

## Problem 7: Atomic Orbitals

One way to describe the shape of atomic orbitals of H-atom is in terms of the nodal surfaces, or nodes, where the electron has zero probability. According to wave mechanics, the number of nodes increases as  $n$  increases. For given set of orbitals  $nlm$ , there are " $n-l-1$ " spherical nodes, " $l$ " angular nodes.

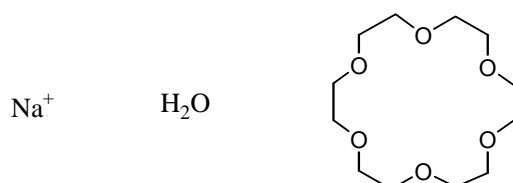
- 7-1 Describe the electron probability distribution for the 1s, 2s and 3s orbitals. How many nodes does each orbital have respectively?
- 7-2 Describe the electron probability distribution for the  $2p_z$  and  $3p_z$  orbitals. How many nodes does each orbital have respectively?
- 7-3 Imagine that you are traveling along the  $z$  axis, beginning your journey at a distance far from the nucleus on the  $z$  axis, passing through the nucleus to a distant point on the  $-z$  axis. How many nodal surfaces would you pass through for each of the following orbitals: 1s, 2s, 3s,  $2p_z$  and  $3p_z$ .

## Problem 8: Intermolecular Forces

Intermolecular forces occur between, rather than within, molecules. Ion-dipole interaction and dipole-dipole interaction are two common types of intermolecular forces.

### Part 1: Ion-Dipole Interactions

The bonding of an ion, such as  $\text{Na}^+$ , with a polar molecule, such as water, is an example of an ion-dipole interaction. Shown below are a sodium ion, a water molecule, and a crown ether compound.

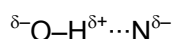


- 8-1-1 Draw the geometrical structure of the product resulting from the interaction between the sodium ion and water molecules.

8-1-2 Draw a diagram showing the interaction between the sodium ion and the crown ether molecule.

## Part 2: Dipole-Dipole Interactions

A hydrogen bond may be regarded as a particular kind of dipole-dipole interaction. Strong hydrogen bonding forces are seen among molecules in which hydrogen is bound to a highly electronegative atom, such as nitrogen, oxygen, or fluorine.



Compared to other intermolecular forces, hydrogen bonds are relatively strong; their energies are of the order of 15 to 40 kJ/mol. Hydrogen bonding is so strong that, in some cases, it survives even in a vapor.

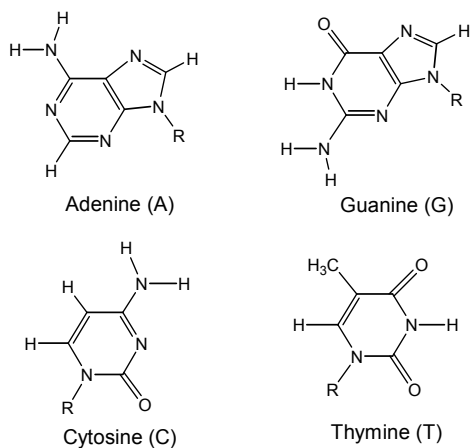
8-2-1 In gaseous hydrogen fluoride, many of the HF molecules are associated into  $(\text{HF})_6$ . Draw the structure of this hexamer.

8-2-2 Draw a diagram showing the hydrogen-bonding interactions between two acetic acid ( $\text{CH}_3\text{CO}_2\text{H}$ ) molecules.

## Part 3: Hydrogen-bonding in Living Matter

Some chemical reactions in living matter involve complex structures such as proteins and DNA, and in these reactions certain bonds must be easily broken and reformed. Hydrogen bonding is the only type of bonding with energies of just the right magnitude to allow this.

The key to DNA's functioning is its double-helical structure with complementary bases on the two strands. The bases form hydrogen bonds to each other.

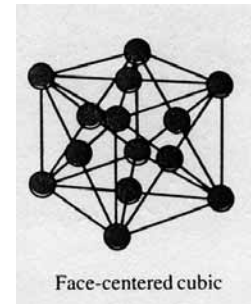
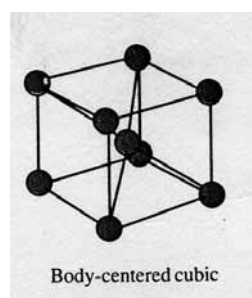
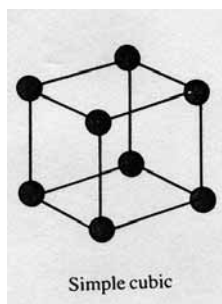


The organic bases found in DNA

- 8-3 There are two kinds of hydrogen-bonded base pairs, T-A and G-C, in DNA. Draw these two base pairs, showing the hydrogen-bonding interactions.

### Problem 9: Crystal Packing

There are three cubic unit cells for the atomic solids, namely, simple cubic, body-centered cubic and face-centered cubic. They are illustrated in the following figures:



- 9-1 How many nearest neighbor atoms are in each packing, respectively?
- 9-2 In each packing, the packing efficiency is defined by

$$f_v = \frac{\text{volume occupied by spheres in the unit cell}}{\text{volume of the unit cell}}$$

What is the value of  $f_v$  in each type of packing, respectively?

- 9-3 Silver crystallizes in a cubic closest packed structure, i.e. face-centered cubic. The radius of a silver atom is 144 pm. Calculate the density of silver.
- 9-4 X-ray diffraction is commonly used for the determination of crystal structures. In one such determination, the emitted X rays were diffracted by a LiF crystal ( $d = 201$  pm), and the first-order diffraction was detected at an angle of  $34.68^\circ$ . Calculate the wavelength of the X-ray emitted by the metal.

## Problem 10: Applications of Transition Metals

The transition metal elements are widely distributed in the Earth's crust. Many of these elements find uses in everyday objects: iron pipes, copper wiring, chromium auto parts, etc.

### Part 1: Properties of Chromium

Chromium is a silvery-white, lustrous metal, whose name (from the Greek chroma, meaning color) alludes to its many colorful compounds. The bright colors of chromium (VI) compounds lead to their use in pigments for artists paints and ceramic glazes.

10-1-1 In an acidic solution, the yellow chromate ion ( $\text{CrO}_4^{2-}$ ) changes into the orange dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ). Write the equation for the reaction.

10-1-2 What is the oxidation state of each metal center in the chromate ion and the dichromate ion?

10-1-3 Is this a redox reaction? Explain.

10-1-4 What is the main factor that controls the equilibrium position?

10-1-5 Draw the three-dimensional structures of  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$ .

### Part 2: Uses of Chromium

An antique automobile bumper is to be chrome plated. The bumper is dipped into an acidic  $\text{Cr}_2\text{O}_7^{2-}$  solution where it serves as the cathode of an electrolytic cell. (The atomic mass of Cr is 51.996;  $1 F = 96,485 C.$ )

10-2-1 Given that oxidation of  $\text{H}_2\text{O}$  occurs at the anode, write equation for the two half-reactions and the overall cell reaction.

10-2-2 How many moles of oxygen gas will be evolved for every 52.0 g of chromium deposited?

10-2-3 If the current is 10.0 amperes, how long will it take to deposit 52.0 g of chromium onto the bumper?

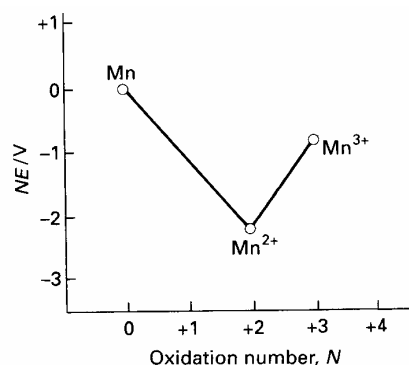
10-2-4 What is the chemical reason that chromium is so useful for decorative plating on metals?

## Problem 11: Electrochemistry of Inorganic Compounds

Some inorganic compounds exhibit a variety of oxidation states, for example, many Mn compounds are known with oxidation states ranging from 0 to +7. The standard reduction potential of a half reaction is measured against the hydrogen electrode. In this problem, the reduction  $\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$ ,  $E^\circ = -1.18\text{V}$  is expressed as  $\text{Mn}^{2+} (-1.18) \text{Mn}$ . For Mn in acidic solution the reduction series:  $\text{Mn}^{3+} \quad \text{Mn}^{2+} \quad \text{Mn}$  can be represented as follows:

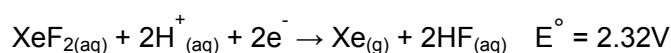


A redox reaction takes place spontaneously if the redox potential is positive. A Frost diagram, a plot of  $nE^\circ$  ( $n$  is the number of electron transferred in the half reaction) of the reduction couple  $\text{X}(N) / \text{X}(0)$  against the oxidation number,  $N$ , of the element, is used to indicate the most stable species of the compounds in different oxidation states. The Frost diagram of  $\text{Mn}^{3+} / \text{Mn}^{2+} / \text{Mn}$  is shown below.



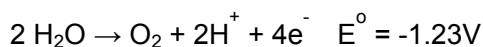
- 11-1 The reduction potential depends on the concentration of the species in solution. The  $K_{sp}$  of  $\text{MnCO}_3$  is  $1.8 \times 10^{-11}$ . Use the Nernst equation to determine the potential at  $25^\circ\text{C}$  for the voltaic cell consisting of  $\text{Mn}_{(s)} | \text{Mn}^{2+}_{(aq)} (1\text{M}) || \text{Mn}^{2+}_{(aq)} / \text{MnCO}_3 | \text{Mn}_{(s)}$ , if the concentration of  $\text{Mn}^{2+}$  in the right hand side of the cell is  $1.0 \times 10^{-8} \text{M}$ .
- 11-2 For oxygen, the standard reduction potential in acidic solution can be represented as:  $\text{O}_2 (0.70) \text{H}_2\text{O}_2 (1.76) \text{H}_2\text{O}$ . Construct the Frost diagram for oxygen, and use the information contained in the diagram to calculate the reduction potential of the half reaction for reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}$ . Could  $\text{H}_2\text{O}_2$  undergo disproportionation spontaneously?

Xenon difluoride can be made by placing a vigorously dried flask containing xenon gas and fluorine gas in the sunlight. The half-reaction for the reduction of  $\text{XeF}_2$  is shown below:



- 11-3 Use the VSEPR model to predict the number of electron-pairs and molecular geometry of

XeF<sub>2</sub>. Show that XeF<sub>2</sub> decomposes in aqueous solution, producing O<sub>2</sub>, and calculate the E° for the reaction. Would you expect this decomposition to be favored in an acidic or a basic solution? Explain.

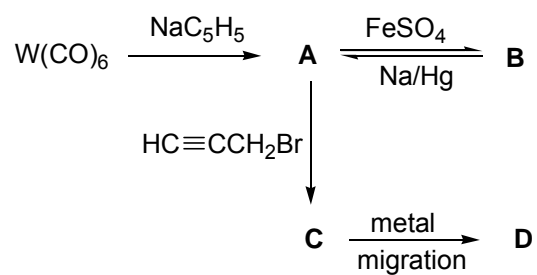


## Problem 12: Metal Carbonyl Compounds

Carbon monoxide, as a two electron donor ligand, coordinates to transition metals to form metal carbonyl compounds. For example, iron forms the pentacarbonyl metal complex, Fe(CO)<sub>5</sub>. Nickel tetracarbonyl, Ni(CO)<sub>4</sub>, has been used for the purification of Ni metal in the Mond process. Electron counts of these metal carbonyl complexes show that they obey the 18-electron rule. Cobalt and manganese react with CO to form dinuclear complexes Co<sub>2</sub>(CO)<sub>8</sub> and Mn<sub>2</sub>(CO)<sub>10</sub>, respectively. (Electronic configuration of Mn is [Ar](3d)<sup>5</sup>(4s)<sup>2</sup>) A metal-metal bond between the metal centers is considered essential in order for the compounds to obey the 18 electron rule. The cyclopentadienyl anion C<sub>5</sub>H<sub>5</sub><sup>-</sup> has also been widely used as a η<sup>5</sup>-ligand. For example, ferrocene (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe, a classical compound, obeys the 18 electron rule.

The reaction of W(CO)<sub>6</sub> with sodium cyclopentadienide NaC<sub>5</sub>H<sub>5</sub> yields an air sensitive compound **A**. Oxidation of **A** with FeSO<sub>4</sub> yields compound **B**. Compound **A** can also be prepared from the reaction of **B** with Na/Hg, a strong reducing agent. In the 1600-2300 cm<sup>-1</sup> region of the IR spectrum, **A** shows absorption bands at 1744 and 1894 cm<sup>-1</sup> and **B** absorption bands at 1904, and 2010 cm<sup>-1</sup>. Compound **A** is a strong nucleophile and a good starting material for the synthesis of organometallic compounds containing metal-carbon bonds. The reaction of **A** with propargyl bromide (HC≡CCH<sub>2</sub>Br) gives compound **C** containing a metal-carbon σ-bond. At room temperature compound **C** undergoes a transformation to yield compound **D**. The same chemical composition was found for compounds **C** and **D**. The chemical shifts (δ) of the CH<sub>2</sub> and CH resonances and coupling constants J<sub>H-H</sub> of propargyl bromide, **C** and **D** in the respective <sup>1</sup>H NMR spectra are listed in the following table.

<sup>1</sup> H NMR	HC≡CCH <sub>2</sub> Br	<b>C</b>	<b>D</b>
δ (CH <sub>2</sub> )	3.86	1.90	4.16
δ (CH)	2.51	1.99	5.49
J <sub>H-H</sub> (Hz)	2.7	2.8	6.7



- 12-1 Explain the differences in the IR spectra of **A** and **B**.
- 12-2 Draw chemical structures for **A**, **B**, **C** and **D**.
- 12-3 The transformation of **C** to **D** involves a migration of the metal on the propargyl ligand. If  $\text{DC}\equiv\text{CCH}_2\text{Br}$  is used for the synthesis of **C**, draw the structures of **C** and **D**.