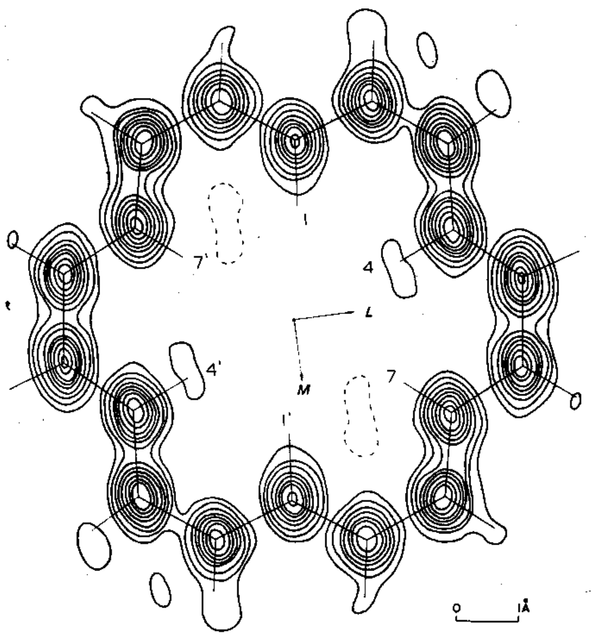
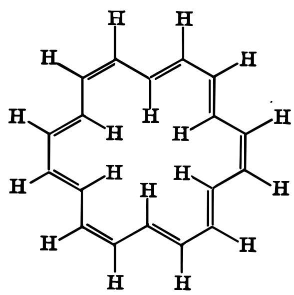
Problem 1: Proton – antiproton atom

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.Å^{-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 $E_n = \frac{h^2N^2}{2m_eL^2}$, 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, ±1, ±2, ±3, …, therefore each level has a two-fold degeneracy except for the zero level which is nondegenerate.

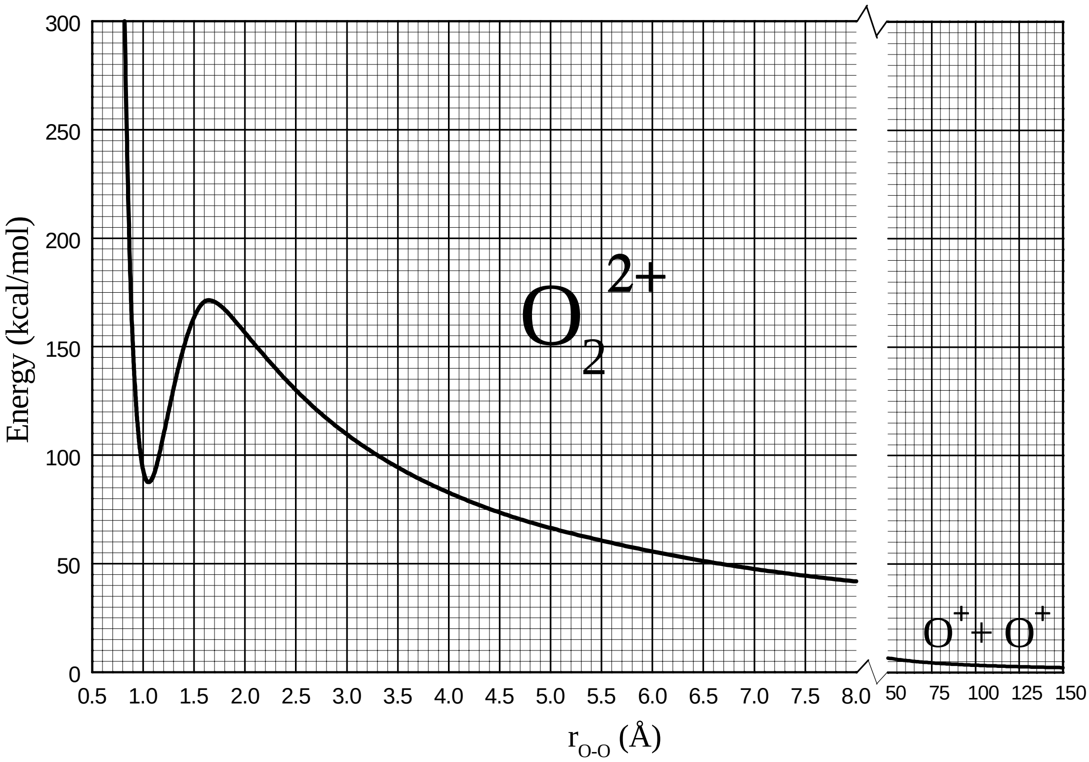
Assuming a mean bond length between carbon atoms equal to 1.40 Å, determine the wavelength of the lowest electronic transition.

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:

$Cd(OH)_2$ (s) + $2e^-$ $\rightarrow$ Cd (s) + $2OH^-$ $\qquad E_1^0 = -0.809$ V

$2NiO(OH)$ (s) + $2H_2O$ + $2e^-$ $\rightarrow$ $2Ni(OH)_2$ (s) + $2OH^-$ $\qquad E_2^0 = -0.490$ V

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 m^3 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/cm^3.

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 CO_2 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 NH_4NO_3 with water in a thermally isolated container. In this problem, 80 g NH_4NO_3 are mixed with 1 kg H_2O 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 NH_4NO_3 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

CO_2 fire extinguishers are metal canisters containing CO_2 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 Å. 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 Å.

(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 (½, 0, ½)], 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?

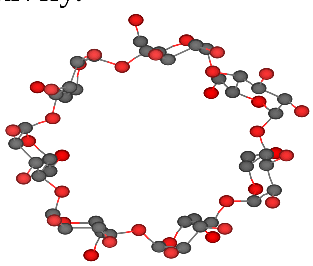
(d) In a similar manner as in (c), calculate the radius of a perfectly fitted interstitial atom *at the center of the γ-Fe unit cell.*

(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^o. Calculate the wavelength of the X-ray beam.

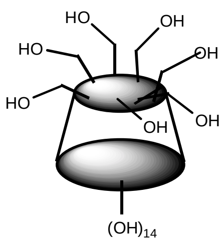
Problem 9: Cyclodextrine

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

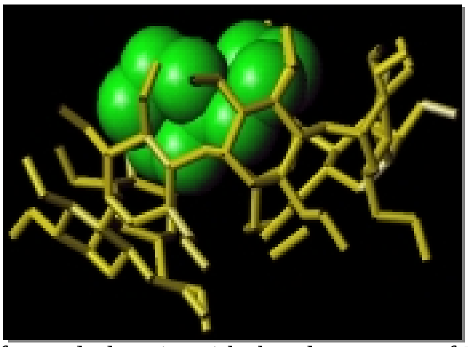


β-cyclodextrin (O atoms are shown in red and C atoms in black)

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 $C_{42}H_{70}O_{35} \bullet C_{12}H_{12}N_2 \bullet 12H_2O$. It crystallizes in space group $P2_1$. Its unit cell dimensions (with uncertainties) are a = 15.394(7) Å, b = 31.995(12) Å, c =15.621(7) Å, β= 103.738(15)°, (α = γ = 90°).

In this unit cell there are four molecules of the inclusion complex (2 molecules in the asymmetric unit). What is the molecular volume in $Å^3$ 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 $t_{½}$ = 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 C_{14}/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 C_{14}/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)]

a) Calculate the age of an isolated sample with a $^{14}C/^{12}C$ ratio which is 0.25 that of a contemporary sample.
b) What happens to a ^{14}C atom when it disintegrates?
c) 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.
d) 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%, $t_{½} = 4.47x10^9$ y) and ^{235}U (0.7%, $t_{1/2} = 7.04x10^8$ y). Both radioisotopes are alpha emitters and were created at the time of nucleosynthesis. Their decay is followed by a different sequence of alpha ($^4He^{2+}$) 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:

$$^{235}U + n \rightarrow U^* \rightarrow \text{fission products} + 2\text{-}3n + 200 \text{ MeV/nucleus } ^{235}U$$

a) Calculate the total number of alpha and beta particles emitted in each of the two complete natural radioactive series ($^{238}U \rightarrow {}^{206}Pb$ and $^{235}U \rightarrow {}^{207}Pb$).
b) Explain why in both radioactive series some chemical elements appear more than once.
c) Assuming that the initial isotopic abundance (i.e., at the time of nucleosynthesis) was equal for the two uranium isotopes ($^{235}U : {}^{238}U = 1:1$), calculate the age of the Earth (i.e., the time that has elapsed since nucleosynthesis).
d) 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:

$$C + O_2 \rightarrow CO_2 + 393.5 \text{ kJ/mol (or 4.1eV/molecule)}$$