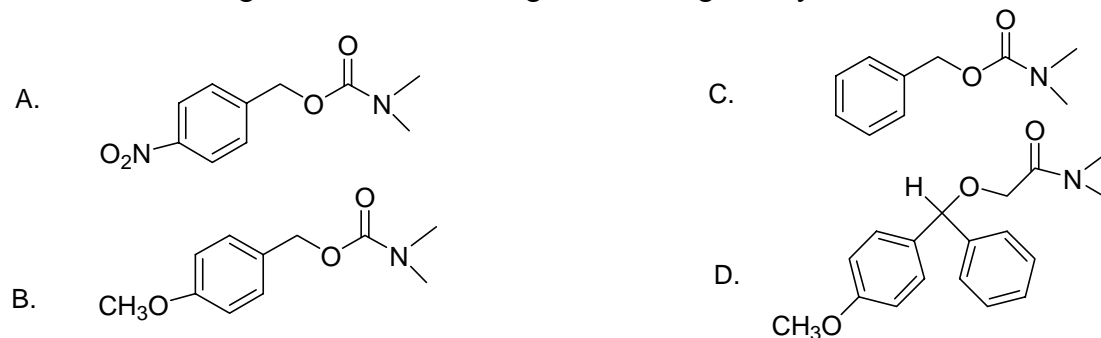
Problem 29: Oleuropein hydrolysis

One of the geographical areas where nutritional habits have drawn attention as a prototype of nutrition is the island of Crete in Greece. In a five countries study, Cretan diet has been associated with low rates of coronary heart disease (CHD). The mortality rate from CHD was 7 in 10000 subjects, while it was 566, 424, 317 and 200 in Finland, USA, the Netherlands and Italy, respectively. This has been attributed to the high olive oil consumption, which is rich in oleuropein (**A**), a powerful antioxidant. (R represents an alkylpolyphenolic group)
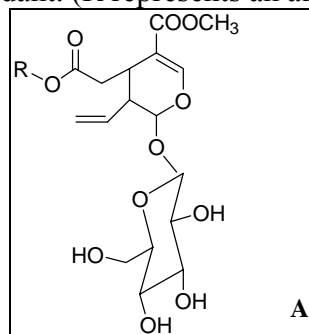
1. The acid-catalyzed hydrolysis of oleuropein gives apart from glucose, two other compounds, one alkylpolyphenolic (A1) and one monoterpenoid (A2).
Indicate with an arrow in the formula of oleuropein:
   (a) The oxygen atom that will be protonated in the acid hydrolysis leading to polyphenolic compound A1.
   (b) The most likely carbon-oxygen bond to be cleaved in order to form glucose.

2. In the mass spectrum of A1, the peak corresponding to the molecular ion is situated at 154 mass units. The 400 MHz ^{1}H-NMR spectrum of compound A1 in DMSO/D$_2$O is shown below. The hydroxylic protons are exchangeable and therefore do not appear in the spectrum:
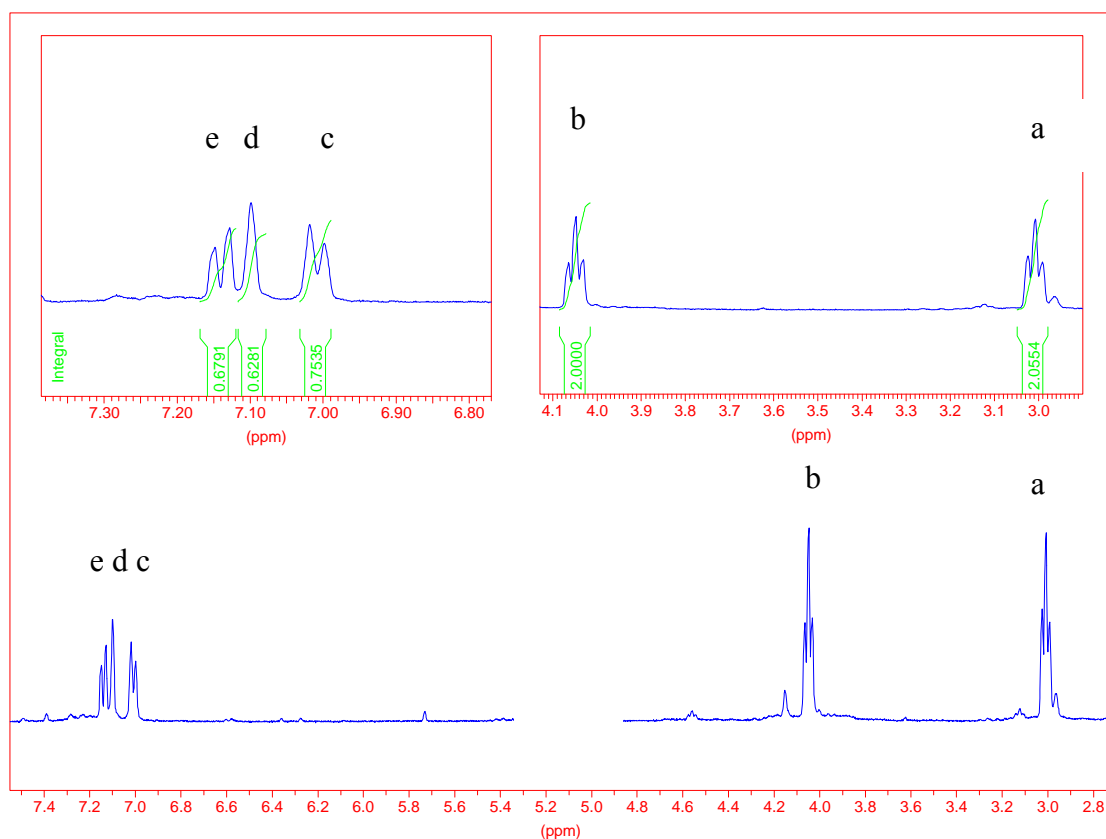
Choose the correct structure of A1 that can be deduced on the basis of the ^{1}H-NMR and mass spectrum information given.
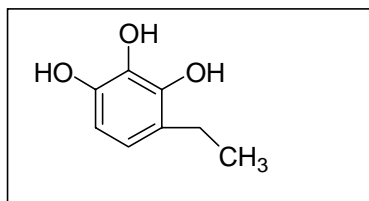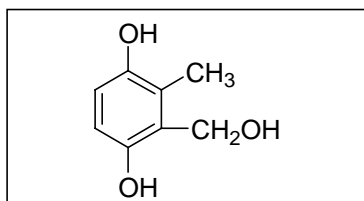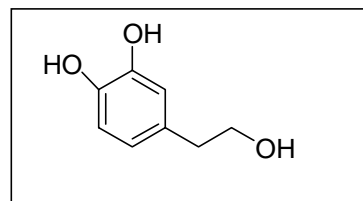

A   B   C

3. Draw the structure of A1 and use the letters a, b, c, d and e to designate the protons that correspond to the respective peaks in the ^{1}H-NMR spectrum.

Problem 30: Stereochemistry of the Addition Reactions to Alkenes

It is known that the addition of bromine to a double bond occurs with anti stereochemistry. Write the products of bromination for the following alkenes, using Fischer projections. Indicate if the products are optically active.

a)

b)

c)

d)
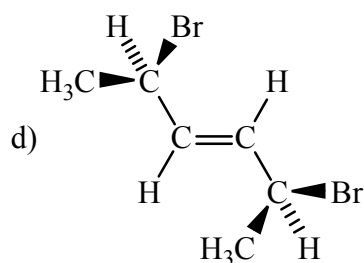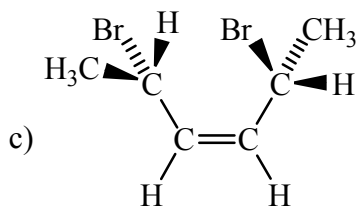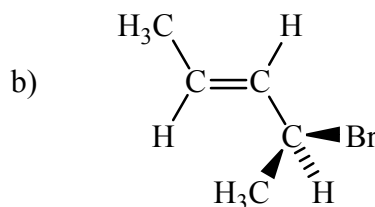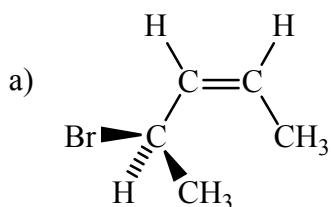
Problem 31: Identification of Organic Compounds

An optically active alkyne A contains 89.52 % C and 10.48 % H. After hydrogenation over a Pd/C catalyst it is converted to 1-methyl-4-propyl cyclohexane. When compound A reacts with CH_3MgBr no gas is liberated. Hydrogenation of A over a Lindlar catalyst, followed by ozonolysis and reaction with $KMnO_4$ gives product B whose ^{13}C NMR spectrum shows a peak at 207 ppm. Product B reacts with $I_2/NaOH$ and gives a yellow precipitate, which is filtered off. Acidification of the filtrate gives an optically active product C, whose ^{13}C NMR spectrum does not have any peak over 175 ppm.
Give the structures of A, B and C and account for all observations.

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Problem 32: Lipases

Lipases are enzymes that hydrolyze the ester bonds of triacylglycerols, while proteases hydrolyze the amide bonds in proteins and peptides. Compounds that inhibit the hydrolysis of triacylglycerols and peptides may be useful for the treatment of various diseases.

The mechanism of action of the above enzymes starts with the attack of the hydroxyl group of serine to the ester or amide bond.

One approach for the development of serine protease inhibitors involves the replacement of the scissile amide bond by an activated carbonyl group. Thus, the hydroxyl of the active site serine reacts with the activated carbonyl forming a stable acyl enzyme adduct, which is not further hydrolyzed.

1. Rank the following carbonyl groups in order of decreasing reactivity against the hydroxyl group of serine:
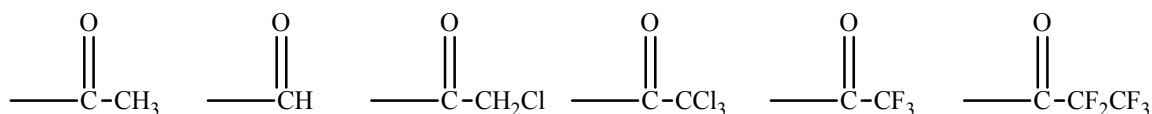
2. Tetrahydrolipstatin is a potent inhibitor of digestive lipases (in clinical use for the treatment of obesity). Indicate with an arrow the carbonyl group of tetrahydrolipstatin that is attacked by the active site serine of lipases.
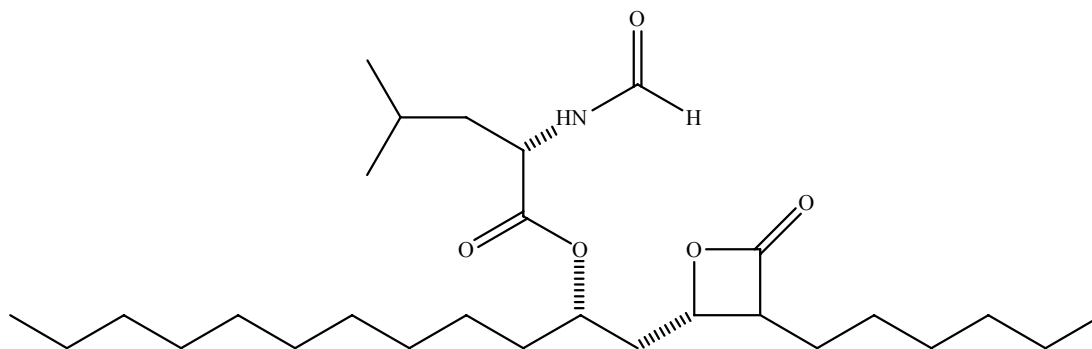

3. Esters and amides can be hydrolyzed under acidic or basic conditions. Rank the following compounds in order of decreasing reactivity towards aqueous hydroxide anion.

$CH_3CO_2CH_3$ $CH_3CO_2CH_2CH_3$ $CH_3CO_2CH_2$—⟨phenyl⟩ $CH_3CO_2C(CH_3)_3$
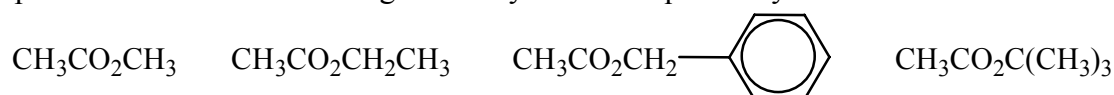
Problem 33: Polymers

Figure 1. The Golden Larnax from the Tomb of the Greek king Philippos of Macedonia, discovered by the late Prof. M. Andronikos of the University of Thessaloniki, in Vergina, a place in Northern Greece close to Thessaloniki. Its cover depicts the 16-rayed star, emblem of the Macedonian Dynasty (Thessaloniki Archeological Museum)
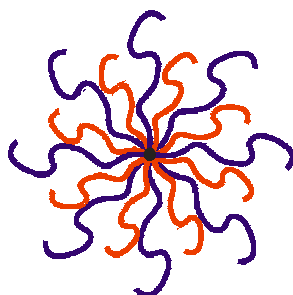

Figure 2. Vergina Star Copolymer: The similarity to the 16-rayed star emblem of the Macedonian Dynasty is obvious

1. The dimensions of the Larnax are 40.9 x 34.1 x 17.0 cm, and the molecular mass of the Vergina star copolymer is 1.0×10^6. If the copolymer density is 0.98 g cm^{-3}, how many Vergina star copolymer molecules are needed in order to fill the Larnax?

2. By using the reactions and the chemical structure of the Vergina star copolymer given below, propose a reaction scheme for the synthesis of the star:
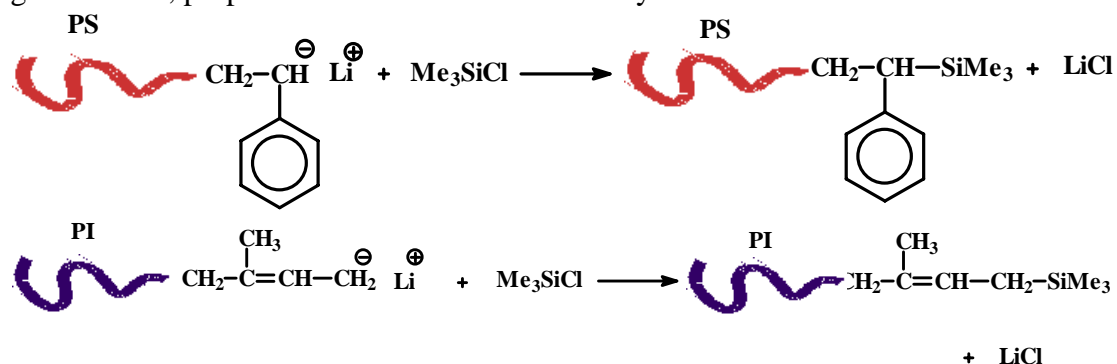
where PS is polystyrene and PI is polyisoprene.
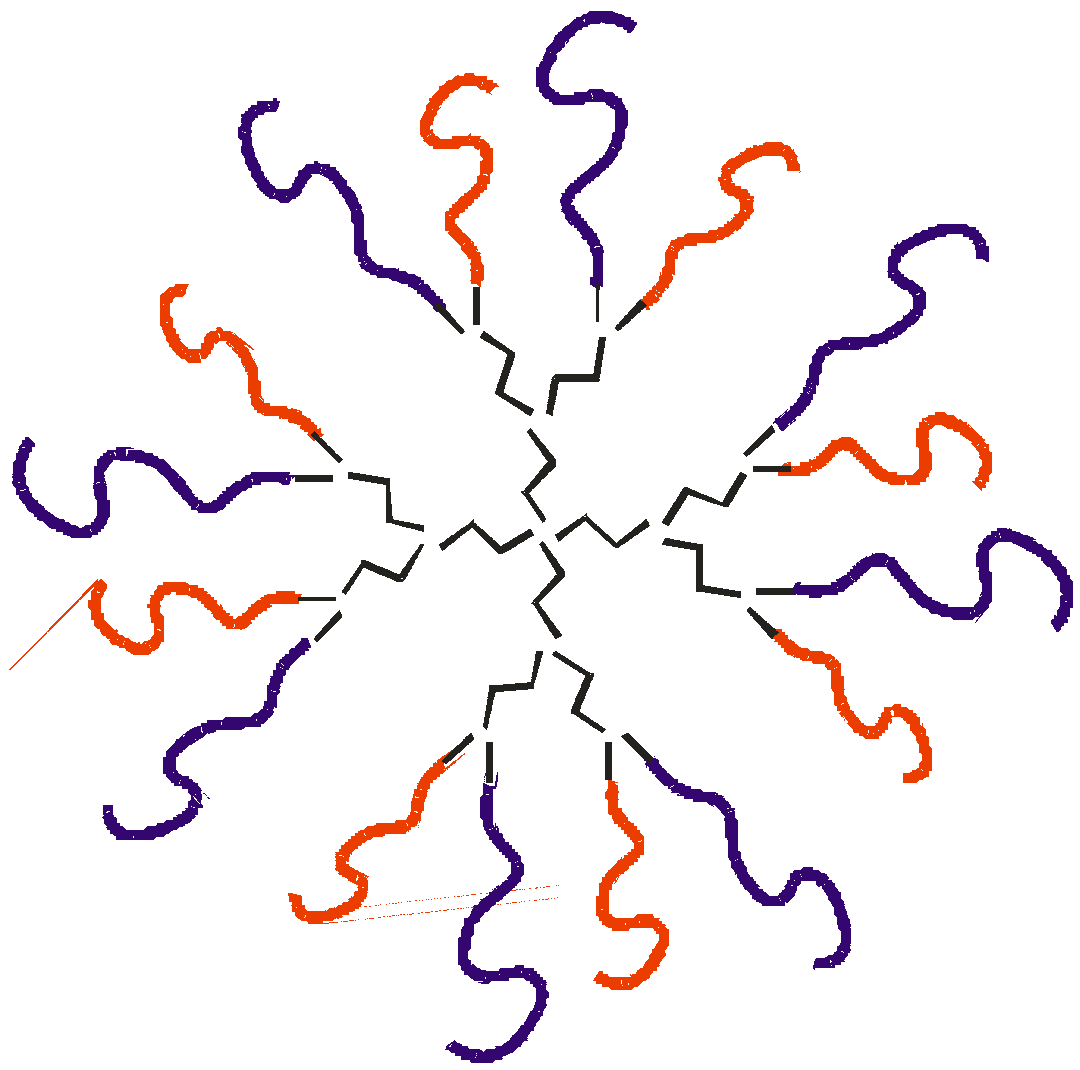
**Problem 34: Preparation of 2,5-Dimethyl-1-Phenylpyrrole**

A. INTRODUCTION

There are many different cyclization reactions that produce nitrogen heterocycles, with the **Paal-Knorr** synthesis being one of the most general. In this reaction, a 1,4-dicarbonyl compound is heated with ammonia or a primary amine to produce a pyrrole.

As an example, the condensation of aniline with 2,5-hexanedione leads to 2,5-dimethyl-1-phenylpyrrole (**1**) (a N-substituted pyrrole) that can be easily carried out in a 3h-undergraduate organic laboratory.

B. REACTION AND MECHANISM

The reaction, which takes place, is the following:

1
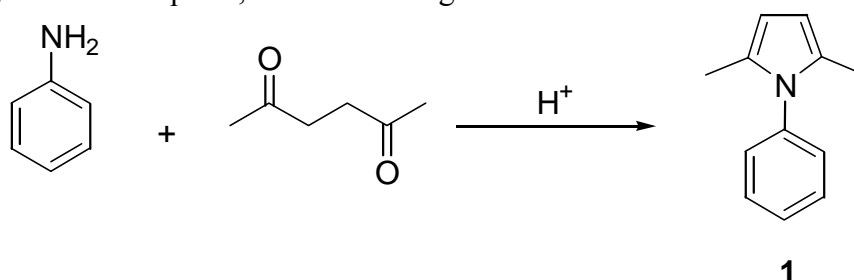
In the first step, the amino-group of aniline attacks one of the protonated carbonyl groups of the 2,5-hexanedione. Afterwards, a second intramolecular nucleophilic attack takes place, resulting in cyclization. Finally, the cyclic compound undergoes two successive dehydrations under acidic treatment to form the final product. The driving force for the two dehydration reactions is the formation of an aromatic system. The proposed mechanism is shown in Scheme 1.
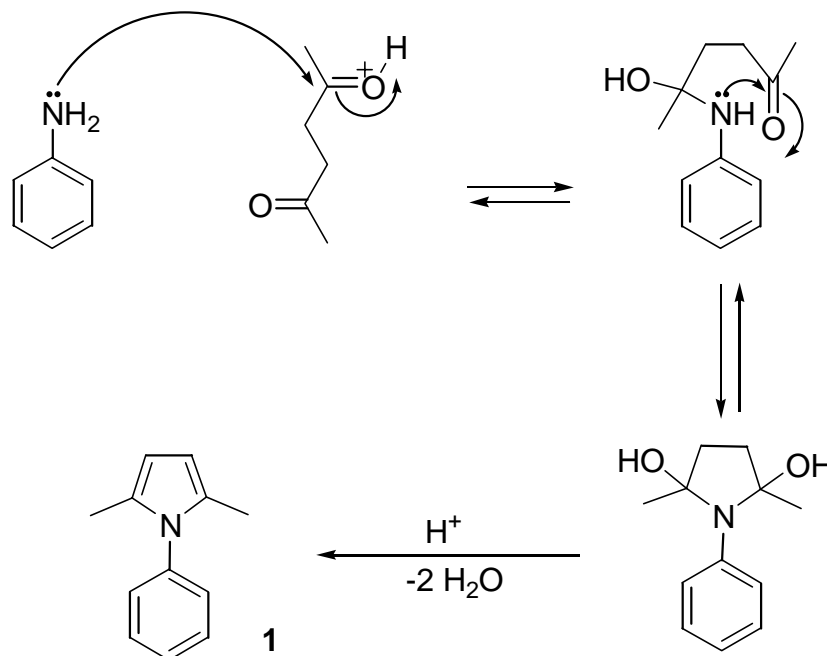
Scheme 1: The proposed mechanism of the 2,5-dimethyl-1-phenyl pyrrole synthesis.

C. LIST OF CHEMICALS:

● Methanol
● Aniline
● 2,5-Hexanedione
● Concentrated HCl
● 0.5 M HCl

D. LIST OF EQUIPMENT FOR EACH STUDENT

1 25 cm^3-round-bottomed flask
1 condenser
3 micrograded syringes
1 10 cm^3 Erlenmeyer flask
1 5 cm^3 volumetric cylinder
5 Pasteur pipettes
1 conical sintered-glass funnel
1 metal spatula
10 capillary tubes
5 TLC plates
1 developing chamber
3 Eppendorf tubes
2 test tubes (diameter 1 cm, length ca. 10 cm)
1 100 cm^3-beaker sand bath on heating plates
ice
UV-lamp (254 nm)
eluent (Ethyl acetate-Hexane 1:3)
balance

E. EXPERIMENTAL

Synthesis of 2,5-Dimethyl-1-phenylpyrrole:

To a 25 cm^3 round-bottomed flask equipped with a reflux condenser, add 186 mg (2.0 mmol) of aniline, 228 mg (2.0 mmol) of 2,5-hexanedione, 0.5 cm^3 of methanol, and 1 drop of concentrated HCl. Heat the mixture (sand bath) to reflux for 15 min, and then add the reaction mixture to 5.0 cm^3 of 0.5 M HCl, which is kept cool in an ice bath.

The crystals formed are collected by suction filtration and recrystallized from 1 cm^3 of 9:1 methanol/water. The isolated recrystallized product is washed twice with 1 cm^3 of the same mixture of methanol/water, and pressed dry on the filter. The solid is then transferred on a piece of filter paper in order to dry further. The dry product is placed in a tare-weighed Eppendorf. The sample tube is closed and weighed. A small amount (ca. 3-5 mg) of the product is placed in another Eppendorf and dissolved in a few drops (~5) of acetone. By means of a capillary tube place a drop of this solution on a TLC plate. A similarly prepared sample of the starting material (aniline) is applied next to the product, as a reference, and the TLC plate is developed with a 1:3 mixture of ethyl acetate-hexane. The plate is observed under UV light (254 nm) and the spots on the plate are drawn with a pencil. The sample tube with the rest of the product is labeled with the name of the product and is given to the supervisor.

PROBLEMS

a. Record the following data:
      I. The weight of your product:
      II. The calculated theoretical yield:
      III. The obtained yield as a percentage of the theoretical:
      IV. The melting point of the product:
b. Give a design of the thin layer chromatographic plate:
c. Estimate the R_f value of the product:
d. The ^{1}H-NMR (CDCl$_3$) data of the product are:
      δ= 2.04 (s, 6H), 5.91 (s, 2H), 7.22 (m, 2H) and 7.44 (m, 3H)

Indicate on the structure below the appropriate δ values on the protons that are shown with arrows
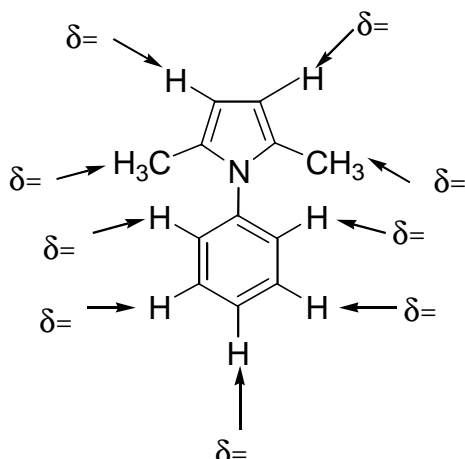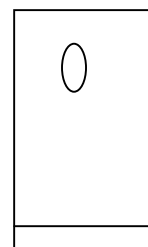

Report

a. Record the following data:

    I. The weight of your product: 178 mg

    II. The calculated theoretical yield: 342 mg

    III. The obtained yield as a percentage of the theoretical: 52%

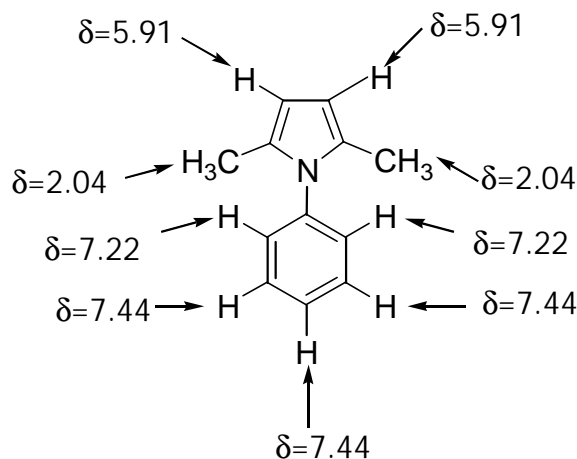   IV. The melting point of the product: 48°C (lit. 50-51°C)

b. Give a design of the thin layer chromatographic plate:

c. Estimate the R_f value of the product: 0.85

d. The ^{1}H-NMR (CDCl$_3$) data of the product are:

    δ= 2.04 (s, 6H), 5.91 (s, 2H), 7.22 (m, 2H) and 7.44 (m, 3H)

Problem 35: Synthesis of the Insect Repellent DEET

A. INTRODUCTION

DEET is the common name for N,N-diethyl-m-toluamide, a multipurpose insect repellent registered for direct application to human skin. DEET is a unique pesticide because it is applied directly to the human body for the purpose of repelling insects. Because DEET was recognised as one of the few products that are effective against mosquitoes and biting flies, it was registered for use by the general public in the USA in 1957. Approximately 230 products containing DEET are currently registered with the Environmental Protection Agency

manufactured by 70 different companies. Every year approximately one-third of the US population is expected to use DEET.

B. THE CHARACTERISTIC FEATURES OF DEET

● The chemical structure is shown below:
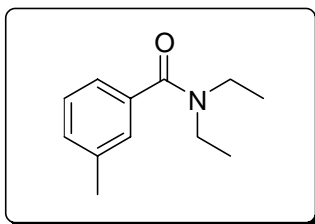
N,N-diethyl-m-toluamide

● Some physical properties are shown in the table below:

|	
Density (25°C)	0.996
Solubility in water	practically insoluble
Solubility in other solvents	soluble in ethanol, ether, chloroform, benzene
Boiling point (at 1 torr)	111°C
Vapour pressure (160°C)	19 torr
Odour	odourless
Colour	colourless

C. SYNTHESIS OF DEET

DEET can be prepared starting from m-methyl-benzoic acid (m-toluic acid). First, m-toluic acid is converted to the corresponding chloride. Next, the desired amide is prepared by reacting the active chloride with diethylamine in the presence of base (NaOH).
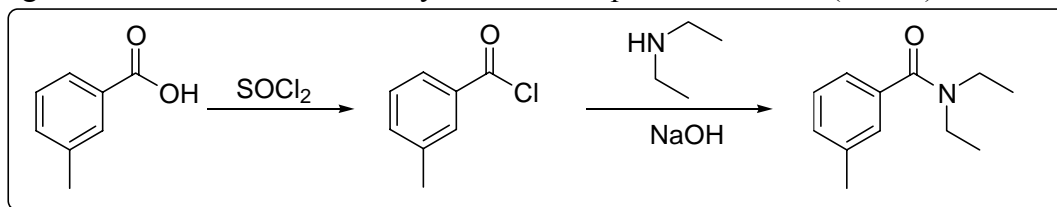
The activation step using thionyl chloride can be accomplished in two alternative ways:
a. By heating the m-toluic acid with thionyl chloride (SOCl$_2$) and
b. By reacting m-toluic acid at room temperature, with SOCl$_2$ in the presence of a catalytic amount of pyridine.

With regards to the yield and purity of the final product, procedure b is preferred over procedure a since the latter leads to the creation of anhydride **3** as a by-product.
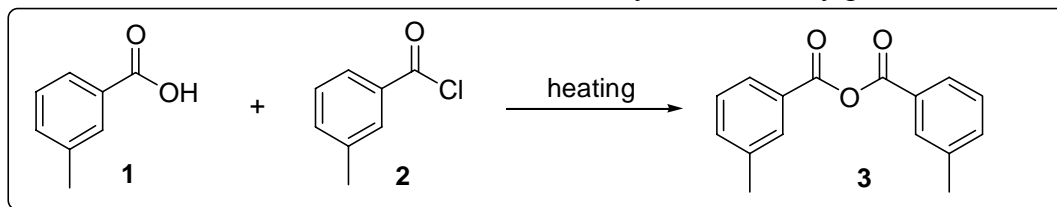
D. EXPERIMENTAL

m-Toluic acid (0.5 g, 3.7 mmol), dry ether (0.2 cm^3), pyridine (2 drops), and 99.5% SOCl$_2$ (0.55 cm^3, 7.6 mmol) are stirred for 8 minutes at room temperature in loosely stoppered 5-cm^3 round-bottom flask. The reaction is performed in a fume hood; alternatively, the liberated HCl gas may be directed to an aspirator. The excess SOCl$_2$ is then removed at room temperature

under water-aspirator vacuum (25 mmHg) and the oil residue is pipetted into a mixture of diethylamine (1.3 cm^3, 12 mmol) in 10% NaOH (5 cm^3) at 0°C. After stirring for 1 minute, the solution is extracted twice with 15-cm^3 portions of ether. The ether fractions are dried over MgSO$_4$ (or Na$_2$SO$_4$) and filtered, and 1 cm^3 of toluene is added to azeotropically remove any traces of both water and pyridine. The solvents are removed under vacuum in a rotary evaporator until dryness. DEET remains as a clear oil in the round-bottom flask.

PROBLEMS

a. Record the following data:
    I. The weight of your product:
    II. The calculated theoretical yield:
   III. The obtained yield as a percentage of the theoretical:
b. During the heating activation of m-toluic acid, the formation of anhydride **3** causes yield reduction because [check the statements that are correct]:
● The anhydride does not react with diethylamine:
● The anhydride reacts with diethylamine affording the desired product as well as some by-products:
● The anhydride reacts readily with diethylamine giving 50% of the desired product plus 50% of the starting m-toluic acid:
c. If we want to use infrared (IR) spectroscopy to identify the anhydride **3** formed during the heating activation step of m-toluic-acid, we should look for the characteristic IR-absorption of [check all that apply]:
    I. The aromatic C-H stretch at ca. 3065 cm^{-1}:
    II. The aliphatic C-H stretch at ca. 2987-2880 cm^{-1}:
    III. The symmetrical and asymmetrical C=O stretch of conjugated anhydride at ca. 1763 cm^{-1} and 1720 cm^{-1}

Report

a. Record the following data:
    I. The weight of your product: 0.68 g
    II. The calculated theoretical yield: 0.70 g
    III. The obtained yield as a percentage of the theoretical: 97%
b. During the heating activation of m-toluic acid, the formation of anhydride **3** causes the yield reduction because:
● The anhydride does not react with diethylamine:
● The anhydride reacts with diethylamine affording the desired product as well as some by-products
● The anhydride reacts readily with diethylamine giving 50% of the desired product plus 50% of the starting m-toluic acid, according to the following reaction: X
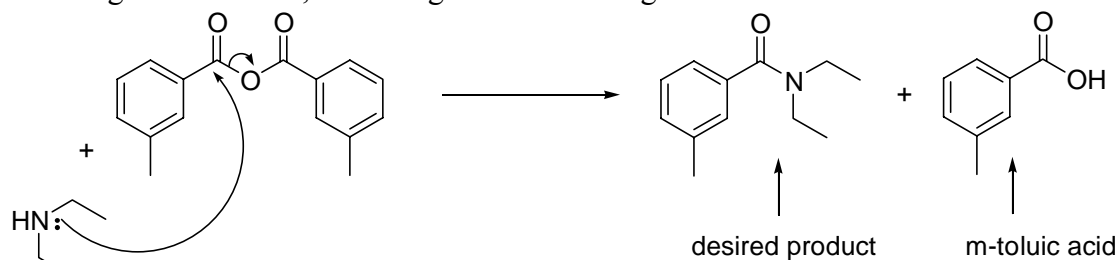

c. The two strong IR bands at 1763 cm^{-1} and 1720 cm^{-1} are characteristic symmetrical and asymmetrical C=O stretches of conjugated anhydrides.

**Problem 36: Solid phase peptide synthesis**

A. INTRODUCTION

Solid phase peptide synthesis (SPPS) was introduced by R. B. Merrifield of Rockefeller University (Nobel Prize 1984). This method is based on sequential addition of α-amino and side-chain protected amino acid residues to an insoluble polymeric support. 2-Chlorotrityl chloride resin (Figure 1), whose use has been pioneered by K. Barlos, is an acid labile resin. The steric bulk and the mild acidic conditions required for cleavage make this resin useful in many applications. The base-labile Fmoc-group is used for N-α-protection of amino acids. After removal of this protecting group, the next protected amino-acid is added using either a coupling reagent or pre-activated protected amino-acid derivative. The resulting peptide is attached to the resin through its C-terminus and may be cleaved to yield a peptide acid or amide (depending on the linker used). Side-chain protecting groups are often chosen so as to be cleaved simultaneously with detachment of the peptide from the resin.
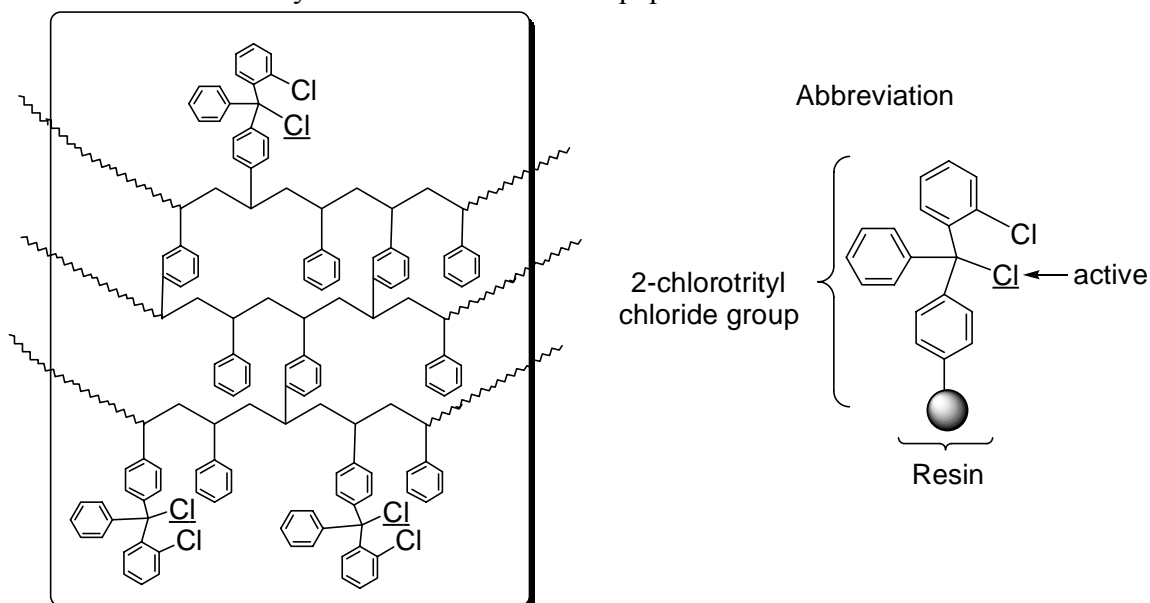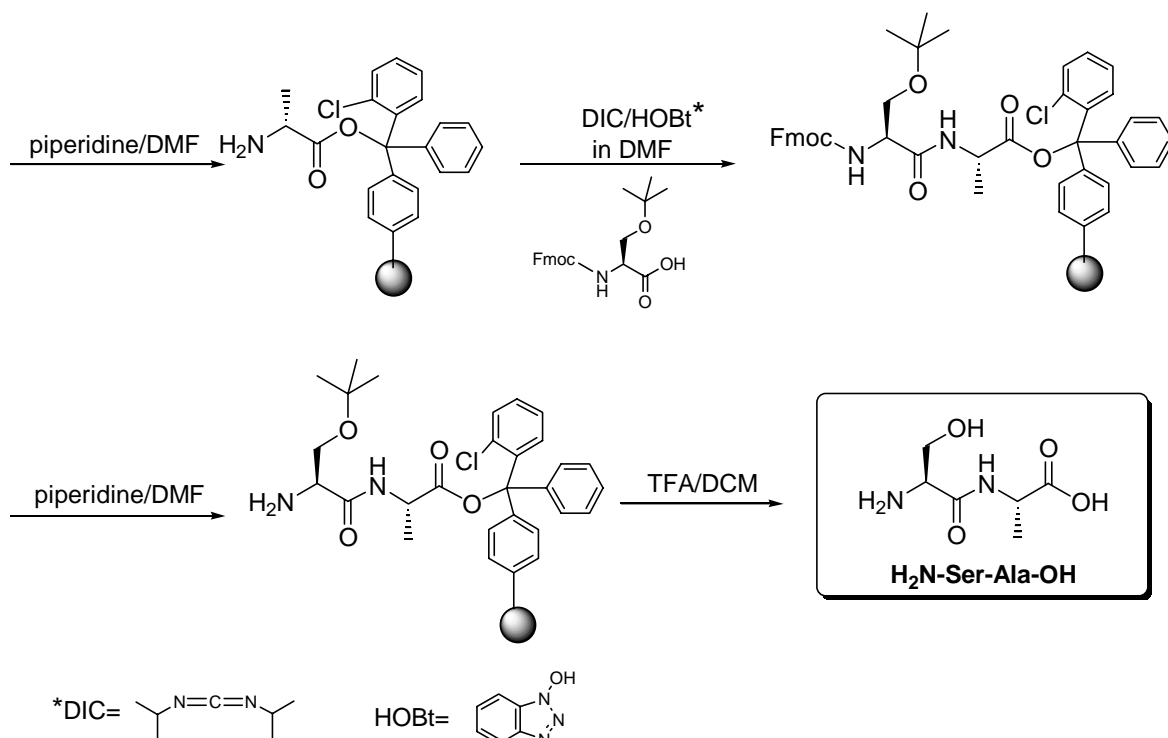

Figure 1: 2-Chlorotrityl chloride group attached to a polymeric support of 1% divinylbenzene cross-linked polystyrene.

B. SYNTHESIS OF THE DIPEPTIDE H₂N-SER-ALA-OH

The synthesis of the above dipeptide is accomplished by the Fmoc-strategy using 2-chlorotrityl chloride resin as the solid support. The reactions that take place are illustrated in Figure 2.
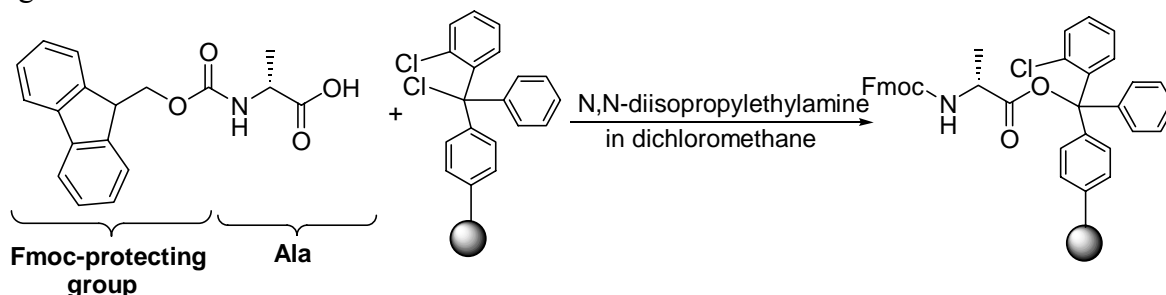
Figure 2a: Synthesis of H$_2$N-Ser-Ala-OH using the Fmoc strategy on 2-chlorotrityl chloride resin (Step 1).

Figure 2b: Synthesis of H_2N-Ser-Ala-OH using the Fmoc strategy on 2-chlorotrityl chloride resin (Steps 2-5). Abbreviations: TFA = CF_3COOH, DCM = CH_2Cl_2, DMF = $HCON(CH_3)_2$

C. ESTIMATION OF LEVEL OF FIRST RESIDUE ATTACHMENT

This procedure takes place after the completion of Step 1.

1. Take a UV cell
2. Weigh 2 mg dry Fmoc-amino acid-resin into the UV cell. Dispense freshly prepared 20% solution piperidine/DMF (3 cm^3) into the cell.
3. Agitate the resin mixture using a Pasteur pipette for 2-3 minutes.
4. Place the cell in a spectrophotometer. Read the absorbance (A_{sample}) at 290 nm.
5. Using another UV cell, read the absorbance of 20% solution piperidine/DMF (3 cm^3) at the same wavelength (A_{blank})
6. Estimate the level of first residue attachment using the equation:

Fmoc loading$=\dfrac{n}{m}=\dfrac{A_{sample}-A_{blank}}{1.75m}$, where n is the amount of Fmoc-amino acid-resin (in mmol) and m the mass of resin (in g).

D. EXPERIMENTAL

Step 1: Dissolve Fmoc-Ala-OH (62 mg, 0.2 mmol) in dry CH_2Cl_2 (DCM, 2 cm^3) by adding DIPEA (N,N-diisopropylethylamine) (139 µL, 0.8 mmol). Add this solution to a fine sintered glass manual SPPS reaction vessel containing 2-chlorotrityl chloride resin (200 mg, 0.2 mmol; loading 1.0 eq Cl/g resin) in 1 cm^3 DCM, shake for 30 minutes and then filter. To end-cap any remaining reactive trityl groups, add HPLC[*] grade methanol (0.2 cm^3) and mix for 15 minutes. Filter the resin and wash it 3x2 cm^3 (DCM/MeOH/DIPEA=17/2/1), 3x2 cm^3 DCM and dry the resin in a dessicator over KOH.

Step 2: Estimate the level of first residue attachment as described before. Remove the Fmoc-protecting group using freshly prepared 20% solution piperidine/dimethyl formamide (DMF, 3 cm^3). Filter after 5 minutes and repeat with another 3 cm^3 of 20% solution piperidine/DMF. Wash the resin with DMF (3x2 cm^3) and DCM (3x2 cm^3).

---

[*] High Performance Liquid Chromatography

Step 3: Dissolve Fmoc-Ser(OBu^t)-OH (383 mg, 1 mmol) and HOBt (135 mg, 1 mmol) in a sample vial in the minimum volume of DMF. Then add dropwise DIC (156 μL, 1 mmol) and stir the mixture for 20 minutes. This results in the formation of the corresponding active ester, which has the structure shown below:
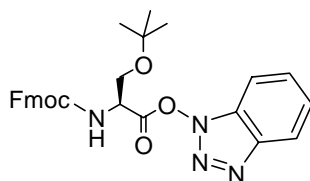
Add this solution to the resin, which has been swollen in 1 cm^3 DMF. Agitate gently for 1 hour and then filter, wash with DMF (3x2 cm^3) and DCM (3x2 cm^3). Then, perform a Kaiser test to ascertain the completeness of the reaction, as described below.

Kaiser test:
Prepare the following solutions:
1. Dissolve 5 g of ninhydrin in 100 cm^3 EtOH.
2. Dissolve 80 g of liquified phenol in 20 cm^3 of EtOH.
3. Add 2 cm^3 of a 0.001 M aqueous solution of potassium cyanide to 98 cm^3 pyridine.
4. Transfer a few resin beads to a small glass tube and add 2 drops of each of the solutions above.
5. Mix well and heat in boiling water for 5 minutes. A positive test indicated by blue resin beads means that the coupling step should be repeated until a negative Kaiser test is achieved.

Step 4: Removal of Fmoc-protecting group is accomplished using the same procedure described in Step 2.

Step 5: Wash resin with isopropanol and ether (3x2 cm^3) and air-dry it by application of vacuum for 10 minutes. Add to the dry resin the cleavage reagent (3 cm^3 0.5% TFA/DCM) and leave to stand at room temperature with occasional agitation for 1 $^1/_2$ hours. Collect the filtrate and wash the resin with the cleavage reagent (3x2 cm^3). Evaporate the combined filtrates until dryness. Add cold ether (5 cm^3) and agitate the solid precipitated with a spatula. Leave for 10 minutes, decant the supernatant liquid and repeat once more with 5 cm^3 of ether. The product H$_2$N-Ser-Ala-OH is obtained by filtration through a sintered glass funnel.

PROBLEMS - Report

a. Record the following data:
I. The weight of your product: 8 mg
II. The calculated theoretical yield: 12.3 mg (for level of first residue attachment 0.35)
III. The obtained yield as a percentage of the theoretical: 65%
IV. The melting point of the product: 210-213°C

b. Give a design of the thin layer chromatographic plate of the following compounds using CHCl$_3$/MeOH=(9/1) as the eluent system:

i)   Fmoc-Ala-OH
ii)   Fmoc-Ser(OBu^t)-OH
iii)   H$_2$N-Ser-Ala-OH
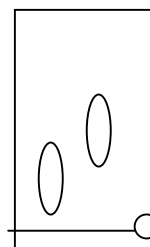
c. Estimate the R$_f$ value of the above products: i) 0.25, ii) 0.40, iii) 0

d. Report the observed angle of rotation α and the specific rotation $[\alpha]_D^t$ of your product using a polarimeter and applying the following equation:

$[\alpha]_D^t = \dfrac{\alpha}{lc}$, where: t = temperature (25 °C), D refers to the sodium D line (589.0 nm), l = 1 dm,

and c = 6 g/100 cm^3 in aq HCl.   α = 1.91°, $[\alpha]_D^t = -31.8°$ dm^{-1} g^{-1} cm^3

Problem 37: Phase diagram and enthalpy of vaporization

Introduction

This experiment will allow you to construct a significant portion of the liquid – gas equilibrium curve in a phase diagram for water. The data will be used to determine an average value for the enthalpy of vaporization for the same compound making use of the Clausius – Clapeyron equation.

Theory

Every liquid can come to equilibrium with its vapor. The vapor pressure of a single-component liquid depends on the nature of the liquid and the temperature. At the temperature where the vapor pressure is equal to the total pressure applied to the liquid, the liquid boils. The normal boiling point is achieved when the pressure is 1 atm (= 1.013 bar = 101 325 Pa).

A phase diagram displays pressure versus temperature (or vice versa). For most compounds there are regions of the diagram where each phase (i.e., solid, liquid, gas) is shown and their boundaries are the two-phase equilibrium curves.

The Clapeyron equation is derived from basic Thermodynamics. It states that the slope of any equilibrium curve is equal to the ratio of the change in molar enthalpy upon phase change over the corresponding molar volume change and over the temperature, viz., $\dfrac{dP}{dT} = \dfrac{\Delta h}{T \Delta V}$. If we are interested in the liquid-gas or solid-gas equilibrium, we may assume that the gas follows the ideal gas state equation and that the molar volume of the gas is much larger than that for the condensed phase. With these assumptions, the Clausius – Clapeyron equation is derived: $\dfrac{d \ln P}{d\left(\frac{1}{T}\right)} = -\dfrac{\Delta h}{R}$. The derivative on the left-hand side of the equation is the slope of the lnP versus T^{-1} diagram.

Method

By trapping water in a sealed container, heating the apparatus and monitoring the pressure and the temperature, we can record a section of the phase diagram.

Apparatus

A simple heater (100-200 W), a 0-200 °C thermometer, a 0-20 bar pressure gauge (Bourdon tube), insulating aluminium foil, a steal tube, H_2O.

Procedure

Assemble the apparatus: wrap tightly together water containing tube (copper tube 10 cm long, 6 mm dia., plugged on one end and fitted with pressure gauge) and thermometer with Al foil; insert assembly in core of heater coil; support properly. Apply power to heater. Monitor pressure and temperature and interrupt heating when either 16 bar or 180 °C are exceeded. Start recording pressure and temperature for every division on the pressure gauge, while the apparatus is cooling down until the temperature has reached below 80 °C. Enter your measurements in a table with 3 columns: point number, pressure (units), temperature (units).

Analysis – Presentation

Draw all recorded points on a P vs. θ graph (phase diagram). Spot out any irregularities, i.e., highly divergent measurements. Extend the above table to include columns for lnP, T, 1/T. Calculate lnP, T, 1/T. Draw diagram of lnP vs. 1/T. Draw a straight line through the points of the latter diagram. Determine the slope of the line and calculate the enthalpy of vaporization for water.

Results – Discussion – Additional questions

Summarize your results. Estimate the normal boiling point of water based on your measurements. Compare to the known value and comment on any divergence. Likewise calculate the cooking temperature in a pressure cooker equipped with a safety valve which weighs 3 N and has a piston diameter of 6 mm.

Problem 38: SOME CHEMISTRY OF IODINE

The following chart contains some of the known compounds of the halogens at various oxidation states. Note that the oxidation number ranges in general from −1 to +7, but fluorine differs significantly from the other halogens in that it has no stable oxyacids.

Oxidation State	Fluorine	Chlorine	Bromine	Iodine
+7		$HClO_4$, ClO_4^-		H_5IO_6, IO_4^-
+5		$HClO_3$, ClO_3^-	$HBrO_3$, BrO_3^-	HIO_3, IO_3^-
+3		$HClO_2$, ClO_2^-		
+1		$HClO$, ClO^-	$HBrO$, BrO^-	HIO, IO^-
0	F_2	Cl_2	Br_2	I_2
-1	HF, F^-	HCl, Cl^-	HBr, Br^-	HI, I^-

A glance at the chart should convince you that oxidation-reduction reactions are a very important part of halogen chemistry.

Although iodine will show some chemistry unique to itself, many of its reactions are typical of other halogens. In this experiment we shall investigate some reactions of iodine and note the influence of hydrogen ion concentration on the equilibria.

PROCEDURE

Caution: Solid iodine and its vapor will cause burns and stains on skin or clothing. Its vapors are poisonous and even small quantities will irritate the mucous membranes, if inhaled. *Avoid unnecessary contact.*

Use 13x100 mm test tubes throughout this experiment except in Part IIb.

Preliminary Experiment-The Starch Iodine Test.

Prepare a dilute solution of iodine by adding one or two small iodine crystals to about 5 cm^3 of tap water. Warm slightly, add 3 or 4 drops of starch solution, and observe. This is a very sensitive test for molecular iodine.

Note: The color is due to a starch-iodine complex which is attributed to the ability of I_2 molecules to fit into the long, hollow spaces between the helical coils which constitute the starch molecule. The fit is close and the interaction strong enough to give the intense color even at very low iodine concentrations.

Part I. Some Reactions of Iodide Ion I^-.

a. To 2 cm^3 of 0.1 M potassium iodide (KI) add an equal volume of 0.1 silver nitrate ($AgNO_3$). Note the result.

b. To 2 cm^3 of 0.1 M potassium iodide (KI) and 5 cm^3 of starch solution add a drop or two of commercial bleach (5% NaOCl) solution. Note the result. Continue to add the bleaching solution until there is a second color change. How do you account for this?

c. To 2 cm^3 of 0.1 M potassium iodide (KI) and 5 cm^3 of starch solution add about 5 drops of 3% H_2O_2. Note the result.

Part II. Some Reactions of Iodate Ion IO_3^-.

a. Pour about 5 cm^3 of saturated solution of KIO_3 into each of two test tubes.

1. Add 3 cm^3 of 0.1 M KI and 2 cm^3 of 6 M H_2SO_4 to one of the test tubes. Decant the supernatant liquid from the solid produced. Filter, if necessary. Wash the solid with water. Do you recognize the solid? Run an identification test you have used previously to confirm your inference.

2. Add 3 cm^3 of 0.1 M KI and 2 cm^3 of 6 M KOH to the second test tube. What do you conclude about the role of hydrogen ion in the reaction between iodide and iodate ions?

3. Add 3 cm^3 of an acidified solution of 0.1 M sodium sulfite (Na_2SO_3), 2 cm^3 of 6 M H_2SO_4 and 3 or 4 drops of starch solution. What do you observe?

Part III. Reaction of I$_2$ in a Basic Solution.

a. To a few crystal (about 0.5 g) of solid iodine add from a dropper about 10 drops of 6 M potassium hydroxide, KOH. Shake the test tube gently until the solid iodine disappears and the solution is colorless. You may need to warm the solution gently and add a few more drops of 6 M KOH. You will identify the product of this reaction in Part d.

b. Cool the solution and make it acidic by adding sufficient (10 drops or slightly more) 6 M HNO$_3$ to neutralize the base added previously. Note the product of this reaction. What do you think it is?

c. Make the solution basic again by adding a few drops of 6 M KOH. Warm gently and add a few drops of 6 M KOH, if necessary, until a color change is observed. Discard the solution.

d. Repeat the procedure outlined in Part a. Cool under the cold water tap until a solid crystallizes from the solution. Decant the supernatant liquid and save it for part (2) below.
   1. Dry the white solid by heating the test tube gently. Allow it to cool. Dissolve the white solid in 5 cm^3 of water. Add 5 cm^3 of 1 M sodium sulfite (Na_2SO_3), 2 cm^3 of 6 M H_2SO_4 and 3 or 4 drops of starch solution. Note the result. Compare it with that obtained in Part IIb.
   2. To the decanted liquid add 5-10 drops of 0.1 M silver nitrate AgNO$_3$; shake the test tube and note the result. Compare the product with that obtained in Part Ia.

QUESTIONS

1. Write the equations for the reactions observed in Parts Ia, Ib, Ic.
2. a. How did the results in Part IIId(1) compare with those obtained in Part IIb?
   b. How did the test with 0.1 M silver nitrate in Part IIId(2) compare with the results of Part Ia?
   c. What do you conclude about the ionic species formed when I$_2$ reacts with 6 M KOH as in Part IIIa?
3. Write the equation for the self-oxidation-reduction reaction of iodine in a basic solution. Write the equation for the reverse reaction in an acid solution.
4. In which oxidation state do the halogens most commonly occur in nature? Explain your answer in terms of the electronic structure of this species for chlorine.
5. How would you prepare elemental fluorine, F$_2$? Consult an oxidation-reduction table to check the feasibility of your method.
6. Find the geometry, using the VSEPR model, for the following anions of the halogen oxoacids: ClO_2^-, ClO_4^-, BrO_3^-, IO_6^{5-}.
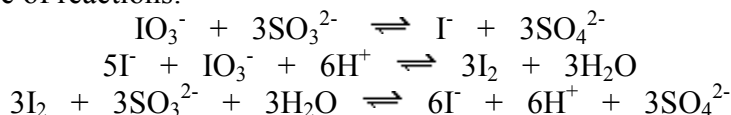
Answers

1. Ia : $I^-(aq) + Ag^+(aq) \rightleftharpoons AgI\downarrow$ (yellow precipitate)

   Ib : $2I^-(aq) + OCl^-(aq) + 2H^+(aq) \rightleftharpoons I_2$ (comp.) $+ Cl^-(aq) + H_2O$

The solution was deep blue colored . The color is due to the starch-iodine complex.

I_2 (comp.) $+ OCl^-(aq) + H_2O \rightleftharpoons IO_3^-(aq) + 5Cl^-(aq) + H^+(aq)$

In excess of NaOCl the iodine was further oxidized to iodate.

   Ic : $2I^-(aq) + H_2O_2 + 2H^+(aq) \rightleftharpoons I_2 + 2H_2O$

The solution was deep blue colored . The color is due to the starch-iodine complex.

2. a. In Part IIb the sulfite ions (SO_3^{2-}) was reacted with an excess of iodic ions (IO_3^-) (saturated solution of KIO_3) and in the presence of starch indicator the deep-blue starch-iodine color increased systematically as a result of the following of reactions:

$$IO_3^- + 3SO_3^{2-} \rightleftharpoons I^- + 3SO_4^{2-}$$
$$5I^- + IO_3^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O$$
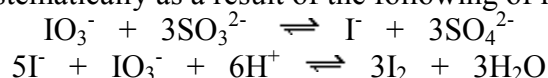
In Part IIId the iodate ions (IO_3^-) are reacted with an excess of sulfite ions (SO_3^{2-}). With the excess of sulfite, free iodine periodically appears and disappears as a result of the following sequence of reactions:

$$IO_3^- + 3SO_3^{2-} \rightleftharpoons I^- + 3SO_4^{2-}$$
$$5I^- + IO_3^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O$$
$$3I_2 + 3SO_3^{2-} + 3H_2O \rightleftharpoons 6I^- + 6H^+ + 3SO_4^{2-}$$

The net reaction is the oxidation of iodates to iodides and the starch indicator oscillates between deep blue and almost colorless as the iodine concentration pulsates.

b. In Part IIId(2) the product is the same (yellow precipitate) with that obtained in Part Ia, following the reaction:

$$I^-(aq) + Ag^+(aq) \rightleftharpoons AgI\downarrow$$
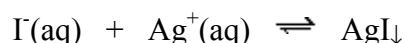
c. The anionic species formed when I_2 reacts with 6 M KOH as in Part IIIa was the iodates (IO_3^-) and iodides (I^-) anions.

3. The equation for the self-oxidation-reduction reaction of iodine in a basic solution is:

$$3I_2 + 6OH^- \rightleftharpoons 5I^- + IO_3^- + H_2O$$
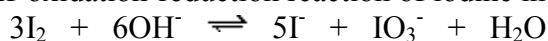
and the reverse of this reaction in an acid solution:

$$5I^- + IO_3^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O$$
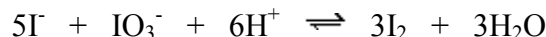
4. As X^-, oxidation state (1-), as the result of their electronic configuration:…..$ns^2 np^5$.

5. The only practicable method of preparing F_2 gas is based on the electrolysis of fluoride salts, i.e., potassium fluoride (KF) dissolved in anhydrous HF:

$$KF + HF \rightleftharpoons F_2 + H_2 \text{ (electrolysis)}$$

$2F^- \rightleftharpoons F_2 + 2e^-$		$E^o = -2.87$ V
$2H^+ + 2e^- \rightleftharpoons H_2$		$E^o = 0.00$ V
$2F^- + 2H^+ \rightleftharpoons F_2 + H_2$		$\Delta E = -2.87$ V
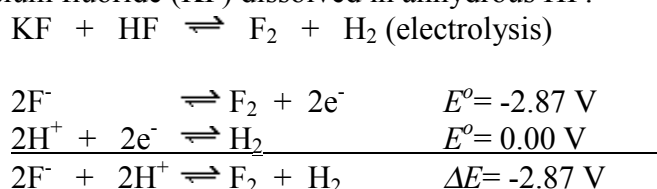
6. ClO_2^-: bent
ClO_4^-: tetrahedral
BrO_3^-: trigonal pyramidal
IO_6^{5-}: octahedral

Problem 39: Preparation of the complex salt $Cu(NH_3)_4SO_4 \cdot H_2O$

Anhydrous copper sulphate, $CuSO_4$, is white. When it is dissolved in water, the resulting solution is sky blue because of the formation of the complex ion $Cu(H_2O)_6^{2+}$, or $Cu(H_2O)_4(H_2O)_2'^{2+}$ or $Cu^{2+}(aq)$. The six water molecules are not equivalent due to the Jahn-Teller effect.
The hydrated solid salt of copper sulfate, $CuSO_4 \cdot 5H_2O$ which may be written as $Cu(H_2O)_4 \cdot SO_4 \cdot H_2O'$ is also blue.
If a solution of NH_3 is added to a solution of $Cu^{2+}(aq)$, the colour becomes intensely blue because of the formation of a new complex:

$$Cu^{2+}(aq) \;+\; 4NH_3 \;\rightleftharpoons\; Cu(NH_3)_4{}^{2+} \;+\; water$$
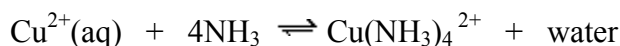
In solutions containing 0.01 to 5 M NH_3 the complex $Cu(NH_3)_4{}^{2+}$ is mainly formed. In lower concentrations of NH_3 formation of complexes containing fewer NH_3 molecules is favored, that is $Cu(NH_3)_3(H_2O)^{2+}$, $Cu(NH_3)_2(H_2O)_2{}^{2+}$ and $Cu(NH_3)(H_2O)_3{}^{2+}$. In concentrations of NH_3 higher than 5 M, $Cu(NH_3)_5(H_2O)^{2+}$ is also formed. Under these conditions the predominant complex is $Cu(NH_3)_4{}^{2+}$.

$$K_{form} = \frac{\left[Cu(NH_3)_4^{2+} \right]}{\left[Cu_{aq}^{2+} \right]\left[NH_3 \right]^4}$$

K_{form} has a large value, that is the equilibrium is shifted to the right, while K_{inst}, which is defined as $1/K_{form}$, is small, hence the complex $Cu(NH_3)_4{}^{2+}$ is <u>stable</u>.

The equilibrium is established quickly, that is, complex $Cu(NH_3)_4{}^{2+}$ is <u>labile</u>.

Complexes in which the corresponding equilibrium is established slowly are called <u>inert</u>.

Due to the lability of the complex $Cu(NH_3)_4{}^{2+}$ the NH_3 molecules that are bound to the central ion Cu^{2+} are quickly and continuously exchanged with non-complexed NH_3 molecules, which are present in the solution as well as with molecules of the solvent (water).

Experiment

1. 6.25 g of hydrated copper sulfate $CuSO_4.5H_2O$ are dissolved in a mixture of 10 cm^3 of concentrated NH_3 solution and 6 cm^3 of distilled water. The intensely blue solutions of the complex $Cu(NH_3)_4{}^{2+}$ will be formed according to the previous equilibrium.

2. The complex salt $Cu(NH_3)_4SO_4 \cdot H_2O$ is less soluble in a mixture of ethanol–water than in water. (Explain why). By adding 10 cm^3 of ethanol to the aqueous solution and cooling, a precipitate is formed. Is the dissolution in a mixture of ethanol – water endothermic or exothermic?

3. The precipitated salt is filtered under vacuum and washed sequentially by (a) a mixture of equal volumes of ethanol and concentrated solution of NH_3, (b) pure ethanol and (c) finally ether.

4. The so obtained crystals are placed in a desiccator. If a drying compound is used that can react with NH_3, e.g. $CaCl_2$, gas phase NH_3 will be bound and the complex will decompose in order to maintain the solid-gas equilibrium. A compound not reacting with NH_3 must be used, like CaO.

5. The binding of Cu(II) with NH_3 can be shown qualitatively as follows:

0.3 g of the starting material $CuSO_4.5H_2O$ are dissolved in 10 cm^3 water, a few drops of Na_2CO_3 2 M solution are added and then a blue precipitate of $CuCO_3$ is formed. A similar solution of $Cu(NH_3)_4SO_4 \cdot H_2O$ does not give the previous reaction since Cu(II) is in the form of $Cu(NH_3)_4{}^{2+}$.

Under which conditions formation of $CuCO_3$ would be possible from the solution of the complex salt $Cu(NH_3)_4SO_4 \cdot H_2O$?

$$Cu(NH_3)_4{}^{2+} \rightleftharpoons Cu^{2+} (aq) \;+\; 4NH_3$$
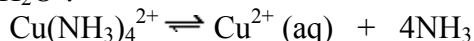
Removal of NH_3 would shift the equilibrium to the right:
 (a) by heating
  (b) by addition of $CaCl_2$
  (c) by addition of HCl.
Why is the complex salt more soluble in water than in ether?

Problem 40: EDTA titration of magensium and calcium in water samples

The term "hardness" of water refers to salts, mainly of Ca^{2+} and Mg^{2+} with the ions Cl^-, SO_4^{2-} and HCO_3^-.

By boiling water, the soluble salts of HCO_3^- are transformed to insoluble salts of CO_3^{2-}:
$$2HCO_3^- \quad <=> \quad H_2O + CO_2 (g) + CO_3^{2-}$$

$$Ca^{2+} + CO_3^{2-}: \quad <=> \quad CaCO_3 \text{ (insoluble)}$$
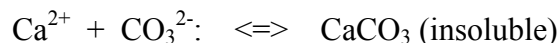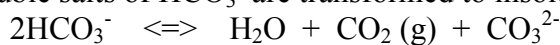
The hardness that is due to such salts disappears by boiling the water, hence the term non-permanent hardness.

The hardness which is due to Cl^- and SO_4^{2-} is permanent because it does not disappear by boiling the water.

Total hardness is the sum of permanent and non-permanent hardness.

The hardness of water is expressed in mg CaO / 100 cm^3 H_2O (Deutch degrees, D^o), in mg $CaCO_3$ / 100 cm^3 H_2O (French degrees, F^o) and in mg $CaCO_3$ / 1000 cm^3 H_2O (American way of expressing hardness).

Procedure:

Determination of the total hardness of water. Titration with EDTA.

1. 50 cm^3 of H_2O are measured accurately. Instead of "hard water" a solution containing a quantity of Mg^{2+} and Ca^{2+} ions may be used.

2-3 cm^3 of buffer solution $NH_3 – NH_4Cl$ having pH=10 are added and 3-4 drops of a solution (in alcohol) of melan eriochrome T, 0.5% (indicator). The solution turns red-violet because of the formation of a complex between Mg^{2+} and the indicator.

2. A solution of the dissodium salt of EDTA of known concentration 0.01 F which is equivalent to 1mg $CaCO_3$ / cm^3 EDTA (question 1) is added with stirring.

The ions Ca^{2+} and Mg^{2+} form 1:1 complexes with EDTA. EDTA will form complexes with all the free Ca^{2+} and Mg^{2+} ions and finally it will also bind with the ions Mg^{2+} which are to the indicator, replacing it. At this point, which is the titration end point, the colour of the solution turns from red to blue because of the liberation of the indicator. At pH=10, the colour change is clear and the determination of the equivalence point more accurate.

If V is the volume of the EDTA solution consumed and C its concentration in mg $CaCO_3$ equivalent to 1 cm^3 of EDTA solution and the volume of the water sample used is 50 cm^3, the hardness of water in mg $CaCO_3$ / 100 cm^3 H_2O is given by: F^o=2VC.

If C=0.01F ~ 1mg $CaCO_3$ / 1 cm^3 EDTA then F^o=2V.

Questions
1. Prove that an EDTA concentration of 0.01F is equivalent to 1mg $CaCO_3$ per 1 cm^3 EDTA.
2. If the volume of water sample is 25 cm^3, how will the hardness in F^o be calculated?
3. Express the experimentally determined hardness in D^o and in mg $CaCO_3$ / dm^3 H_2O.
4. If the water contains Ca^{2+} but no Mg^{2+}, is it possible to use the above method for the determination of the concentration of Ca^{2+} ? Which modification of the method is necessary?
5. Fluoride ions are added to the water supply of many cities for the protection of teeth. If the water non-permanent hardness is 1.0×10^{-3} M, is it possible for the fluoride concentration to reach the desired value of one part per million before it starts to form insoluble CaF_2? For the solubility product of CaF_2 use the value 1.7×10^{-10}.

Problem 1: Proton – antiproton atom

We can use the expression for hydrogen-like atoms to calculate the energy levels.

$$E_n = -\frac{2\pi Z^2 e^4 \mu}{(4\pi\varepsilon_0)^2 h^2 n^2}$$ where Z is the total number of charges in the nucleus (= 1), e is the electron charge (= 1.6022×10^{-19} C), μ is the reduced mass of the system with $\mu = (m_1^{-1} + m_2^{-1})^{-1}$ and $m_1 = m_2 = m_p = 1.6726 \times 10^{-27}$ kg, thus $\mu = \frac{1}{2} m_p$, ε_0 is the permittivity of vacuum (= 8.8542×10^{-12} C^2 J^{-1} m^{-1}) [note: $(4\pi\varepsilon_0)^{-1}$ is Coulomb's constant], h is the Planck constant (= 6.626076×10^{-34} J s) and n is the principal quantum number of the system taking values 1, 2, …

For n = 1, $E_1 = -m_p \left(\frac{e^2}{4h\varepsilon_0}\right)^2 = -2.00129 \times 10^{-15}$ J and for n = 2, $E_2 = \frac{E_1}{4}$, hence

$$\Delta E \equiv E_2 - E_1 = \frac{3}{4} E_1 = 1.50097 \times 10^{-15} \text{ J}$$

$\Delta E = h\nu$, hence $\nu = \frac{\Delta E}{h} = \frac{1.50097 \times 10^{-15} \text{ J}}{6.626076 \times 10^{-34} \text{ J s}} = 2.2652 \text{ s}^{-1}$.

$c = \lambda\nu$, hence $\lambda = c/\nu = \lambda = \frac{c}{\nu} = \frac{2.997925 \times 10^8 \text{ m s}^{-1}}{2.2652 \text{ s}^{-1}} = 1.3234 \times 10^{-10} \text{ m} = 1.3234 \text{ Å}$.

The Bohr radius is given by

$$\alpha = \frac{h^2 (4\pi\varepsilon_0)}{4\pi^2 \mu e^2} = \frac{2h^2 \varepsilon_0}{\pi m_p e^2} = 5.76397 \times 10^{-14} \text{ m}$$ which is 1836/2 times smaller than the hydrogen radius due to the difference in reduced mass of the "atom".

Problem 2: Annulene

The number of π electrons is 18. Two electrons can occupy each state due to the Pauli exclusion principle. Each state above the lowest is two-fold degenerate. Based on these pieces of information, we can fill this table:

N	max number of e⁻ per state	total e⁻ up to this state
0	2	2
1	4	6
2	4	10
3	4	14
4	4	18

States up to N = 4 are fully occupied with 18 electrons. The lowest possible transition is from state N = 4 to state N = 5. The path forming a circular well is L = 18 x 1.4 Å. Hence

$$\Delta E = E_5 - E_4 = (5^2 - 4^2)\frac{(6.6260755 \times 10^{-34} \text{ J s})^2}{2 \times (18 \times 1.4 \text{ Å})^2 \times 9.109389 \times 10^{-31} \text{ kg}} = 3.415 \times 10^{-19} \text{ J}$$

The transition frequency is $\nu = \Delta E/h = 5.1544 \times 10^{14}$ s^{-1} and the corresponding wavelength is $\lambda = c/\nu = 581.6$ nm.

Problem 3: Chemical bonding: The molecular ion O_2^{2+}

1. 171.9 kcal/mol
2. No

3. Yes

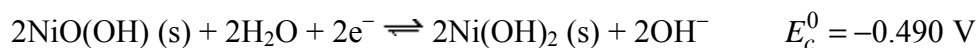**4.** 85.6 kcal/mol

5. $(171.9 - 85.6)$ kcal/mol $= 86.3$ kcal/mol or $(86.3/N_A)$ kcal/molecule $= 1.43 \times 10^{-23}$ kcal/molecule.
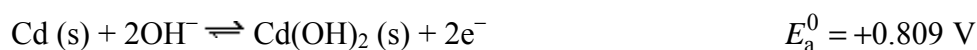
6. ~1.1 Å

7. ~1.6 Å

Problem 4: Electrochemistry: Nicad batteries

$2NiO(OH)\ (s) + 2H_2O + 2e^- \rightleftharpoons 2Ni(OH)_2\ (s) + 2OH^- \qquad E_c^0 = -0.490$ V

$$E_c = E_c^0 - \frac{RT}{2F} \ln\left[OH^- \right]^2$$

$Cd\ (s) + 2OH^- \rightleftharpoons Cd(OH)_2\ (s) + 2e^- \qquad\qquad E_a^0 = +0.809$ V

$$E_a = E_a^0 - \frac{RT}{2F} \ln \frac{1}{\left[OH^- \right]^2}$$

$Cd\ (s) + 2NiO(OH)\ (s) + 2H_2O \xrightleftharpoons[\text{charge}]{\text{discharge}} 2Ni(OH)_2\ (s) + Cd(OH)_2\ (s)$
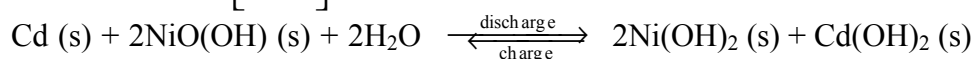
$E = E_a - E_c = E_a^0 - E_c^0 = 0.809$ V $- (-0.490$ V$) = 1.299$ V.

700 mAh $= 0.700$ A $\times 3600$ s $= 2520.0$ C

2520.0 C $\rightarrow \dfrac{2520.0}{2 \cdot 96485}$ moles of Cd $= 0.013$ moles of Cd $\rightarrow 0.013 \times 112.4 = 1.47$ g of Cd.

Problem 5: Boiler

Tank capacity: $m = V\rho = 4$ m^3 x 0.73 g cm^{-3} = 2920 kg

Heating power P = 116 kW

Consumption rate $\dfrac{m}{t} = \dfrac{P}{\Delta h\big/ m} = \dfrac{116\,\text{kJ s}^{-1}}{4.3 \times 10^7\,\text{J kg}^{-1}} = 2.70 \times 10^{-3}$ kg s$^{-1}\left(= 9.73\,\text{kg h}^{-1}\right)$

Operation duration $t = \dfrac{m}{m\big/ t} = \dfrac{2920\,\text{kg}}{2.70 \times 10^{-3}\,\text{kg s}^{-1}} = 1.08 \times 10^8$ s $= 300$ h $= 12.5$ days

$C_nH_{2n+2} + \frac{1}{2}(3n+1)\ O_2 \rightarrow nCO_2 + (n+1)H_2O$
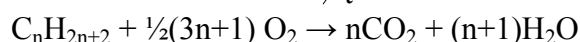
$\dfrac{m_{CO_2}}{m_{C_nH_{2n+2}}} = \dfrac{44n}{14n + 2} = \dfrac{22}{7 + \dfrac{1}{n}}$ This ratio does not depend heavily on n; for a representative value of n = 10, the ratio takes the value of 3.1.

Since $\dfrac{m_{C_nH_{2n+2}}}{t} = 9.73$ kg h^{-1},

$m_{CO_2} = \dfrac{m_{C_nH_{2n+2}}}{t} \dfrac{m_{CO_2}}{m_{C_nH_{2n+2}}} = 9.73$ kg h^{-1}x3.1 = 30.2 kg h^{-1}

Problem 6: Ammonium nitrate

Mixing is endothermic and the process is adiabatic, thus heat has to be provided by the solution itself. Since water is at its freezing point, it will tend to freeze, but the solution created will experience a depression of freezing point due to the presence of

dissolved ions. The large amount of heat required for solvation will necessitate some freezing of water.

A Hess cycle of 3 steps will be considered.

A. mixing at 0 °C with $\Delta H_1 > 0$

B. lowering of the temperature of the mixture to its final temperature with $\Delta H_2 < 0$

C. freezing of some water m_s with $\Delta H_3 < 0$

The final temperature is given by $\theta_2 = -K_f 2 \dfrac{n}{m - m_s}$ where K_f is the cryoscopy constant, 2 is the number of particles per formula weight for NH_4NO_3, n the number of moles of NH_4NO_3 $n = \dfrac{80\,g}{80\,g\,mol^{-1}} = 1\,mol$, m = 1000 g.

$\Delta H_1 = \Delta h_s\, n = $ -25.69 kJ mol^{-1} x 1 mol = -25.69 kJ

$\Delta H_2 = c_P \dfrac{m}{M} \theta_2$ where c_P is the molar heat capacity of water and M its molecular mass (18 g mol^{-1}).

$\Delta H_3 = -\Delta h_f \dfrac{m_s}{M}$ where Δh_f is the molar enthalpy of fusion.

$\Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_{total} = 0$ because no heat is allowed to be exchanged between the system and its surroundings.

Substituting for θ_2 and solving for m_s yields the following expression

$$m_s = \frac{m}{2} + \frac{\Delta h_s}{\Delta h_f}\frac{nM}{2} \pm \sqrt{\left(\frac{m}{2} - \frac{\Delta h_s}{\Delta h_f}\frac{nM}{2}\right)^2 + \frac{2nK_f c_P m}{\Delta h_f}}$$

We discount the solution derived from the + sign as unphysical ($m_s > m$) and arrive at the result m_s = 28.52 g ice.

Hence θ_2 = -3.83 °C.

If we made the simplification that we expect $m_s \ll m$, then θ_2 is immediately calculated as –3.72 °C, which yields a value for m_s = 29.9g. If this result is used to improve the θ_2 value using the exact expression, we get θ_2 = -3.83 °C. Then, m_s can be further improved to 28.5 g.

The process is spontaneous, irreversible, one where separation of components is possible, adiabatic, isobaric, isenthalpic, nearly isoenergetic.

The equation $\Delta G = \Delta H - T \Delta S$ can be used here because T varies less than 2%. $\Delta G < 0$ because the process is spontaneous and $\Delta H = 0$, hence $\Delta S > 0$. This is also to be expected from stability criteria under the constraint $\Delta H = 0$.

Problem 7: Carbon dioxide

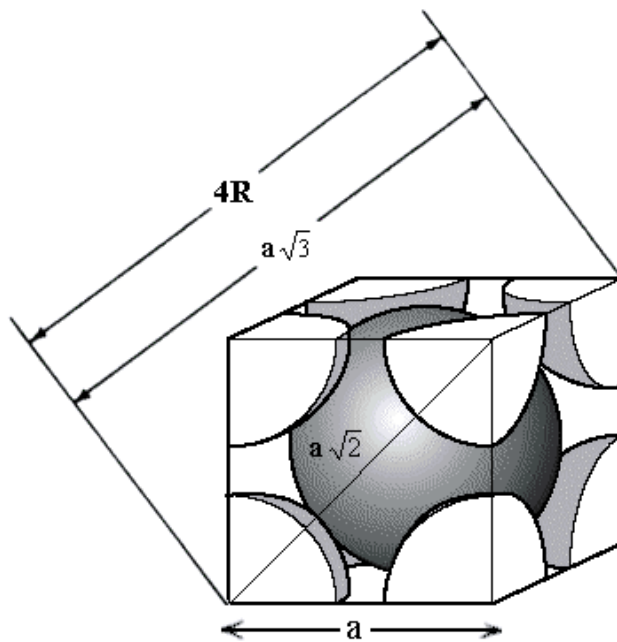A rather accurate phase diagram for CO_2 is shown here using data from Landolt-Börnstein New Series IV/20B, p. 22 which has been based on Dykyi, J. Repas, M.: Saturated Vapor Pressure of Organic Compounds, Bratislava, Czech.: Slovakian Academy of Science, 1979.
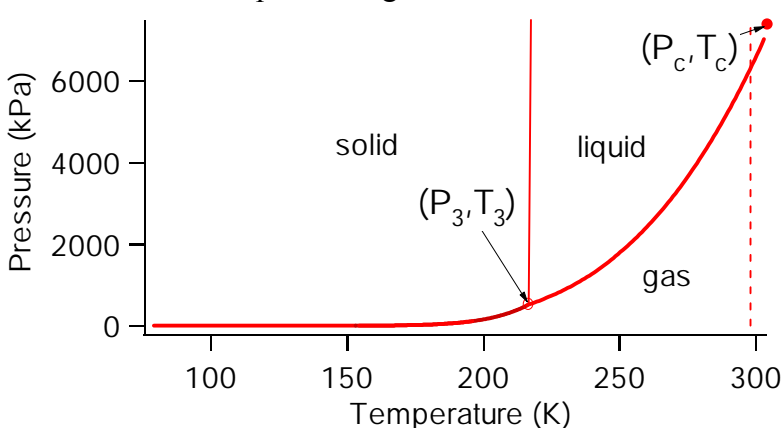
A qualitative one can be drawn based on the triple and the critical points. Since the room temperature is well above the triple point, there is no way there can be any solid CO_2 in the fire extinguisher. At 298 K, the CO_2 vapor pressure is 63.1 bar. This value can be estimated by drawing a straight line between the triple and the critical points. It can be calculated also based on the empirical Antoine equation, viz.,

$$\log \frac{P}{kPa} = A - \frac{B}{C + T/K} \quad \text{with } A = 6.46212, B = 748.28 \text{ and } C = -16.9.$$

Problem 8: Iron crystal

(a) Let **R** be the atomic radius of iron and **a** =2.87 Å the length of the unit cell edge. Then, as atoms touch each other along the body diagonal and from a Pythagorean theorem in the cube:

$a\sqrt{3} = 4R \Rightarrow R = (a\sqrt{3})/4 \Rightarrow R = 1.24$ Å

The Avogadro number (N_A) can be calculated from the density (ρ) formula. The latter is obtained by finding the number of atoms per unit cell, multiplying this number by the mass of each atom ($\frac{\text{mole of atoms}(g/mol)}{N_A (\text{atoms}/mol)}$) and, eventually, dividing the result by the volume of the unit cell (a^3). Note that each bcc unit cell contains two whole spheres, that is 2 Fe atoms.

$$\rho(g/cm^3) = \frac{2 \times (55.847/N_A)g}{a^3 (cm^3)} \Rightarrow$$

$$N_A = \frac{2 \times 55.847 \, g}{7.86 \times (2.87 \times 10^{-8})^3 \frac{g}{cm^3} cm^3} \Rightarrow N_A \approx 6.01 \times 10^{23}$$

(b) By applying the Pythagorean theorem in the cube, one finds:
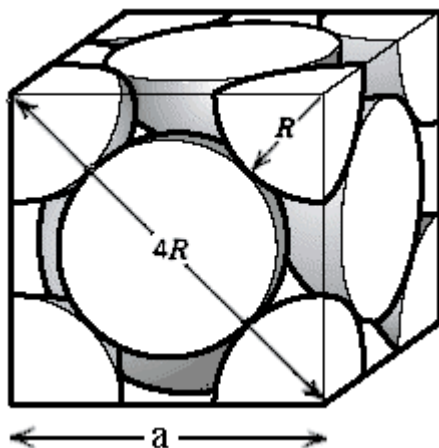
$a^2 + a^2 = (4R)^2 \Rightarrow a = 2R\sqrt{2} \Rightarrow R = \frac{a\sqrt{2}}{4} \Rightarrow R = 1.27$ Å (slightly different from the value found above for bcc structure, because of the different packing, having an influence on the atomic radius or at least its estimation).

As for the density, recalling that each fcc unit cell contains four whole spheres, that is 4 Fe atoms, once again one has:

$$\rho(g/cm^3) = \frac{4 \times (55.847/N_A)g}{a^3 (cm^3)} =$$

$$\frac{4 \times 55.847\,g}{6.023 \times 10^{23} \times (3.59 \times 10^{-8})^3\,cm^3} = 8.02\ g/cm^3$$

The higher value of γ-Fe density, as compared with α-Fe, points at the fact that the fcc structure is denser than bcc. fcc represents the, so called, *cubic close packed* structure which, together with the *hexagonal close packed,* are the most efficient ways of packing together equal sized spheres in three dimensions.

(c) and (d) The unit cells below are illustrated by using reduced size spheres. Note that, in hard spheres packing model <u>the represented atoms must be in contact one to each other</u>.
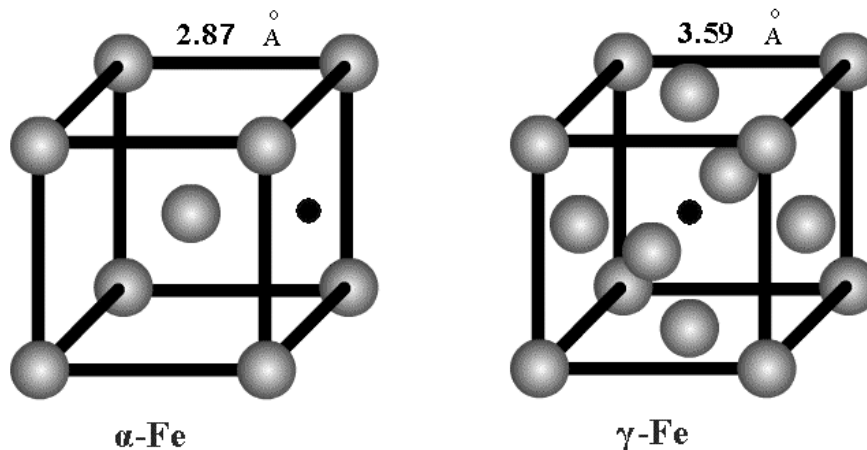
According to the left figure, a perfectly fitted interstitial atom centered at (½, 0, ½) in an α-Fe cell, would have a radius of:

$R_{interstitial}$ = ½ a - R_{Fe}, where a = 2.87 Å and R_{Fe} = 1.24 Å [(see question (a)].
Therefore: $R_{interstitial}$ (α-Fe) ≈ 0.20 Å

Similarly, according to the figure in right, a perfectly fitted interstitial atom centered at (½, ½, ½) in an γ-Fe cell, would have a radius of:

$R_{interstitial}$ = ½ a - R_{Fe}, where a =3.59 Å and R_{Fe}= 1.27 Å   [(see question (b)].
Therefore: $R_{interstitial}$ (γ-Fe) ≈ 0.53 Å

(e) 1 nm = 10 Å. Thus:

For α-Fe: $\dfrac{R_{carbon}}{R_{int\,erstitial}} = \dfrac{0.77\,Å}{0.20\,Å} = 3.85$

For γ-Fe: $\dfrac{R_{carbon}}{R_{int\,erstitial}} = \dfrac{0.77\,Å}{0.53\,Å} = 1.45$

Therefore, the carbon atom is roughly four times too large to fit next to the nearest iron atoms in α-Fe without strain, while it is only 1.5 times oversize to fit in the γ-Fe structure. The above estimations explain well the low solubility of carbon in α-Fe (< 0.1 %).

(f) The wavelength (λ) of the X-rays will be calculated from Bragg's law, assuming first order diffraction: 2d sinθ = λ, where θ is the angle of diffraction equal to 32.6° and d is the interplanar spacing of the (200) set of parallel lattice planes, that is, the perpendicular distance between any pair of adjacent planes in the set. The (200) planes are shown
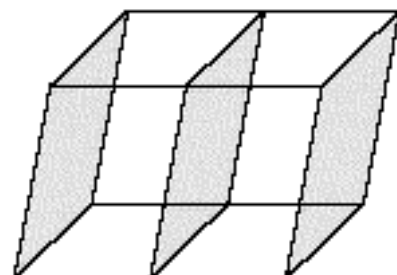
shaded in the figure.

Let a be the length of the cubic unit cell edge. Then, from previous data for α-Fe: a = 2.87 $\overset{\circ}{A}$, so the distance between adjacent (200) planes is: d = $\dfrac{a}{2}$ = 1.44 Å Therefore,

from Bragg's law: λ = 2d sinθ = 2×1.44×sin(32.6°) $\Rightarrow$ $\lambda \approx$ 1.55 Å
This value corresponds to the $K_{\alpha 1}$ transition of iron.

Problem 9: Cyclodextrine

a) V = a x c · b = a b c sin(β) = 7474 Å^3, V_m = 7474 Å^3 /4 = 1868 Å^3
b) FW = 1535.4 g mol^{-1}, ρ = FW 4/(V N_A), hence ρ = 1.3646 g cm^{-3}

Problem 10: Infrared spectroscopy

1. The number of vibrational modes is given by 3N-6 for non-linear and 3N-5 for linear molecules, where N is the number of atoms in the molecule. Hence
CO: 1, H_2O: 3, C_6H_6: 30, C_{60}: 174
2. The fact that the molecules have a vibrational infra red absorption implies that the molecules have a permanent dipole moment, hence these diatomic molecules must be heteronuclear.
For a simple harmonic oscillator-type diatomic molecule, the eigen frequency is given

by the equation $\nu = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{\mu}}$, where k is the force constant and μ the reduced mass of

the molecule. In the absence of any further information, nothing can be said about the reduce masses or the force constants (though bond strength is not related to k, but more likely to bond dissociation energy). The eigen frequency is equal to the frequency of the absorbed photons because the vibrational energy is given by E_v = (v+½) h ν and the energy for the resonance transition is $\Delta E = E_{v=1} - E_{v=0}$ = h ν.
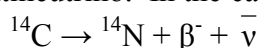
Problem 11: Radioactivity and chemical reactivity

1. γ-rays are a form of high energy electromagnetic radiation.
2. There are no stable (non-radioactive) isotopes beyond Bi.
3. There are numerous light isotopes that are radioactive.
4. Xe compounds such as XeF_2 are commercially available.
5. Cs is the element with the lowest ionization potential (3.89 eV).

Problem 12: Carbon dating

a) Let N_0 be the $^{14}C/^{12}C$ ratio in living systems and N the same ratio found in a sample coming from a system that died t years ago. Then, the following relation between them is true: $N = N_0 e^{-\lambda t}$, where λ (= ln 2 / $t_{\frac{1}{2}}$) the disintegration constant for ^{14}C. The above equation becomes

$$t = \dfrac{-\ln \dfrac{N}{N_0}}{\lambda} = -\dfrac{t_{\frac{1}{2}}}{\ln 2} \ln \dfrac{N}{N_0} = -5700y \dfrac{\ln 0.25}{\ln 2} = 11400y$$

b) The β decay scheme is based on the nuclear reaction n → p + β + $\overline{\nu}_e$, where p is a proton and $\overline{\nu}_e$ an electron antineutrino. In the case of ^{14}C we have
$$^{14}C \rightarrow {}^{14}N + \beta^- + \overline{\nu}$$
hence C becomes a (common) ^{14}N atom.

c) If an organic molecule contains ^{14}C, the consequence of its disintegration can be grave for the structure of the molecule, causing great damage to the molecule in

the vicinity of the ^{14}C atom. At least the chemical bond is raptured since ^{14}N is a chemically different atom than ^{14}C. Free radicals may also be created.

d) The total carbon inside a human body of 75 Kg is 75 kg x 0.185 = 13.9 kg. The total radioactivity (R) is R = 0.277 Bq / g x13.9 kg = 3850 Bq

The amount of ^{14}C present is estimated from the total radioactivity as follow:

$$R \equiv -\frac{dN}{dt} = \lambda N$$

Then

$$N = \frac{A}{\lambda} = A\frac{t_{\frac{1}{2}}}{\ln 2} = 3850s^{-1}\frac{5700\,y}{0.693}\frac{60x60x24x365.25\,s}{y} = 1.00x10^{15}\,atoms = 1.66\,nmol$$

Problem 13: Uranium

a) alpha decay: $X(A,Z) \rightarrow X(A-4, Z-2) + {}^4He^{2+}(2p+2n)$ (ΔA = -4, ΔZ= -2)

beta decay: $X(A,Z) \rightarrow X(A, Z+1) + \beta + \bar{v}_e$ (ΔA = 0, ΔZ = +1)

Since changes in the mass number (ΔA) are due to the emission of alpha particles only, in each series we have:

total alpha particles emitted = $\Delta A_{total}/4$

Alpha emission also changes the atomic number (Z) (ΔZ = -2), so the total decrease in Z due to the total alpha particles emitted would be twice their total number. But Z of the final (stable) element of the radioactive series is higher than the expected Z based on alpha emission. This difference in Z is due to the number of beta particle emitted. Thus

^{238}U $\rightarrow$ ^{206}Pb, α = ΔA/4 = (238-206)/4 = 32/4 = 8, β = 2α - ΔZ = 18 -(92-82) = 6

^{235}U $\rightarrow$ ^{207}Pb, α = ΔA/4 = (235-207)/4 = 28/4 = 7, β = 2α - ΔZ = 14-(92-82) = 4

b) This occurs when an alpha decay (ΔZ = -2) is followed by two successive beta decays (ΔZ = +2).

c) For each radioisotope of uranium we can write

^{235}N = ^{235}N$_0$ exp(-λ_{235} t) and ^{238}N = ^{238}N$_0$ exp(-λ_{238} t)

where N the number of nuclei at time t, N$_0$ at time t = 0 and λ = ln 2 / t$_{\frac{1}{2}}$ = 0.693 / t$_{\frac{1}{2}}$ the disintegration constant.

At t = 0, ^{235}N$_0$ = ^{238}N$_0$, then

$$\frac{\exp(-\lambda_{238}t)}{\exp(-\lambda_{235}t)} = \frac{{}^{238}N}{{}^{235}N} = \frac{99.3}{0.7} = 142$$

Thus

λ_{235} t - λ_{238} t = ln 142 = 4.95

λ_{238} = 0.693/t$_{\frac{1}{2}}$ = 0.693/4.5x10^9 = 1.54x10^{-10} y^{-1}

λ_{235} = 0.693/t$_{\frac{1}{2}}$ = 0.693/7.1x10^8 = 9.76x10^{-10} y^{-1}

$$t = \frac{4.95}{(9.76-1.54)x10^{-10}\,y^{-1}} = \frac{4.95x10^{10}\,y}{8.22} = 6.0x10^9\,y$$

d) The energy released by the complete fission of 1g ^{235}U is

E = (1/235) x 6.022 x 10^{23} x 200 MeV = 5.13 x10^{23} MeV

and the energy released upon combustion of 1 g C is

E = (1/12) x 6.022 x 10^{23} x 4.1 eV = 2.06 x 10^{23} eV = 2.06x10^{17} MeV

Hence the amount of carbon that would release the same amount of energy as the fission of 1 g ^{235}U is

m = (5.13x10^{23})/(2.06x10^{17}) = 2.49 x 10^3 kg C

Problem 14: Lead iodide

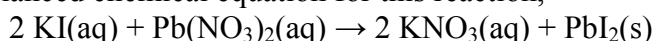**1.** The graph obtained is one of two straight lines, meeting at a peak of about 2.50 g $Pb(NO_3)_2$.

Data according to the reaction
$2 KI(aq) + Pb(NO_3)_2(aq)$
$\rightarrow 2 KNO_3(aq) + PbI_2(s)$

Mass of $Pb(NO_3)_2$ (g)	Mass of PbI_2 (g)
0.500	0,696
1.000	1.392
1.500	2.088
4.000 (1.000 g KI)	1.389
3.000 (2.000 g KI)	2,778

Mass of $Pb(NO_3)_2(aq)$ in g
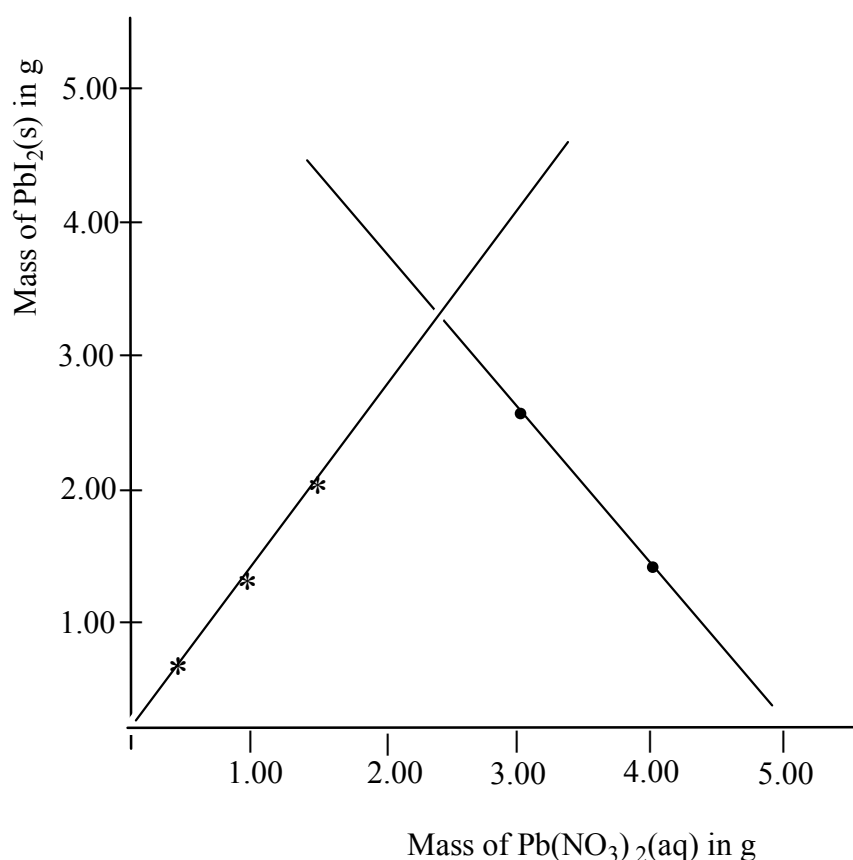
2. The total quantity of reactant is limited to 5.000 g. If either reactant is in excess, the amount in excess will be "wasted", because it cannot be used to form product. Thus, we obtain the maximum amount of product when neither reactant is in excess; there is a stoichiometric amount of each.

The balanced chemical equation for this reaction,
$$2 KI(aq) + Pb(NO_3)_2(aq) \rightarrow 2 KNO_3(aq) + PbI_2(s)$$
shows that stoichiometric quantities are two moles of KI (166.00 g/mol) for each mole of $Pb(NO_3)_2$ (331.21 g/mol). If we have 5.000 g total, we can let the mass of KI equal x g, so that the mass of $Pb(NO_3)_2 = (5.000 - x)$ g. Then we have

$$\text{amount KI} = x \text{ g KI} \times \frac{1 \text{ mol KI}}{166.00 \text{ g KI}} = \frac{x}{166.00}$$

$$\text{amount Pb(NO}_3)_2 = (5.000 - x) \text{ g Pb(NO}_3)_2 \times \frac{1 \text{ mol Pb(NO}_3)_2}{331.21 \text{ g Pb(NO}_3)_2} = \frac{5.000 - x}{331.21}$$

At the point of stoichiometric balance, amount KI = 2 × amount $Pb(NO_3)_2$

$$\frac{x}{166.00} = 2 \times \frac{5.000 - x}{331.21} \quad \text{or} \quad 331.21x = 10.00 \times 166.00 - 332.00x$$

$$x = \frac{1660.0}{331.21 + 332.00} = 2{,}503 \text{ g KI} \times \frac{1 \text{ mol KI}}{166.00 \text{ g KI}} = 0.01508 \text{ mol KI}$$
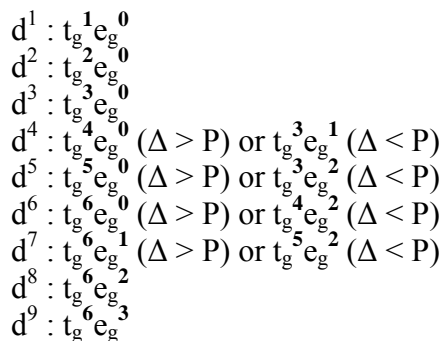
$$5.000 - x = 2.497 \text{ g Pb(NO}_3)_2 \times \frac{1 \text{ mol Pb(NO}_3)_2}{331.21 \text{ g Pb(NO}_3)_2} = 0.007539 \text{ mol Pb(NO}_3)_2$$

To determine the proportions precisely, we use the balanced chemical equation.
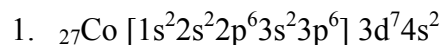
49

$$\text{maximum PbI}_2 \text{ mass} = 2.503 \text{ g KI} \times \frac{1 \text{ mol KI}}{166.00 \text{ g KI}} \times \frac{1 \text{ mol PbI}_2}{2 \text{ mol KI}} \times \frac{461.0 \text{ g PbI}_2}{1 \text{ mol PbI}_2} =$$
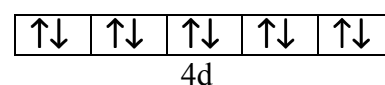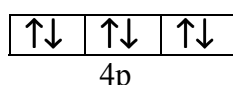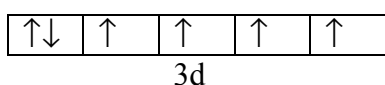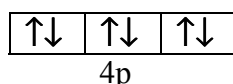
3.476 g PbI$_2$

Problem 15: Octahedral complexes

$d^1 : t_g{}^1 e_g{}^0$
$d^2 : t_g{}^2 e_g{}^0$
$d^3 : t_g{}^3 e_g{}^0$
$d^4 : t_g{}^4 e_g{}^0 \ (\Delta > P) \text{ or } t_g{}^3 e_g{}^1 \ (\Delta < P)$
$d^5 : t_g{}^5 e_g{}^0 \ (\Delta > P) \text{ or } t_g{}^3 e_g{}^2 \ (\Delta < P)$
$d^6 : t_g{}^6 e_g{}^0 \ (\Delta > P) \text{ or } t_g{}^4 e_g{}^2 \ (\Delta < P)$
$d^7 : t_g{}^6 e_g{}^1 \ (\Delta > P) \text{ or } t_g{}^5 e_g{}^2 \ (\Delta < P)$
$d^8 : t_g{}^6 e_g{}^2$
$d^9 : t_g{}^6 e_g{}^3$

Problem 16: Isomerism in Inorganic Chemistry

1. $_{27}\text{Co} \ [1s^2 2s^2 2p^6 3s^2 3p^6] \ 3d^7 4s^2$
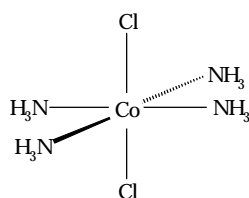
   Ar

   $\text{Co}^{3+} \ [\text{Ar}] 3d^6$

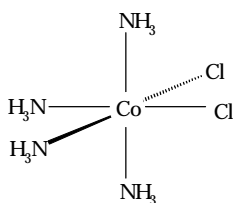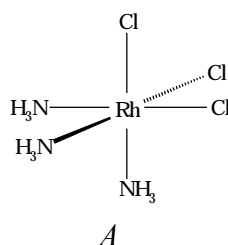2. dative covalent by the ligand into an empty metal orbital. d^2sp^3 hybridization
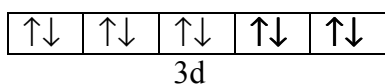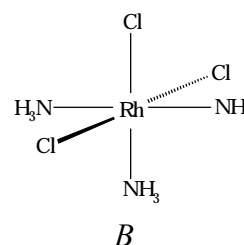

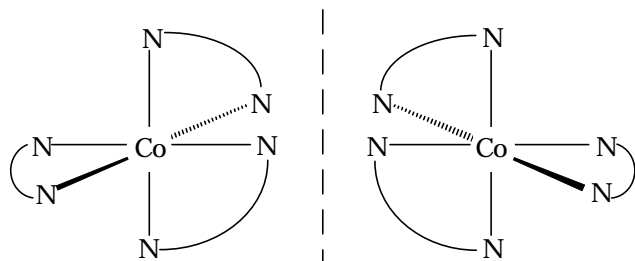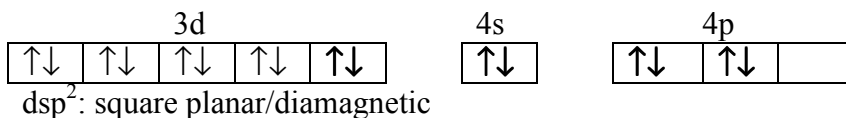   outer sphere paramagnetic complex

3. *trans*   *cis*

4. *fac*   *mer*

   A   *B*

5.   2 enantiomers $\pm \text{Co(en)}_3{}^{3+}$

Problem 17: Tetrahedral and square complexes

sp^3: tetrahedral/paramagnetic

dsp^2: square planar/diamagnetic
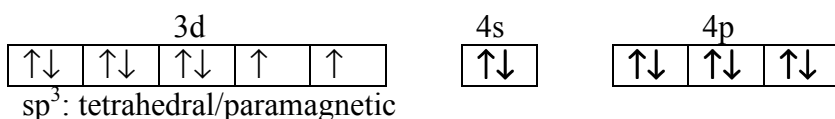
Problem 18: Copper enzyme

1. Cu: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$, Cu(I): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$,
   a. Cu(II): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$
2. Oxidised PC
3. A=ε.c.l $\Rightarrow$ c = 0.700 / (4500 x 1) = 1.56 x 10^{-4} mol dm^{-3}. 5 cm^3 of the solution contain 1.56 x 10^{-4} x 5 x 10^{-3} x 10500 x 1000 = 8.2 mg PC. #Cu atoms = 1.56 x 10^{-4} x 5 x 10^{-3} x 6.0221 x 10^{23} = 4.7 x 10^{17}
4. Electronic configurations :
   Zn(II): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$, Cd(II): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}$, Co(II): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7$, Ni(II): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$. Redox inactive are the Zn(II) and Cd(II) reconstituted Blue Copper Proteins.

Problem 19: Palladium nanoclusters

1. $N = \dfrac{N_o \cdot \rho \cdot V}{Atomic\,Weight}$ = 307 Pd(0) atoms per nanocluster

V = the volume of a nanocluster = $\dfrac{4}{3}\pi\left(\dfrac{D}{2}\right)^3$

According to the equation $y=10n^2+2$, the number of Pd(0) atoms in a 4 full-shells nanocluster is N = 1+12+42+92+162 = 309, hence it is a full shell cluster.

2. From Fig. 4 the H$_2$ uptake is ΔP_{H_2} = 4.15 − 2.05 = 2.10 atm in 184 min.

$\Delta P_{H_2} V = \Delta n_{H_2} RT$, hence Δn_{H_2} = 0.029 mol where V = 400-55=345 cm^3

Initially $n_{C_6H_{12}} = \dfrac{V\rho}{M} = \dfrac{5\,cm^3 x\,0.81\,g\,cm^{-3}}{(6x12.0107 + 12x1.00794)g\,mol^{-1}}$ = 0.048 mol

(i) Conversion = $\dfrac{reacted\,moles}{initial\,moles} = \dfrac{0.029}{0.048}$ = 0.60 = 60%

(ii) The catalytically active Pd(0) atoms are $\dfrac{162}{309}$ = 0.524 = 52.4% of the total Pd(0)

amount. So: $TON = \dfrac{n_{H_2}}{n_{Pd}} = \dfrac{0.029\,mol}{0.524x50x10^{-6}\,mol}$ = 1106 and

$TOF = \dfrac{TOF}{t} = \dfrac{1106}{184\,min}$ = 6.0 min^{-1}

3. The spectral regions (δ / ppm) and the respective relative integrals in the ^{1}H-NMR spectrum of hex-1-ene (Fig. 5a and Table) are assigned as follows:

1 2 3 4 5 CH$_3$(CH$_2$)$_2$CH$_2$CH=CH$_2$	1	2	3	4	5
	0.88-0.96 (3)	1.15-1.32 (4)	1.99-2.08 (2)	5.65-5.79 (1)	4.85-4.98 (2)

The integral ratios of the second ^{1}H-NMR spectrum (Fig. 5b and Table) suggest that both hex-1-ene and hexane are present. The differences in the integral values of the spectral regions 0.88-0.96 ppm and 1.12-1.37 ppm must be due to the presence of hexane. The relative integrals of second spectrum are converted as shown in the table below:

	δ / ppm	relative integral
Solution of the reaction (Fig. 5b)	0.88-0.96	3+6
	1.12-1.37	4+8
	1.99-2.08	2
	4.85-4.98	2
	5.65-5.79	1

So, the spectral regions (δ / ppm) and the respective relative integrals in the ^{1}H-NMR spectrum corresponding to hexane are assigned as follows:

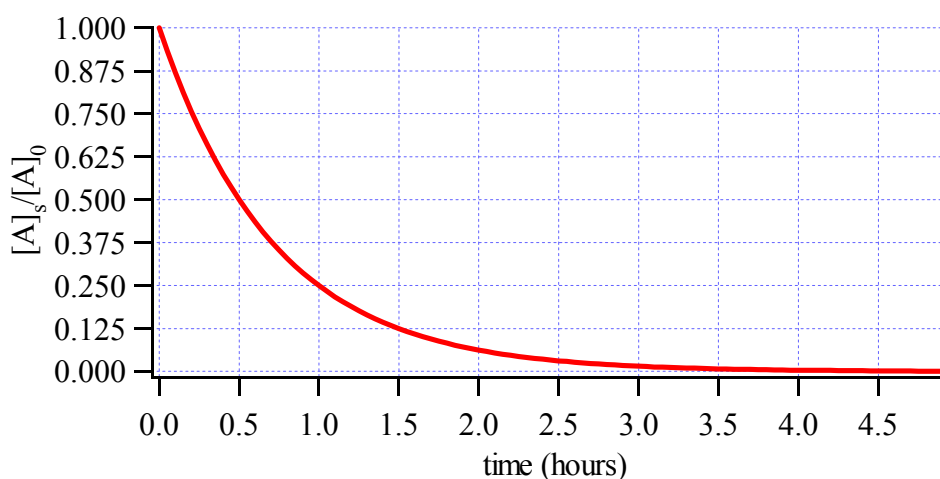| **1' 2' 1'** $CH_3(CH_2)_4CH_3$	1' 0.88-0.96 (6)	2' 1.15-1.32 (8)

Finally, comparing the integral values per proton for the hex-1-ene and hexane the % conversion of hex-1-ene to hexane, after 30 min is 50%

Problem 20: Drug kinetics

$$A_s \xrightarrow{k_1} A_b \longrightarrow products \quad (1)$$
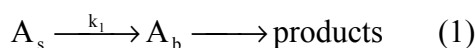
$$-\frac{d[A]_s}{dt} = k_1[A]_s \quad (2)$$

Integration of Eq. 2 gives $[A]_s = [A]_o \exp(-k_1t)$, where $[A]_o$ the concentration of the drug in the stomach at zero time.

$$\frac{[A]_o - [A]_s}{[A]_o} = 0.75 \Rightarrow \frac{[A]_s}{[A]_o} = 0.25 = \left(\frac{1}{2}\right)^2$$ Since ¼ of the initial amount remains after one hour, $(¼)^2 = 1/16 = 0.625$ will remain after 2 hours, which corresponds to 4 half lives. That is 6.25% of $[A]_s$ is left.

Problem 21: Br$_2$ + CH$_4$ reaction mechanism

1 The rate of formation of CH$_3$Br is given by the equation:

$$v = +\frac{d[CH_3Br]}{dt} = k_3[CH_3][Br_2] \quad (1)$$

The "steady state" approximations for CH$_3$ and Br are given by the equations:

$$\frac{d[CH_3]}{dt} = k_2[Br][CH_4] - [CH_3](k_3[Br_2] + k_4[HBr]) = 0 \quad (2)$$

$$\frac{d[Br]}{dt} = 2k_1[Br_2][M] - k_2[Br][CH_4] + [CH_3](k_3[Br_2] + k_4[HBr]) - 2k_5[Br]^2[M] = 0 \quad (3)$$

From equation (**2**):

$$[CH_3]_{st} = \frac{k_2[Br][CH_4]}{k_3[Br_2] + k_4[HBr]} \quad (4)$$

From equations (**3**) and (**4**):

$$[Br]_{st} = \left(\frac{k_1}{k_5}[Br_2]\right)^{\frac{1}{2}} \quad (5)$$

By combining equations (**1**), (**4**) and (**5**) the expression for the rate of formation of CH$_3$Br as a function of the concentrations of the stable species that are involved in the reaction is given by equation (**6**):

$$v = \left(\frac{k_1}{k_5}\right)^{\frac{1}{2}} k_2 \cdot \frac{[Br_2]^{\frac{1}{2}}[CH_4]}{\dfrac{k_4[HBr]}{k_3[Br_2]} + 1} \quad (6)$$

2

Start of the reaction	**II**
Steady state condition	**I**
Near to the end of the reaction	**III**

3

Start of the reaction	[Br$_2$] >> [HBr] and since k$_3$ ≈ k$_4$: k$_3$ [Br$_2$] >> k$_4$[HBr], so k$_4$[HBr] / k$_3$ [Br$_2$] << 1
Steady state condition	-
Near to the end of the reaction	[Br$_2$] << [HBr] and since k$_3$ ≈ k$_4$: k$_3$ [Br$_2$] << k$_4$[HBr], so k$_4$[HBr] / k$_3$ [Br$_2$] >> 1

Problem 22: Buffer solutions

1. The equilibrium, which governs the concentration of H^+ within the solution is
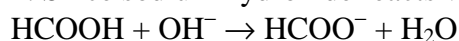
$$HCOOH \rightleftharpoons HCOO^- + H^+$$

Hence $K_a = \dfrac{[H^+][HCOO^-]}{[HCOOH]} = 2.1 \times 10^{-4}$

and since $[HCOOH] \approx 0.200$ M and $[HCOO^-] \approx 0.150$ M

$$[H^+] = 2.1 \times 10^{-4} \times \frac{0.200}{0.150} = 2.8 \times 10^{-4} \text{ M}$$

and **pH = 3.55**.

2. Since sodium hydroxide reacts with formic acid:

$$HCOOH + OH^- \rightarrow HCOO^- + H_2O$$

the concentration of formic acid in the solution is reduced to

$$[HCOOH] = 0.200 \text{ M} - 0.0100 \text{ M} = 0.190 \text{ M}$$

and the concentration of formate is increased to

$$[HCOO^-] = 0.150 \text{ M} + 0.0100 \text{ M} = 0.160 \text{ M}$$

Therefore: $[H^+] = 2.1 \times 10^{-4} \times \dfrac{0.190}{0.160} = 2.5 \times 10^{-4}$ M

and **pH = 3.60**

Note that the addition of sodium hydroxide, which is a strong base, causes a very small increase of the pH of the solution.

3. Let V the volume of the solution of sodium hydroxide. Therefore, the final volume of the solution will be $(100.0 + V)$ mL and the number of mmol of CH_3COOH and OH^- which are mixed are 100.0 mL $\times$ 0.150 mmol/mL = 15.00 mmol and V mL $\times$ 0.200 mmol/mL = 0.200$\times$V mmol, respectively. From the reaction:

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$$
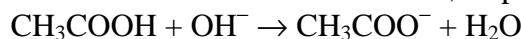
it is obvious that the amount of acetate produced is 0.200$\times$V mmol and the amount of acetic acid which remains unreacted is $(15.00 - 0.200 \times V)$ mmol. Hence, the concentration of each constituent in the buffer solution is:

$$[CH_3COOH] = \frac{(15.00 - 0.200 \times V)}{100.0 + V} \text{ M}$$

and $[CH_3COO^-] = \dfrac{0.200 \times V}{100.0 + V}$ M

From the acid dissociation constant expression of acetic acid

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

it can be derived $\dfrac{[CH_3COO^-]}{[CH_3COOH]} = \dfrac{K_a}{[H^+]}$

and $\dfrac{\dfrac{0.200 \times V}{100.0 + V} \text{ M}}{\dfrac{(15.00 - 0.200 \times V)}{100.0 + V} \text{ M}} = \dfrac{1.8 \times 10^{-5}}{1.0 \times 10^{-5}}$

from which **V = 48.21 cm^{-3}**.
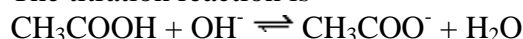
4. a

5. (i) c, (ii) b
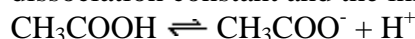
6. (i) b, (ii) d

7. (i) c, (ii) c

8. (i) b, (ii) c

Problem 23: Titrations of weak acids

The titration reaction is

$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$

a) Initial pH

The pH of the solution before the titration begins, is calculated by the acid dissociation constant and the initial concentration of CH_3COOH:

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

From the acid dissociation constant expression:

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

the concentration of H^+ can be calculated:

$[H^+] = \sqrt{1.8 \times 10^{-5} \times 0.1000} = 1.34 \times 10^{-3} \, M$ and $pH = 2.87$

b) pH after the addition of 10.00 cm^3 of titrant

The solution contains acetic acid and sodium acetate. Therefore it is a buffer solution. The concentration of each constituent is calculated:

$$[CH_3COOH] = \frac{(50.00 \, cm^3 \times 0.1000 \, M) - (10.00 \, cm^3 \times 0.1000 \, M)}{60.00 \, cm^3} = 0.0667 \, M$$

$$[CH_3COO^-] = \frac{10.00 \, cm^3 \times 0.1000 \, M}{60.00 \, cm^3} = 0.01667 \, M$$

These concentrations are then substituted into the dissociation constant expression of acetic acid for calculating the concentration of $[H^+]$:

$$[H^+] = 1.8 \times 10^{-5} \times \frac{0.0667}{0.01667} = 7.20 \times 10^{-5} \, M \text{ and } pH = 4.14$$

c) pH at the equivalence point

At the equivalence point, all acetic acid has been converted to sodium acetate and the pH is calculated from the hydrolysis of acetate ions:

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$
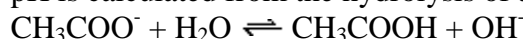
The volume of titrant required for the equivalence point (V_{ep}) is calculated:

$$V_{ep} = \frac{50.00 \, cm^3 \times 0.1000 \, M}{0.1000 \, M} = 50.00 \, cm^3$$

and the total volume of solution is 100.0 cm^3. Therefore, at this point of the titration $[CH_3COOH] = [OH^-]$ and

$$[CH_3COO^-] = \frac{50.00 \, cm^3 \times 0.1000 \, M}{100.0 \, cm^3} - [OH^-] \approx 0.0500 \, M$$

$$\frac{[OH^-]^2}{0.0500 \, M} = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

$[OH^-] = \sqrt{0.0500 \times 5.56 \times 10^{-10}} = 5.27 \times 10^{-6} \, M$

$pOH = 5.28$ and thus $pH = 14 - 5.28 = 8.72$

d) pH after the addition of 50.10 cm^3 of titrant

At this stage, all acetic acid has been converted to sodium acetate and the pH of the solution is calculated by the excess of sodium hydroxide, which has been added:

$$[OH^-] = \frac{(50.10 \, cm^3 \times 0.1000 \, M) - (50.00 \, cm^3 \times 0.1000 \, M)}{100.1 \, cm^3} = 1.0 \times 10^{-4} \, M$$

Therefore $pOH = 4.00$ and $pH = 10.00$
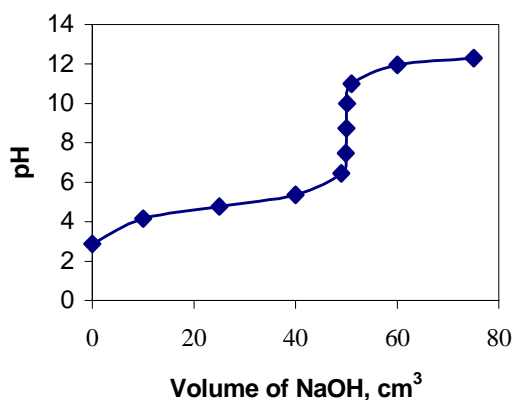
Titration curve of 0.1000 M acetic acid with 0.1000 M NaOH

e) Selection of indicator

Since the pH at the equivalence point is 8.72, the appropriate acid base indicator is phenolphthalein.

2. (i) b, (ii) c, (iii) a, (iv) b, (v) c, (vi) d

Problem 24: Separation by extraction

1 Starting with an amount W_0 of S in phase 1, after the extraction this amount is distributed between the two phases as follows:

$$W_0 = (C_S)_1 V_1 + (C_S)_2 V_2$$

Since $D = (C_S)_2 / (C_S)_1$, we have

$$W_0 = (C_S)_1 V_1 + D(C_S)_1 V_2 = (DV_2 + V_1)(C_S)_1$$

Therefore, after removing phase 2, the remaining amount of S in phase 1 is:

$$W_1 = (C_S)_1 V_1 = W_0 \frac{V_1}{DV_2 + V_1}$$

By repeating extraction with a fresh portion of volume V_2 of phase 2, the amount W_1 of S is similarly distributed. After removing phase 2, the remaining amount of S in phase 1 is:

$$W_2 = (C_S)_1 V_1 = W_1 \frac{V_1}{DV_2 + V_1} = W_0 \left(\frac{V_1}{DV_2 + V_1} \right)^2$$

and so on. Therefore after n extractions with a fresh portion of volume V_2 of phase 2, the remaining amount of S in phase 1 will be:

$$W_n = W_0 \left(\frac{V_1}{DV_2 + V_1} \right)^n$$

2. (a) The remaining fraction of S after 1 extraction with 100 mL of chloroform is calculated using Equation 1.4:

$$f_1 = \frac{W_1}{W_0} = \left(\frac{50}{3.2 \times 100 + 50} \right)^1 = 0.135,$$

therefore the percentage of S extracted is $100 - 13.5 = $ **86.5%**

(b) The remaining fraction of S after 4 extractions with 25 mL of chloroform each time is similarly calculated:

$$f_4 = \frac{W_4}{W_0} = \left(\frac{50}{3.2 \times 25 + 50} \right)^4 = 0.022,$$

therefore the percentage of S extracted is $100 - 2.2 = \mathbf{97.8\%}$. The result is indicative of the fact that successive extractions with smaller individual volumes of extractant are more efficient than a single extraction with all the volume of the extractant.

3. Using Equation 1-4 we have:

$$0.01 = \left(\frac{100.0}{9.5 \times 25.0 + 100.0} \right)^n \quad \text{or} \quad 0.01 = 0.2963^n \text{ hence } n = \log(0.01)/\log(0.2963) =$$

3.78, therefore at least **4** extractions are required.

4. The equilibria involved are represented schematically as follows:
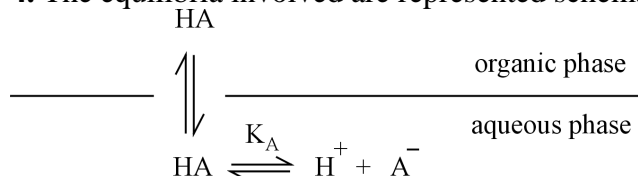
We have (subscripts w and o denote concentrations in aqueous and organic phase, respectively)

$$D = \frac{(C_{HA})_o}{(C_{HA})_w} = \frac{[HA]_o}{[HA]_w + [A^-]_w}$$

$K_D = [HA]_o / [HA]_w \quad \text{and} \quad K_a = [H^+]_w [A^-]_w / [HA]_w$

Combining all three equations we finally obtain:

$$D = \frac{K_D [H^+]_w}{[H^+]_w + K_a} \tag{1.5}$$

Last equation predicts that if $[H^+]_w \gg K_a$ (strongly acidic aqueous phase), then $D \approx K_D$ (i.e. D acquires the maximum possible value) and the acid is extracted (or prefers to stay) in the organic phase. On the other hand, if $[H^+]_w \ll K_a$ (strongly alkaline aqueous phase), we have $D \approx K_D[H^+]_w / K_a$, and because of the small value of D the acid is then extracted (or prefers to stay) in the aqueous phase. In this way, by regulating the pH of the aqueous phase, the course of extraction is shifted towards the desired direction.

5. (a) By using the previously derived Equation 1.5, we obtain the following plots of the D/K_D ratio vs. pH.
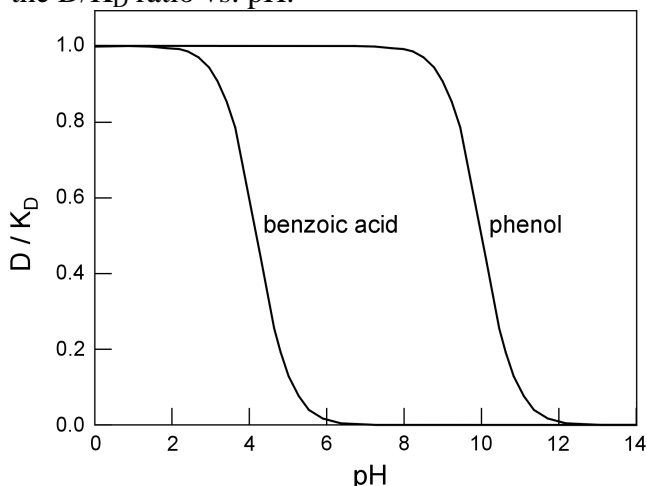
(b) From these plots it is clear that at the pH region 7-8 the distribution ratio for benzoic acid will be practically 0, whereas that of phenol will acquire the maximum possible value. Therefore, phenol can be efficiently separated from an aqueous solution of both compounds by extraction with diethylether, provided that the pH of this solution has been adjusted in the range 7 to 8 (e.g. by the presence of excess of $NaHCO_3$).

6. (a) The equilibria involved are represented schematically as follows:

$$OxH$$
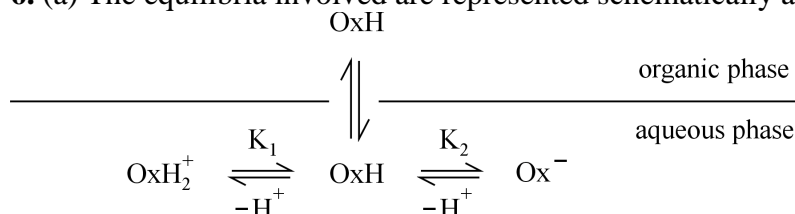
We have the expressions

$$D = \frac{(C_{OxH})_o}{(C_{OxH})_w} = \frac{[OxH]_o}{[OxH_2^{\,+}]_w + [OxH]_w + [Ox^-]_w}$$

$$K_D = [OxH]_o / [OxH]_w = 720$$

$$K_1 = \frac{[OxH]_w [H^+]_w}{[OxH_2^{\,+}]_w} = 1 \times 10^{-5}$$

$$K_2 = \frac{[Ox^-]_w [H^+]_w}{[OxH]_w} = 2 \times 10^{-10}$$

Combining all four equations, we have the sought-for expression

$$D = \frac{[OxH]_o}{\dfrac{[OxH^+]_w [H^+]_w}{K_1} + [OxH]_w + \dfrac{K_2 [OxH]_w}{[H^+]_w}}$$

$$= \frac{[OxH]_o}{[OxH]_w} \cdot \frac{1}{\dfrac{[H^+]_w}{K_1} + 1 + \dfrac{K_2}{[H^+]_w}} = \frac{K_D}{\dfrac{[H^+]_w}{K_1} + 1 + \dfrac{K_2}{[H^+]_w}}$$

(b) Using last equation we obtain the following D-pH plot:
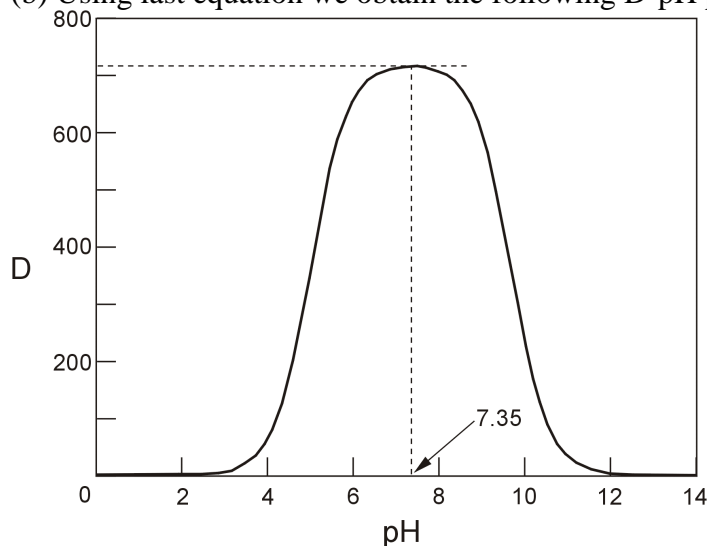
(c) We calculate the 1st and 2nd derivative of the denominator, i.e.,

$$F([H^+]_w) = \frac{[H^+]_w}{K_1} + 1 + \frac{K_2}{[H^+]_w}$$

whereupon we have the 1st derivative $F'([H^+]_w) = \dfrac{1}{K_1} - \dfrac{K_2}{[H^+]_w^2}$

and for the 2nd derivative $F''([H^+]_w) = \dfrac{2K_2}{[H^+]_w^3}$

Since always $F''([H^+]_w) > 0$, then when $F'([H^+]_w) = 0$, $F([H^+]_w)$ is minimum under these conditions. Consequently, the distribution ratio is maximum when

$$\frac{1}{K_1} - \frac{K_2}{[H^+]^2} = 0 \text{ or } [H+]_w = \sqrt{K_1 \, K_2} = \sqrt{(1\times10^{-5})(2\times10^{-10})} = 4.5\times10^{-8} \text{ M}$$

or pH = **7.35**

Problem 25: Mass spectroscopy

1 The ionic fragment $SiCl_2^+$ will be represented by the following peaks:

M = 98	$^{28}Si\,^{35}Cl_2^+$
M+1 = 99	$^{29}Si\,^{35}Cl_2^+$
M+2 = 100	$^{28}Si\,^{35}Cl\,^{37}Cl^+$ + $^{30}Si\,^{35}Cl_2^+$
M+3 = 101	$^{29}Si\,^{35}Cl\,^{37}Cl^+$
M+4 = 102	$^{30}Si\,^{35}Cl_2^+$ + $^{28}Si\,^{35}Cl\,^{37}Cl^+$
M+5 = 103	$^{29}Si\,^{37}Cl_2^+$
M+6 = 104	$^{30}Si\,^{37}Cl_2^+$

Therefore, the correct answer is **7**.

2 The expected peaks and the corresponding probabilities are:

m/z = 45	$^{10}B\,^{35}Cl$:	$0.199\times0.7577 = 0.151$
m/z = 46	$^{11}B\,^{35}Cl$:	$0.801\times0.7577 = 0.607$
m/z = 47	$^{10}B\,^{37}Cl$:	$0.199\times0.2423 = 0.048$
m/z = 48	$^{11}B\,^{37}Cl$:	$0.801\times0.2423 = 0.194$

Hence, the base peak has nominal mass M = 46 and the relative intensities are:

M−1 = 45	(0.151/0.607)×100	= 24.9%
M = 46		= 100%
M+1 = 47	(0.048/0.607)×100	= 7.9%
M+2 = 48	(0.194/0.607)×100	= 32.0%

Therefore, the correct answer is **C**.

3 For the ion N_2^+ we have:

M: $^{14}N\,^{14}N = (0.99634)^2 = 0.9927$

M+1: $^{14}N\,^{15}N + ^{15}N\,^{14}N = 2\times(0.99634\times0.00366) = 0.007293$

hence, (M+1)/M = 0.007293/0.9927 = 0.00735 or 0.735%

For the ion CO^+ we have:

M: $^{12}C\,^{16}O = 0.989\times0.99762 = 0.9866$

M+1: $^{12}C\,^{17}O + ^{13}C\,^{16}O = (0.989\times0.00038) + (0.011\times0.99762) = 0.01135$

hence, (M+1)/M = 0.01135/0.9866 = 0.0115 or 1.15%

For the ion CH_2N^+ we have:

M: $^{12}C\,^1H_2\,^{14}N = 0.989\times(0.99985)^2\times0.99634 = 0.9851$

M+1: $^{13}C\,^1H_2\,^{14}N + ^{12}C\,^1H\,^2H\,^{14}N + ^{12}C\,^2H\,^1H\,^{14}N + ^{12}C\,^1H_2\,^{15}N = $
$0.011\times(0.99985)^2\times0.99634+2\times0.989\times0.99985\times0.00015\times0.99634+$
$+0.989\times(0.99985)^2\times0.00366 = 0.01487$

hence, (M+1)/M = 0.01487/0.9851 = 0.0151 or 1.51%

For the ion $C_2H_4^+$ we have:

M: $^{12}C_2\,^1H_4 = (0.989)^2\times(0.99985)^4 = 0.9775$

M+1: $^{13}C\,^{12}C\,^1H_4 + ^{12}C\,^{13}C\,^1H_4 + ^{12}C_2\,^2H\,^1H_3 + ^{12}C_2\,^1H\,^2H\,^1H_2 +$
$+ ^{12}C_2\,^1H_2\,^2H\,^1H + ^{12}C_2\,^1H_3\,^2H = 2\times0.011\times0.989\times(0.99985)^4 +$
$+ 4\times0.989\times0.00015\times(0.99985)^3 = 0.02234$

hence, (M+1)/M = 0.02234/0.9775 = 0.0229 or 2,29%

Therefore the correct answer is (b) CO^+

Problem 26 Chemical Structure and Absolute Stereochemistry of Coniine
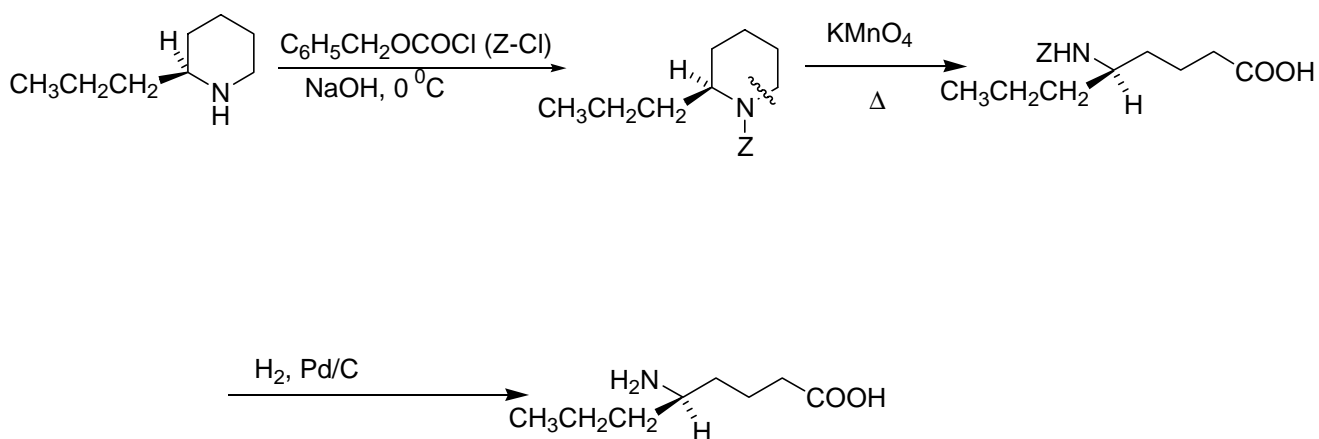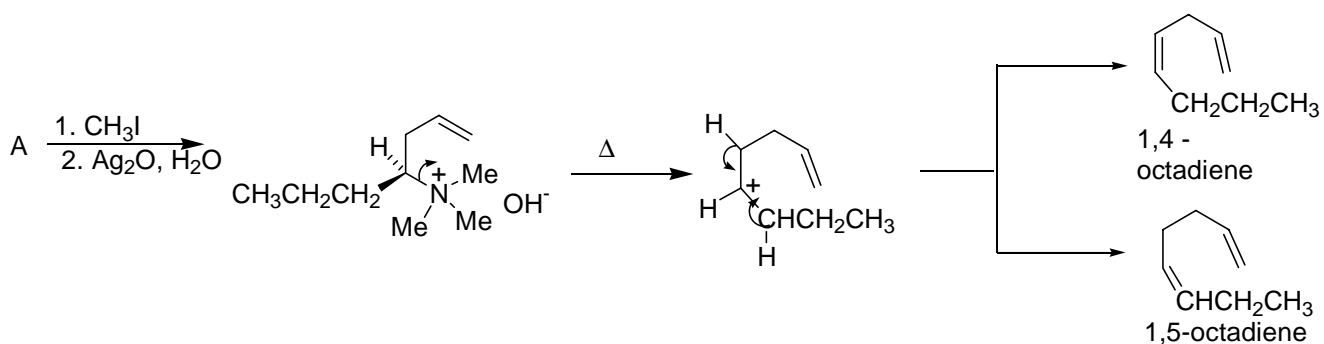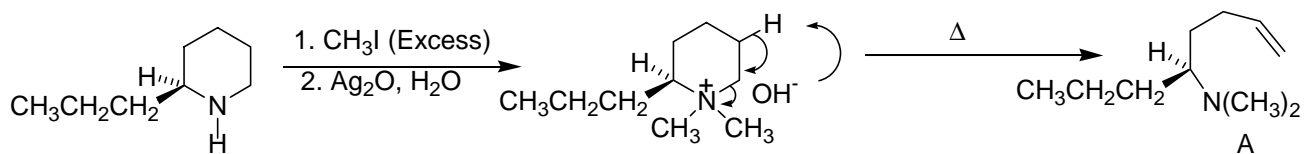
(S)- 5-aminooctanoic acid

The KMnO$_4$ oxidation reaction step is based on A. M. Castano, J.M. Cuerva, A. M. Echavarren, *Tetrahedron Letters,* 35, 7435-7438 (1994)

Problem 27: The chemistry and identification of flavonoids

1.
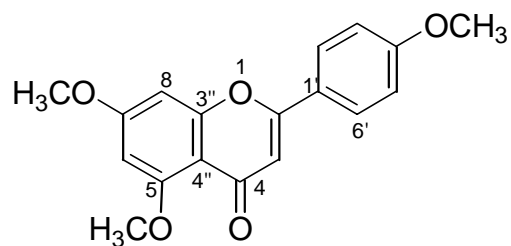
B
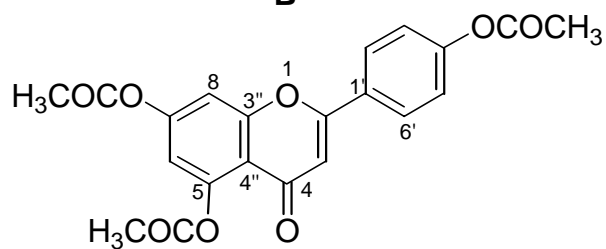
C

2. a) down field. The ^{1}H-NMR resonance of phenolic proton involvement in hydrogen bonding will be observed at very low magnetic field (~ 12ppm).

3.
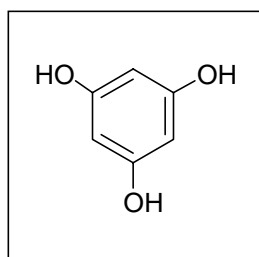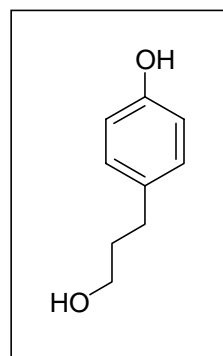
D   **E**

4. ^{13}C-NMR would be expected to show three characteristic peaks of the three different carbonyl groups.

C

Problem 28: Synthesis of peptides

1
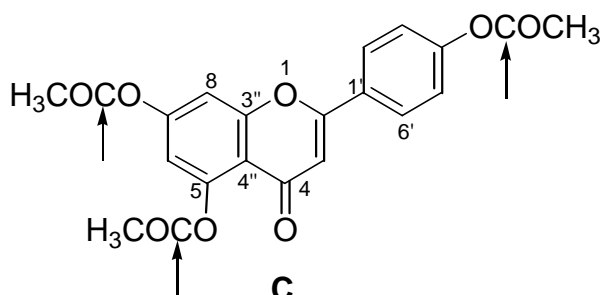
Dipeptide I

Dipeptide II

Dipeptide III
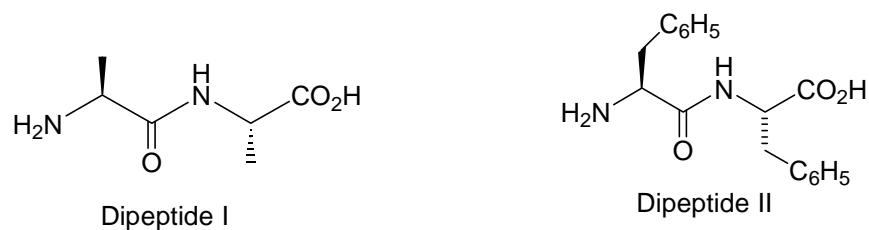
Dipeptide IV

The cyclic dipeptides (diketo piperazines) must also be considered:

DP-I

DP-II

DP-III
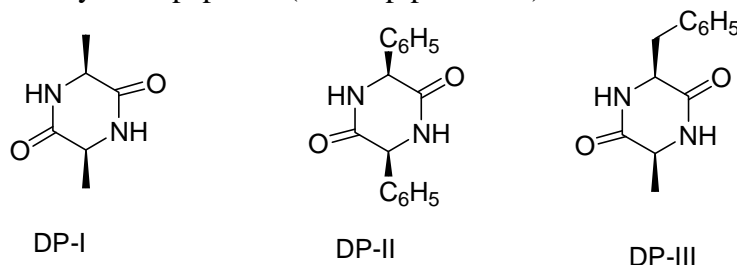
2. Best answers are 5 and 2.

3.
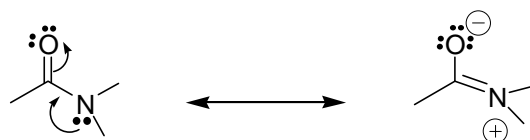
4. Benzyl chloroformate, reagent N° 4, would react easily with an amine in the following way:

$$C_6H_5CH_2OCOCl + H_2NR \xrightarrow{\text{base}} C_6H_5CH_2OCONHR + HCl$$
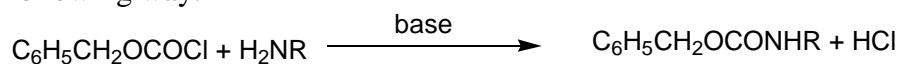
5. If we assume the intermediate formation of a carbonium ion, the ease of formation of such ion would parallel its stability. Electron delocalization is most extensive in case D:
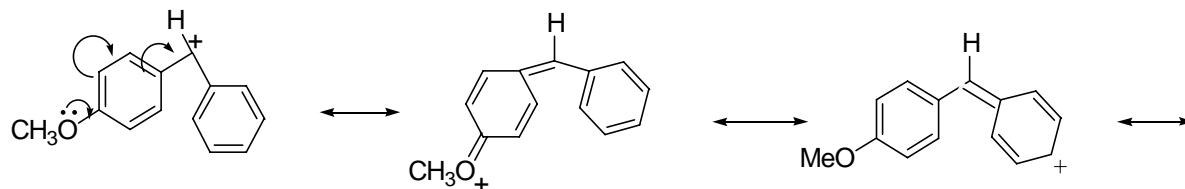
And least effective in case A:
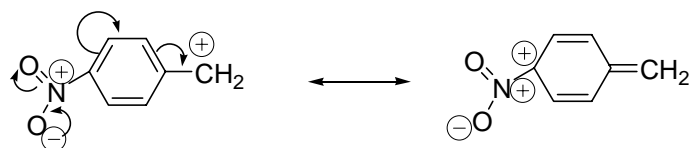
In the same way the cation from B is better stabilized than the cation from C. Therefore, the order of increasing lability is: A<C<B<D.

Problem 29: Oleuropein hydrolysis

1.
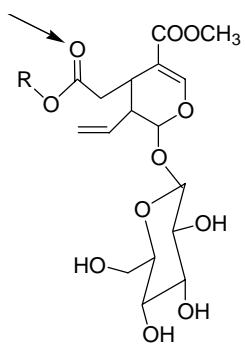
(a)
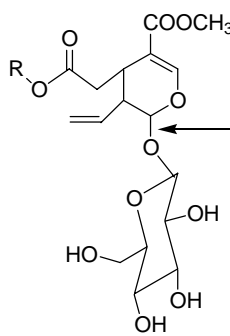
(b)

2.
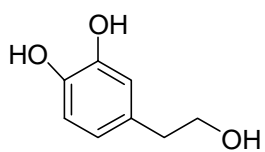
The correct structure is C

3.
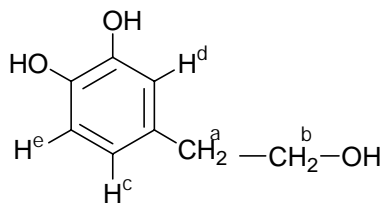
Problem 30: Stereochemistry of the Addition Reactions to Alkenes

a)

	CH$_3$			CH$_3$	
H—		—Br	Br—		—H
Br—		—H	H—		—Br
H—		—Br	H—		—Br
	CH$_3$			CH$_3$	

No   **Yes**

b)

	CH$_3$			CH$_3$	
H—		—Br	H—		—Br
H—		—Br	Br—		—H
H—		—Br	Br—		—H
	CH$_3$			CH$_3$	

No   **Yes**

c)

	CH$_3$			CH$_3$	
Br—		—H	Br—		—H
H—		—Br	Br—		—H
Br—		—H	H—		—Br
Br—		—H	Br—		—H
	CH$_3$			CH$_3$	

Yes   **Yes**

d)

	CH$_3$			CH$_3$	
H—		—Br	H—		—Br
H—		—Br	Br—		—H
H—		—Br	Br—		—H
H—		—Br	H—		—Br
	CH$_3$			CH$_3$	

No   **No**
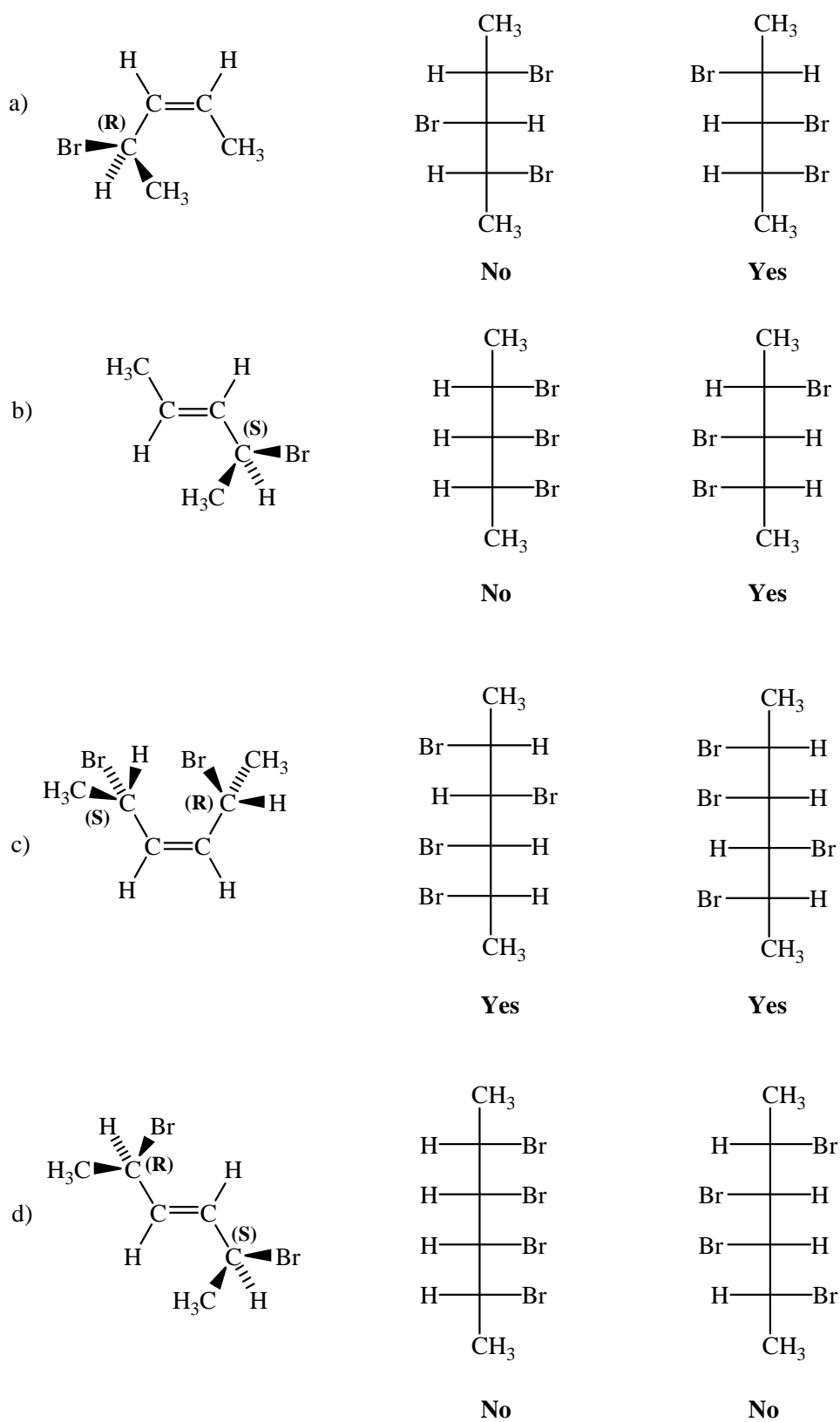
Problem 31: Identification of Organic Compounds

Problem 32: Lipases

a)

(6)	(5)	(4)	(3)	(2)	(1)

b)

c)

CH₃CO₂CH₃   CH₃CO₂CH₂CH₃   CH₃CO₂CH₂—⟨phenyl⟩   CH₃CO₂C(CH₃)₃

(1)	(2)	(3)	(4)

Problem 33: Polymers

1. The volume of the Larnax is 40.9 cm x 34.1 cm x 17.0 cm = 23.7 dm^3. Consequently, the Larnax will be filled with m=V d = 23.2 kg

This quantity corresponds to (23200/10^6) x N$_A$ Vergina Star Copolymers, or 0.0232 x N$_A$ Vergina Star Copolymers, where N$_A$ is the Avogadro number.

2. The following reaction scheme should be followed in order to synthesize the Vergina Star Copolymer:

(A)

Due to the steric hindrance of the styrillithium anion, only one polymeric chain can react with each –SiCl$_2$ group.

$+$ 8 LiCl

Due to the lower steric hindrance of the polyisoprenyllithium living ends, the reaction goes to completion.

Fundamental constants

Quantity	Symbol	Value	Unit
Speed of light	c	299 792 458	$m\ s^{-1}$
Permeability of vacuum	μ_0	$4\pi \times 10^{-7} =$ $12.566\ 370\ 614\ldots \times 10^{-7}$	$N\ A^{-2}$
Permittivity of vacuum	ε_0	$1/\mu_0 c^2 =$ $8.854\ 187\ 817 \times 10^{-12}$	$C^2\ m^{-2}\ N^{-1}$ or $F\ m^{-1}$
Planck constant	h	$6.626\ 068\ 76 \times 10^{-34}$	$J\ s$
Electron charge	e	$1.602\ 176\ 462 \times 10^{-19}$	C
Electron mass	m_e	$9.109\ 381\ 88 \times 10^{-31}$	kg
Proton mass	m_p	$1.672\ 621\ 58 \times 10^{-27}$	kg
Avogadro constant	N_A	$6.022\ 141\ 99 \times 10^{23}$	mol^{-1}
Faraday constant	F	96 485.3415	$C\ mol^{-1}$
Boltzmann constant	k	$1.380\ 650\ 3 \times 10^{-23}$	$J\ K^{-1}$
molar gas constant	R	8.314 472	$J\ K^{-1}\ mol^{-1}$
atomic mass unit	u	$1.660\ 538\ 73 \times 10^{-27}$	kg

Source: *Physics Today* **55** BG6 (2002)

The unit 1 M is commonly used as an abbreviation for 1 mol dm^{-3}.
1 cal = 4.184 J

The constants listed on this page and the periodic table will be available to students during the 35th IChO.

Periodic Table of the Elements

Legend:
- Atomic number, Symbol
- Mean atomic mass (u)
- Melting point (°C)
- Boiling point (°C)

Z	Symbol	Mean atomic mass (u)	Melting point (°C)	Boiling point (°C)
1	H	1.00794	-259.34	-252.87
2	He	4.002602		-268.93
3	Li	6.941	180.5	1342
4	Be	9.012182	1287	2471
5	B	10.811	2075	4000
6	C	12.0107	4440	
7	N	14.00674	-210.00	-195.79
8	O	15.9994	-218.79	-182.95
9	F	18.998403	-219.66	-188.12
10	Ne	20.1797	-248.59	-246.08
11	Na	22.989770	97.80	883
12	Mg	24.3050	650	1090
13	Al	26.981538	660.32	2519
14	Si	28.0855	1414	3265
15	P	30.973761	44.15	280.5
16	S	32.066	115.21	444.60
17	Cl	35.4527	-101.5	-34.04
18	Ar	39.948	-189.35	-185.85
19	K	39.0983	63.38	759
20	Ca	40.078	842	1484
21	Sc	44.955910	1541	2836
22	Ti	47.867	1668	3287
23	V	50.9415	1910	3407
24	Cr	51.9961	1907	2671
25	Mn	54.938049	1246	2061
26	Fe	55.845	1538	2861
27	Co	58.933200	1495	2927
28	Ni	58.6934	1455	2913
29	Cu	63.456	1084.62	2562
30	Zn	65.39	419.53	907
31	Ga	69.723	29.76	2204
32	Ge	72.61	938.25	2833
33	As	74.92160		614
34	Se	78.96	221	685
35	Br	79.904	-7.2	58.8
36	Kr	83.80	-157.36	-153.22
37	Rb	85.4678	39.31	688
38	Sr	87.62	777	1382
39	Y	88.90585	1522	3345
40	Zr	91.224	1855	4409
41	Nb	92.90638	2477	4744
42	Mo	95.94	2623	4639
43	Tc	(98)	2157	4265
44	Ru	101.07	2334	4150
45	Rh	102.90550	1964	3695
46	Pd	106.42	1554.9	2963
47	Ag	107.8682	961.78	2162
48	Cd	112.411	321.07	767
49	In	114.818	156.60	2072
50	Sn	118.710	231.93	2602
51	Sb	121.760	630.63	1587
52	Te	127.60	449.51	988
53	I	126.90447	113.7	184.4
54	Xe	131.29	-111.75	-108.04
55	Cs	132.90545	28.44	671
56	Ba	137.327	727	1897
57	La	138.9055	918	3464
72	Hf	178.49	2233	4603
73	Ta	180.9479	3017	5458
74	W	183.84	3422	5555
75	Re	186.207	3186	5596
76	Os	190.23	3033	5012
77	Ir	192.217	2446	4428
78	Pt	195.078	1768.4	3825
79	Au	196.96655	1064.18	2856
80	Hg	200.59	-38.83	356.73
81	Tl	204.3833	302	1473
82	Pb	207.2	327.46	1749
83	Bi	208.98038	271.40	1564
84	Po	(209)	254	962
85	At	(210)	302	
86	Rn	(222)	-71	-61.7
87	Fr	(223)	27	
88	Ra	(226)	7000	
89	Ac	(227)	1051	3198
104	Rf	(261)		
105	Db	(262)		
106	Sg	(263)		
107	Bh	(262)		
108	Hs	(265)		
109	Mt	(266)		
110	Uun	(269)		
111	Uuu	(272)		
112	Uub	(277)		
113				
114				

Lanthanide series

Z	Symbol	Mean atomic mass (u)	Melting point (°C)	Boiling point (°C)
58	Ce	140.116	798	3443
59	Pr	140.90765	931	3520
60	Nd	144.24	1021	3074
61	Pm	(145)	1042	3000
62	Sm	150.36	1074	1794
63	Eu	151.964	822	1529
64	Gd	157.25	1313	3273
65	Tb	158.92534	1356	3230
66	Dy	162.50	1412	2567
67	Ho	164.93032	1474	2700
68	Er	167.26	1529	2868
69	Tm	168.93421	1545	1950
70	Yb	173.04	819	1196
71	Lu	174.967	1663	3402

Actinide series

Z	Symbol	Mean atomic mass (u)	Melting point (°C)	Boiling point (°C)
90	Th	232.0381	1750	4788
91	Pa	231.03588	1572	
92	U	238.0289	1135	4131
93	Np	(237)	644	
94	Pu	(244)	640	3228
95	Am	(243)	1176	2011
96	Cm	(247)	1345	3100
97	Bk	(247)	1050	
98	Cf	(251)	900	
99	Es	(252)	860	
100	Fm	(257)	1527	
101	Md	(258)	827	
102	No	(259)	827	
103	Lr	(262)	1627	

Additions and corrections to the preparatory problems

Problem 24: (p. 17)
6. In the structures of OxH_2^+, OxH and Ox^-, N is part of the ring, not of an attached group.

Problem 25: (p.19)
3 … change "peak is 1.15" to "peak 1.15% of the base peak".

Problem 27: (p. 20-21)
3 When treated with 2 M NaOH (under reducing conditions)

(top of p. 21) Apigenin → NaOH 2M (above arrow), Na-Hg amalgam (below arrow)

Spectrum I, Compound D ($C_6H_6O_3$). 200 MHz ^{1}H-NMR (simulated spectrum (ACD-data bases). Note that phenolic H atoms do not appear due to rapid exchange.

Spectrum II, Compound E ($C_9H_{12}O_2$): 60 MHz ^{1}H-NMR spectrum in DMSO-d_6 + $CDCl_3$.

Problem 36: (p. 34)
C. 6. Fmoc loading: mmol/g resin=(A_{sample}-A_{blanc})/1.75 x mg of resin, or, equivalently,

Fmoc loading=$\dfrac{n}{m} = \dfrac{A_{sample} - A_{blank}}{1750\, m}$, where n is the amount of Fmoc-amino acid attached to resin (in mmol) and m the mass of resin (in g).

Solution to problem 1: (p. 42)
In the 1st equation π should be π^2.

Solution to problem 6: (p. 44)
The answer to the second question is A (as implied by the solution for the first question).