Chemistry 121(01) Winter 2009

Introduction to Organic Chemistry and Biochemistry
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TR 9::00 - !0:00 am & 1:00-2:00 pm.

December 19, Test 1 (Chapters 12-14)
January 2 Test 1 (Chapters 15-16)
February 6 (Chapters 17-19)
February 27, (Chapters 20-22)
March 2, 2009, Make Up Exam:
Bring Scantron Sheet 882-E

Chem 120: Background for Organic and Biochemistry

Chapters 1-11

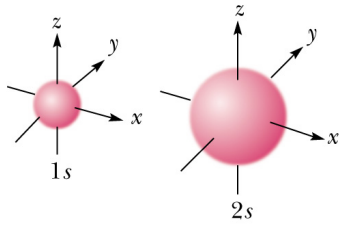
Chapter 3: Atomic Structure and Periodic Table

Chapter 3: Atomic Structure and Periodic Table

Shapes of s Atomic Orbitals

All *s* orbitals have the shape of a sphere, with its center at the nucleus

- **of the *s* orbitals, a 1*s* orbital is the smallest, a 2*s* orbital is larger, and a 3*s* orbital is larger still**



Atomic Orbitals

s orbital - a spherical-shaped atomic orbital; can hold a maximum of 2 electrons

p orbital - a dumbbell-shaped atomic orbital; the three p orbitals (p_x, p_y, p_z) can hold a maximum of 2 electrons each

Electrons always fill starting with the lowest-energy orbital:

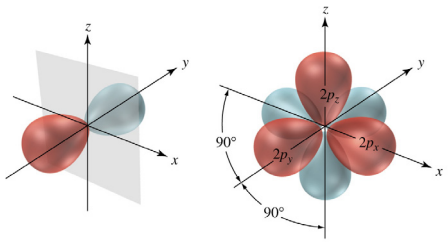
lower energy higher energy

$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$

We will be concerned with only the valence electrons which are the outermost electrons involved in forming bonds.

Shapes of p Atomic Orbitals

- A *p* orbital consists of two lobes arranged in a straight line with the center at the nucleus



Electronic Structure of atoms

Ground state electronic configuration of atoms in core format

Carbon (C):): [He] $2s^2$, $2p^2$

or [He] $2s^2$, $2p_x^1 3p_y^1 3p_z^0$

Potassium (K): Ar] $4s^1$

Phosphorous (P): [Ne] $3s^2$, $3p^3$

Valence shell electronic configuration

Carbon (C):): $3s^2$, $3p^2$

Potassium (K): $4s^1$

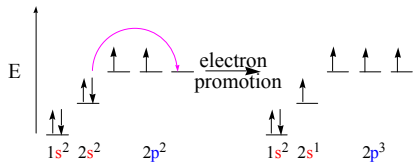
Phosphorous (P): $3s^2$, $3p^3$

How you get the electronic configuration of an atom from the periodic table?

Excited State Valence Electron Configuration

Carbon (C):

Ground state: $2s^2$, $2p^2$ or $2s^2$, $2p_x^1 3p_y^1 3p_z^0$



Excited State: $2s^1$, $2p^3$ or $2s^1$, $2p_x^1 3p_y^1 3p_z^1$

Chapter 4: Ionic Bond Model

Lewis structure of atoms (Review)

1A	2A	3A	4A	5A	6A	7A	8A
H·							He:
Li·	Be·	·B·	·C·	·N:	:O:	:F:	:Ne:
Na·	Mg·	·Al·	·Si·	·P:	:S:	:Cl:	:Ar:

Cations and Anions

Cations

- What elements lose electrons? And how many?
- What is the positive charge on their cations?

Anions

- What elements gain electrons?
- What is the positive charge on their anions?

Covalent bonds

- How many covalent bonds are formed?
- What elements share electrons?

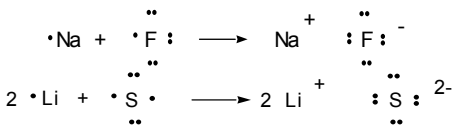
C	X· X· X· X· X· X· X·
N	X· X· X· X· X· X· X·
Na^+	X· X· X· X· X· X· X·
O	X· X· X· X· X· X· X·

Ionic model of bonding model (Review)

Ionic bond - results from the electrostatic attraction between a cation and an anion of two atoms typically involves a metal and a nonmetallic element.

Anion: An atom that gains electrons becomes a negative ion

Cation: An atom that loses electrons becomes a positive ion



Chapter 5. Chemical Bonding: The Covalent Bond Model

Lewis Model of bonding (Review)

"octet rule"

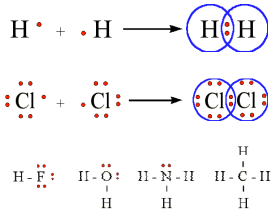
atoms tend to gain, lose or share electrons so as to have eight electrons in their outer electron shell

"Lewis structure of atoms"

Shows only valence electrons, is a convenient way of representing atoms to show their chemical bonding pattern.

Covalent model of bonding (Review)

Covalent bonds - results from the sharing of electrons between two atoms typically involves two nonmetallic elements



Types of electrons

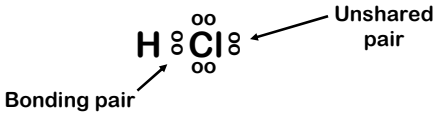
Bonding pairs

Two electrons that are shared between two atoms.

A covalent bond.

Unshared (nonbonding) pairs

A pair of electrons that are not shared between two atoms. Lone pairs or nonbonding electrons.



Drawing Lewis structure molecules and ions (Review)

3) Draw the skeletal structure by connecting the atoms with single bonds.

4) Give each of the atoms an octet (8 e-). Adding unshared pairs of electrons

5) Count the total number of e- used through step 4 and compare to the number calculated in step 2.

a) If it results in zero, the structure is correct.

b) For every two electrons too many, another bond is added (minimize formal charges).

Multiple bonds form only with C, N, O and S.

Total number of bonds to neutral atoms:

- 4 bonds to C
- 3 bonds to N, P
- 2 bonds to O, S
- 1 bond to H, F, Cl, Br, I

Drawing Lewis structure molecules and ions (Review)

1) Predict arrangement of atoms.

a) H is always a terminal atom.

b) Halogens and oxygen are often terminal.

c) The central atom of binary compounds is usually written

d) first and has the lowest subscript.

e) Most organic compounds have more than two central atoms.

f) These are mainly C, but N, O and S can also be central atoms.

2) Total number of valence electrons (e-)

a) Add all valence electron of atoms in the molecule from the formula.

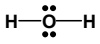
b) Add the ion charge for negative ions or subtract for positive ions.

Calculation of formal charges of atoms in the Lewis structure

1. For a neutral molecule, the sum of the formal charges equals zero. For a polyatomic ion, the sum of the formal charges equals the charge on the ion.
2. Formal charge of each atom is calculated by:

   (group #) - (# unshared e-) - ½ (# shared e-)
3. Formal charges are shown as + or - on the atom with that charge.
4. An atom with the same number of bonds as its group number has no formal charge.
5. In a molecule if two different elements can be assigned a negative charge, then the more electronegative element gets the charge; the same sign should not be given to bonded atoms.

Lewis Structures (Review)



H_2O (8)
Water

HCl (8)
Hydrogen chloride

CH_4 (8)
Methane

NH_3 (8)
Ammonia

- How many bonding electron pairs are in the molecule?
- How many bonding electron pairs are in each atom?
- How many nonbonding electron pairs are in the molecule?

Draw Lewis structure of molecules

$CHCl_3$

C_2H_4

C_3H_8O

$CH_3CH_2CH_2OH$

$CH_3CH_2OCH_3$

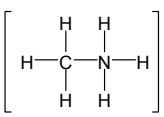
CH_3CO_2H

CH_3CHO

Draw Lewis structure and assign formal charges

$CH_3NH_3^+$

C = (group #)of C - (# unshared e- in C) - ½ (# shared e- in C) = 4 - 0 - 1/2(8) = 0



C = 4 - 0 - 1/2(8) = 0
N = 5 - 0 - 1/2(8) = +1
H = 1 - 0 - 1/2(2) = 0

CH_3O^-

Valence-Shell Electron-Pair Repulsion (VSEPR) model (Review)

For predicting shapes of molecules and polyatomic Ions based on the repulsion of valence pairs of electrons making them as far apart as possible around an atom of a Lewis structure.

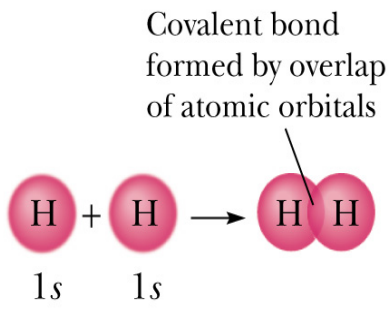
1) Draw the Lewis structure for the molecule or ion.

2) Determine the number of bonding and unshared pairs attached to the central atom.

One single, double or triple bond counted as a bonding pair

3) Choose the appropriate case from the given chart.

Orbital Overlap Model



Hybrid Atomic Orbitals

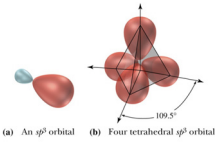
Hybridization is the mixing up of two or more atomic orbitals

There are three types of hybrid atomic orbitals for carbon

- sp^3 (one *s* orbital + three *p* orbitals give four sp^3 orbitals)
- sp^2 (one *s* orbital + two *p* orbitals give three sp^2 orbitals)
- *sp* (one *s* orbital + one *p* orbital give two *sp* orbitals)

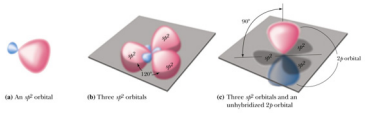
s and p hybrids

Four sp^3 hybrids



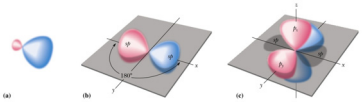
(a) An sp^3 orbital (b) Four tetrahedral sp^3 orbitals

Three sp^2 hybrids



(a) An sp^2 orbital (b) Three sp^2 orbitals (c) Three sp^2 orbitals and an unhybridized 2p orbital

Two sp hybrids



(a) (b) (c)

Electronegativity (Review)

Is the attraction of an atom for its valence electrons

increases →

increases ↑

H						
2.1						
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0

Nonpolar/polar-covalent and ionic bonds. (Review)

We classify chemical bonds as polar covalent, nonpolar covalent and ionic based on the difference in electronegativity between the atoms

Difference in Electronegativity Between Bonded Atoms	Type of Bond
less than 0.5	nonpolar covalent
0.5 to 1.9	polar covalent
greater than 1.9	ionic

Covalent or Ionic

Identify covalent and ionic compounds:

$NaCl$, C_2H_5OH, CH_3COOH, Na_2CO_3, CH_3OK, KOH

Covalent :

Ionic:

Classify following bonds nonpolar-covalent, polar-covalent or ionic bonds

N-H nonpolar-covalent, polar-covalent or ionic bonds

O-H nonpolar-covalent, polar-covalent or ionic bonds

C-H nonpolar-covalent, polar-covalent or ionic bonds

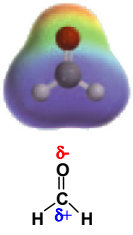
C-F nonpolar-covalent, polar-covalent or ionic bonds

Na-Cl nonpolar-covalent, polar-covalent or ionic bonds

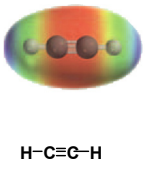
Al-Cl nonpolar-covalent, polar-covalent or ionic bonds

Polar and nonpolar molecules

Ammonia (polar)



Formaldehyde (polar)



Acetylene (nonpolar)

Predict the bond angles of molecules from their Lewis structures. (Review)

Molecule	Bonding pairs	unshared pairs	Shape
H_2O	two	two	bent
NH_3	three	one	Trigonal pyramid
CH_2O	three	none	Trigonal planar
$CHCl_3$	four	none	tetrahedral
CH_4	four	none	tetrahedral
CCl_4	four	none	tetrahedral

Molecular Shape and Polarity (Review)

Molecule	Bonding pairs and unshared pairs	Electron pair distribution	Polarity
H_2O	**four**	**asymmetric**	**polar**
NH_3	**four**	**asymmetric**	**polar**
CH_2O	**three**	**asymmetric**	**polar**
$CHCl_3$	**four**	**asymmetric**	**polar**
CH_4	**four**	**symmetric**	**Non-polar**
CCl_4	**four**	**symmetric**	**Non-polar**

σ and π bonds in single and multiple bonds

single bond - one shared pair of electrons between two atoms; a σ bond

double bond - two shared pairs of electrons between two atoms; one s bond and one π bond

triple bond - three shared pairs of electrons between two atoms; one s bond and two p bonds

Predicting hybridization of atoms in a Lewis structure

Count sigma bonds and unshared electrons around the atom

If the total number of pairs:

2 sp hybridization

3 sp^2 hybridization

4 sp^3 hybridization

Chapter 10. Acids, Bases, and Salts

10.1 Arrhenius Acid-Base Theory

10.2 Bronsted-Lowry Acid-Base Theory

10.3 Mono-, Di-, and Triprotic Acids

10.4 Strengths of Acids and Base

10.5 Ionization Constants for Acids K_a and Bases K_b

10.6 Salts

10.8 Self-Ionization of Water

10.9 The pH Concept

10.10 The pK_a Method for Expressing Acid Strength

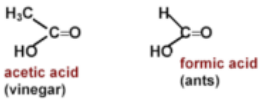
10.12 Buffers

10.13 The Henderson-Hasselbalch Equation

Acids and Bases

There are many compounds when dissolved in water changes the Hydrogen ion (H^+) (related to pH) concentration of to water to acid or basic sides

a) Binary acids: E.g. HF, HCl, HBr, HI, H_2S
b) Oxyacid: E.g. HNO_3, H_2SO_4 , $HClO_4$
c) Organic acids: E.g.



d) Hydroxy bases: NaOH, $Ca(OH)_2$
e) Amine bases: CH_3NH_2 (methylamine)
$(CH_3)_2NH$ (dimethylamine)

Arrhenius acids and bases

This is the first acid/base concept to be developed to describe typical acid/base reactions.

Arrhenius Acid:

A substance that produces H^+, or (protons) H^+_3O, (hydronium ion) in an aqueous solution.

Arrhenius Base:

A substance that produces OH^-, or hydroxide ion in an aqueous solution.

E.g. HCl (acid), NaOH (base).

Bronsted Lowery acid and bases

This is the second acid/base concept to be developed to include proton, H^+ transfer reactions to base other than those containing OH^-. This definition also uses conjugate acid/base concept .

Bronsted Acid:

A substance that donates protons (H^+): E.g. HCl (acid),

Bronsted Base:

A substance that accepts protons. E.g. NH_3 (base) non-hydroxy bases such as amines.

Lewis acid and bases

Lewis was successful in including acid and bases that catalyze organic reactions without proton or hydroxyl ions.

Lewis Acid: A substance that accepts an electron pair.

Lewis base: A substance that donates an electron pair.

E.g. $BF_3(g) + :NH_3(g) \rightarrow F_3B:NH_3(s)$

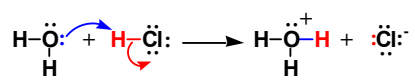
Lewis Acid Lewis base Lewis acid/base adduct

the Lewis base donates a pair of electrons to the acid forming a coordinate covalent bond common to coordination compounds. Lewis acids/bases will be discussed later in describing reaction mechanism

Bronsted Lowery Equilibria Acids/bases and Conjugate Acid/bases

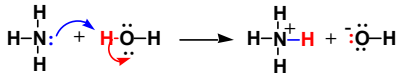
$H_2O(l)$ + $HCl(aq)$ ⇌ $H_3O^+(aq)$ + $Cl^-(aq)$

base acid conjugate acid conjugate base

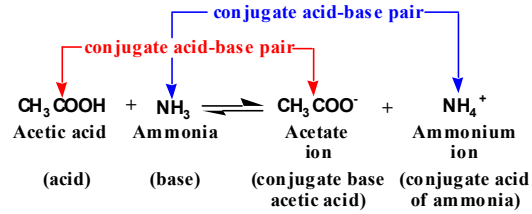


$NH_3(aq) + H_2O(l)$ ⇌ $NH_4^+ + OH^-(aq)$

base acid conjugate acid conjugate base



Strength of conjugate acid/bases



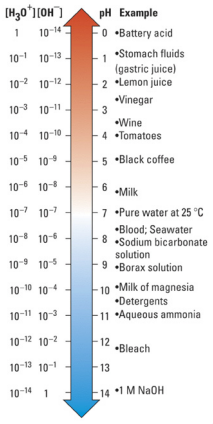
Weak acid + Weak base ⇌ Strong conjugate base + Strong conjugate acid

Other combinations

Weak acid + Strong base ⇌ weak conjugate acid + Strong conjugate base

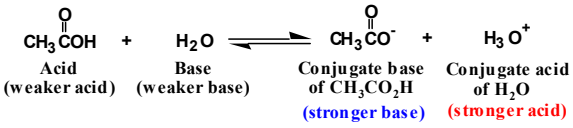
strong acid + Weak base ⇌ weak conjugate acid + Strong conjugate acid

pH of Aqueous Solutions



K_a and pK_a from acid/base equilibria

E.g. acetic acid is incompletely ionized in aqueous solution



The equation for the ionization of a weak acid, HA, is

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

$$K_a = K_{eq}[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

$$pK_a = -\log K_a$$

Relative acidity/basity

Higher the K_a : higher the acidity.

Higher the K_b : higher the basity.

Higher the pK_a : lower the acidity.

Higher the pK_b : lower the basity.

Which one is weaker acid?

HNO_2 ; $K_a = 4.0 \times 10^{-4}$. $pK_a = 3.39$

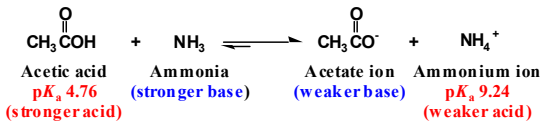
$HOCl_2$; $K_a = 1.2 \times 10^{-2}$. $pK_a = 1.92$

HOCl ; $K_a = 3.5 \times 10^{-8}$. $pK_a = 7.46$

HCN ; $K_a = 4.9 \times 10^{-10}$. $pK_a = 9.31$

pK_a in Acid-Base Equilibrium

Equilibrium favors reaction of the stronger acid and stronger base to give the weaker acid and the weaker base



Molecular Structure and acidity

Binary acids

E.g. HF, HCl, HBr, HI, H_2S

The acidity of the haloacid: (HX; X = F, Cl, Br, I)

Series increase in the following order:

HF < HCl < HBr < HI

(Going down a group it increase for binary acids)

Oxo acids

Acidity depends oxo groups $HClO_4$,

Acidity: $HClO_4 > HClO_3 > HClO_2 > HClO$

$HNO_3 > HNO_2$

$H_2SO_4 > H_2SO_3$

Molecular Structure and acidity

Organic acids

Higher the pK_a higher the acidity

The most important factor in determining the relative acidity of an organic acid is the relative stability of the anion, A^-, formed when the acid, HA, transfers a proton to a base

There are three factors:

- the electronegativity of the atom bonded to H in HA
- resonance stabilization of A^-
- the inductive effect

Electronegativity of the atom bonded to H in HA

Acid	CH_3CH_2-H	CH_3NH-H	CH_3O-H
pK_a	51	38	16
	increasing acidity →		
Electronegativity of A in A-H	2.5	3.0	3.5
Anion	$CH_3CH_2^-$	CH_3NH^-	CH_3O^-
	increasing anion stability →		