

## Chapter 1. A Review of General Chemistry: Electrons, Bonds, and Molecular Properties

### 1.1. Introduction to Organic Chemistry

*Organic*: of, relating to, or obtained from living things

*Organic Chemistry* - The study of the structure and reactivity of carbon-based compounds. Organic compounds also contain H, O, N, S, P, and halides.

Organic chemistry includes the study of biological molecules, drugs, solvents, dyes, etc.

CH <sub>4</sub> (methane)	vitamins	peptide & proteins
H <sub>2</sub> CO (formaldehyde)	antibiotics	nucleic acids
C <sub>6</sub> H <sub>6</sub> (benzene)	carbohydrate	polysaccharides

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How and why do organic reactions occur?

- molecular collisions
- bonds break and bonds form – changes in bonding

*Focus on the electrons*

What are the factors that allow us to predict if an organic reaction will occur and what product(s) are formed?

Structure – arrangement of the atoms and electrons within a molecule

Reactions – conversion of a substrate to a product

Mechanism – how reactions occur

Synthesis – making larger (more complex) compound from simpler one. Require that you are able to predict reactivity

Friedrich Wohler (1828): synthesized urea (organic from ammonium cyanate (inorganic))

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## 1.2. The Structural Theory of Matter

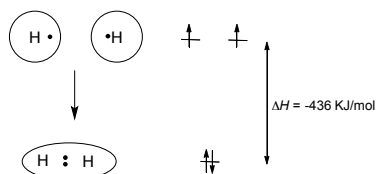
Both the atoms and their arrangement (bonding) are important. Dimethyl ether and ethanol have the same molecular formula ( $C_2H_6O$ ), but very different properties.

Valency: number of bonds an element usually forms

$$C = 4, H = 1, N = 3, O = 2, X = 1$$

## 1.3 Electrons, Bonds, and Lewis Structures.

Lewis theory of bonding – Covalent bonds result from two atoms sharing a pair or pairs of valence electrons in order to achieve a noble gas electronic configuration (octet rule).



Each H of  $H_2$  has the electron configuration of He - closed (filled) valence shell

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Covalent bond – energy vs. internuclear distance for the H–H.

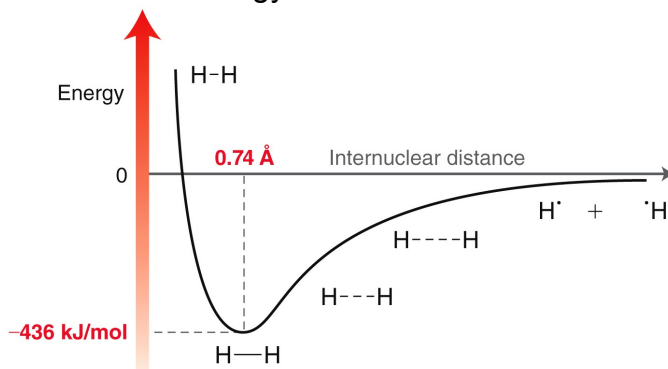


Figure 1.2

Atoms - protons- (+)-charge, mass =  $1.6726 \times 10^{-27}$  kg  
 neutrons- no charge, mass =  $1.6750 \times 10^{-27}$  kg  
 electrons- (-)-charge, mass =  $9.1096 \times 10^{-31}$  kg

For neutral atoms, the number of protons and electrons are the same

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Each atom of F<sub>2</sub> has eight valence electrons and the electron configuration of Ne.


The C of CH<sub>4</sub> has the electron configuration of Ne, while the H's have the electron configuration of He

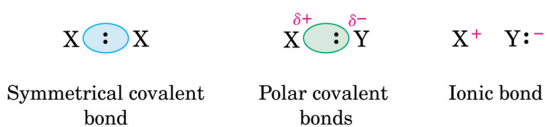
**1.4 Identifying Formal Charges.** proper Lewis structures must have the proper formal charge

$$\text{formal charge} = \left( \begin{array}{c} \# \text{ of valence } e^{-}\text{'s} \\ \text{of the free atom} \end{array} \right) - \left( \frac{\# \text{ of bonding } e^{-}\text{'s}}{2} \right) - \left( \# \text{ of non-bonding } e^{-}\text{'s} \right)$$

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**1.5 Induction and Polar Covalent Bonds.** covalent bonds in which the electrons are not equally shared between the two atoms – results in a net dipole.

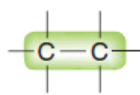
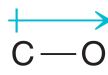




*Electronegativity:* intrinsic ability of an atom to attract electrons. In general, the greater the electronegativity difference between two bonded atoms, the more polar the bond. Electronegativity tends to decrease down a period, and increase across a row (from left to right).

H	Li	Be	B	C	N	O	F
2.1	1.0	1.6	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
	K	Ca					Br
	0.8	1.0					2.8
							I
							2.5

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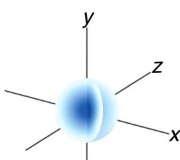
<p>covalent C-C, C-H</p> 	<p>polar covalent C-O, C-N C-X</p>  <p><math>\delta+</math> <math>\delta-</math> C-O</p>	<p>ionic NaOH</p> <p>HO<sup>-</sup> Na<sup>+</sup></p>
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**1.6 Atomic Orbitals.**  
 Quantum mechanics - electrons have properties of both a particle and energy. Energy of an electron is given by a wave function ( $\psi$ ) - electrons have a series of discrete energy levels.  
 Schrödinger wave equation ( $\psi$ ) gives the total energy of an electron at a given point in space (x,y,z)  
 $\psi^2$  = probability of finding an electron at a given point in space  
 Orbital = space where an electron spends ~90% of its time.

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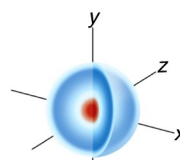
1st (K) shell: one 1s-orbital  
 2nd (L) shell: one 2s-orbital and three 2p-orbitals

1s-orbital: no nodes



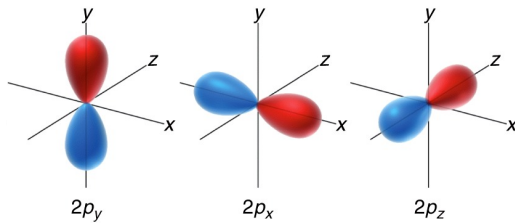
1s

2s-orbital: one nodes



2s

p-orbitals: one node



$2p_y$        $2p_x$        $2p_z$

Nodes: points, planes, surfaces where  $\psi^2 = 0$

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### Atomic orbitals (AOs)

- electrons are arranged in “shells” at various distances from the nucleus
- shells are arranged by increasing energy
- within each shell, electrons are paired into orbitals with each orbital holding two electrons
- paired electrons within an orbital have opposite spins – Pauli exclusion principles

Periodic chart is organized according to the electron shells and AOs

Please review and understand electronic configuration:

Aufbau principle, Pauli exclusion principle, Hund’s rule

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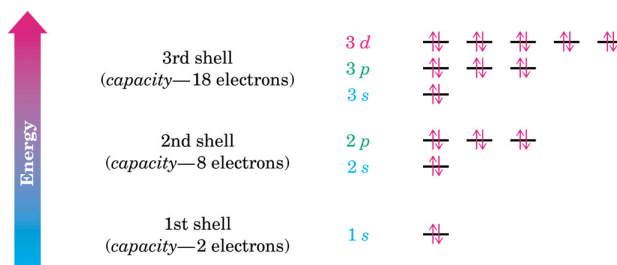
### Types of AOs

1 s-orbital - spherical (2 e<sup>-</sup> s)

3 p-orbitals - dumbbell shaped (6 e<sup>-</sup> s)

5 d-orbitals - four clover leaf and one dumbbell w/ a ring (10 e<sup>-</sup> s)

7 f-orbitals - (14 e<sup>-</sup> s)



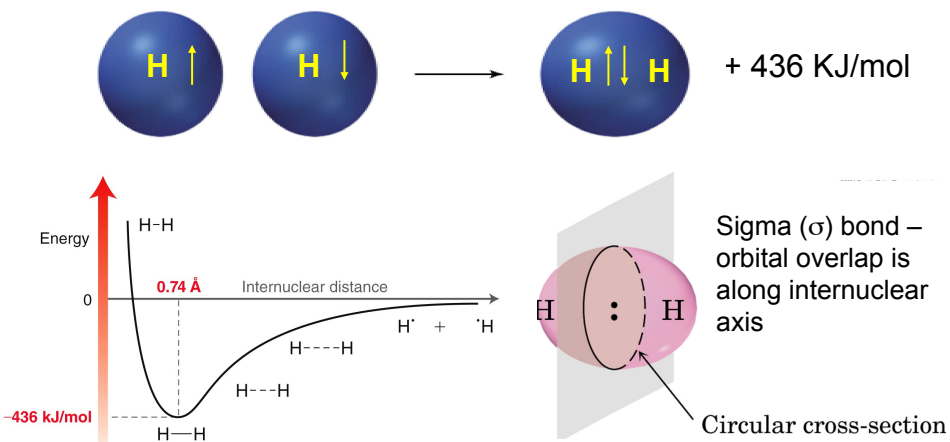
Valence electrons: electrons in the outermost shell; valence electrons are involved in bonding

Octet rule- atoms will give up, accept, or share electron in order to achieve a noble gas electronic configuration

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### 1.7 Valence Bond Theory.

Bond: sharing of electrons between two nuclei as a result of overlap of atomic orbital.



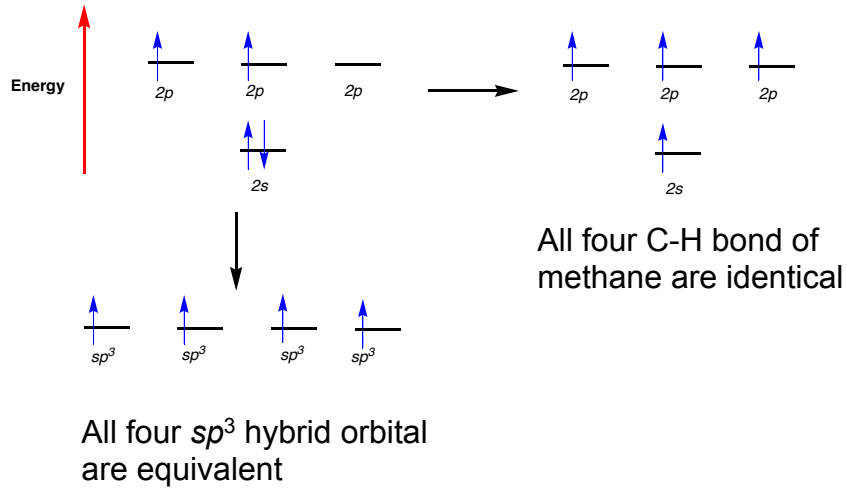
Principle of maximum overlap (L. Pauling) - the strength of a bond is directly proportional to the amount of orbital overlap <sup>11</sup>

**1.8 Molecular Orbital Theory:** Molecular orbitals (MOs) are linear combinations of atomic orbitals (AOs)

LCAO: # of MOs = # of AOs

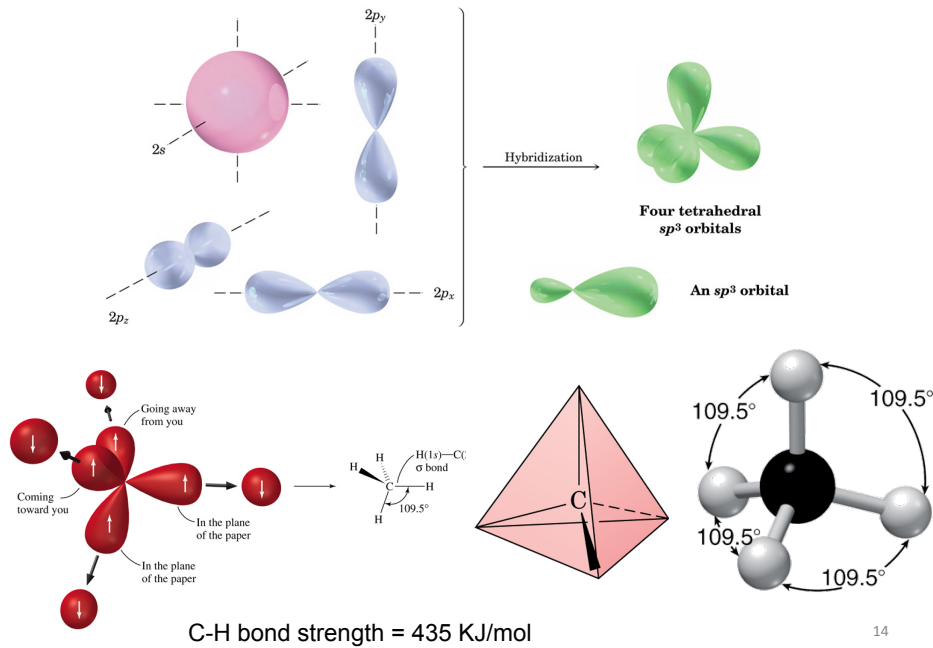
## 1.9 Hybridized Atomic Orbitals

### Methane and $sp^3$ Hybridization ( $CH_4$ )



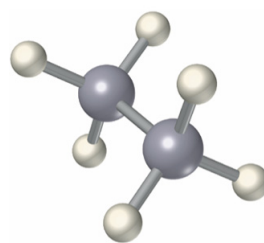
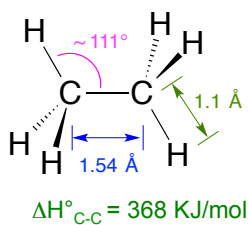
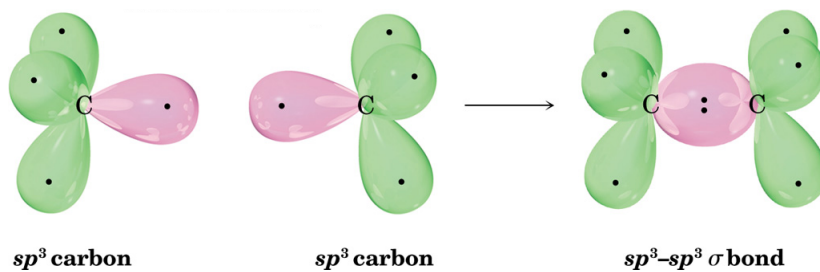
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$sp^3$  Hybridized Orbitals = 1 part s-orbital + 3 parts p-orbitals



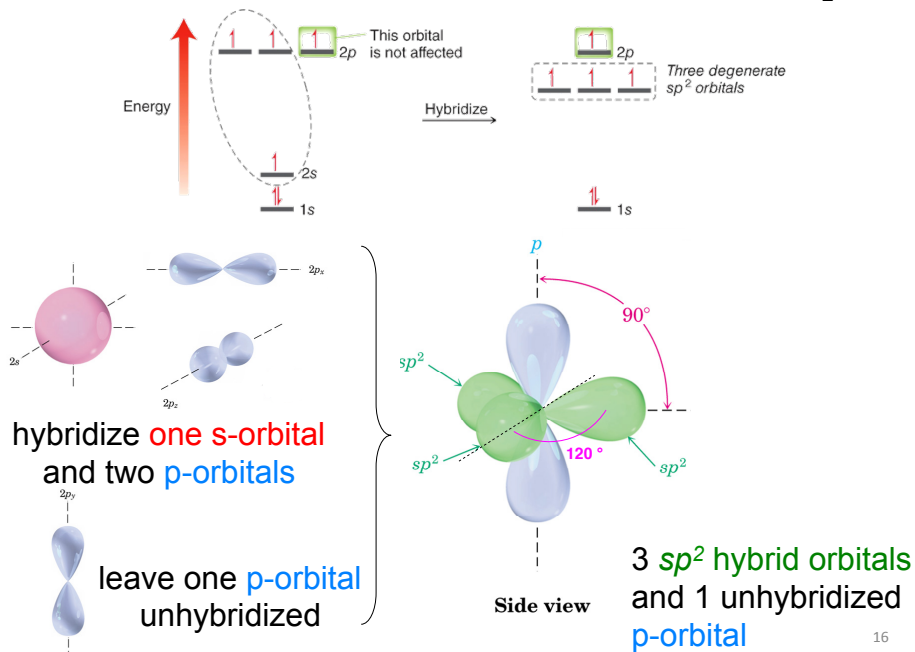
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Ethane ( $C_2H_6$ ) - ethane contains a C-C  $\sigma$ -bond and 6 C-H  $\sigma$ -bonds



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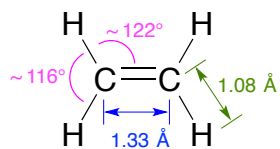
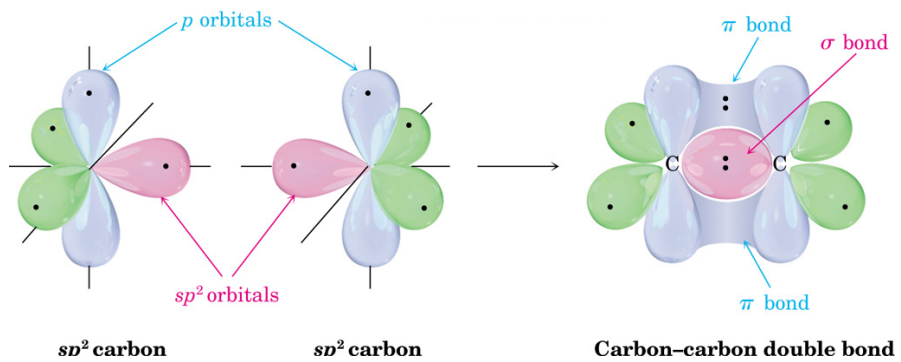
Double Bonds and  $sp^2$  Hybridization – ethene (ethylene,  $C_2H_4$ )



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### C=C double bonds- ethylene (C<sub>2</sub>H<sub>4</sub>)



$$\Delta H^\circ_{\text{C}=\text{C}} = 632 \text{ KJ/mol}$$

$$\Delta H^\circ_{\text{C}-\text{C}} = 368 \text{ KJ/mol}$$

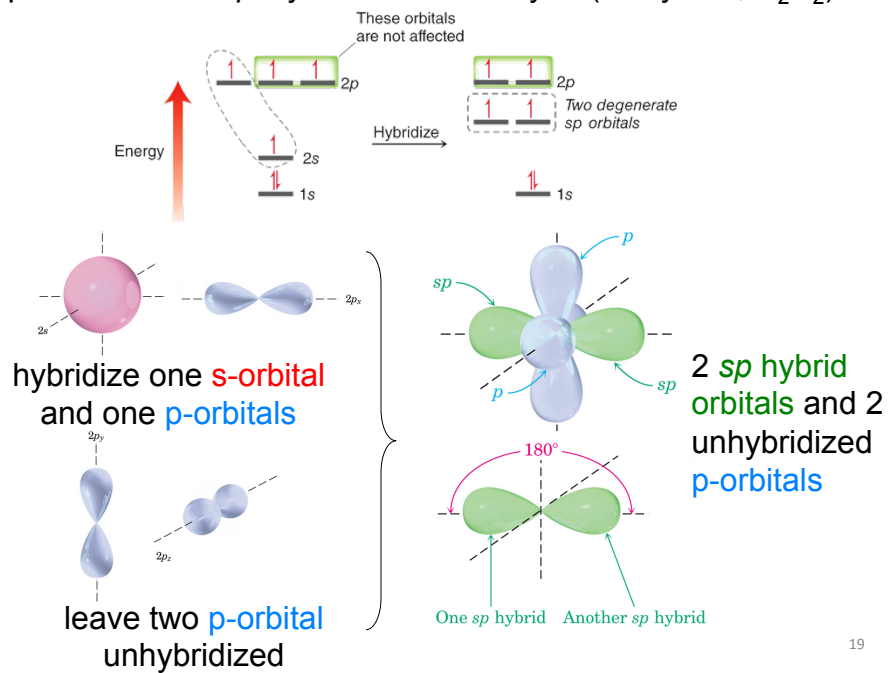
$$\Delta H^\circ_{\pi\text{-bond}} = 264 \text{ KJ/mol}$$

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### Molecular Orbitals of C=C double bond

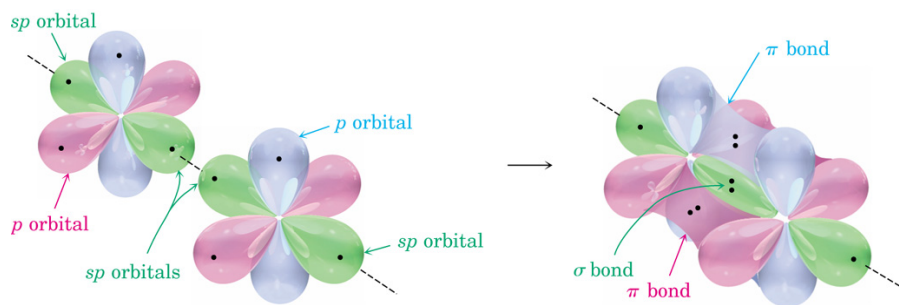
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### Triple Bonds and $sp$ Hybridization – ethyne (acetylene, $C_2H_2$ )

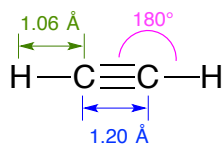


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### $C\equiv C$ triple bonds- acetylene ( $C_2H_2$ ) one C-C $\sigma$ -bond and two C-C $\pi$ -bonds



#### Carbon-carbon triple bond

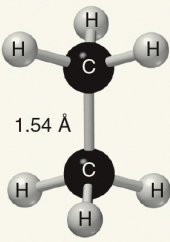
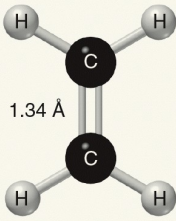
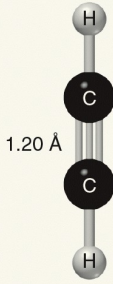


$\Delta H^\circ_{C\equiv C}$	= 820 KJ/mol
$\Delta H^\circ_{C-C}$	= 368 KJ/mol
$\Delta H^\circ_{1st \pi\text{-bond}}$	= 264 KJ/mol
$\Delta H^\circ_{2nd \pi\text{-bond}}$	= 188 KJ/mol

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## Bond Strength and Bond Length

TABLE 1.2 COMPARISON OF BOND LENGTHS AND BOND ENERGIES FOR ETHANE, ETHYLENE, AND ACETYLENE

	ETHANE	ETHYLENE	ACETYLENE
Structure			
C—C bond length	1.54 Å	1.34 Å	1.20 Å
Bond energy	368 kJ/mol	632 kJ/mol	820 kJ/mol

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### 1.10 VSEPR Theory: Predicting Geometry

Molecules are not flat! They are three dimensional.

Valence Shell Electron Pair Repulsion (VESPR): molecules will adopt a three dimensional geometry so that electron pairs, either in bonds or non-bonding pairs, are as far away from one another as possible.

Atoms in which the number of substituents and/or nonbonding electron pairs (steric number) is . . .

- . . . four, then the hybridization is  $sp^3$  and the geometry will be tetrahedral (methane)
- . . . three, then the hybridization is  $sp^2$  and the geometry will be trigonal planar (ethylene)
- . . . two, then the hybridization is  $sp$  and the geometry will be linear (acetylene)

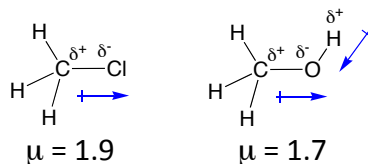
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### 1.11 Dipole Moment and Molecular Polarity

Dipole moment ( $\mu$ ): molecular property, which is the vector sum of all individual bond dipoles

$$\mu = e \cdot d \quad e = \text{charge, } d = \text{distance; units: Debye (D)}$$

Inductive Effect: atom's (or group of atoms) ability to polarize a bond through electronegativity differences



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### 1.12 Intermolecular Forces and Physical Properties

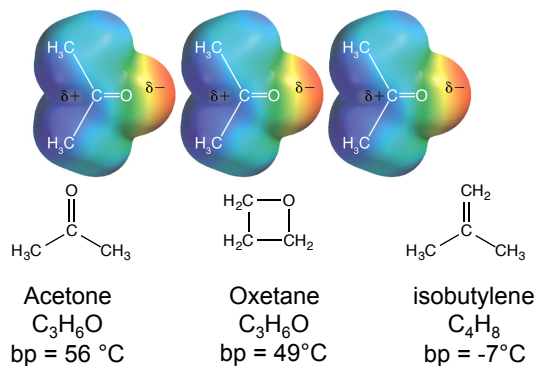
Many properties (solubility, boiling point, melting point, etc.) are affected by the weak attractions between molecules.

Dipole-dipole interactions

Hydrogen bonding

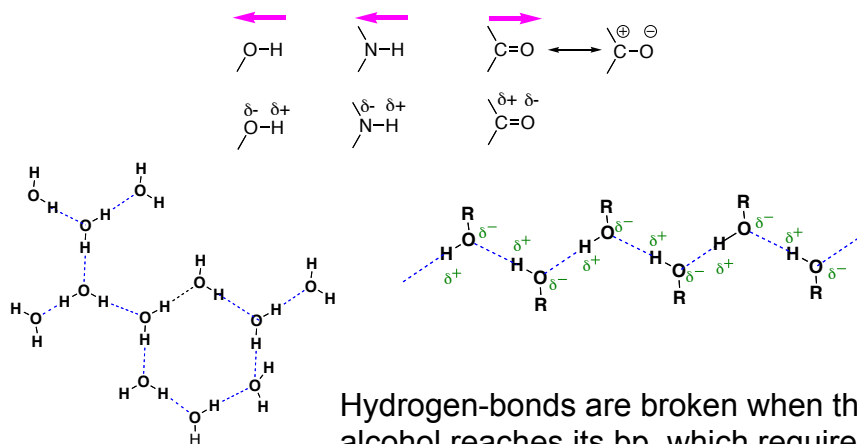
Dispersion forces (London forces or van der Waal)

Dipole–Dipole: Electrostatic interaction of opposite partial charges between dipolar molecules.



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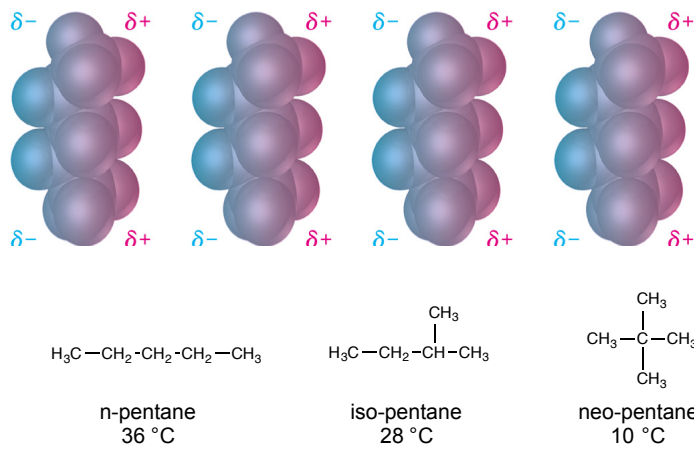
Hydrogen Bond – electrostatic interaction between a proton ( $\delta^+$ ) bonded to a highly electronegative atom (O or N) and another highly electronegative atom ( $\delta^-$ ).



Hydrogen-bonds are broken when the alcohol reaches its bp, which requires additional energy

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Dispersion forces (London or van der Waal forces) small temporary dipoles that result from distortions of the electron clouds. There is an attraction between molecules as result of these temporary dipoles.



1.13 Solubility (please read)

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