

CHEM 321 Organic Chemistry I - Professor Kathleen V. Kilway
"Organic Chemistry" by Maitland Jones, 3rd edition

Homework problems for Chapter 1 - 1, 2, 3, 6, 7, 8, 9, 10, 11, 12, 19, 20, 21, 22, 23, 26, 29, 30, 31, 32, 33, 35, 36, 41, 48, 50, 51.

CHAPTER 1: ATOMS AND MOLECULES; ORBITALS AND BONDING

Section 1.1

I. Preview

Section 1.2

II. Atoms and Atomic Orbitals

A- Neutral Atom

- 1- Contains a nucleus at its core.
 - a- The nucleus is an area of positively charged protons and neutral neutrons.
 - b- The nucleus is surrounded by negatively charged electrons, which are equal in number to the protons.
- 2- Ion
 - a- Occurs when protons and electrons are not equal.

B- Anion

- 1- Negatively charged atom or molecule.

C- Cation

- 1- Positively charged atom or molecule.

D- Ionization Potential

- 1- Form of Energy.
- 2- Energy required to take an electron away from an atom.
- 3- Forms a cation.
- 4- In general, increases as you go up the column and across a row.

E- Octet Rule

- 1- An atom's goal is to achieve the electron configuration of the noble gases.
- 2- The octet rule helps us understand that we need to fill certain shells to reach a stable configuration.
- 3- First shell: 1s holds 2 electrons.
- 4- Second shell: 2s and 2p are subshells.
 - a- They hold a total of 8 electrons.
 - b- 2 electrons in 2s and 6 electrons in 2p.
- 5- Please look at Figure 1.1 on page 4 in the text.

F- Electron Affinity

- 1- This is a way of measuring the tendency of an atom or molecule to accept an electron.
- 2- It is measured in electron volts (eV).

- 3- Noble gases = low electron affinity.
- 4- When you add an electron to an atom and complete the noble gas configuration = high electron affinity.
 - a- A prime example if this is fluorine. See Figure 1.2 on page 4 in the text.

For a pictorial representation of the periodic table, go to a Phoenix College website:
<http://chemlab.pc.maricopa.edu/periodic/periodic.html>

G- Wave Functions

- 1- This is the volume of space occupied by an electron.
- 2- They are also called orbitals.
- 3- The function is determined by a set of quantum numbers.
 - a- The first quantum number is n .
 - 1- It may have integral values of 1,2,3,4....
 - 2- It also relates the distance of the electron to the nucleus.
 - 3- So the higher the n , the greater the distance and thus the greater the energy.
 - 4- It also determines the row occupied by the atom in the periodic table.
 - 5- When $n = 1$, then 1 orbital; when $n = 2$, 2 orbitals and so on.
 - b- The second quantum number is l .
 - 1- It may have integral values of 0, 1, 2, ... up to $n - 1$
 - 2- It is related to the shape of the orbital.
 - 3- When $n = 1$, l must be 0; when $n = 2$, l can be 0 or 1, and so on.
 - 4- When $l = 0$, then it's called an s orbital; when $l = 1$, it's a p orbital; when $l = 2$, it's a d orbital; when $l = 3$, it's a f orbital.
 - c- The third quantum number is m_l .
 - 1- It may have integral values 0, ± 1 , ± 2 , ± 3 ,
 - 2- It depends on l .
 - 3- It gives the orientation of the orbitals in space.
 - d- The fourth quantum number is s .
 - 1- It is the spin quantum number which is only $s = \pm 1/2$.
 - e- See Table 1.4 on page 6 for the relationship of the quantum numbers.

For a general chemistry review of quantum chemistry, check out Professor Kent Wilson's group page at:

<http://www.wilson.ucsd.edu/education/gchem/atomorbs/qmbasics.html>

H- Pauli Principle

- 1- It states that no 2 electrons in an atom or molecule may have the same values for all of the 4 quantum numbers.
- 2- For example, ${}_2\text{He}: 1s^2$
 Electron number 1: $n = 1, l = 0, m_l = 0, s = +1/2$.
 Electron number 2: $n = 1, l = 0, m_l = 0, s = -1/2$.
- 3- See Figure 1.4 on page 7 for an example.

I- Aufbau Principle

- 1- It states that when you add electrons to a system of orbitals, you need to fill the lowest energy first.
- 2- For example, ${}_{14}\text{N}$: $1s^2 2s^2 2p_x 2p_y 2p_z$ (Note: $2p_x$ is equal to $2p_x^1$); first 1s, then 2s, then 2p.

J- Hund's Rule

- 1- It states that for a set of equi-energetic orbitals, the electron configuration with the maximum number of parallel spins has the lowest energy.
- 2- Give all p orbitals (x, y, z) one electron with the same spin orientation, before adding a second electron.
- 3- See Figure 1.5 on page 7 for an example.

K- Wave Functions (ψ)

- 1- The solutions to the Schrödinger's equations.
- 2- The square of the wave function (ψ^2) is related to electron density.
- 3- A node is a stationary point which is neither positive nor negative.

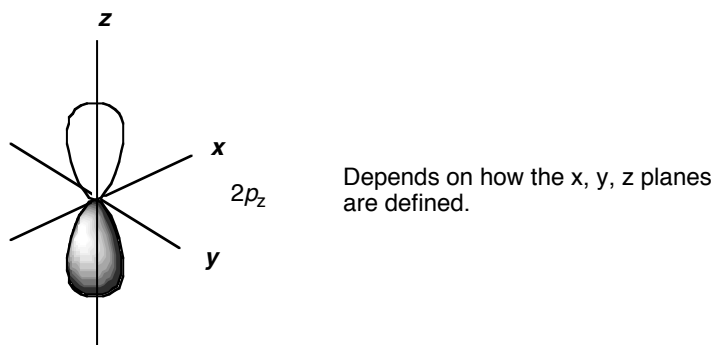


Figure 1

Section 1.3**III. Covalent Bonds and Lewis Structures****A- Covalent Bond**

- 1- A type of bond which is formed by equally sharing a pair of electrons (e.g., Br_2 , Cl_2 , ...).

B- Lewis Structures

- 1- A way of writing molecules, which are formed by covalent bonds.
 - a- See Figure 1.14 on page 13 for the construction of a Lewis structure.

C- Polar Covalent Bonds

- 1- These molecules contain electrons which are unequally shared (e.g., H-F, Cl-CCl_3 , F- BF_2 , ...).

D- Dipole Moments

- 1- This is a result of 2 opposite charges being separated.
 - a- A small arrow is used to show the direction of the dipole as well as the partial positive or negative charge.

b- See Figure 1.15 on page 14 for an example.

E- Electronegativity

- 1- This is the tendency for an atom to attract electrons.
 - a- Table 1.8 on page 14 gives examples of some electronegativity values.
 - b- The most electronegative atoms are found to the right of the periodic table.
 - c- These atoms also have high electron affinities.
 - d- In general, electronegativity increases up the column and across the row.

Section 1.4

IV. Introduction to Resonance Forms

A- Resonance Forms

- 1- This is a representation of 2 or more equivalent electronic forms.
 - a- Number of charges never changes.
 - b- A good example is Figure 1.28 on page 23 and below.

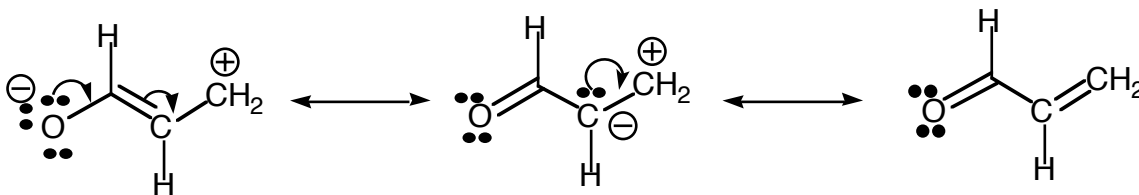


Figure 2

- c- A double-headed arrow is used to indicate resonance structures.
- d- Only by moving electrons not atoms (see below).

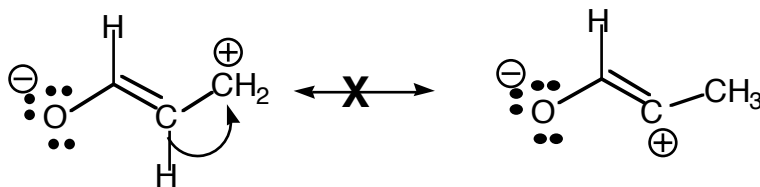


Figure 3

For more examples, check out the website of Brenda Wojciechowski and Paul Cerpovicz at Georgia Southern University:

<http://www2.gasou.edu/chemdept/general/molecule/resonan.htm>

Another useful site is by CHEMystery which is a virtual textbook:

<http://library.advanced.org/3659/structures/resonance.html>

Additional problems are provided by Professor John G. Russell:

<http://kekule.chem.csus.edu/jr/chem20/addprob.html>

Section 1.5

V. The Covalent Bond: Hydrogen (H₂)

A- Bonding Molecular Orbital Φ_B

- 1- This is the occupation of the bonding orbital by an electron, which is overall stabilizing.
- 2- See Figure 1.32 on page 28.
 - a- This shows the bonding of 2 hydrogen 1s orbitals.

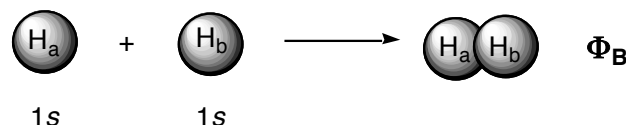


Figure 4

B- Antibonding Molecular Orbital Φ_A

- 1- This is the occupation of the antibonding molecular orbital by an electron, which is overall destabilizing.
- 2- See Figure 1.33 on page 28.
- 3- A node is formed between H_a and H_b .

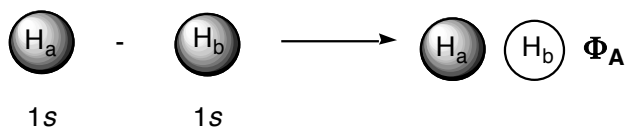


Figure 5

C- Overall molecular energy diagram for H_2

- 1- # of molecular orbitals resulting from this combination must = the # of atomic orbitals used.
- 2- See Figure 1.35 on page 30.

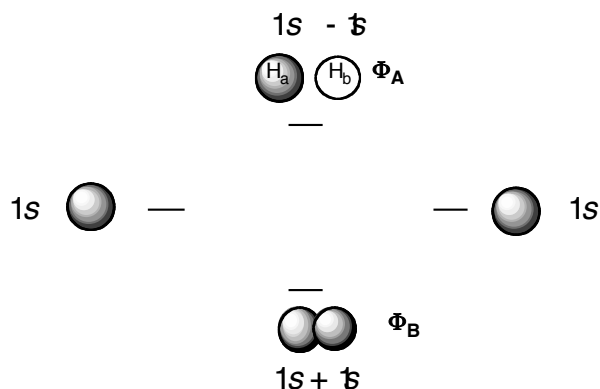


Figure 6

D- Other Orbital Interactions

- 1- Orthogonal orbitals - bonding interactions are exactly balanced with antibonding interactions. A net zero interaction.
- 2- See Figure 1.36 on page 31.

Section 1.6**VI. Bond Strength****A- Exothermic Reaction**

- 1- Here the products are more stable than the starting materials. Energy is evolved from this reaction, usually in the form of heat.

B- Endothermic Reaction

- 1- Here the products are less stable than the starting materials. Instead of energy being evolved it must be supplied, again usually in the form of heat.

C- Bond Dissociation Energy (BDE)

- 1- This is the amount of energy required for homolytic cleavage.
 - a- Homolytic Cleavage.
 - 1- This is the breaking of the bond into a pair of neutral species.
 - 2- See Figure 1.39 on page 34.

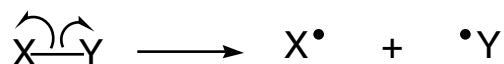


Figure 7

- b- See Table 1.9 on page 36 for examples of Bond Dissociation Energies.

D- Heterolytic Cleavage

- 1- This is where the breaking of a bond produces a pair of oppositely charged ions.
- 2- See figure 1.39 on page 34. One example is pictured below.

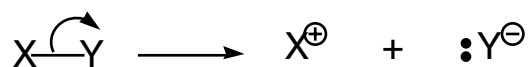


Figure 8

Section 1.7**VII. An Introduction to Reactivity: Acids and Bases****A- Interactions which lead to stabilization**

- 1- Two singly occupied orbitals overlap to form a bond.
- 2- A filled orbital (Lewis base) and an empty orbital (Lewis acid) interact.
- 3- See Figure 1.42 on page 39.

Check out these useful Web Sites:

For a QuickTime movie of addition of atomic orbitals go to Professor Kent Wilson's page:

<http://www-wilson.ucsd.edu/education/gchem/molecorbs/QuickTime/molorbbs.qt>

A good place to browse is the Chemist's Art Gallery:

<http://www.csc.fi/lul/chem/graphics.html>