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Organic Chemistry

Third Edition

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Chapter 1

A Review of General Chemistry: Electrons, Bonds, and Molecular Properties

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1.1 Organic Chemistry

- The study of carbon-containing molecules and their reactions
- What happens to a molecule during a reaction?
 - molecules collide
 - bonds are broken and bonds are made



- Why do reactions, like the one above, occur?
 - We will need at least 2 semesters of your time to answer this question
 - FOCUS ON THE ELECTRONS

1.1 Organic Chemistry

• Why do we distinguish between organic and inorganic compounds?

Organic compounds contain carbon atoms

• Why are organic compounds important? Organic compounds make up things like:



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1.2 Structural Theory

- In the mid 1800s, it was first suggested that substances are defined by a specific arrangement of atoms.
 - Why is a compounds formula not adequate to define it?
 Because compounds differ in the specific ways in which atoms are bonded together
- Compounds with the same molecular formula but different structures are **constitutional isomers**.



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1.2 Structural Theory

- Atoms that are most commonly bonded to carbon include N,
 O, H, and halides (F, Cl, Br, I).
- With some exceptions, each element generally forms a specific number of bonds with other atoms



• Practice with SkillBuilder 1.1

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1.3 Covalent Bonding

• A covalent bond is a PAIR of electrons shared between two atoms. For example...



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1.3 Covalent Bonding

• How do potential energy and stability relate?



- What forces keep the bond at the optimal length?
 - Attractive forces between positively charged nuclei and negatively charged electrons
 - Repulsive forces between the two positively charged nuclei
 - Repulsive forces between the two negatively charged electrons

1.3 Atomic Structure

- A review from General Chemistry
 - Protons (+1 charge) and neutrons (neutral) reside in the nucleus
 - Electrons (-1 charge) reside in orbitals outside the nucleus.
 - Valence electrons are the electrons in the outermost shell
 - Look at carbon for example. Which electrons are the valence electrons?

Valence electrons are our focus: because they involved in bonding! WILEY

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1.3 Counting Valence Electrons

- You can always calculate the number of valence electrons by analyzing the e- configuration.
- Or, for Group A elements only, just look at the Group number on the periodic table (Group number = # of valence electrons)



• Practice with SkillBuilder 1.2

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1.3 Simple Lewis Structures

- For simple Lewis Structures...
 - 1. Draw the individual atoms using dots to represent the valence electrons.
 - 2. Put the atoms together so they **share pairs** of electrons to make complete octets.
- Take NH₃, for example...



Note the nitrogen has a lone pair of electrons

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1.3 Simple Lewis Structures

- For simple Lewis Structures...
 - 1. Draw the individual atoms using dots to represent the valence electrons.
 - 2. Put the atoms together so they share pairs of electrons to make complete octets.
- **Skillbuilder 1.3**: Try drawing a Lewis structure for CH₂O

1.4 Formal Charge

• Recall the terms we use to describe atoms with an unbalanced or FORMAL charge.

Anion = negatively charged atom Cation = positively charged atom

- Atoms in molecules (sharing electrons) are typically neutral, but can also be anionic or cationic
- To to determine the formal charge for an atom in a given molecule, compare the number of valence electrons that *it owns* (based on its bonding pattern) to the number of valence electrons that the atom needs to be neutral.

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1.4 Formal Charge

• Consider the formal charge on the atoms in the structure below, and determine if any of the atoms should have a formal charge



- **Carbon** needs **4 valence electrons** to be neutral (Group IV)
- Carbon is surrounded by 8 electrons here, but it **only owns 4** of them (1 from each of the bonds).
- Since carbon owns 4 electrons, and needs 4 electrons to be neutral, it does not have a formal charge.

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1.4 Formal Charge

• Now determine if the oxygen atom has a formal charge here.



- **Oxygen** needs 6 valence electrons to be neutral (Group VI)
- Oxygen is surrounded by 8 electrons here, but it only owns 7 of them (1 from the bond, plus 3 lone pairs).
- Since oxygen owns 7 electrons here, and needs 6 electrons to be neutral, it **has an extra electron**, and therefore has a **-1 charge**.
- Practice with SkillBuilder 1.4

• Electronegativity - how strongly an atom attracts shared electrons



 If you remember that F is the most electronegative atom, then you can always remember the relative electronegativity of the atoms in the same column or the same row of the PTE
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• There are three types of bonds:

COVALENT BOND: electrons shared between two atoms, where electronegativity difference is less than 0.5

POLAR COVALENT BOND: electrons shared between two atoms with electronegativity difference between 0.5 and 1.7

IONIC BOND: the electrons are not really shared, the two atoms differ in electronegativity by more than 1.7, and so the more electronegative atom owns the electrons.







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• Electrons tend to shift away from lower electronegativity atoms to higher electronegativity atoms.



• The greater the difference in electronegativity, the more polar the bond.



• Some bonds are acceptable to write as a covalent bond or an ionic bond, as in the following example:

• The electronegativity difference is 1.5, so it is on the cusp of polar covalent and ionic, according to just one method used for determining electronegativity values. So, the *absolute* difference in electronegativity is to be taken with a grain of salt.

• Practice with SkillBuilder 1.5

General Chemistry review

- In the 1920s, Quantum Mechanics was established as a theory to explain the wave properties of electrons
- The solution to wave equations are wave functions; The 3D plot of a (wave function)² gives an image of an atomic orbital



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1.6 Atomic Orbitals = Electron Density

- The type of orbital is identified by its shape (s, p)
- Electron density: term used to refer to probability of finding an electron (the orbital shape is 90-95% of the space where an electron "probably" is)



• We think of an **atomic orbital** as a cloud of **electron density**

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1.6 Phases of Atomic Orbitals

- Electrons behave as both particles and waves. How can they be BOTH? Maybe the theory is not yet complete
- The theory does match experimental data, and it has predictive capability.
 - Like a wave on a lake, an electron's wavefunction can have a positive (+) value, a negative (-) value, or zero (a node).



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- Because they are generated mathematically from wavefunctions, orbital regions can also be (-), (+), or ZERO
 - The sign of the wave function has nothing to do with electrical charge.
- In this p-orbital, there is a nodal plane. The sign of the wavefunction will be important when we look at orbital overlapping in bonds.



- Electrons are most stable (lowest in energy) if they are in the 1s orbital?
- The 1*s* orbital, like every atomic orbital, can have up to 2 electrons in it. If there are more electrons in the atom they fill up the 2s the 2p orbitals



Common elements and their electron configurations



 The placement of electrons are governed by the following: Aufbau principle, Pauli exclusion principle, and Hund's Rule

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1.7 Valence Bond Theory

• A bond occurs when atomic orbitals overlap. Overlapping orbitals is like overlapping waves



• Only constructive interference results in a bond

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1.7 Valence Bond Theory

• The bond for a H₂ molecule results from constructive interference



 The bonded electrons spend most of their time in the overlapping atomic orbital space... which is called a sigma (σ) bond WILEY

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- Atomic orbital wavefunctions overlap to form MOs that extend over the entire molecule.
- MOs are a more complete analysis of bonds, because they include both constructive and destructive interference.
- The number of MOs created must be equal to the number of AOs that were used.



Molecular Orbitals for H₂

• The antibonding MO has higher energy because it has one node.



When the AOs overlap the electrons go into the bonding MO rather than the antibonding MO in order to achieve a lower energy state

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- The are more than two MOs that exist for CH₃Br.. But let's focus on only two of them here
 - There are many areas of atomic orbital overlap, and nodes as well
 - Notice how the MOs extend over the entire molecule



- Each MO can hold two electrons?
- In the ground state, electrons occupy lower energy MO's while the higher energy ones remain unoccupied





- These two IVIO's nere are the most important ones: The highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO)
- These are the MO's in play when undergoing a chemical rxn

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 the ground state electron configuration for carbon can't explain how carbon makes four bonds



 If considering the excited state, it still doesn't explain how carbon makes 4 *equivalent* bonds, like the 4 bonds to H in a methane molecule

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- The carbon must undergo hybridization to form 4 equal **atomic** orbitals, with symmetrical geometry
- The **atomic** orbitals must be equal in energy to form four equalenergy symmetrical C-H bonds





 the shape of an sp³ orbital results from have 25% s-character, and 75% p-character



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• To make CH₄, the 1*s* atomic orbitals of four H atoms will overlap with the four *sp*³ hybrid atomic orbitals of C



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• Consider ethene (ethylene).



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 Each carbon in ethene must bond to three other atoms, so only three hybridized atomic orbitals are needed



 An sp² hybridized carbon will have three equal-energy sp² orbitals and one unhybridized p orbital



 the shape of an sp² orbital results from have 33% s-character, and 67% p-character

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• The sp^2 atomic orbitals overlap to form sigma (σ) bonds



• The *p* orbitals, here, overlap to form a pi bond

 The pi (π) bond is formed by SIDE-BY-SIDE overlap of the p orbitals. The electron density of the pi bond is spread out above and below the plane of the molecule, as shown below



• Pi bonds are weaker than sigma bonds.

• The pi bond is described in a similar way according to MO theory.



• Consider ethyne (acetylene).

Acetylene

 Each carbon in ethyne must bond to two other atoms, so only two hybridized atomic orbitals are needed



 The sp atomic orbitals overlap HEAD-ON to form sigma (σ) bonds while the unhybridized p orbitals overlap SIDE-BY-SIDE to form pi bonds



• Practice with Skillbuilder 1.7

1.9 Bond Strength and Length

• Which should be stronger, a pi bond or a sigma bond?

The sigma bond is considered stronger as it requires almost twice the bond energy of a pi bond to break it

 Which should be longer, an sp³ – sp³ sigma bond overlap or an sp – sp sigma bond overlap? Realize the more s-character in the orbitals, the shorter they will be

sp³ bond lengths are the longest, followed by sp², and then sp bonds.

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1.9 Bond Strength and Length

• Rationalize the bond strengths and lengths below



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1.10 Molecular Geometry

• Valence shell electron pair repulsion (VSEPR theory)

Valence electrons (shared and lone pairs) repel each other

• To determine molecular geometry, start with the **steric number**... which gives us a quick prediction



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1.10 Molecular Geometry

- The steric number translate to the hybridization of the central atom
 - If the Steric number is 4, then it is sp^3
 - If the Steric number is 3, then it is sp^2
 - If the Steric number is 2, then it is *sp*



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1.10 Molecular Geometry – *sp*³

- For any sp³ hybridized atom, the 4 valence electron pairs will form a tetrahedral electron group geometry
- Methane has 4 equal bonds, so the bond angles are equal

- The bond angles in ammonia are a little smaller
- The bond angles in oxygen are even smaller still



1.10 Molecular Geometry – *sp*³

• The **molecular geometry** is described for **only the atoms** bonded to the central atom; **electron group geometry includes lone pairs**

TABLE 1.3	COMMON MOLECULAR SHAPES THAT CAN BE PREDICTED WITH VSEPR THEORY				
EXAMPLE	BONDING ELECTRON PAIRS (BONDS)	NONBONDING ELECTRON PAIRS (LONE PAIRS)	STERIC NUMBER	PREDICTED ARRANGEMENT OF ELECTRON PAIRS	PREDICTED MOLECULAR GEOMETRY
CH ₄	4	0	4	Tetrahedral	Tetrahedral
NH ₃	3	1	4	Tetrahedral	Trigonal Pyramidal
H ₂ O	2	2	4	Tetrahedral	Bent
BF ₃	3	0	3	Trigonal Planar	Trigonal Planar
BeH ₂	2	0	2	Linear	Linear



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1.10 Molecular Geometry – *sp*²

- Calculate the steric number for BF₃
- The electron pairs in sp² hybridized orbitals (either bonded electrons or lone pairs) will form a <u>trigonal planar electron group geometry (steric number = 3 = trigonal planar)</u>



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1.10 Molecular Geometry – *sp*²

 Realize that the boron atom, in BF3, is *sp2* hybridized. The three bonds are made with *sp2* orbitals, and the unhybridized *p* orbital remains empty



1.10 Molecular Geometry – *sp*

 When steric number = 2, the geometry will be linear and the atom will be sp-hybridized



 Draw a Lewis structure for CO₂. Are the *p* orbitals on the C atom also empty in this compound, like they are with Be in the previous example?

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1.10 Molecular Geometry – Summary



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- Electronegativity differences result in polar bonds
- Induction (shifting of electrons within an orbital) results in a dipole moment.
- Dipole moment = (the amount of partial charge) x (the distance the δ + and δ are separated)
- Dipole moments are reported in units of debye (D)
- 1 debye = 10^{-18} esu · cm

- Consider the dipole for CH₃Cl
- Dipole moment (μ) = charge (e) x distance (d)
 - Plug in the charge and distance
- $\mu = (1.056 \times 10^{-10} \text{ esu}) \times (1.772 \times 10^{-8} \text{ cm})$
 - Note that the amount of charge separation is less than what it would be if it were a full charge separation (4.80 x 10⁻¹⁰ esu)
- $\mu = 1.87 \times 10^{-18} \text{ esu} \cdot \text{cm}$
 - Convert to debye
- μ = **1.87 D**





- What would the dipole moment be if CH₃Cl were 100% ionic?
- μ = charge (e) x distance (d)
 - Plug in the charge and distance, using the full charge of an electron
- $\mu = (4.80 \times 10^{-10} \text{ esu}) \times (1.772 \times 10^{-8} \text{ cm})$
- $\mu = 8.51 \times 10^{-18} \text{ esu} \cdot \text{cm} = 8.51 \text{ D}$
- What % of the C-Cl bond is ionic?
- 22% ionic character means the C-Cl bond is mostly covalent



$$\frac{1.87 \text{ D}}{8.51 \text{ D}} \times 100\% = 22\%$$

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The polarity of some other common bonds



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• Why is the C=O double bond so much more polar than the C-O single bond?



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• For molecules with multiple polar bonds, the dipole moment is the vector sum of all of the individual bond dipoles



- you have to know the molecule's geometry before analyzing its polarity
- If you have not drawn the molecule with the proper geometry, it may cause you to assess the polarity wrong as well
- Would water have a different dipole moment if it were linear instead of bent?





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• Electrostatic potential maps are often used to give a visual depiction of polarity



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Practice with SkillBuilder 1.9

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1.12 Intermolecular Forces

- Many properties such as solubility, boiling point, density, state of matter, melting point, etc. are affected by the attractions between separate molecules
- Neutral molecules (polar and nonpolar) are attracted to one another through...
 - Dipole-dipole interactions
 - Hydrogen bonding
 - Dispersion forces (a.k.a. London forces or fleeting dipoledipole forces)

1.12 Dipole-Dipole Attractions

• Dipole-dipole forces result when polar molecules line up their **opposite** charges.



- Note acetone's permanent dipole results from the difference in electronegativity between C and O
- The dipole-dipole attractions BETWEEN acetone molecules increases acetone's boiling and melting points while similar molecules without dipole-dipole interactions, such as isobutylene, have lower boiling and melting points.

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1.12 Dipole-Dipole Attractions

 Isobutylene and acetone have such different MP and BPs because of dipole-dipole interactions. Isobutylene lacks a significant dipole moment.



Isobutylene Melting point = $-140.3^{\circ}C$ Boiling point = $-6.9^{\circ}C$

isobutylene is less polar, has weaker dipole-dipole attractions and therefore a lower BP



Acetone Melting point = -94.9° C Boiling point = 56.3° C

Acetone is more polar, and so it has a higher BP

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- Hydrogen bonds are an especially strong type of dipole-dipole attraction
- Hydrogen bonds are strong because the partial + and charges are relatively large
- **H-bonding** is the **attractive force** between an H bonded to an electronegative atom (N, O and F) and a lone pair on another electronegative atom.



- Only when a hydrogen shares electrons with a highly electronegative atom (O, N, F) will it carry a large partial positive charge
- The large δ + on the H atom can attract large δ charges on other molecules



• Even with the large partial charges, H-bonds are still about 20 times weaker than covalent bonds

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Solvents that engage in H-bonding are called protic solvents.
Solvents that do not H-bond are aprotic



 Increasing the amount and extent of hydrogen bonding explains why the following isomers have different boiling points

$$H_3C - N - CH_3$$

Trimethylamine Boiling point = $3.5^{\circ}C$



Ethylmethylamine Boiling point = $37^{\circ}C$



Propylamine Boiling point = 49°C

 H-bonds are among the forces that cause DNA to form a double helix and some proteins to fold into an alpha-helix



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- If two molecules are nonpolar (dipole = 0 D), they still will have an attractive force between them
 - This occurs due to an induced, transient dipole moment, called London Dispersion Forces

- Nonpolar molecules normally have their electrons (–) spread out evenly around the nuclei (+) completely balancing the charge
- However, the electrons are in constant random motion within their MOs

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- The constant random motion of the electrons in the molecule will sometimes produce an electron distribution that is NOT evenly balanced with the positive charge of the nuclei
- Such uneven distribution produces a temporary dipole, which can induce a temporary dipole in a neighboring molecule



• The result is a fleeting attraction between the two molecules



- Such fleeting attractions are generally weak.
- But like any weak attraction, if there are enough of them, they can add up to be significant

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- The greater the surface area of a molecule, the more temporary dipole attractions are possible
- Consider the feet of Gecko. They have many flexible hairs on their feet that maximize surface contact
 - The resulting London dispersion forces are strong enough to support the weight of the Gecko



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1.12 London Dispersion Forces

• London dispersion forces are the reason why molecules with more mass generally have higher boiling points



• Practice with SkillBuilder 1.10

1.12 London Dispersion Forces

• The more branching in a molecule, the lower it's surface area, and the weaker the London dispersion forces.



1.13 Solubility

- As you learned in general chemistry, like-dissolves-like
- Polar compounds **generally** mix well with other polar compounds
 - If the compounds mixing are all capable of H-bonding and/or strong dipole-dipole, then there is no reason why they shouldn't mix
- Nonpolar compounds generally mix well with other nonpolar compounds
 - If none of the compounds are capable of forming strong attractions, then no strong attractions would have to be broken to allow them to mix

1.13 Solubility

- We know it is difficult to get a polar compound (like water) to mix with a nonpolar compound (like oil)
 - We can't use just water to wash oil off our dirty cloths
- To remove nonpolar oils, and grease, and dirt... we need soap



1.13 Solubility

• Soap molecules organize into micelles in water, which form a nonpolar interior to carry away dirt.





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