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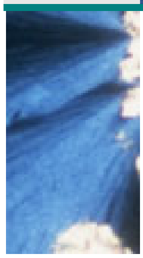

Chemical Bonding and Chemical Structure

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The glossary in this and subsequent chapters is a list of the key terms and concepts contained in the chapter. These terms and concepts will be used throughout the text. It probably will not help you to memorize the exact definitions given in the text; rather, define each of these terms and concepts in your own words and give an example if appropriate.

CONCEPTS

I. ATOMS

A. Basics

1. A neutral atom of each element contains a number of both protons and electrons equal to its atomic number.
2. The ease with which neutral atoms lose electrons to form positive ions increases to the left and towards the bottom of the periodic table.
3. The ease with which neutral atoms gain electrons to form negative ions increases to the right and towards the top of the periodic table.
4. Two different species that have the same number of electrons are said to be isoelectronic.
5. Chemistry happens because of the behavior of electrons in atoms and molecules.
   a. Organic chemistry is the branch of science that deals generally with compounds of carbon. Initially, the term organic implied a connection with living things.
   b. In the modern concept, organic chemistry deals with compounds of carbon regardless of their origin.
   c. As a science, organic chemistry lies at the interface of the physical and biological sciences.

B. Valence Electrons

1. The electrons in the outermost shell (the valence shell) of an atom are called valence electrons.
2. The number of valence electrons for any neutral atom in an A group of the periodic table (except He) equals its group number.
3. Stable ions are formed when atoms gain or lose valence electrons in order to have the same number of electrons as the noble gas of closest atomic number.

II. CHEMICAL BONDS

A. Ionic Bonds

1. The ionic bond—a force that hold atoms together within molecules—is an electrostatic attraction between ions of opposite charge.
2. The ionic bond is most likely to form between atoms at opposite ends of the periodic table.
3. The formation of ions tends to follow the octet rule—each atom is surrounded by eight valence electrons (two electrons for hydrogen).
4. The ionic bond is the same in all directions; that is, it has no preferred orientation in space.
5. When an ionic compound dissolves in water:
   a. ionic bonds are broken;
   b. the ionic compound dissociates into free ions.

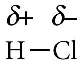
$$\mathrm{Na^+Cl^-} \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+} + \mathrm{Cl^-}$$

B. Covalent Bonds

1. Covalent bonds are formed when the orbitals of different atoms overlap and share electrons.
2. Both electrons in a covalent bond are shared between the bonding atoms.
3. Covalent bonding can be understood to arise from the filling of bonding molecular orbitals by electron pairs.
4. The bonding in covalent compounds tends to follow the octet rule—each atom is surrounded by eight valence electrons (two electrons for hydrogen).
5. The covalent bond has a definite direction in space.
6. All organic molecules contain covalent bonds.

C. Polar Covalent Bonds

1. In polar covalent compounds, electrons are shared unequally between bonded atoms, and a bond dipole results.
   a. The tendency of an atom to attract electrons to itself in a covalent bond is indicated by its electronegativity.
   b. A polar bond is a bond between atoms of significantly different electronegativities.
2. Partial charge in a polar covalent bond is indicated by a delta (δ), which is read "partially" or "somewhat."

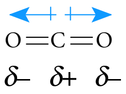


$$\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{Cl}}$$

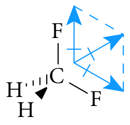
3. The uneven electron distribution in a compound containing covalent bonds is measured by the dipole moment μ in units of debyes D:

$$\mu = q\mathbf{r}$$

   where q is the magnitude of the separated charge and $\mathbf{r}$ is a vector from the site of positive charge to the site of negative charge.
   a. Dipole moments of typical polar organic molecules are in the 1–3 D range.
   b. Each polar bond has associated with it a dipole moment contribution, called a bond dipole.
4. A bond dipole is a vector quantity and μ and $\mathbf{r}$ have the same direction; the dipole moment is oriented from the partial positive charge to the partial negative charge.
   a. The vector sum of all bond dipoles in a molecule is its dipole moment.
   b. Two vectors of equal magnitude oriented in opposite directions always cancel.



$$\underset{\delta-}{\mathrm{O}}=\underset{\delta+}{\mathrm{C}}=\underset{\delta-}{\mathrm{O}}$$



5. Molecules that have permanent dipole moments are called polar molecules.
6. The polarity of a molecule can significantly affect its chemical and physical properties.

D. Octet Rule

1. An atomic species tends to be especially stable when its valence shell contains eight electrons.
2. The tendency of atoms to gain or lose valence electrons to form ions with the noble-gas configuration is known as the octet rule.
   a. The octet rule is often obeyed in covalent bonding.
   b. The sum of all bonding electrons and unshared pairs for atoms in the second period of the periodic table will under no circumstances be greater than eight (octet rule). These atoms may, however, have fewer than eight electrons.
   c. In some cases, atoms below the second period of the periodic table may have more than eight electrons. However, these cases occur so infrequently that rule b should be followed until exceptions are discussed.
3. To determine if an atom has a complete octet, count all unshared valence electrons and all bonding electrons.

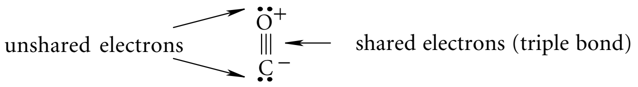
E. Lewis Structures

1. Lewis structures are molecular structures that use lines and/or dot symbols between atoms to denote bonds and dot symbols on atoms to denote unshared electrons.
   a. Nonvalence electrons are not shown in Lewis structures.
   b. A hydrogen can share no more than two electrons.
2. A bond consisting of one electron pair is called a single bond (bond order = 1).
3. A bond consisting of two electron pairs is called a double bond (bond order = 2).

4. A bond consisting of three electron pairs is called a triple bond (bond order = 3).

F. Formal Charge

1. Formal charge is an electronic bookkeeping system that assigns a charge to specific atoms.
2. The sum of the formal charges on the individual atoms must equal the total charge of the ion.
   a. Assign a valence electron count to the atom by adding all unshared valence electrons on the atom and one electron from every covalent bond to the atom.
   b. Subtract this electron count from the group number of the atom in the periodic table (equal to the number of valence electrons in the neutral species).
   c. The resulting difference is the formal charge.



III. MOLECULAR STRUCTURE

A. General

1. The structure of a molecule is determined by its molecular connectivity (how atoms are connected) and molecular geometry (how they are situated in space).
2. Sources of molecular structure are
   a. X-Ray crystallography
   b. electron diffraction
   c. microwave spectroscopy
3. How a molecule reacts chemically is closely linked to its structure.

B. Bond Lengths

1. The bond length is the distance between the centers of the bonded nuclei (in Å; Å = 10^{-10} m).
2. Bond lengths are governed, in order of importance, by:
   a. The row of the periodic table from which the bonded atoms are derived: longer bonds are associated with higher periods (lower rows).
   b. Bond order (the number of covalent bonds shared by two atoms): bonds of higher order are shorter.
   c. The column of the periodic table from which the bonded atoms are derived: longer bonds are associated with higher atomic number.

C. Bond Angles

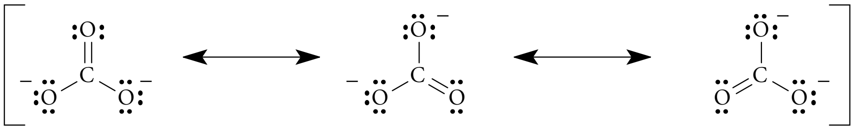
1. The bond angle is the angle between each pair of bonds to the same atom.
2. The bond angles within a molecule determine its shape.
3. Approximate bond angles can be predicted by assuming that the groups bound to a central atom are as far apart as possible.
   a. An atom bonded to four groups has tetrahedral geometry (bond angle = 109.5°).
   b. An atom bonded to three groups has trigonal planar geometry (bond angle = 120°).
   c. An atom bonded to two groups has linear geometry (bond angle = 180°).
   d. An unshared electron pair can be considered as a bond without a nucleus at one end.

D. Molecular Geometry

1. The geometry of a molecule is the spatial relationship of the bonds on adjacent atoms and is important for molecules that contain many atoms.
2. The angular relationship of bonds on adjacent atoms when projected onto the same plane is called the dihedral (torsional) angle.
3. The geometries of a molecule are described by specifying the bond lengths, bond angles, and dihedral angles between bonds on adjacent atoms.

E. Resonance Structures

1. A molecule that is not adequately described by a single Lewis structure is represented as a resonance hybrid.
   a. A resonance hybrid is a weighted average of two or more fictitious Lewis structures.
   b. When resonance structures are identical, they are equally important descriptions of the molecule.
   c. Resonance between two Lewis structures is shown by a double-headed arrow.
   d. Resonance structures are not in equilibrium; a molecule has a single structure that is a hybrid of its fictitious Lewis structures.



2. A molecule represented by resonance structures is more stable than its fictional resonance contributors and is said to be resonance-stabilized.

IV. NATURE OF THE ELECTRON

A. Wavelike Properties

1. In the submicroscopic world of the electron and other small particles, there is no real distinction between particles and waves.
   a. The behavior of very small objects simultaneously as waves and particles is called the wave-particle duality.
   b. Orbitals are descriptions of the wave properties of electrons in atoms and molecules, including their spatial distribution.
   c. As a consequence of their wave properties, electrons in atoms and molecules can exist only in certain allowed energy states (orbitals).
   d. Waves have peaks and troughs, which are regions where the waves are, respectively, at their maximum and minimum heights.
   e. A node is a point, or in a three-dimensional wave, a surface, at which the wave is zero.
   f. An atomic orbital in physics is described by a mathematical function called a wavefunction.
      i. The sign of the wavefunction for an electron is not the same as the charge on the electron.
      ii. A wave peak is a region in which the wavefuntion has a positive (+) sign.
      iii. A wave trough is a region in which the wavefuntion has a negative (–) sign.
      iv. The wavefunction is zero at a node.
2. The theory that describes the behavior of electrons in molecules is called quantum mechanics.
   a. Heisenberg uncertainty principle: the exact position and velocity of an electron cannot be specified; only the probability that it occupies a certain region of space can be specified.
   b. Pauli exclusion principle: no two electrons may have all four quantum numbers the same. A maximum of two electrons may be placed in any one atomic orbital, and these electrons must have opposite spins.
   c. Hund's rules: electrons are distributed among identical orbitals of equal energy, single electrons are placed into separate orbitals before the orbitals are filled, and the spins of these unpaired electrons are the same.
   d. Aufbau principle: to determine the electronic configuration of an atom, electrons are placed one by one into orbitals of the lowest possible energy in a manner consistent with the Pauli exclusion principle and Hund's rules.
3. Electron density within an orbital is a matter of probability (Heisenberg uncertainty principle); think of an orbital as a "smear" of electron density.

B. Quantum Numbers

1. Electrons in orbitals are characterized by quantum numbers which, for atoms, are designated n, ℓ, m, and s.

  a. The principal quantum number n can assume any integral value greater than zero ($n = 1, 2, 3, \ldots$).
  b. The angular momentum quantum number ℓ depends on the value of n and can assume any integral value from zero through $n - 1$ ($\ell = 0, 1, 2, \ldots, n - 1$) where $\ell = 0 \Rightarrow s$; $\ell = 1 \Rightarrow p$, $\ell = 2 \Rightarrow d$, and $\ell = 3 \Rightarrow f$.
  c. The magnetic quantum number m depends on the value of ℓ and can assume integral values between $-l$ and $+l$.
  d. The spin quantum number s can assume a value of $+\frac{1}{2}$ or $-\frac{1}{2}$.

2. Each orbital is described by a series of three quantum numbers:
  a. The principal quantum number n governs the energy and size of an orbital; orbitals of higher n have higher energy.
  b. The angular momentum quantum number ℓ governs the shape of an orbital: $\ell = 0$ (s orbitals) are spheres; orbitals with $\ell = 1$ (p orbitals) are dumbbells.
  c. The magnetic quantum number m governs the orientation (directionality) of an orbital.

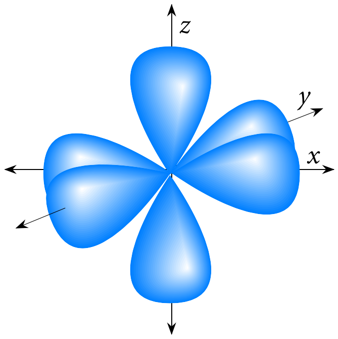
C. Energies

1. The energy of an electron is quantized, that is, limited to certain values.
  a. The higher the principal quantum number n of an electron, the higher the energy.
    i. In atoms other than hydrogen, the energy is also a function of the ℓ quantum number.
    ii. Electrons with the same principal quantum number n but different values of ℓ have different energies.
  b. Gaps between energy levels become progressively smaller as the principal quantum number increases.
  c. The energy gap between orbitals that differ in principal quantum number is greater than the gap between two orbitals within the same principal quantum number.

V. ORBITALS

A. Atomic Orbitals

1. Some orbitals contain nodes which separate the wave-peak parts of the orbitals from the wave-trough parts.
  a. An orbital with principal quantum number n has $n - 1$ nodes.
  b. The number of nodes in an atomic orbital increases with its principal quantum number.
  c. The greater number of nodes in orbitals with higher n is a reflection of their higher energies.
2. Each atomic orbital is characterized by a three-dimensional region of space in which the electron is most likely to exist.
  a. The size of an atomic orbital is governed by its principal quantum number n; that is, the larger is n, the larger the region of space occupied by the orbital.
  b. The angular momentum quantum number ℓ governs the shape of an atomic orbital.
  c. The magnetic quantum number m governs the directionality of an atomic orbital.
3. Atomic orbitals are populated with electrons according to the Aufbau principle.
4. The distribution of electron density in a given type of orbital has a characteristic arrangement in space:
  a. An electron in an s atomic orbital is a smear of electron density in the shape of a sphere.
  b. An electron in a p orbital has a smear of electron density in the shape of a dumbbell consisting of two lobes that are part of the same orbital and are directed in space.
  c. The three p orbitals are mutually perpendicular.



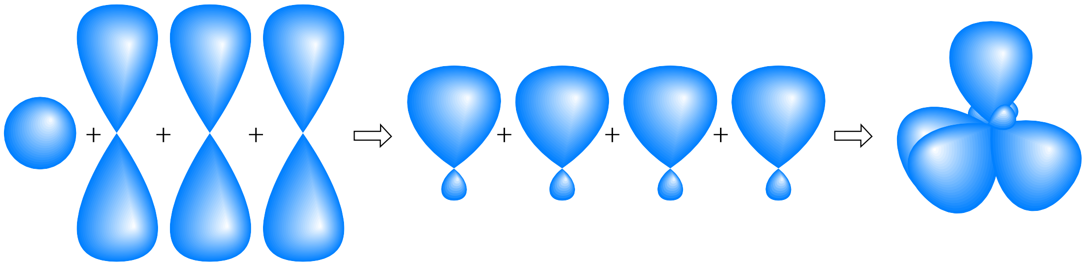
5. The electronic configuration of an atom or ion describes the distribution of electrons among the atomic orbitals.

chlorine atom $1s^2 2s^2 2p^6 3s^2 3p^5$

6. Within the A group elements, the valence electrons of an atom are the electrons that occupy the orbitals with the highest principal quantum number.
   a. The valence orbitals of an atom are the orbitals that contain the valence electrons.
   b. Chemical interactions between atoms involves their valence electrons and valence orbitals.

B. Hybrid Orbitals

1. Hybrid orbitals arise from the mixing of atomic orbitals on the same atom with different ℓ quantum numbers.
2. The hybridization of an atom and the geometry of the attached atoms are closely related.
   a. Hybridization affords bonds that are as far apart as possible.
   b. Hybridization of an atom provides orbitals that have the bulk of their electron density directed toward the nuclei of the bonded atoms.
   c. Hybridization gives stronger, more stable bonds.
3. One $2s$ orbital and three $2p$ orbitals can be mixed to give four equivalent orbitals which are one part s character and three parts p character, called sp^3 orbitals.
   a. The electron density of an sp^3 orbital is highly directed in space.
   b. One of the lobes is very large and is directed towards the bonded atom; the other lobe is very small.
   c. All sp^3-hybridized atoms have tetrahedral geometry.



4. Unshared electrons are in orbitals with more s character.
   a. Orbitals with greater s character occupy more space.
   b. Unshared pairs have a greater spatial requirement than bonds.

C. Molecular Orbitals

1. Chemical bonding is an energetically favorable process.
2. When atoms combine into a molecule, the electrons of each atom are no longer localized on individual atoms but "belong" to the entire molecule.

3. Combination of x atomic orbitals gives x molecular orbitals.
    a. One molecular orbital of the hydrogen molecule is formed by the addition (additive overlap) of the individual atomic orbitals (a bonding molecular orbital).
        i. Bonding molecular orbitals arise through wave peak-wave peak or wave trough-wave trough interactions.
        ii. The energy of an electron in the bonding molecular orbital is lower than that of an electron in an isolated atom.
    b. The second molecular orbital of the hydrogen molecule is generated by the subtraction (subtractive overlap) of the individual atomic orbitals (an antibonding molecular orbital).
        i. Antibonding molecular orbitals arise through wave peak-wave trough interactions.
        ii. The energy of an electron in an antibonding molecular orbital is higher than that of an electron in an isolated atom.
4. Molecular orbitals of greater energy have more nodes.
5. Molecular orbitals have different energies and are arranged in order of increasing energy, then populated with electrons according to the Pauli principle, Hund's rules, and the Aufbau principle.
    a. The electrons occupy the bonding molecular orbitals before occupying the antibonding orbitals.
    b. The most common bonding situations occur when bonding molecular orbitals contain electron pairs and antibonding molecular orbitals are empty.
6. The Lewis view of the electron-pair bond is approximately equivalent to the quantum-mechanical idea of a bonding molecular orbital occupied by a pair of electrons.
    a. Bonds that have cylindrical symmetry about the internuclear axis are called σ bonds (sigma bonds).
    b. The carbon in methane has an arrangement of orbitals that is different from the orbitals in atomic carbon.

SCIENTISTS

Marcellin Berthelot (1827–1907)	1.1B
Jöns Jacob Berzelius (1779–1848)	1.1B
Petrus (Peter) Josephus Wilhelmus Debye (1884–1966) [Chemistry 1936]	1.2D
Friedrich Hermann Hund (1896–1997)	1.7
Alfred Wilhelm Hermann Kolbe (1818–1884)	1.1B
Walter Kossel (1888–1956)	1.2A
Antoine Laurent Lavoisier (1743–1794)	1.1B
Gilbert Newton Lewis (1875–1946)	1.2C
Wolfgang Ernst Pauli (1900–1958) [Physics 1945]	1.7
Linus Carl Pauling (1901–1994) [Chemistry 1954, Peace 1962]	1.9A
Theophrastus Bombastus von Hohenheim (alias Paracelsus) (ca. 1493–1541)	1.1B
Friedrich Wöhler (1800–1882)	1.1B

Dates in brackets refer to Nobel Prize awards.