

Electronic Structure of the Atom

A century ago, the atom was considered to be “solid”.

Rutherford’s experiments showed however that atoms are mostly “empty” and eventually it was realized that atoms consist of a massive nucleus (**protons** and **neutrons**) and much less massive **electrons** (about 1/2000 the mass of a proton).

Diameter of an atom is about 10^{-10} meters or 1 Angstrom (\AA)

Diameter of the nucleus is only about 10^{-14} meters or 0.0001 \AA .

Elements are characterized by the number of their protons in the nucleus. Atoms with the same number of protons but different numbers of neutrons are called isotopes.

^{12}C (most): 6 protons, 6 neutrons, mass 12

^{13}C (1.1%): 6 protons, 7 neutrons, mass 13

^{14}C (<0.1%): 6 protons, 8 neutrons, mass 14

^{14}C is radioactive, *beta* emitter, half-life 5730 years.

(See links for radiocarbon dating and ^{14}C to ^{14}N decay)

Einstein’s equation was discovered (photo-ionization). This law states that electrons can have only certain amounts of energy.

The electrons are responsible for the bonding between atoms and their description is thus of particular relevance.

The Bohr Model of the Atom

Electrons are thought of as particles that move around the atom's nucleus. This motion may occur in different shells. The shells are named with capital letters starting with the innermost shell; K, L, M, ...

The closer the electron is to the nucleus, the lower is its energy, that is, the more energy will be required to remove it. You may think of it in electrostatic terms: The nucleus and the electron attract each other and this interaction depends on the distance. Why different shells? It turns out that there is only a certain number of electrons allowed in each shell: $2n^2$ where n is the number of the shell starting with K.

| | | |
|---|-------|--------------|
| K | $n=1$ | 2 electrons |
| L | $n=2$ | 8 electrons |
| M | $n=3$ | 18 electrons |
| N | $n=4$ | 32 electrons |

There are a few problems with this model. Classical physics tells us that accelerated charge emits radiation. Moving electrons are accelerated (direction change), but atoms do not radiate. There are other problems that we need not go into.

The Quantum-Mechanical Atom

Heisenberg's uncertainty principle leads to the modern view of the electronic structure of atoms. The principle says: You cannot know the energy and the location of a moving particle accurately at the same time.

If you know the energy, then the location is uncertain.

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Photoionization shows that atoms have well defined energy levels. Hence, the location of the electron must be uncertain!

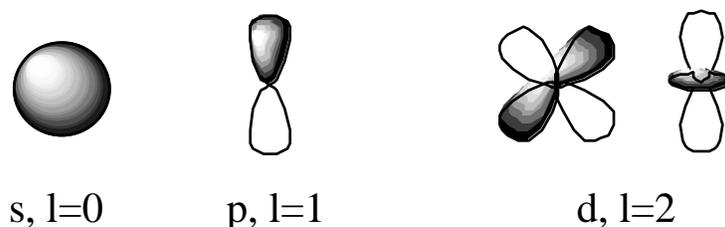
Electrons are no longer thought of as particles. It is recognized that the electron may be described by a wave function and that the electrons in atoms are standing wavefunctions. We no longer describe the electron by place and energy but instead by its energy and the probability of finding the electron at a certain place in space. The regions in which an electron moves are called the orbitals. The orbitals are solutions to the Schroedinger Equation. It is the square of the orbitals, ψ^2 , that represents the electron density distribution.

Orbitals have sign information (left). Electron density distributions, ψ^2 , do not have sign information (right).



Shapes of Atomic Orbitals

There are different shapes of orbitals. Shapes of atomic orbitals (AOs) are specified by the small letter s, p, d, f ... indicating second quantum numbers (l) of 0, 1, 2, 3, ... and so on.

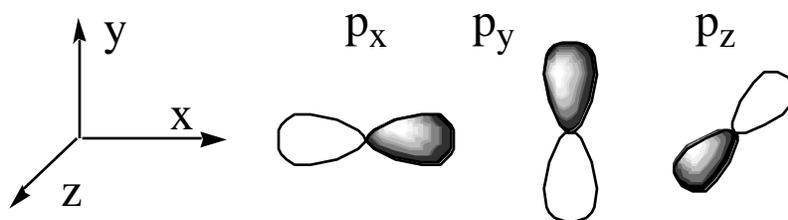


Number and Degeneracy of Atomic Orbitals

For a given main quantum number, l can assume values that are between 0 and $n-1$. Depending on the type of AO, there are different numbers of AOs allowed: $2l+1$.

- $l=0$, s-AO, not degenerate
- $l=1$, p-AO, 3-fold degenerate
- $l=2$, d-AO, 5-fold degenerate
- $l=3$, f-AO, 7-fold degenerate

This has to do with possible orientations in space.



Occupation of Atomic Orbitals

Each orbital may only be occupied by two electrons with opposite spin (Pauli Rule).

In the particle picture, spin has a very clear meaning. The particle rotates around its own axis. This rotation can occur in two ways: clockwise or counter-clockwise.

In the quantum world, there are no particles and “spin” becomes impossible to visualize. But again, there are two possibilities for the spin. They are called alpha and beta. Up and down arrows are used for these spin states as well.

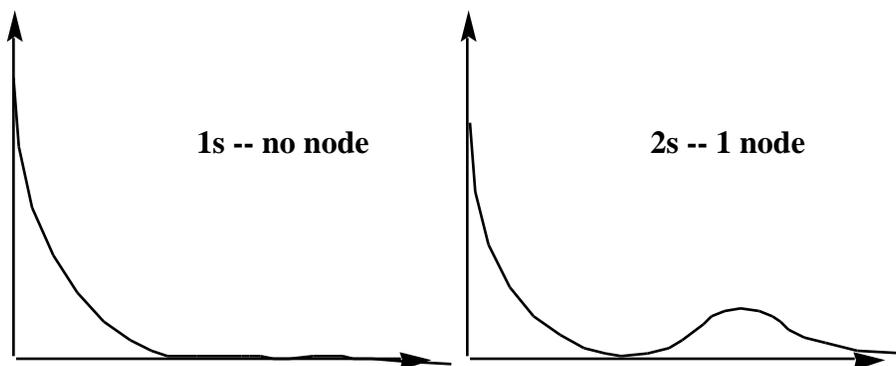
Number and Type of AOs per Shell

Each energy level (“shell”) allows only for a certain number of orbitals. The rule is that the second quantum number l can be lower or equal but may not exceed $n-1$.

| Level n | $l=0$ | $l=1$ | $l=2$ | Max. # |
|-----------|-------|---------------|-----------|--------|
| 1 | 1s | | | 2 |
| 2 | 2s | 2p (px,py,pz) | | 8 |
| 3 | 3s | 3p (px,py,pz) | 3d (five) | 18 |

Spherical Nodes of Atomic Orbitals

The s-orbitals in different shells need to be different in some way. The difference is with the number of spherical nodes. A node is a surface on which the electron density is zero. E. g.: 1s *versus* 2s.



The total number of nodes for any AO is $n-1$.

The number of node planes is given by l .

The number of node spheres is given by the difference between $n-1$ and l .

3s-AO: $n=3$, # of nodes=2

no node planes ($l=0$), 2 spherical nodes.

3p-AO: $n=3$, #of nodes=2

one node plane ($l=1$), 1 spherical node.

View graphical displays of atomic orbitals on the web!

Use the links embedded in the online Schedule.

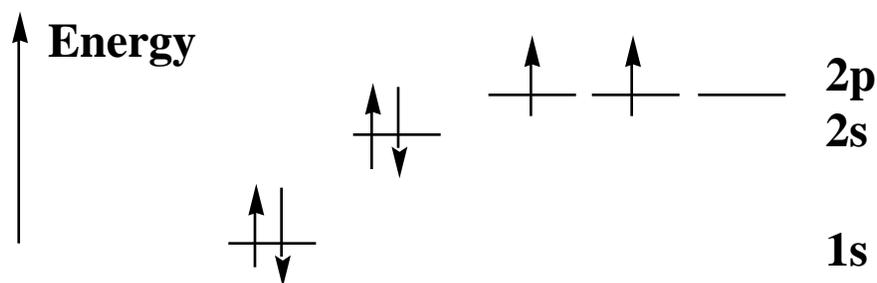
Aufbau Principle - Filling the Atomic Orbitals

Two rules:

- Fill the AOs with low energy first.
- Within a set of degenerate orbitals, fill each AO once before you start double occupation. Fill them such that all the unpaired electrons have the same spin: Seek “Maximum spin multiplicity” (Hund Rule).

To apply rule (a) we need to know the relative energies of the AOs. For H itself, all of the AOs in a given level have the same energy. For all other atoms, within an energy level the energy increases $s < p < d \dots$ So, we start filling s before p and later d.

Thus, we take the energy level diagram (occupation for C is shown) and fill in the electrons considering the above rules. Let's do that for the first two rows of the elements. Make sure you can do this also for the next row of elements.



Electron Configurations of H & He and of the “First-Row Atoms”

| Element | Atomic Number | Electron Configuration |
|---------|------------------|--|
| H | 1 | 1s ¹ |
| He | 2 | 1s ² |
| Li | 3 | 1s ² , 2s ¹ |
| Be | 4 | 1s ² , 2s ² |
| B | 5 | 1s ² , 2s ² , 2p _x ¹ |
| C | 6 | 1s ² , 2s ² , 2p _x ¹ , 2p _y ¹ |
| N | 7 | 1s ² , 2s ² , 2p _x ¹ , 2p _y ¹ , 2p _z ¹ |
| O | 8 | 1s ² , 2s ² , 2p _x ² , 2p _y ¹ , 2p _z ¹ |
| F | 9 | 1s ² , 2s ² , 2p _x ² , 2p _y ² , 2p _z ¹ |
| Ne | 10 | 1s ² , 2s ² , 2p _x ² , 2p _y ² , 2p _z ² |

Valence Electrons: Electrons in the outermost shell.

Core Electrons: Electrons that are not valence electrons.

Atomic Radius

To determine a radius of an atom we need to know where the atom ends! Well, it doesn't really end anywhere. Let's look at a more practical solution then.

Determination of Atomic Radii of Diatomics

Atomic radii are determined by measuring bond lengths of the covalent diatomic molecules and dividing by 2.

E.g.: $d(\text{H-H}) = 0.74 \text{ \AA}$; radius 0.37 \AA .

Determination of Atomic Radii of Other Elements

Determine the bond lengths of XH_n molecules.

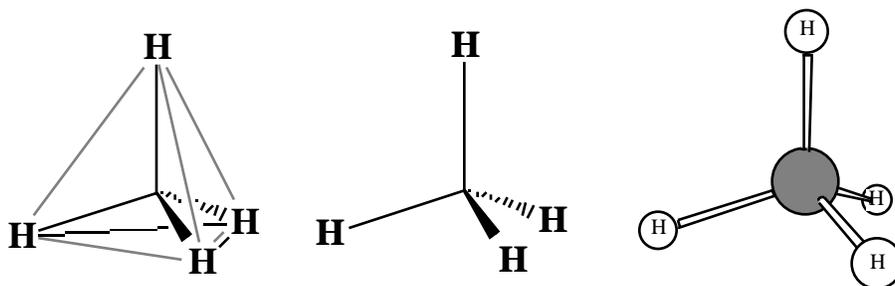
Some Numbers

The atomic radii vary systematically as we move to the right in the PSE or as we move down in the PSE. (a) They increase as we move down in the PSE. (b) They are decreased as we move to the right in the same row.

| | | | | | | | |
|-------------|-------------|-------------|-------------|-----------|-----------|-------------|--|
| H 0.37 | | | | | | | |
| Li 1.225 | Be 0.889 | B 0.80 | C 0.771 | N 0.74 | O 0.74 | F 0.72 | |
| Na 1.573 | Mg 1.364 | Al 1.248 | Si 1.173 | P 1.10 | S 1.04 | Cl 0.994 | |

See the PSE on the Course Web Site!

Introduction to the Chemical Bonding



The connectivity and the spatial arrangement of atoms in molecules were not realized until about 150 years ago! It was only in 1915 that a general method for the description of the connectivity of atoms became widely accepted. The dot structures of Lewis.

1858 August Kekule & Archibald Couper:

C is tetravalent with 4 single bonds

Alexander Brown: C-C double bond in ethylene

Emil Erlenmeyer: C-C triple bond in acetylene

1865 August Kekule: Ring structure of benzene

1874 Joseph Le Bel: Specific direction of the bonds

Jacobus van't Hoff: Tetrahedral orientation in 3-d

1915 Gilbert N. Lewis: Lewis dot structures

Kekule writes dashes instead of two dots.

Nothing but connectivity information!

Bond Formation and the “Octet Rule”

The origin of all types of bonding lies with the aim of obtaining *noble gas electronic configurations* for all atoms in the molecules. Noble gases have totally symmetric fully occupied shells and that is lowest in energy. Organic chemistry is mostly a chemistry of polar covalent bonds.

The types of bonds can vary rather significantly depending on the nature of the bonding partner. The broadest classification of the nature of the bond relates to the magnitude of charge transfer during bond formation. Classically we differentiate between ionic and covalent bonds. Ionic bonding involves transfer of electrons between atoms. Covalent bonding involves sharing of electrons. All intermediate situations may occur.

Ionic: Na^+Cl^- example (2 Ne configurations, **octet**)

Ionic: Li^+Cl^- example (He and Ne configs., **duett & octet**)

Ionic: $\text{Mg}^{2+}(\text{Cl}^-)_2$ example (3 Ne configurations, **octet**)

Covalent: H-H example (2 He configurations, **duett**)

Covalent: F-F example (2 Ne configurations, **octet**)

Covalent: Cl-Cl example (2 Ar configurations, **octet**)

Covalent: H-Cl example (1 He and 1 Ar conf., **duett & octet**)

Ionic Bonding

Stable electron configurations are reached through electron transfer and the formed ions attract each other electrostatically.

Three terms are involved:

- (a) ionization energy,
- (b) electron affinity, and
- (c) ion pairing energy.

Ionization energy

is the energy required to remove a valence electron from the neutral atom to produce a cation.



Removal of a valence electron is facile for the elements on the left in the PES and harder for the ones on the right. The elements with high IEs are said to be *electronegative* (that is, they attract their valence electrons strongly) and the others are *electropositive*.

| | | | |
|----|-------------------|-----------------|--------------|
| Li | loses 2s electron | Li ⁺ | 125 kcal/mol |
| Na | loses 3s electron | Na ⁺ | 119 kcal/mol |
| C | loses 2p electron | C ⁺ | 259 kcal/mol |
| F | loses 2p electron | F ⁺ | 401 kcal/mol |
| Ne | loses 2p electron | Ne ⁺ | 497 kcal/mol |

See the course web site for links to databases that contain the ionization energies of all elements (NIST). There also are links to databases that contain ionization energies of molecules.

Electron affinity

is the energy associated with the capture of an electron by an atom to form an anion.



This energy is released, electron affinities are negative numbers. The trends are just opposite to those found for the IEs. Electron affinities are smaller in magnitude compared to ionization energies.

| | | | |
|----|---------------------|-----------------|----------------|
| Li | gains a 2s electron | Li ⁻ | -13.6 kcal/mol |
| C | gains a 2p electron | C ⁻ | -28.9 kcal/mol |
| F | gains a 2p electron | F ⁻ | -79.6 kcal/mol |
| Cl | gains a 3p electron | Cl ⁻ | -83.0 kcal/mol |

Ion Pairing Energies

are the energies associated with bringing a cation and an anion close together. This interaction always is attractive and the ion pairing energy makes ionic bonding overall an exothermic process. Nature does not like to make charges, only pairs of charges.

Example LiF: The ionization of Li requires 125 kcal/mol. The electron capture by F releases -80 kcal/mol. Overall the ion formation consumes 45 kcal/mol. But when the ions are brought together to form an “ion pair” the Coulomb interaction renders the ionic bond forming process overall advantageous.

Example NaCl: The ionization of Na requires 119 kcal/mol. The electron capture by Cl releases -83 kcal/mol. Overall the ion formation consumes 36 kcal/mol. But when the ions are brought together to form an “ion pair” the Coulomb interaction renders the ionic bond forming process overall advantageous.

Covalent Bonds

Here bonding electron pairs are shared. Electrons no longer are transferred, but shared such that *each bonding partner reaches the next higher filled shell*. At the simplest level, covalent bond formation also can be explained in terms of electrostatic Coulomb interactions (although the “exchange terms” are just as important and neglected in this simple picture). The sharing of electrons basically allows the shared electrons to benefit from attraction to both nuclei. This effect is more beneficial than is the additional electron-electron and nuclear-nuclear repulsion that also are associated with bond formation. If the bond length would get too short, then the latter two repulsions increase sharply.

Lewis Dot Structures

are used to indicate covalent bonds. Instead of drawing the dots, it is also common to draw a line for an electron pair. Strictly speaking the resulting structures are Kekule structures or Lewis-Kekule structures, but they often are called Lewis structures as well.

How to Draw Lewis and Kekule Structures

Write down the atoms.

Mark each valence electron with a dot.

Combine the dots (pair the electrons)

Optionally: Draw dash instead of dots.

Try to make octets except for bonds involving H.

Electrons might be left over and form lone pairs.

Show: H₂, Cl₂, O₂ (double bond), N₂ (triple bond).

Number of Covalent Bonds

For each vacancy in the valence electron shell, there should be one bond formed to attain the stable noble gas electron configuration.

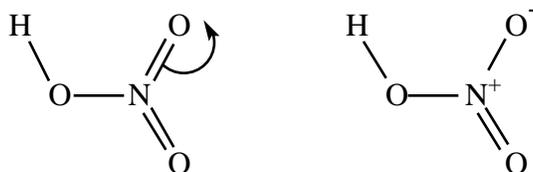
Show: H with H, C with H, C with Cl.

Example: Show C₂H₆O (alcohol and ether) in these steps:

- (1) Number of valence electrons for the atoms?
- (2) Draw Cs and O.
- (3) “Saturate” with hydrogens.
- (4) Distribute the electrons.

Formal Charges

In some cases the prescription leads to structures with atoms that have too many bonds. An example is HNO_3 . To obtain an octet at N, we need to reduce the number of bonds to N. To do this, we formally shift a bond pair onto an O.

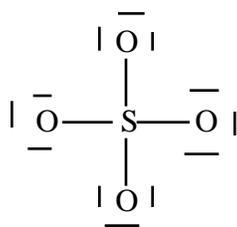


Note that the shift really means that we transfer an electron from N to O. So, we need to keep track of that and assign the formal charges as shown.

If you are given an LK structure and you need to determine the formal charges, proceed in these steps:

- determine number of valence electrons of the atoms, NVE
- determine the number of bonds the atom engages in, NB
- determine the number of unshared electrons, NUE
- $\text{FC} = \text{NVE} - \text{NB} - \text{NUE}$

Example 1: Sulfate Dianion



For S: $FC = 6 - 4 - 0 = +2$

For O: $FC = 6 - 1 - 6 = -1$

The total charge of this molecule is thus 2-. The sulfate dianion.

Example 2: Nitromethane

Example 3: Methylnitrate

Example 4: Dimethylsulfoxide

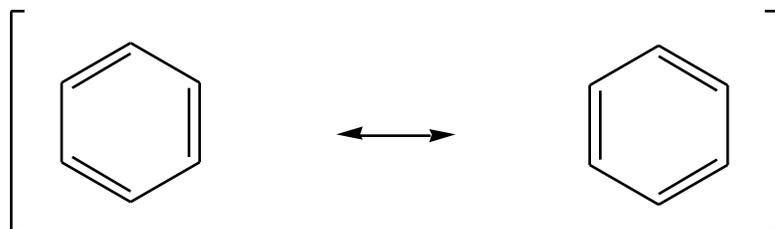
Example 5: Diazomethane

Resonance

Many compounds are not adequately represented by just a single Lewis-Kekule structure. Whenever several LK structures are needed to represent a molecule, then we say that these structures are in “resonance”, they are “resonance forms”. Instead of resonance forms, one also uses the terms “mesomeric forms” and “canonical forms”.

All resonance forms must be valid LK structures only (# of electrons, formal charges). There should be no change in multiplicity between resonance forms. Resonance forms are interconverted by shifting electron pairs (use curved arrows).

Resonance forms are written between [] brackets (often neglected) and separated by a double-sided single-line arrow “ \longleftrightarrow ”. E.g. [A \longleftrightarrow B]

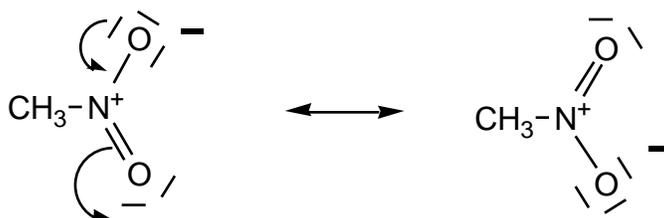


Major Contributors

- (1) Largest number of bonds. (often, but not always)
- (2) Largest number of octets. (often, but not always)
- (3) Negative charge best on electronegative atoms.
- (4) Positive charge best on electropositive atoms.

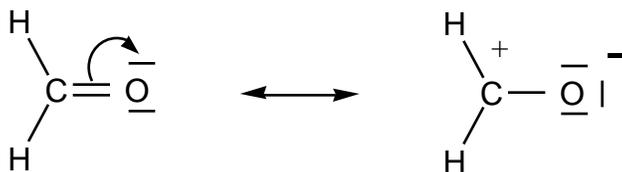
When To Use Resonance Forms?

(a) Cases where there are several possibilities to draw “all-octet” LK structures. E.g. Nitromethane.

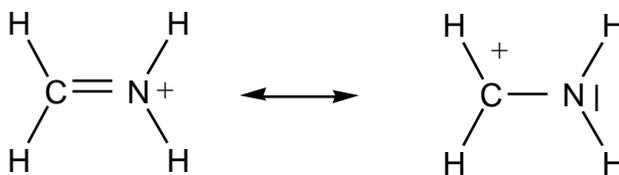


(b) Cases where structures become important that are not “all-octet” LK structures. (It should be realized that the octet rule is just an empirical thing; there is no strict law that requires octets or forbids anything else.)

E.g. Formaldehyde. In the case of formaldehyde, the polar structure actually is the major contributor.



E.g. Amino-subst. Carbenium Ion. The major contributor is the one on the right!



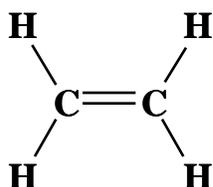
Chemical Formulas in Organic Chemistry

Empirical formula tells us the types of atoms in a molecule and their ratio. (Result of elemental analysis.)

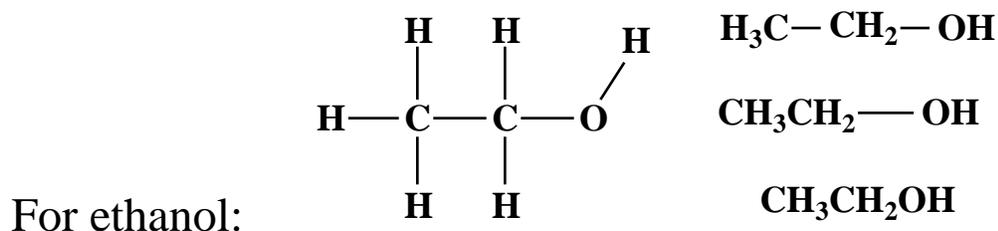
Molecular formula tells us the types of atoms in the molecule and their number.

Structural formula tells us the types of atoms in the molecule and their number and their connectivity.

For ethene (SF, MF, EF)

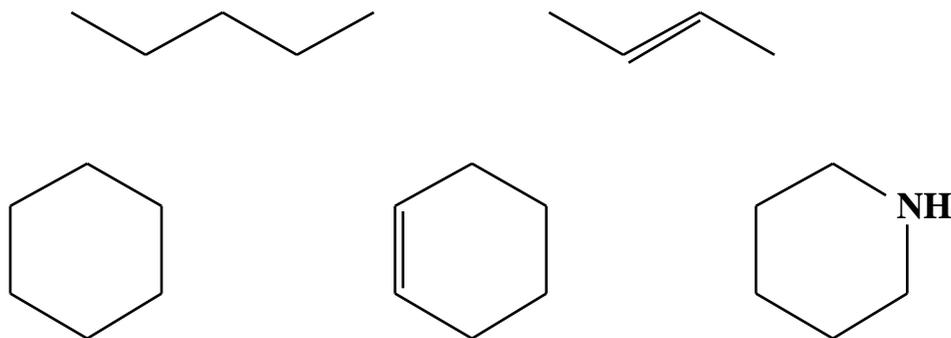


Condensed structural formulas omit the bonds but keep the groups together in the correct fashion. Most often used. Often, some bonds are indicated, e.g. those bonds that are being formed or broken.



Line-Angle Formulas or Bond-Line Formulas or Stick Figures or Skeletal Structures or Polygon Structures

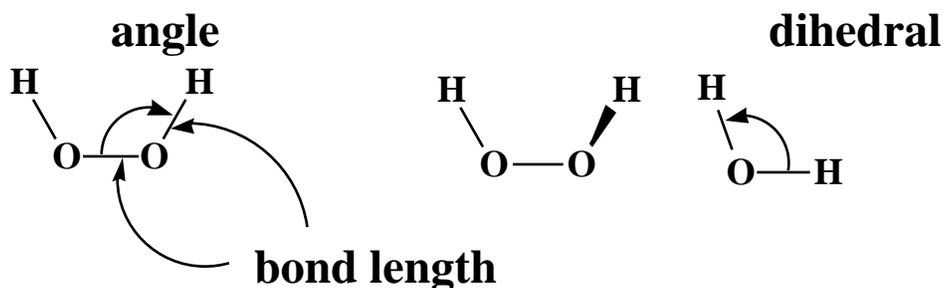
For further simplification, we usually omit C and H. Open chain alkanes become zig-zag lines and cyclic compounds become polygons. Each corner is a carbon (with the appropriate number of hydrogens). Some examples:



Bond Lengths, Angles, and Dihedrals

Structures of molecules can be determined in a number of ways. Small molecules can be explored by spectroscopic techniques, for example, and solid materials can be studied by X ray diffraction methods. Without going into detail, it is nowadays possible to obtain rather accurate structural details of just about any molecule.

Thus: We can determine the bond lengths, the bond angles, and the dihedral angles. This means that we don't have to draw our structures in 2 dimensions, instead we may indicate the relative position in 3d space in some fashion.



We'll learn some methods later, that tell us what the geometries around certain atoms are like.

Types of Bond Dissociation

There are two fundamentally different types of bond cleavage processes. Either the bonding electron pair is moved to one of the bonded fragments or it is split up between them. The different ways can be illustrated best using *curved arrows*.



Homolytic cleavage results in radical species, that is, molecules with unpaired electrons. The unpaired electron is represented as a dot. Radicals are very reactive.

Relation Between Homolytic and Heterolytic Bond Dissociation Energies

Homolytic and heterolytic dissociation energies are related with each other through the ionization energy of one of the radicals and the electron affinity of the other radical formed in the homolytic dissociation.

Homolytic Bond Dissociation Energies

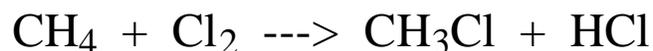
Homolytic bond dissociations have been studied extensively and a wide variety of bond dissociation energies are available in the literature. These energies play an important role as they tell us whether reactions might be possible or not. Suppose there is a reaction in which one bond is broken and one is formed. Will this reaction occur? It will most likely occur if the bond that is formed is more stable than the one that is broken.

Some Important Numbers (in kcal/mol)

| | | | |
|--------------------------------------|------|----------------------------------|-----|
| Hydrogen | | Halogens | |
| H-H | 104 | F-F | 37 |
| H-Cl | 103 | Cl-Cl | 58 |
| | | Br-Br | 46 |
| | | I-I | 36 |
| Substitution | | Saturation | |
| H ₃ C-Cl | 83.5 | H ₃ C-CH ₃ | 88 |
| H ₃ C-H | 104 | H ₂ C=CH ₂ | 163 |
| H ₃ CCH ₂ -H | 98 | HCCH | 230 |
| (CH ₃) ₂ CH-H | 94.5 | | |
| (CH ₃) ₃ C-H | 91 | | |

An Application of Bond Dissociation Energies

The reaction between methane and chlorine. Will it go?



| | | |
|----------|---------------------------|-----------------------------|
| Breaking | a H ₃ C-H bond | requires 104 kcal/mol |
| | a Cl-Cl bond | requires 58 kcal/mol |
| | | required total 162 kcal/mol |

| | | |
|---------|----------------------------|---------------------------|
| Forming | a CH ₃ -Cl bond | gain 83.5 kcal/mol |
| | a H-Cl bond | gain 103 kcal/mol |
| | | gain total 186.5 kcal/mol |

Thus: Overall the bonds formed are 24.5 kcal/mol more stable than the ones that are broken. Yes, it will go.

Bond Dissociation Energies of Polar and Unpolar Bonds

Pauling observes

$$D_{AB} = D_{A-A} + D_{B-B} - [D_{A-A} \cdot D_{B-B}]^{1/2}$$

Interpretation

"... the energy of an actual bond between unlike atoms is greater than (or equal to) the energy of a normal covalent bond between these atoms. This additional bond energy is due to the additional ionic character of the bond; that is, it is the additional ionic resonance energy that the bond has as compared with a bond between like atoms."

Link to an Atom Property

$$D_{AB} = 30 (\chi_A - \chi_B)^2$$

Electronegativity is a measure of an atom's attraction for its outer bonding electrons. The electronegativity affects the bond polarity and has major consequences for chemical reactivity.

Electronegativity

Ionic and covalent bonds are merely describing limiting cases. All kinds of bond polarities are possible -- from the very high polarity resulting from complete charge transfer in ionic species to the very low polarity in covalent bonds between atoms of the same type. Whenever a “covalent“ bond is formed between atoms of a different type, the resulting bond will be somewhat polar because of the inductive effect. We use electronegativity to discuss just that.

Trends

Rule I. As we add electrons to the same energy level (across a row) the attraction between the nucleus and the electrons increases more than the electron-electron repulsion. Thus, EN increases as we move to the right in the PSE.

Rule II. EN decreases within a group. The valence electrons are farther away from the nucleus and less attracted to it.

Electronegativity Numbers

The ones given in bold face should be remembered.

| | | | | | | |
|------------------------|-----------|-----------|------------------------|------------------------|------------------------|------------------------|
| H 2.1 | | | | | | |
| Li 1.0 | Be 1.6 | B 2.0 | C 2.5 | N 3.0 | O 3.5 | F 4.0 |
| Na 0.9 | Mg 1.2 | Al 1.5 | Si 1.8 | P 2.1 | S 2.5 | Cl 3.0 |

This is the **Pauling** scale. There are others and the numerical values may differ slightly. Elements with low EN values may be called “electropositive”; doesn’t make much sense (!) but it’s used.

Difference in EN between bonded atoms causes a shift of the bonding electron pair toward the more electronegative atom. Bond Polarization. Polar covalent bonds result. Aside from EN, the *polarizability* of the atoms also plays a role. The outer electrons can be deformed easier (deviation from spherical distribution). The larger the atom the larger is its polarizability.

Covalent -- Semi-Polar -- Polar -- Ionic Bond

Bond Polarity

The polarity is indicated by partial charges. Also possible is the indication of the direction of the polarization *via* a dipole moment vector. Several bonds: Dipole for each.

Example 1: Hydrogenchloride



Example 2: Chloromethane. Show the molecule, show partial charges + and -, indicate bond dipole moment with an arrow from C to Cl. Carbon is positive pole.

Example 3: Tetraethyllead (in gas). Here, carbon is negative pole.

Bond Dipole Moments and Molecular Dipole Moments

Bond Dipole Moments

Dipole moments are defined as the product between the (partial) charge and the distance between them. Their units are Debye (D). For unit charges to be separated by 1 Angstrom, the dipole moment is 4.8 Debye. Dipoles of most organic molecules range from 0 up to 3.

| | | |
|--------------|------------|-------------|
| C-N = 0.22 | C-O = 0.86 | C-F = 1.51 |
| Some Numbers | | C-Cl = 1.56 |
| | | C-Br = 1.48 |
| | | C-I = 1.29 |

Molecular Dipole Moments

The sum of the bond dipole moments. Vector addition!

Molecules with very strongly polar bonds may have very small dipole moments (e.g. CCl_4). (Note that the molecular dipoles are measured and the bond dipoles are the derived values.)

Remember: Dipole moment of water is 1.85 D

Bond dipole moment of H-O bond is 1.51 D.

Symmetry is often more important for dipole considerations than is the knowledge of bond dipole moments. Symmetry allows you to compare relative dipole moments very easily.

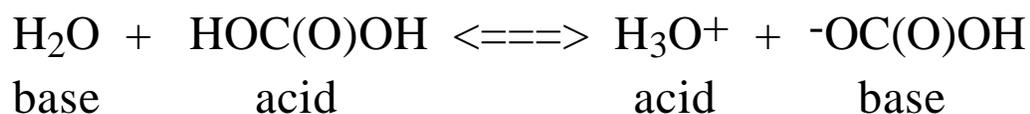
Example: CCl_4 (0) CHCl_3 (1.0 D), CH_2Cl_2 , CH_3Cl (1.9 D) and CH_4 .

Brønsted Acids and Bases

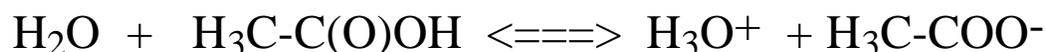
Brønsted: H^+ donors are acids and H^+ acceptors are bases

In organic chemistry we mostly deal with weak acids, that is not totally dissociated acids. We have to consider equilibria.

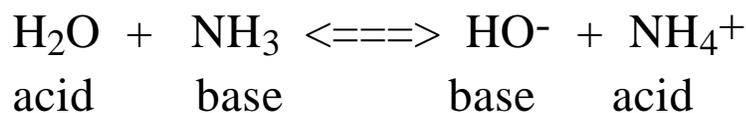
Example 1: Carbonic Acid. Only ONE weak deprotonation.



Example 2: Acetic Acid; a molecule with a *carboxyl* group.



Example 3: Amines in water. Organic bases are rel. weak.



Conjugate Acids and Bases

If water accepts a proton, it acts as a base. The resulting ion, the hydronium ion, will be an acid, the conjugate acid of the base water.

If water donates a proton, it acts as an acid. The resulting ion, hydroxide ion, will be a base, the conjugate base of the acid water.

Same with others. Acetate is the conjugate base of acetic acid. Ammonium ion is the conjugate acid of the base ammonia.

The weaker an acid the stronger is its conjugate base.

And vice versa.

The weaker a base the stronger is its conjugate acid.

And vice versa.

Factors Affecting Acidity

- * In the same group, the acidity increases with the size of the atom to which H is bonded. The reason is, that the stability of the formed X^- anion increases with the size.
- * In the same row, the acidity increases with electronegativity. Again, the stability of the formed anion is increased.
- * Note, that the acidity is not only a function of the X-H bond strength. Products also need to be considered.

Acidity and Basicity Constants

- (1) Write equation for the acid dissociation (e.g. acetic acid)
- (2) K_a is defined as the ratio $[\text{Products}] / [\text{Reagents}]$
- (3) pK_a is the negative log of K_a .

Large pK_a means weak acid, small or negative pK_a means strong acid.

- (1) Write equation for the base hydrolysis (e.g. NH_3)
- (2) K_b is defined as the ratio $[\text{Products}] / [\text{Reagents}]$
- (3) pK_b is the negative log of K_b .

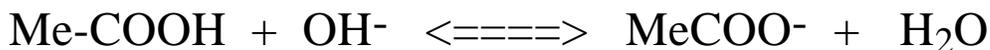
Large pK_b means weak base, small pK_b means strong base.

Practice Problem 1:

Predicting Acid-Base Reactions from pK_a values

Will acetic acid donate a proton to hydroxide anion? Hydroxide anion is the conjugate base of the weak acid water. Water is a much weaker acid than acetic acid. In general, any acid will donate a proton to the conjugate base of an acid with a higher pK_a -- that is a weaker acid.

A corollary: Reaction that convert strong acid and strong base into weaker acid and weaker base will occur.



$$pK_a = 4.7$$

Strong acid strong base

$$pK_a = 15.7$$

weak base weak acid

Practice Problem 2:

Acetylene has $pK_a = 25$. Water has a $pK_a = 15.7$. Can acetylene be deprotonated by the hydroxide ion? **No**, because acids can protonate only the conjugate base of a weaker acid.

Practice Problem 3:

The pK_a of acetic acid is 4.72. What is [proton] in 0.1 M acetic acid?

(1) Write definition for K_a .

(2) Solve for $X = [\text{proton}]$. Use $[\text{proton}] = [\text{acetate}]$ and $[\text{acid}] = 0.1$ (because it is weak and hardly dissociated).

(3) Solve numerically at home. Find solution $1.4 \cdot 10^{-3}$ M.

Lewis Acids and Bases

Lewis Acid:

Acceptor of electron pair (BF_3 , AlBr_3 , ZnCl_2) --- Sextet.

Lewis Base:

Donor of electron pair (NH_3 , OH_2) --- Has Lone pair.

These are broad definitions that include the Br nsted cases. The proton acids all allow for the generation of the proton which is the simplest Lewis acid. Other Lewis acids are metal cations and all *systems with low-lying unoccupied orbitals*.

The characteristic reaction is the complex formation between a Lewis acid and a Lewis base. Many of these reactions are important for discussions of reaction mechanisms.

Example 1: Boron trifluoride (LA) and dimethyl ether (LB).

Example 2: Alum. trichloride (LA) and trimethylamine (LB).

Example 3: Acetone and Acetic acid (two ways) being protonated by sulfuric acid.