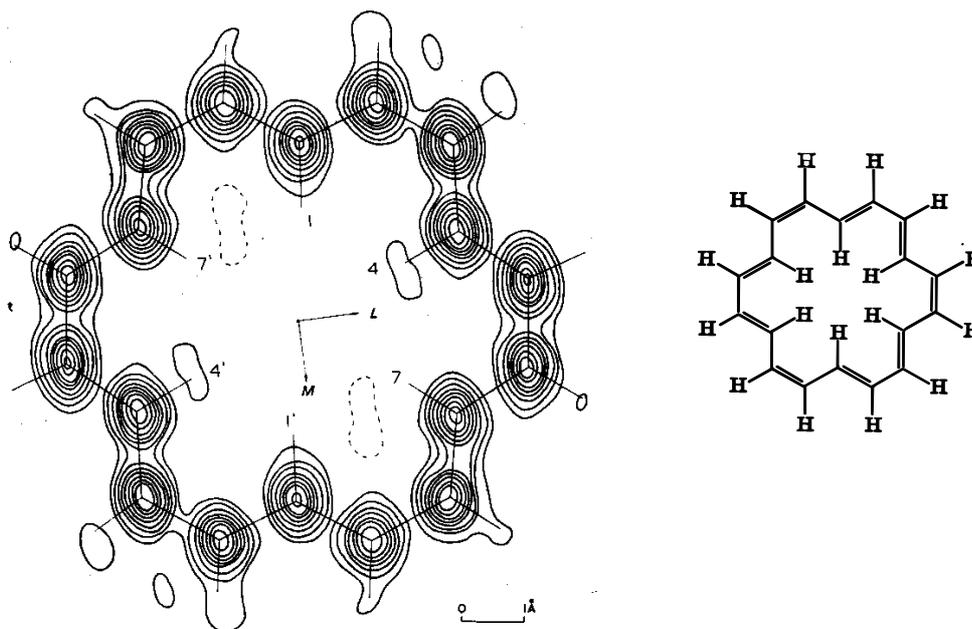


Problem 1: Proton – antiproton atom

Experimental and theoretical work has shown that for each of the fundamental particles such as protons (p) and electrons (e) there exist antiparticles which differ from their counterparts usually in one property only, but have the same mass. Antielectrons (or positrons) are positively charged, whereas antiprotons (\bar{p}) are negatively charged. Antimatter composed of antiparticles had not been observed until very recently. Antihydrogen consisting of positrons attached to antiprotons was created in laboratories in 2002 (*Nature* **419**, 456 (2002)). An even more exotic form of an atom would consist of a combination of a proton and an antiproton ($p\bar{p}$). Assuming that the $p\bar{p}$ atom is hydrogen-like, (a) what is its ionization energy and its Bohr radius? (b) What is the wavelength of the transition from the ground electronic state to the first excited state?

Problem 2: Annulene

The crystallographic structure of [18] annulene ($C_{18}H_{18}$) has been determined with x-ray crystallography (*Acta Cryst.* **19**, 227 (1965)). The following figure shows the electron density in the mean molecular plane; the contours are shown at intervals of $1 e.\text{\AA}^{-3}$. The absorption spectrum of this molecule has been studied too. The location of



the absorption maximum can be estimated using the model of "the particle on a ring".

The energy of a particle moving on a circular well is given by $E_n = \frac{h^2 N^2}{2m_e L^2}$, where h

is Planck's constant, m_e the mass of the electron, L the full path of the electron and N its quantum number. N takes the integer values $0, \pm 1, \pm 2, \pm 3, \dots$, therefore each level has a two-fold degeneracy except for the zero level which is nondegenerate.

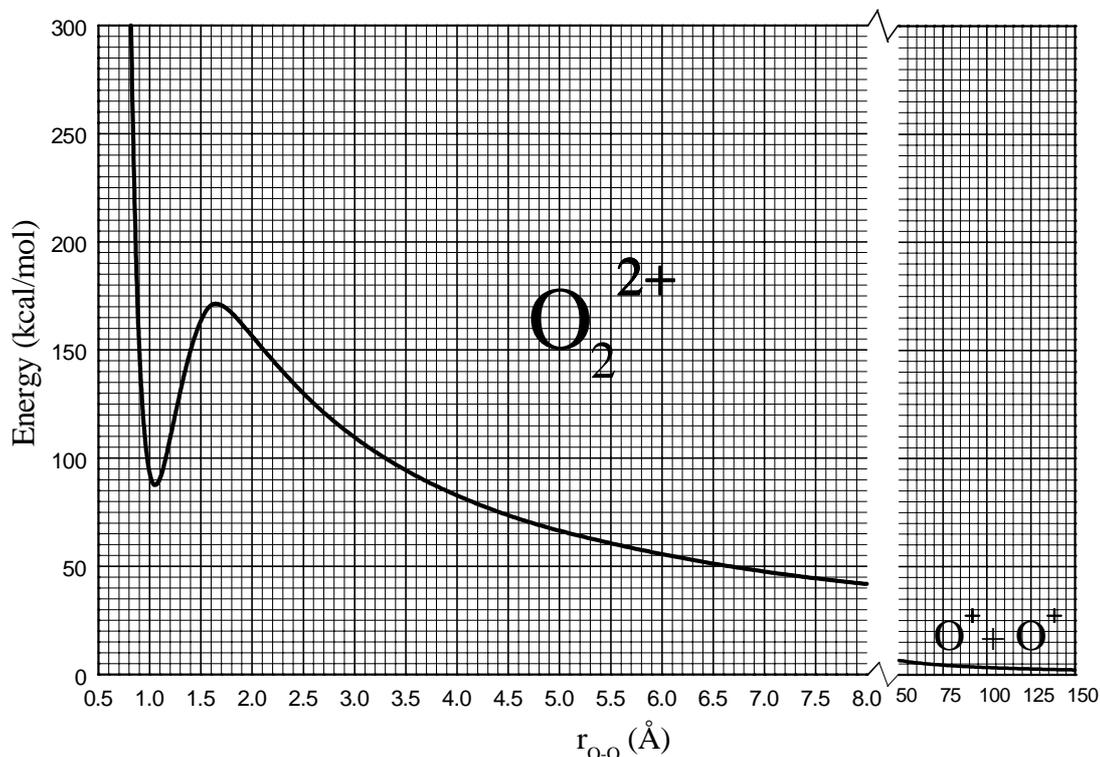
Assuming a mean bond length between carbon atoms equal to 1.40 \AA , determine the wavelength of the lowest electronic transition.

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

O_2^{2+} is a strange molecule because its existence is unexpected. Indeed, one would expect that two approaching O^+ cations should repel each other so that the energy of

the system rises and formation of O_2^{2+} is impossible. However, the molecular cation O_2^{2+} was first observed experimentally in the early sixties. This means that although coulombic repulsion is important at short distances, covalent bonding must be very strong and, indeed, takes over stabilizing the system. A triple bond is formed by the coupling of the three unpaired p electrons on each O^+ yielding $[O \equiv O]^{2+}$.

The potential energy curve of this molecule is shown in the graph below, and because of its particular shape, it is often called “volcano-type potential”.

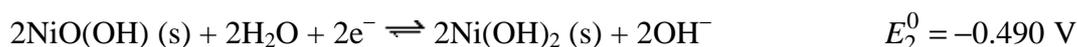


Questions

1. What should be the minimum kinetic energy of two colliding O^+ cations in order for them to form O_2^{2+} ?
2. Is O_2^{2+} thermodynamically stable? Yes No
3. Is O_2^{2+} kinetically stable (metastable)? Yes No
4. How much energy is needed to cause dissociation of O_2^{2+} ?
5. It is claimed that O_2^{2+} could be used for storing energy. If true, give the energy that could be stored per molecule of O_2^{2+} .
6. What is the $O^+ - O^+$ bond length?
7. What is the minimum approach distance between two O^+ cations in order to form O_2^{2+} ?

Problem 4: Electrochemistry: Nicad batteries

Sealed type Ni – Cd batteries (“Nicad”) are widely used in portable devices such as cordless power tools, cellular telephones, camcorders, portable computers, etc. Ni – Cd batteries are cost-effective and have high cycle lives and excellent low or high-temperature performance. They require no maintenance and can be recharged up to 2000 times. A typical sealed type Ni – Cd cell consists of the following two half-cells:



where E_1^0 , E_2^0 are standard reduction potentials at 25°C.

Questions:

1. Which reaction occurs at the cathode? Give the corresponding Nernst equation for the potential.
2. Which reaction occurs at the anode? Give the corresponding Nernst equation for the potential.
3. Write a balanced equation that shows the reaction that occurs spontaneously as the cell discharges.
4. Calculate the electromotive force E of the cell at 25°C.
5. What is the mass of Cd contained in a cellular telephone Ni – Cd battery of a nominal capacity of 700 mAh?

Problem 5: Boiler

A medium size apartment house is equipped with a heating furnace (boiler) for generating hot water during the cold months. The nominal heating power of the furnace is 116 kW. The building has an oil tank with a storage capacity of 4 m³ of heating oil. The enthalpy of combustion of the oil, which consists mostly of heavy liquid saturated hydrocarbons, is 43000 kJ/kg and its density is about 0.73 g/cm³.

1. Indicate how long the heater can operate continuously before it becomes necessary to refill the tank.
A. 5h B. 2.2 days C. 12 days D. 3.3 weeks E. 2.1 months.
2. What is the approximate amount of CO₂ generated and released into the atmosphere per hour when the furnace is operating?
A. 300 g B. 1 kg C. 5 kg D. 10 kg E. 30 kg

Problem 6: Ammonium nitrate

One elementary laboratory demonstration in introductory Chemistry is the mixing of NH₄NO₃ with water in a thermally isolated container. In this problem, 80 g NH₄NO₃ are mixed with 1 kg H₂O which are both initially at 0 °C. Determine the final state of the system.

Given are: heat capacity of liquid water 76 J mol⁻¹ K⁻¹, enthalpy of fusion for water 6.01 kJ mol⁻¹, enthalpy of solution of NH₄NO₃ in water 25.69 kJ mol⁻¹, cryoscopic constant for water 1.86 K kg mol⁻¹,

The final temperature is equal to A. 1.86 K, B. 3.72 K, C. 3.72 °C, D. 1.86 °C, E. -3.72 °C, F. -3.72 K, G. 1.86 K, H. -1.86 °C, I. -3.83 °C.

The final state of the system consists of A. 1 liquid and 1 solid phase, B. 1 liquid and 2 solid phases, C. 1 liquid phase, D. 1 solid phase, E. 2 liquid phases, F. 2 solid phases, G. 2 liquid and 1 solid phase.

The mixing process can be described as (check all that apply)

induced, spontaneous, reversible, irreversible, one where separation of components is impossible by any means, adiabatic, non-adiabatic, isobaric, isothermal, isochoric, isenthalpic, isoenergetic.

The change in entropy (ΔS) of the system is A. > 0, B. = 0, C. < 0, D. indeterminate.

Problem 7: Carbon dioxide

CO₂ fire extinguishers are metal canisters containing CO₂ under pressure higher than 1 atm. Given are [NIST Webbook of Chemistry, CRC]: Critical point $P_c = 73.75$ bar,

$T_c = 304.14$ K; Triple point $P_3 = 5.1850$ bar, $T_3 = 216.58$ K. Assume room temperature is 25°C .

1. What is the required pressure in the fire extinguisher for the coexistence of solid and liquid CO_2 ?

A. 2 bar B. 5.185 bar C. 20 bar D. 73.8 bar E. not possible under any pressure

2. What is the required pressure in the fire extinguisher for the coexistence of liquid and gaseous CO_2 ?

A. about 2 bar, B. 5.1850 bar, C. about 20 bar, D. about 63 bar, E. 73.8 bar, F. about 100 bar, G. not possible under any pressure

Problem 8: Iron crystal

The crystalline form of iron, known as α -Fe, has a *body centered cubic* (bcc) unit cell with an edge length of 2.87 \AA . Its density at 25°C is 7.86 g/cm^3 . Another - higher temperature - crystalline form, known as γ -Fe, has a *face centered cubic* (fcc) unit cell with an edge length of 3.59 \AA .

(a) Calculate the atomic radius of iron in α -Fe and use the above facts to estimate Avogadro's number, assuming that the atoms in α -Fe touch each other *along the body diagonal*.

(b) Calculate the atomic radius of iron in γ -Fe as well as the density of γ -Fe, assuming that the atoms touch each other *along the face diagonal*.

(c) Assume that an interstitial atom (other than Fe) fits perfectly *at the center of α -Fe cube face* [i.e., a position with fractional coordinates $(\frac{1}{2}, 0, \frac{1}{2})$], hence it just touches the surface of an iron atom at the center of the unit cell. What is the radius of the interstitial atom?

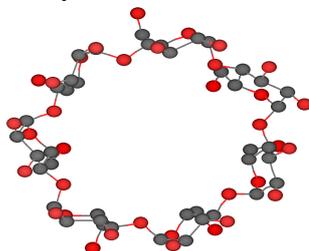
(d) In a similar manner as in (c), calculate the radius of a perfectly fitted interstitial atom *at the center of the γ -Fe unit cell*.

(e) How much oversize is a carbon atom, having a radius of 0.077 nm , as compared with the interstitial atoms in questions (c) and (d)?

(f) The (200) lattice planes of a cubic structure coincide with the faces of the unit cell as well as those planes that cut the axis at half of the cell edge (see figure). Suppose that a monochromatic X-ray beam, incident on a α -Fe crystal, is diffracted on these planes at an angle of 32.6° . Calculate the wavelength of the X-ray beam.

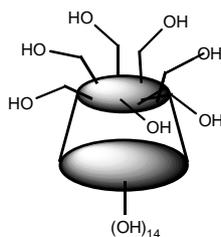
Problem 9: Cyclodextrine

Cyclodextrins are cyclic sugars commonly composed of 6,7,or 8 glucose units called α , β , γ -cyclodextrins respectively.



β -cyclodextrin (O atoms are shown in red and C atoms in black)

Their shape resembles a truncated cone with a hydrophobic cavity and a hydrophilic exterior lined with hydroxyl groups.



A plethora of hydrophobic molecules can be encapsulated in the cavity forming inclusion complexes



Structure of a cyclodextrin with the pheromone of *Dacus Oleae*

This property in combination with the fact that they are natural, water soluble compounds makes them suitable candidates for many applications, especially as carriers for pharmaceutical compounds.

Cyclodextrin inclusion complexes form crystals the molecular structure of which can be determined by X-ray crystallography. Consider a crystal of such an inclusion complex of β -cyclodextrin with the empirical formula $C_{42}H_{70}O_{35} \cdot C_{12}H_{12}N_2 \cdot 12H_2O$. It crystallizes in space group $P2_1$. Its unit cell dimensions (with uncertainties) are $a = 15.394(7) \text{ \AA}$, $b = 31.995(12) \text{ \AA}$, $c = 15.621(7) \text{ \AA}$, $\beta = 103.738(15)^\circ$, ($\alpha = \gamma = 90^\circ$).

In this unit cell there are four molecules of the inclusion complex (2 molecules in the asymmetric unit). What is the molecular volume in \AA^3 of the inclusion complex and what is the density of the crystal.

Problem 10: Infrared spectroscopy

1. How many vibrational modes does a CO, a H_2O , a benzene, or a C_{60} molecule undergo? Pick the most appropriate answer for each molecule.

A. 1, B. 2, C. 3, D. 4, E. about 30, F. 54, G. 120, H. 174, I. 720, J. not possible to determine based on information provided

2. Two unknown diatomic molecules show a single peak of vibrational absorption in the infrared region of the electromagnetic spectrum. Molecule XY absorbs at a higher frequency than molecule WZ. Which of the following statements are correct?

1. XY and WZ are heteronuclear
2. XY has a stronger bond than WZ
3. XY has a larger mass than WZ
4. The vibrational eigen frequency of XY is higher than that of WZ

A. 1 B. 2 C. 3 D. 4 E. 1 and 2 F. 1 and 3 G. 1 and 4 H. 2 and 3 I. 2 and 4 J. 3 and 4 K. 1, 2 and 3 L. 1, 2 and 4 M. 1, 3 and 4 N. 2, 3 and 4 O. 1, 2, 3 and 4 P. all are incorrect

Problem 11: Radioactivity and chemical reactivity

Give a “yes” or “no” answer to the following questions:

1. Is the γ -radiation of radioactive objects electromagnetic in nature?
2. Do any non-radioactive exist with atomic number greater than 83?
3. Do any radioactive isotopes exist with atomic number less than 82?
4. Do noble gases form compounds with other elements?

5. Is Cs the most easily ionizable non-radioactive element?

Problem 12: Carbon dating

^{14}C is a β radioactive isotope of carbon with a half-life $t_{1/2} = 5700$ y. It exists in nature because it is formed continuously in the atmosphere as a product of nuclear reactions between nitrogen atoms and neutrons generated by cosmic rays.

We assume that the rate of formation has remained constant for thousands of years and is equal to the rate of decay, hence the amount of ^{14}C in the atmosphere has reached steady state. As a result ^{14}C accompanies the stable isotopes ^{12}C and ^{13}C in the atmosphere and participates indistinguishably in all carbon chemical reactions. It forms CO_2 with oxygen and enters all living systems through photosynthesis under constant $\text{C}_{14}/\text{C}_{12}$ isotopic ratio, labeling the organic molecules.

This fact is used for dating samples of biological origin (e. g., silk, hair, etc.) which have been isolated by some way after the death of the organism (e.g., in an ancient grave). The $\text{C}_{14}/\text{C}_{12}$ ratio in these samples does not remain constant, but decreases with time because the ^{14}C present is disintegrating continuously.

The specific radioactivity of ^{14}C in living systems is 0.277 bequerel per gram of total carbon [1 Bq = 1dps (disintegration per second)]

- Calculate the age of an isolated sample with a $^{14}\text{C}/^{12}\text{C}$ ratio which is 0.25 that of a contemporary sample.
- What happens to a ^{14}C atom when it disintegrates?
- What do you expect will happen to a ^{14}C containing organic molecule (e.g., DNA, protein, etc.) of a living organism when this ^{14}C atom disintegrates.
- Calculate the radioactivity of a 75 kg human body due to ^{14}C and the number of ^{14}C atoms in the body, given that the amount of total carbon is about 18.5 %.

Problem 13: Uranium

Uranium (U, $Z=92$) is a naturally occurring radioactive element which occurs as a mixture of ^{238}U (99.3%, $t_{1/2} = 4.47 \times 10^9$ y) and ^{235}U (0.7%, $t_{1/2} = 7.04 \times 10^8$ y). Both radioisotopes are alpha emitters and were created at the time of nucleosynthesis. Their decay is followed by a different sequence of alpha ($^4\text{He}^{2+}$) and beta (β^-) disintegration's, which lead through successive transmutations of intermediate radioactive products to stable lead isotopes, ^{206}Pb and ^{207}Pb , respectively (Pb, $Z=82$). These sequences form two (out of a total of three) so-called radioactive series. Gamma radiation, which appears in various disintegrations, does not affect the transmutations.

^{235}U is less stable than ^{238}U and reacts more easily with thermal neutrons to undergo fission, a fact which makes ^{235}U a suitable fuel for nuclear reactors. The fission reaction is as follow:



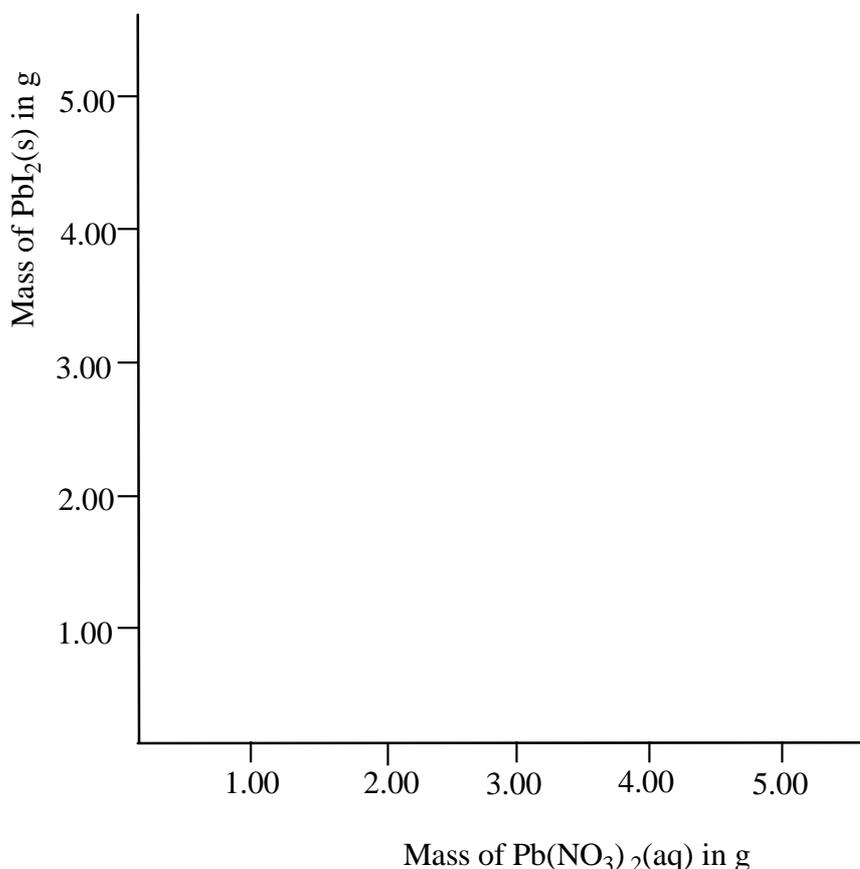
- Calculate the total number of alpha and beta particles emitted in each of the two complete natural radioactive series ($^{238}\text{U} \rightarrow ^{206}\text{Pb}$ and $^{235}\text{U} \rightarrow ^{207}\text{Pb}$).
- Explain why in both radioactive series some chemical elements appear more than once.
- Assuming that the initial isotopic abundance (i.e., at the time of nucleosynthesis) was equal for the two uranium isotopes ($^{235}\text{U} : ^{238}\text{U} = 1:1$), calculate the age of the Earth (i.e., the time that has elapsed since nucleosynthesis).
- Calculate the amount (in g) of carbon required to release energy equal to the energy released by the complete fission with neutrons of 1g ^{235}U , using to the following oxidation reaction:



Problem 14: Lead iodide

Lead nitrate ($\text{Pb}(\text{NO}_3)_2$) 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



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 $\text{Pb}(\text{NO}_3)_2$.

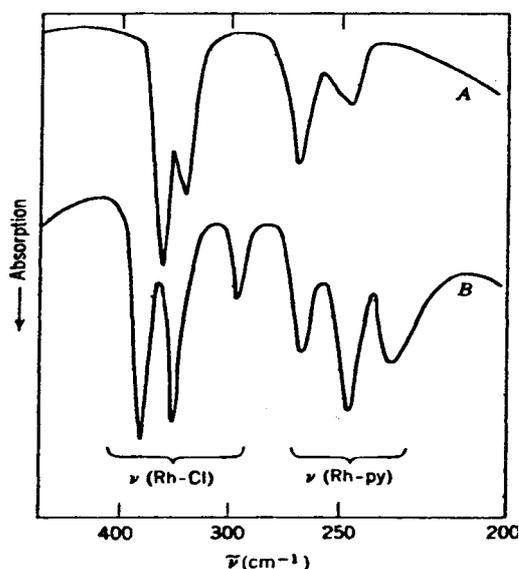
Problem 15: Octahedral complexes

The doubly charged metal ions of the first row transition elements with the configuration d^1, d^2, \dots, 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 $\text{M}(\text{g})^{2+}$, 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 Werner¹ 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 $\text{Co}(\text{NH}_3)_6^{3+}$. Thus, there are two isomers corresponding to the chemical formula $\text{CoCl}_3 \cdot 4\text{NH}_3$, the *praseo* and *violeo* complexes. There are also two structural isomers for the complex $\text{Rh}(\text{py})_3\text{Cl}_3$ (py: pyridine – only its N-atom



need be considered). The far infrared spectra in the $450\text{--}200\text{ cm}^{-1}$ 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*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ complex, there are two *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ 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 $\text{Co}(\text{NH}_3)_6^{3+}$?
2. What is the type of bonding of NH_3 in $\text{Co}(\text{NH}_3)_6^{3+}$, 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 $\text{Rh}(\text{py})_3\text{Cl}_3$ complexes. Assign the spectra to each of the two complexes.
5. How many isomers does the complex with the formula $[\text{Co}(\text{en})_3]\text{I}_3$ exhibit?

Problem 17: Tetrahedral and square complexes

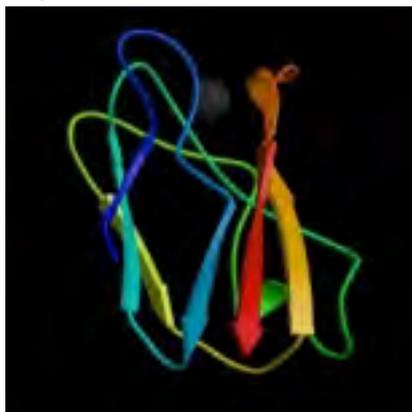
Four coordination is much less common than six coordination in first row d-block elements, mainly due to energy stabilization by the ligands. The most symmetric spatial location of ligands about a central ion is the tetrahedron, but square planar complexes are also well known. In tetrahedral geometry 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 $[\text{Ar}]3\text{d}^8$. With chloride ion a paramagnetic NiCl_4^{2-} complex ion is formed, whereas with cyanide (CN^-) ion a diamagnetic $\text{Ni}(\text{CN})_4^{2-}$ 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 $4500 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$). 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).

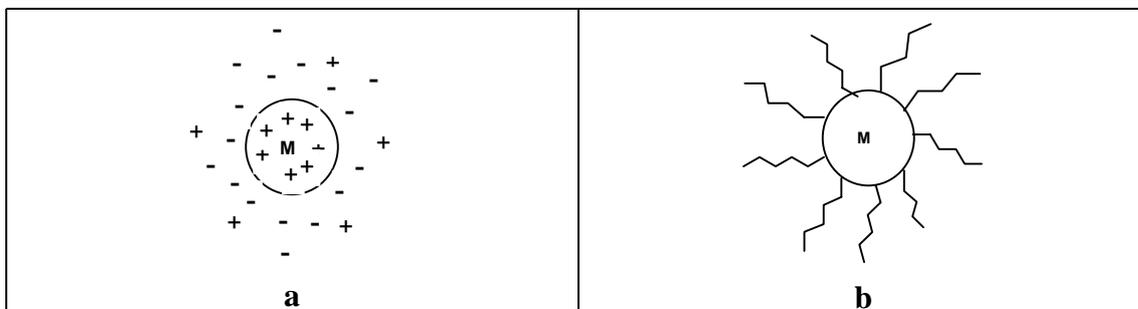


Figure 1. A schematic illustration for (a) an electrostatically stabilized metal (M) particle and (b) a sterically stabilized metal particle.

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 $y = 10n^2 + 2$ ($n = 1, 2, 3, \dots$) (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.

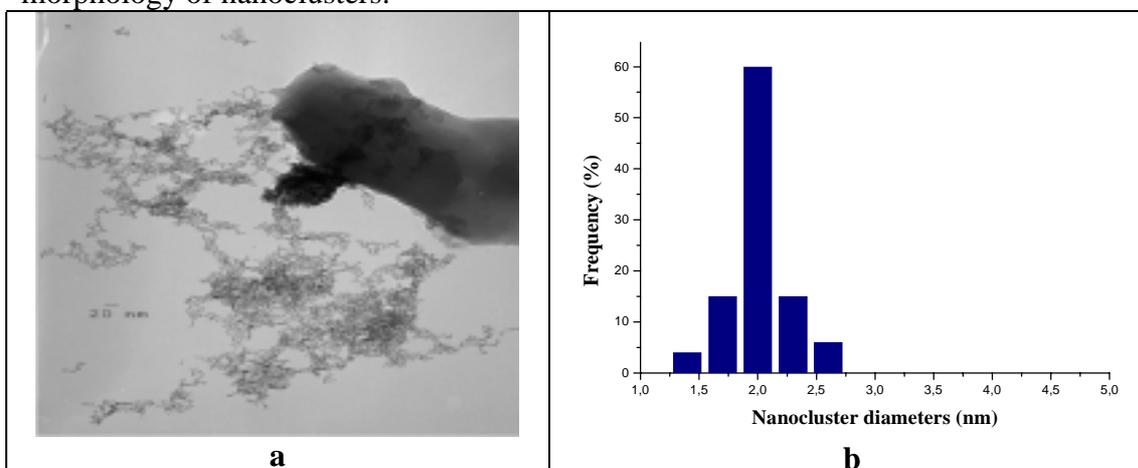
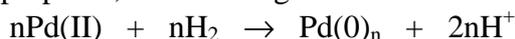


Figure 3. (a) Transmission electron microscopy image of Pd(0) nanoclusters stabilized by a polymer. (b) Histogram of the Pd(0) nanocluster diameters.

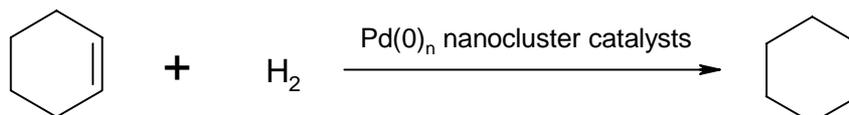
1 By direct reaction of Pd(II)-polymer complex (1 mM in water solution) with gas H₂, Pd(0) nanoclusters are prepared, as following:



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, $\rho = 12.02 \text{ g/cm}^3$.

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 H₂ reaction:



In a 400 cm³ 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 cm³ of acetone, followed by the addition of 5 cm³ of cyclohexene. The reactor was then sealed, purged several times with prepurified H₂ (dry and O₂ free) and the H₂ 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. H₂ pressure vs. time until the end of the reaction is presented in Fig. 4.

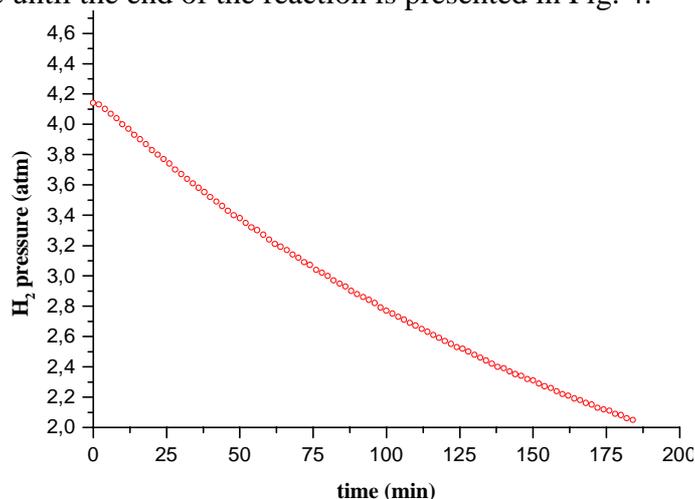
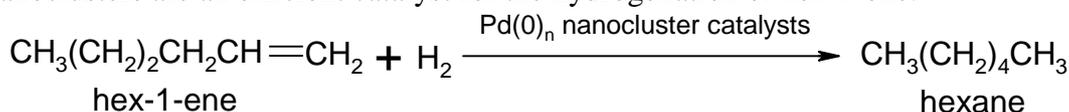


Figure 4. Hydrogen uptake curve. Temperature 30°C, 0.5 μmol of Pd(0), 5 cm³ of cyclohexene.

(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 $TON = \text{moles } H_2 \text{ consumed} / \text{moles of catalytically active Pd(0)}$ and the turnover frequency, TOF, where $TOF = \text{moles } H_2 \text{ consumed} / \text{moles of catalytically active Pd(0)} / \text{time (min) of the consumption}$. Density of cyclohexene, $\rho = 0.81 \text{ g cm}^{-3}$.

3 The polymer-protected Pd(0)_n nanocluster catalyst are also used for the catalytic hydrogenation of hex-1-ene by H₂. The experiment was performed under the conditions cited above, except 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 $^1\text{H-NMR}$ 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.

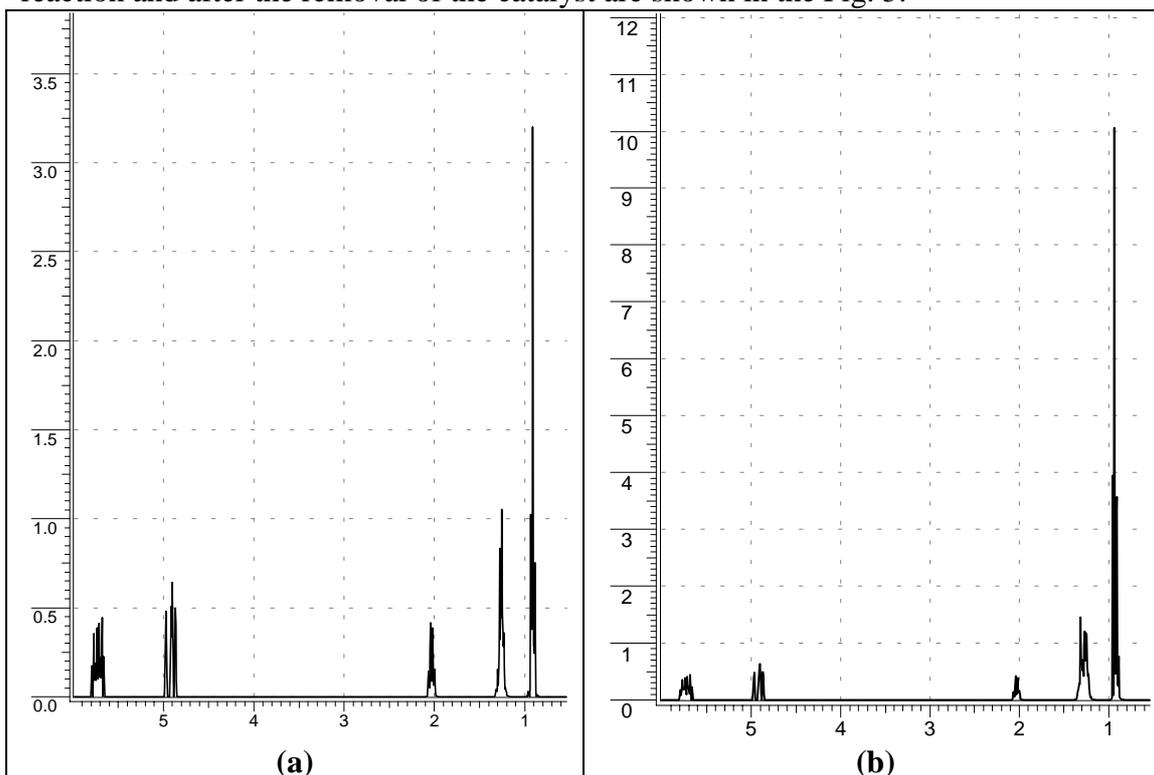


Figure 5. 300 MHz $^1\text{H-NMR}$ spectra of (a) hex-1-ene and (b) the solution of the reaction after 30 min of reaction and after the elimination of the catalyst and the solvent.

The relative integrals of the $^1\text{H-NMR}$ 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

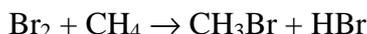
Calculate the % conversion of hex-1-ene to hexane after 30 min.

Problem 20: Drug kinetics

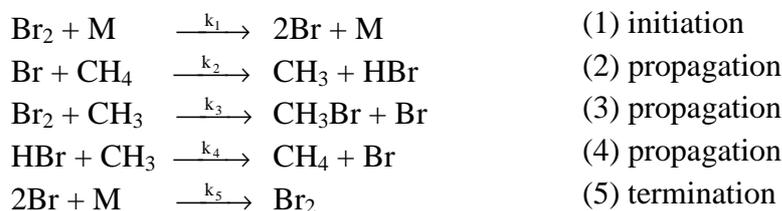
The absorption of a drug by an organism often follows simple kinetics though the mechanism is very complicated. Consider a drug delivered orally in a common capsule. Let $[A]_s$ be its concentration in the stomach and assume that the rate of its introduction into the blood stream is first order with 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: Br₂ + CH₄ reaction mechanism

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



The proposed mechanism for this reaction is as follows:



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 CH₃ 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: $\frac{d[\text{CH}_3]}{dt} = 0$ and $\frac{d[\text{Br}]}{dt} = 0$. This is called the “steady state” condition or

approximation for the CH₃ and Br radicals. Find the expression for the rate of formation of CH₃Br 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 CH₃ and Br radicals and near the end of the reaction:

$v = \frac{k_1^{1/2} k_2}{k_5^{1/2}} \cdot \frac{[\text{Br}_2]^{1/2} [\text{CH}_4]}{\frac{k_4 [\text{HBr}]}{k_3 [\text{Br}_2]} + 1}$	(I)
$v' = \frac{k_1^{1/2} k_2}{k_5^{1/2}} \cdot [\text{Br}_2]^{1/2} [\text{CH}_4]$	(II)
$v'' = \frac{k_1^{1/2} k_2 k_3}{k_5^{1/2} k_4} \cdot \frac{[\text{Br}_2]^{3/2} [\text{CH}_4]}{[\text{HBr}]}$	(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	<input type="text"/>
Steady state condition	<input type="text"/>
Near the end of the reaction	<input type="text"/>

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 $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$) or a weak base and its conjugate acid (for example $\text{NH}_3/\text{NH}_4^+$). 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:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

where K_a is the acid dissociation constant of the weak acid HA and $[\text{HA}]$ and $[\text{A}^-]$ 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 ($\text{K}_a = 2.1 \times 10^{-4}$) 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 , $\text{K}_a = 1.8 \times 10^{-5}$) in order to prepare a buffer solution with $\text{pH} = 5.00$.
4. The pH of a buffer solution containing 0.0100 M benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$, $\text{K}_a = 6.6 \times 10^{-5}$) 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 ($\text{K}_a = 1.8 \times 10^{-5}$), 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 ($\text{K}_a = 1.8 \times 10^{-5}$), 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.

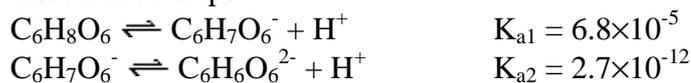
Questions

1. Construct the titration curve by calculating a few characteristic points and select indicator for the titration of 50.00 cm³ of 0.1000 M of acetic acid (CH₃COOH, 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, C₆H₈O₆) is a weak acid and undergoes the following dissociation steps:



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

50.00 cm³ 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 cm³, b. 35.00 cm³, c. 25.00 cm³, d. 20.00 cm³

(iii) The pH of the solution after the addition of 12.5 cm³ 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 cm³ of titrant is:

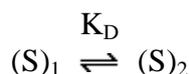
a. 13.30, b. 11.30, c. 11.00, d. 11.42

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 2, then we have the following equilibrium



where K_D is the **distribution coefficient** given by

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

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

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

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.

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

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

or

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

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.

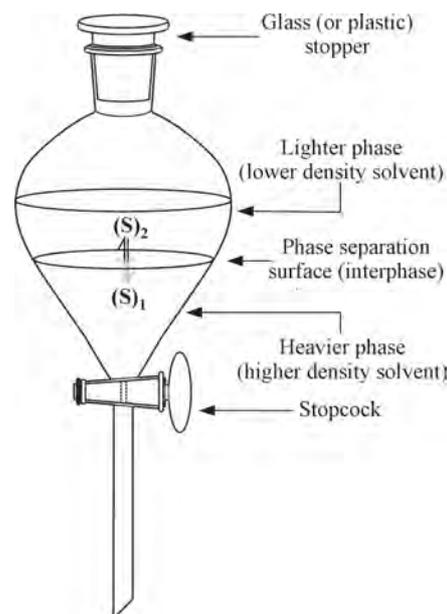


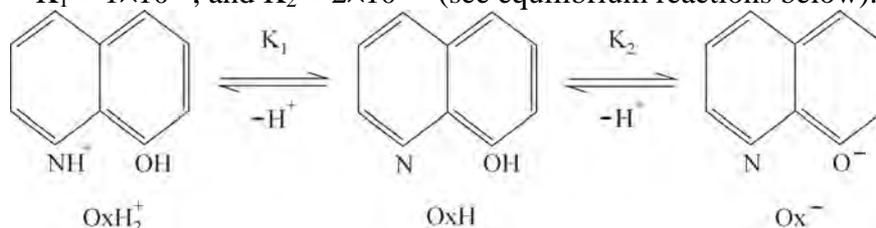
Figure 1. A typical separatory funnel.

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-cm³, and (b) four 25-cm³ 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 cm³ of an aqueous solution containing 0.500 g of X, if each extraction is carried out with 25.0 cm³ 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 constants 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: $K_1 = 1 \times 10^{-5}$, and $K_2 = 2 \times 10^{-10}$ (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 ($R \approx 300-1000$) 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 $^{12}\text{C}^1\text{H}_3^+$) up to 19 (fragment $^{13}\text{C}^2\text{H}_3^+$).

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 $^{12}\text{C}^1\text{H}_3^+$, the next in intensity but much smaller than peak M ($M+1=16$) is attributed to both $^{13}\text{C}^1\text{H}_3^+$ and $^{12}\text{C}^1\text{H}_2^2\text{H}^+$, whereas peak $M+4$, attributed to $^{13}\text{C}^2\text{H}_3^+$, 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 $M = 49$	$^{12}\text{C}^1\text{H}_2^{35}\text{Cl}$	$0.989 \times (0.99985)^2 \times 0.7577 =$	0.7491
Fragments $M+1 = 50$	$^{13}\text{C}^1\text{H}_2^{35}\text{Cl}$	$0.011 \times (0.99985)^2 \times 0.7577 =$	0.00833
	$^{12}\text{C}^2\text{H}^1\text{H}^{35}\text{Cl}$	$0.989 \times 0.00015 \times 0.99985 \times 0.7577 =$	0.00011
	$^{12}\text{C}^1\text{H}^2\text{H}^{35}\text{Cl}$	$0.989 \times 0.99985 \times 0.00015 \times 0.7577 =$	<u>0.00011</u> 0.00855
Fragments $M+2 = 51$	$^{13}\text{C}^2\text{H}^1\text{H}^{35}\text{Cl}$	$0.011 \times 0.00015 \times 0.99985 \times 0.7577 =$	1.25×10^{-6}
	$^{13}\text{C}^1\text{H}^2\text{H}^{35}\text{Cl}$	$0.011 \times 0.99985 \times 0.00015 \times 0.7577 =$	1.25×10^{-6}
	$^{12}\text{C}^1\text{H}_2^{37}\text{Cl}$	$0.989 \times (0.99985)^2 \times 0.2423 =$	<u>0.240</u> 0.240
Fragments $M+3 = 52$	$^{13}\text{C}^2\text{H}_2^{35}\text{Cl}$	$0.011 \times (0.00015)^2 \times 0.7577 =$	1.9×10^{-10}
	$^{13}\text{C}^1\text{H}_2^{37}\text{Cl}$	$0.011 \times (0.99985)^2 \times 0.2423 =$	0.00266
	$^{12}\text{C}^1\text{H}^2\text{H}^{37}\text{Cl}$	$0.989 \times 0.99985 \times 0.00015 \times 0.2423 =$	3.59×10^{-5}
	$^{12}\text{C}^2\text{H}^1\text{H}^{37}\text{Cl}$	$0.989 \times 0.00015 \times 0.99985 \times 0.2423 =$	<u>3.59×10^{-5}</u> 0.0027
Fragments $M+4 = 53$	$^{13}\text{C}^2\text{H}^1\text{H}^{37}\text{Cl}$	$0.011 \times 0.00015 \times 0.99985 \times 0.2423 =$	4.0×10^{-7}
	$^{13}\text{C}^1\text{H}^2\text{H}^{37}\text{Cl}$	$0.011 \times 0.99985 \times 0.00015 \times 0.2423 =$	4.0×10^{-7}
	$^{12}\text{C}^2\text{H}_2^{37}\text{Cl}$	$0.989 \times (0.00015)^2 \times 0.2423 =$	<u>5.4×10^{-9}</u> 8.1×10^{-7}
Fragment $M+5 = 54$	$^{13}\text{C}^2\text{H}_2^{37}\text{Cl}$	$0.011 \times (0.00015)^2 \times 0.2423 =$	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 $M+1 = 50$:	$(0.00855/0.7491) \times 100 = 1.14\%$

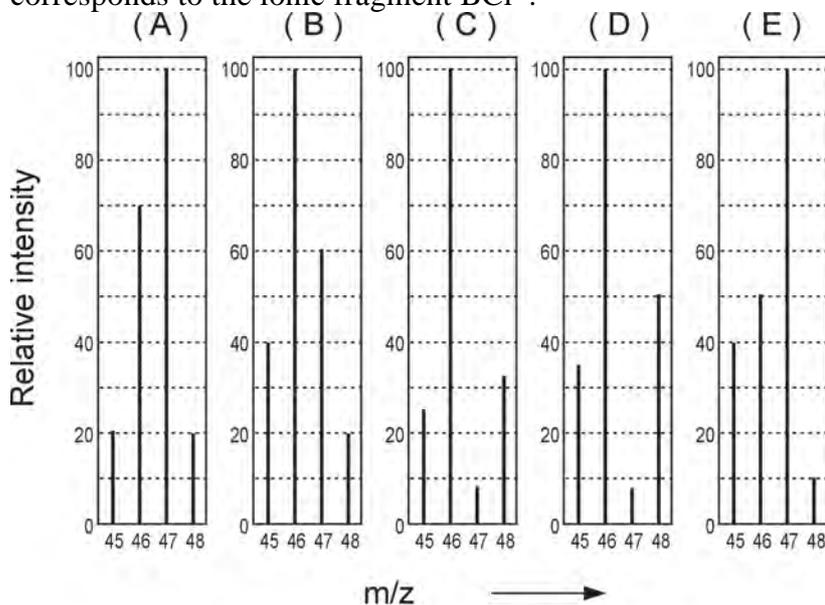
Relative intensity for M+2 = 51: $(0.240/0.7491) \times 100 = 31.98\%$
 Relative intensity for M+3 = 52: $(0.0027/0.7491) \times 100 = 0.36\%$
 Relative intensity for M+4 = 53: $(8.1 \times 10^{-7}/0.7491) \times 100 = 1 \times 10^{-4}\%$
 Relative intensity for M+5 = 54: $(6 \times 10^{-11}/0.7491) \times 100 = 8 \times 10^{-9}\%$

[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^+ ?



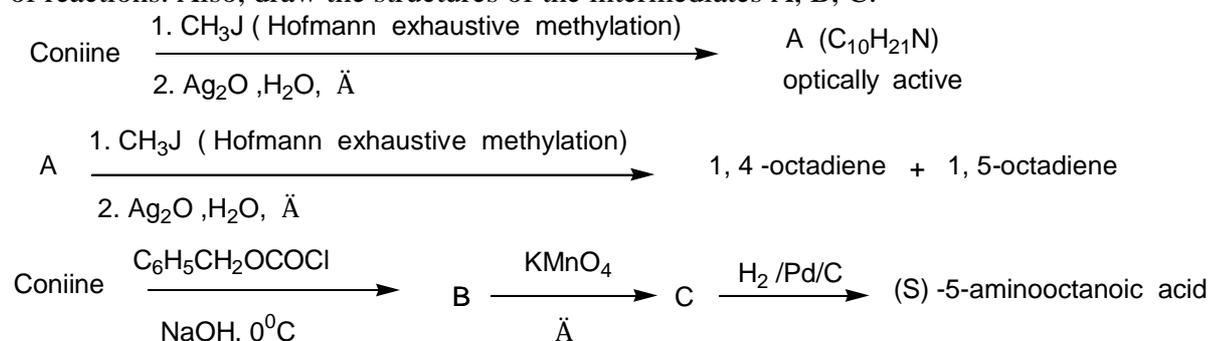
3. All the following ionic fragments: (a) N_2^+ , (b) CO^+ , (c) CH_2N^+ , (d) C_2H_4^+ have nominal mass $M = 28$ and they cannot be resolved with a low resolution mass spectrometer. However, based on the relative intensity of the M+1 peak, identification still can be achieved. Identify the ionic fragment 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 and Stereochemical Structure 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.

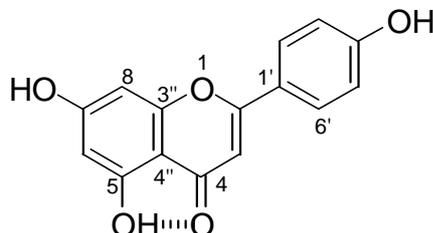
Find the chemical and stereochemical structure of coniine by completing the following series of reactions. Also, draw the structures of the intermediates A, B, C.



Problem 27: The Chemistry and Identification of Flavonoids

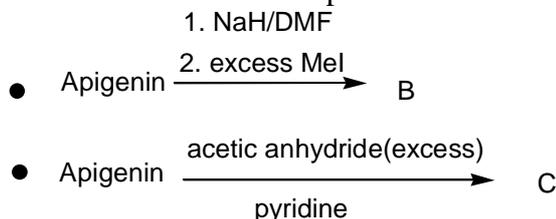
Cistus L is an aromatic, erect branched shrub and is a significant element of Greek flora. It can be found in stony slopes and hills and it can also be found in pinewoods. In folk medicine the flower branches of *Cistus monspeliensis* have been used for asthma, while the leaves may replace tea. Flavonoids 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, enzymes 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.

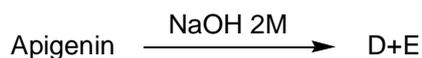


2 **Apigenin** can form a hydrogen bond between the phenolic hydroxyl group attached to C-5 and the carbonyl group at C-4.

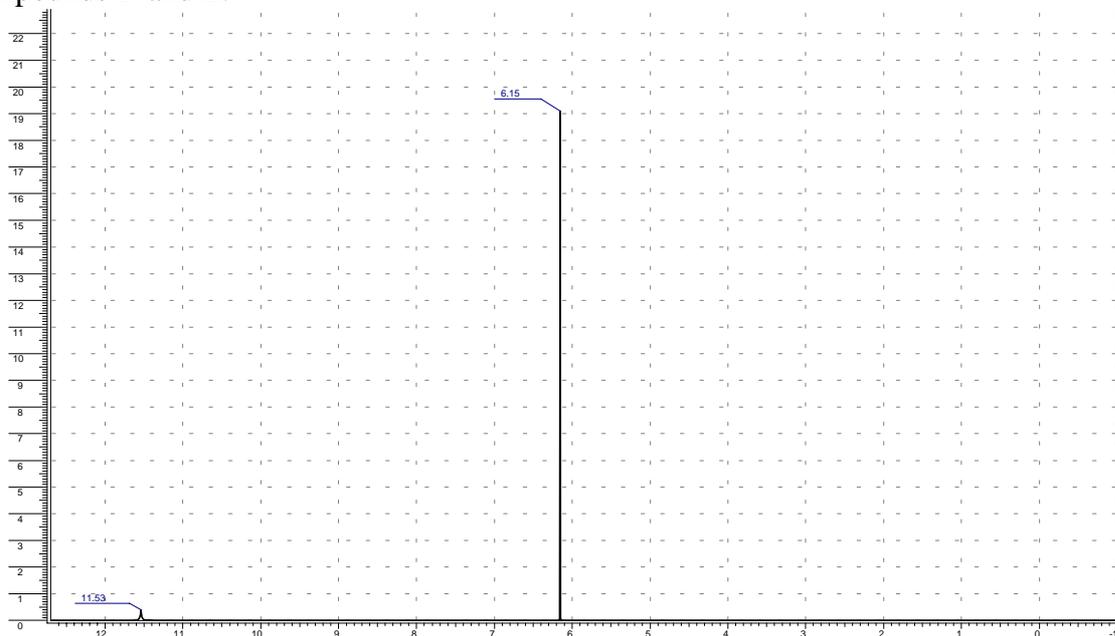
The $^1\text{H-NMR}$ resonance of the phenolic proton at C-5 will be shifted due to hydrogen bond:

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

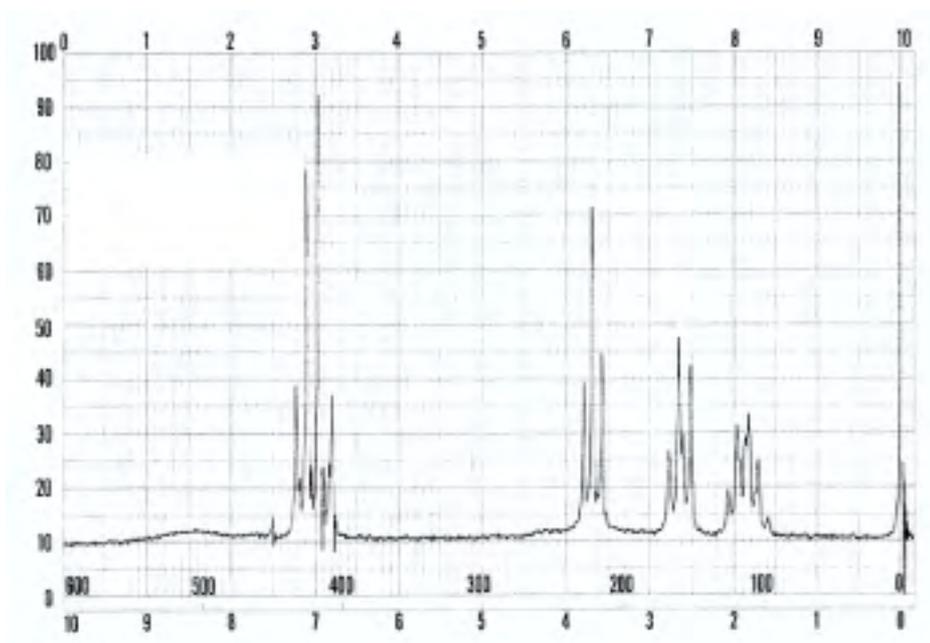
3 When treated with 2M NaOH, **apigenin** gives among others products D and E



Compound D ($\text{C}_6\text{H}_6\text{O}_3$) gives a positive test with FeCl_3 and its ^1H NMR spectrum consists of only one aromatic single peak (spectrum I). Compound E ($\text{C}_9\text{H}_{12}\text{O}_2$) also gives a positive test with FeCl_3 . In the ^1H -NMR spectrum the aliphatic region shows two triplet and one multiplet peaks while the aromatic region consists of two doublets (spectrum II). Draw the structure of compounds D and E.



Spectrum I, Compound D ($\text{C}_6\text{H}_6\text{O}_3$)



Spectrum II, Compound E ($\text{C}_9\text{H}_{12}\text{O}_2$)

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.

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 (employed in the form of ester) to which each successive aminoacid unit (employed in the form of N- aminoacid derivative) is linked, followed by removal of the N substituent before the next unit is added. The substituent most often employed is an alkoxy carbonyl group ROCO- and the derivatives are then called carbamates.

Why does the presence of such a substituent (protecting group) 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.

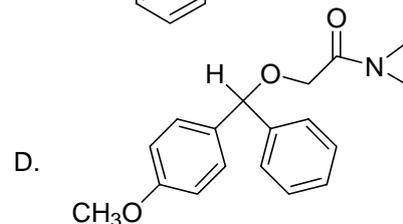
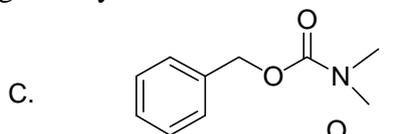
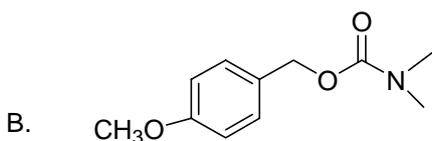
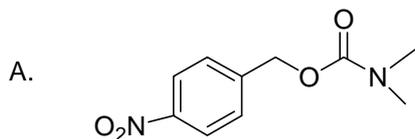
4. Which of the following reagents would you use to prepare the benzyl carbamate of an amine (Bergmann-Zervas protecting group)? Write the reaction

1. $C_6H_5CH_2OCOCNH_2$, 2. $C_6H_5CH_2OCO_2CH_3$, 3. $C_6H_5CH_2OCO_2C(CH_3)_3$, 4. $C_6H_5CH_2)C)Cl$, 5. C_6H_5OCOC

5. The removal of an alkoxy carbonyl protecting group is often accomplished by the action of acid that triggers a fragmentation represented schematically as follows:

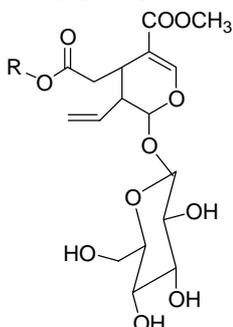


Rank the following carbamates according to increasing lability under acidic conditions:



Problem 29: Oleuropein hydrolysis

One of the geographical areas where nutritional habits have drawn attention as a prototype of nutrition is Crete. In a five country 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 is mainly attributed to the high olive oil consumption, which is rich in oleuropein (A), a powerful antioxidant. (R represents an alkylpolyphenolic group)



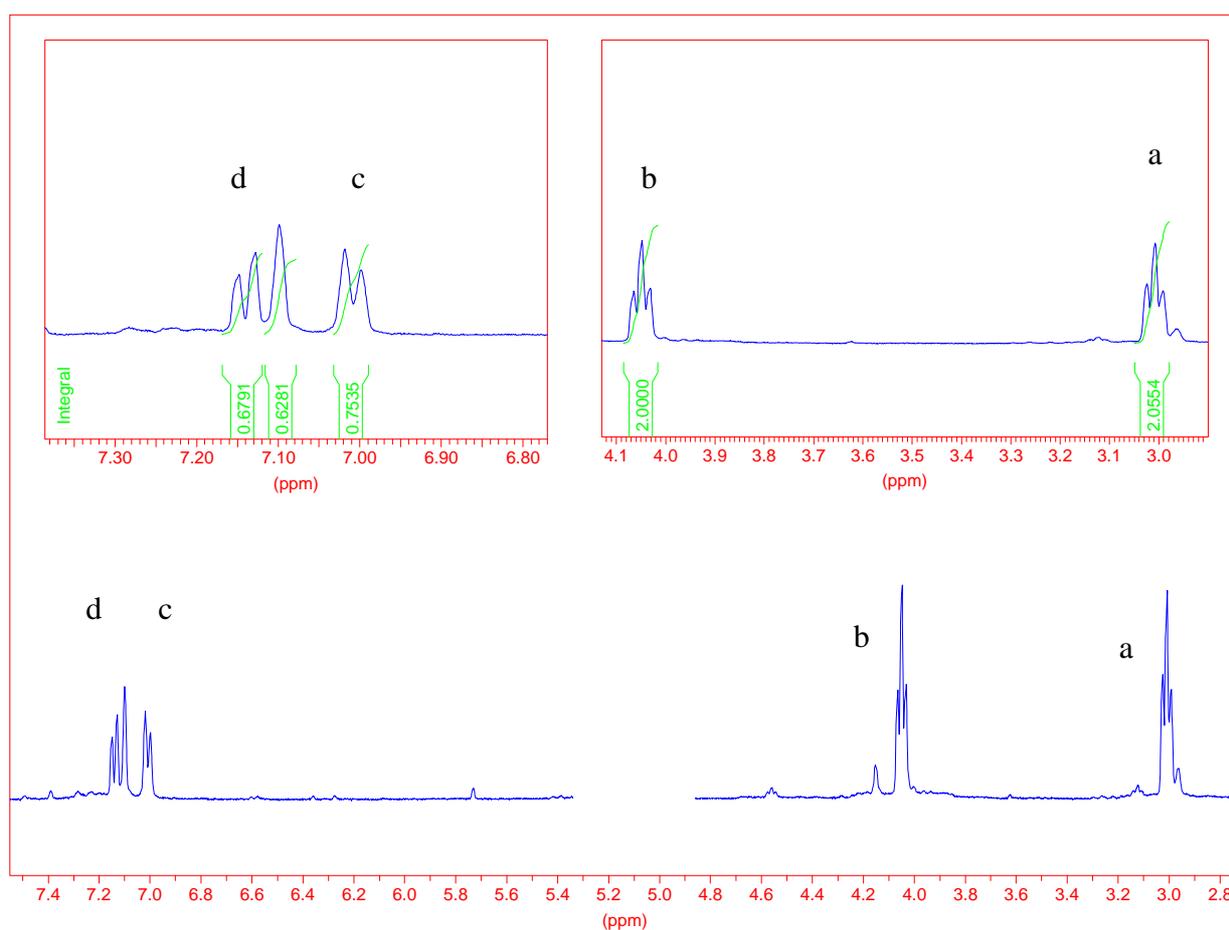
A

1. The acid-catalyzed hydrolysis of oleuropein gives apart from glucose, two other compounds, one polyphenolic (A1) and one monoterpene (A2).

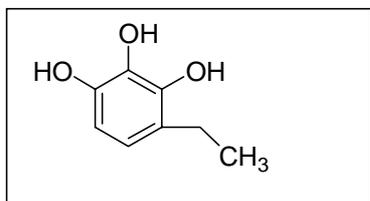
Indicate with an arrow in the formula of oleuropein:

- The oxygen atom that will be protonated in the acid hydrolysis leading to polyphenolic compound A1.
- The carbon-oxygen bond that will be cleaved in order to form glucose.

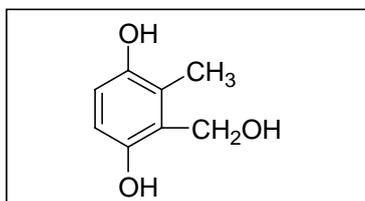
2. In the mass spectrum of A1, the peak corresponding to the molecular ion is situated at 154 mass units. The ¹H-NMR spectrum of A1 is shown below. The hydroxylic protons are exchangeable and therefore do not appear in the spectrum:



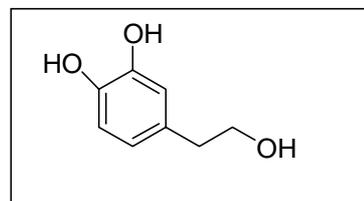
Choose the correct structure of A1 that can be deduced on the basis of $^1\text{H-NMR}$ and mass spectrum information given.



A



B

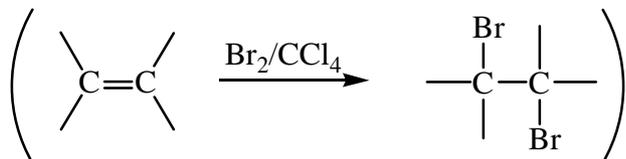


C

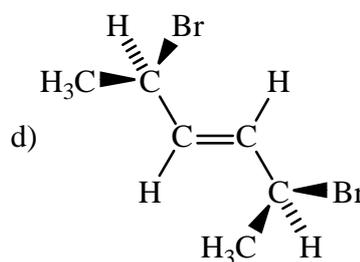
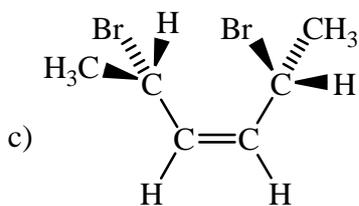
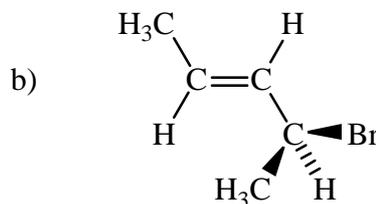
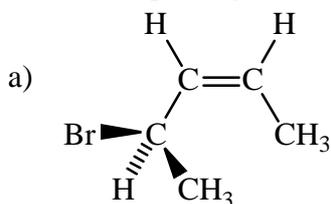
3 Draw the structure of A1 and use the letters a, b, c and d to designate the protons that correspond to the respective peaks in the $^1\text{H-NMR}$ spectrum.

Problem 30: Fischer projections and optical activity

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.



Problem 31: Alkyne identification

An optically active alkyne A contains 89,5% C and 10,4% H. After hydrogenation over 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 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. 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.

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.

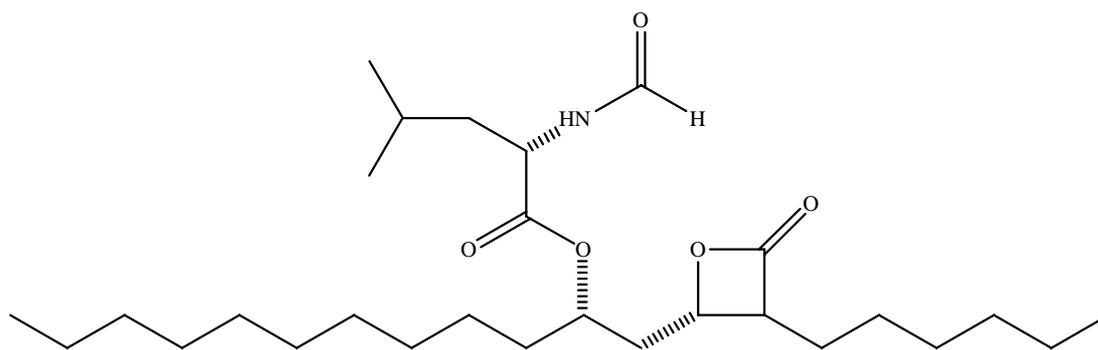
The mechanism of action of the above enzymes starts with the attack of the hydroxyl group of serine to the ester or amide bond.

Our approach for the development of serine proteases 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 by 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 acid or basic conditions. Rank the compounds by decreasing reactivity towards aqueous hydroxide ion.

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)

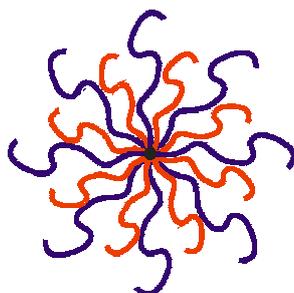
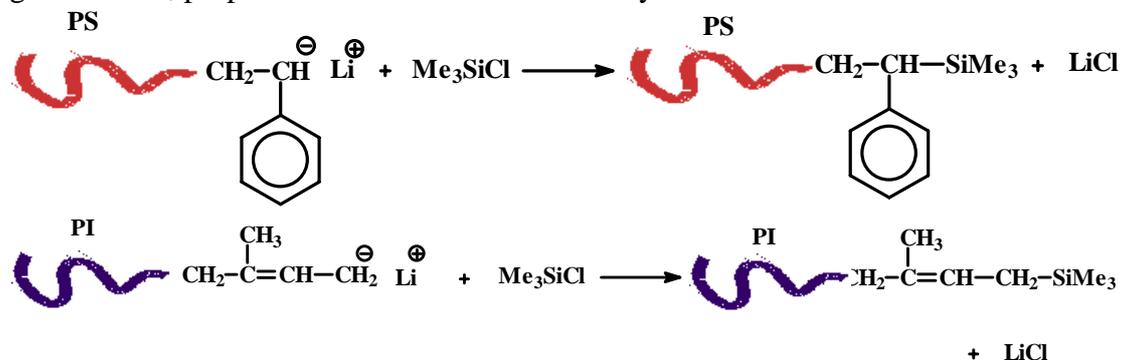


Figure 2. Vergina Star Copolymer: The similarity to the 16-rayed star emblem of the Macedonian Dynasty is obvious

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.

