1. Structure and Bonding; Acids and Bases

Foundation of Organic Chemistry (mid-1700)

1. **Alchemist** noticed *unexplainable differences* between compounds derived from living sources and those derived from minerals.

2. **Torbern Bergman** was the first to express the difference between **organic** and **inorganic** substances in 1770. – *The chemistry of compounds from living organisms (vital force)*

3. **Friedrich Wöhler** discovered in 1828 that it was possible to convert the **inorganic salt** ammonium cyanate into **urea**. ($NH_4^{+-}OCN$ → urea)

Mid-1800

The only distinguishing characteristic of organic compounds is that all contain the element **carbon**.

Carbon

1. Group 4A element
2. Four valence electron and form four strong covalent bond
3. Form long chains or rings
4. Form an immense diversity of compounds

Medicines, dyes, polymers, plastics, pesticides etc. are prepared in the laboratory.

Organic chemistry is a subject that touches the lives of everyone.

H, O, N, S, P, X also appear in organic molecules.

1.1 Atomic structure

Nucleus: a dense, positively charged, consists of neutrons and protons

Electrons: negatively charged

The diameter of a typical atom is about 2×10^{-10} m.

Thin pencil line is about 3 million carbon atoms wide. chapter_01_01.ppt

Atomic number (Z): the number of protons in the nucleus

Mass number (A): the total number of protons and neutrons

Isotopes: atoms that have the same number of protons in their nuclei but different numbers of neutrons – chemical properties are largely the same, but their masses are differ.

Atomic weight: the average mass in atomic mass unit

Electronic distribution

The behavior of a specific electron in an atom can be described by a mathematical expression called ***wave equation***. The solution of the wave equation is **wave**

function or **orbital** (ψ: psi). chapter_01_02.ppt

Orbital: a region of space around the nucleus where the electron can most likely be found.

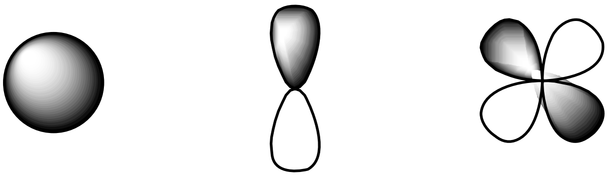
Orbitals are organized into different layers, or **shells**, of successively larger size and energy.

The first shell – 1s (2 electrons)

The second shell – 2s, and three 2p orbitals (8 electrons)

The third shell – 3s, three 3p orbitals, and five 3d orbitals (18 electrons)

The shape of orbitals



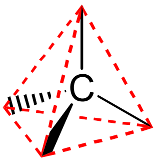
1.2 Electron Configuration of Carbon

Carbon (6 electrons): ($1s^2$) $2s^2$ $2p^2$

1.3 Chemical Bonding Theory

1858 August Kekule and Archibald Couper independently proposed that carbon has four “**affinity units**.” – ***Tetravalent***

1874 Jacobus van’t Hoff and Joseph Le Bel added a 3-dimensional idea. ***Tetrahedron***



1.4 The Nature of Chemical Bonds

Why do atoms bond together?

Atoms bond together because the compound that results is more stable (**less energy**) than the separate atoms.

How can bonds be described?

Eight electrons – an electron octet – in the outermost shell (or valence shell) impart special stability to the noble-gas element in group 8A.

Ionic Bond

To form a noble-gas configuration, each atom loses or gains (an) electron(s).

The resulting ions are held together in compounds like NaCl by an **electrostatic attraction**.

Covalent Bond

Carbon bonds to other atoms, not by losing or gaining electrons, but by **sharing electrons**.

1916 G. N. Lewis proposed shared-electron bonds

The neutral collection of atoms held together by covalent bonds is called a **molecule**.

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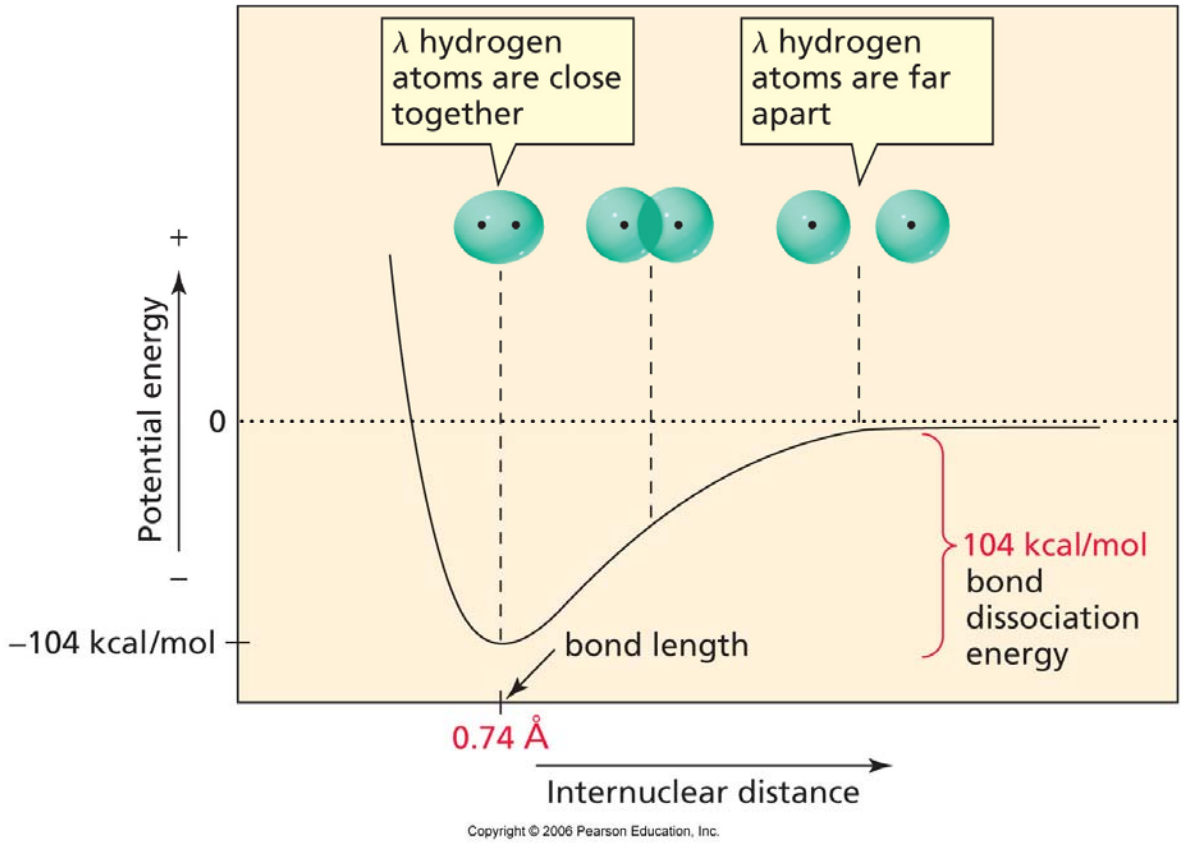
Potential energy vs. internuclear distance diagram



The internuclear distance at minimum energy is the length of the covalent bond

Lewis structures – electron dot structures

An atom's valence electrons are represented by dots.

A stable molecule results when a noble-gas configuration is achieved for all atoms – an octet rule. e.g.) CH_4, NH_3, H_2O, CH_3OH

Nonbonding electrons (lone-pair electrons): valence electrons not used for bonding

Kekule structures (or line-bond structures)

The two electrons of a covalent bond are indicated simply by a line between the atoms.

1.5 Forming Covalent Bonds: Valence Bond Theory

How does **electron sharing** between atoms occur?

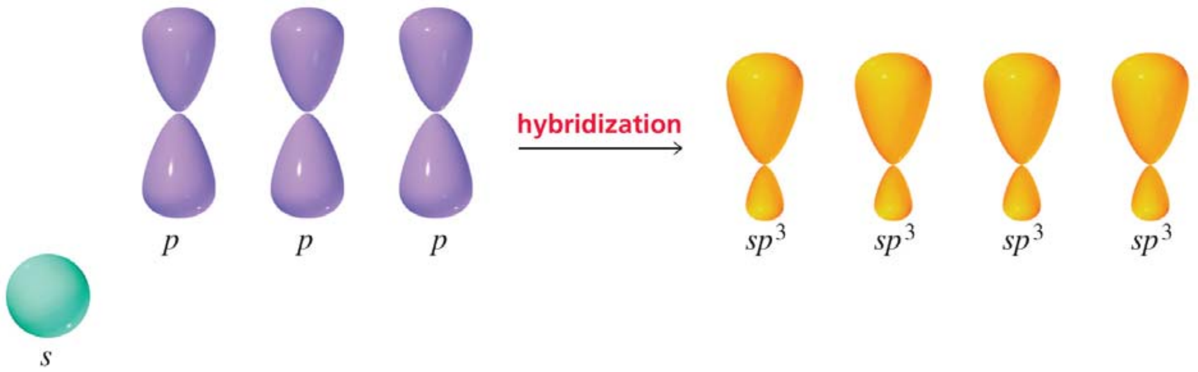
When two atoms approach each other closely, a singly occupied orbital on one atom overlaps a singly occupied orbital on the other. The electrons are now paired in the overlapping orbitals and are attracted to the nuclei of both atoms, thereby bonding the atoms together.

Bond strength: energy released when a bond is formed, or energy required to break a bond (104 kcal/mol or 436 kJ/mol for H_2).
Bond length: an optimum distance between nuclei that leads to maximum bond stability (0.74 Å for H_2).

1.6 Hybridization: sp^3 Orbitals and the Structure of Methane

Methane (CH_4)

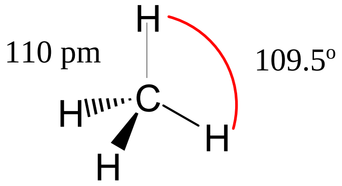
4 electrons in valence shell ($2s^2$, $2p^2$), and can form four bonds to hydrogens.
All four C–H bonds in methane are identical and spatially oriented toward the four corners of a regular tetrahedron.
1931 Linus Pauling proposed the concept of ***hybridization***.
An s orbital and three p orbitals can combine, or hybridize to form four equivalent atomic orbitals (**sp^3 hybrid orbitals**)

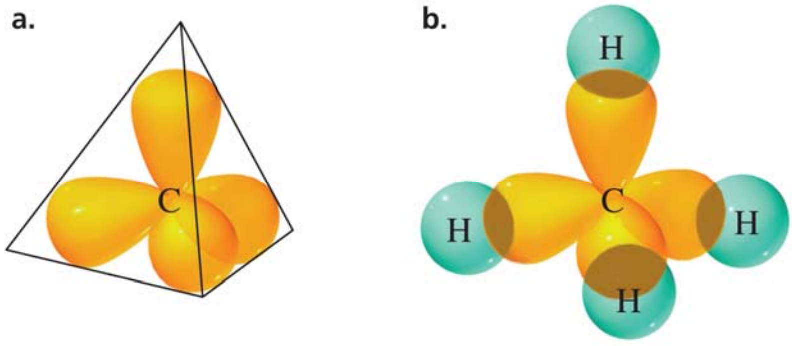


Why?

One of the two lobes of the hybrid orbital is much larger than the other. When this larger lobe overlaps with another orbital to form a bond, the electrons are better shared between the two bonding nuclei than if unhybridized s or p orbitals were to overlap, which results in the **formation of a stronger bond**.

Each C–H **sigma (σ) bond** in methane has a strength of 438 kJ/mol (105 kcal/mol), a bond length of 110 pm. The bond angle (H–C–H) is 109.5°.





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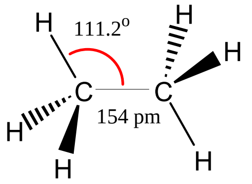
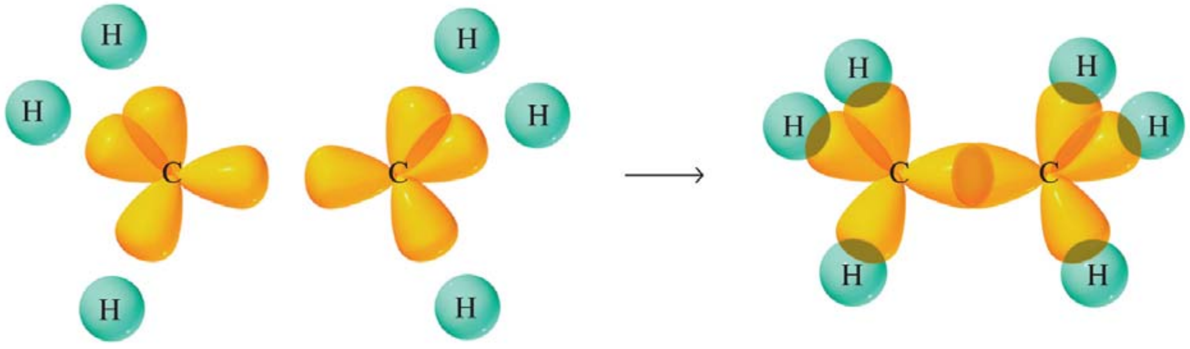
a) Four sp^3 orbitals are directed toward the corners of a tetrahedron causing each bond angle to be 109.5 degrees. b) An orbital picture of methane showing the overlap of each sp^3 orbital of the carbon with the *s* orbital of hydrogen

1.7 Hybridization: sp^3 Orbitals and the Structure of Ethane

C-H in ethane has a strength of 420 kJ/mol, C-C of 376 kJ/mol





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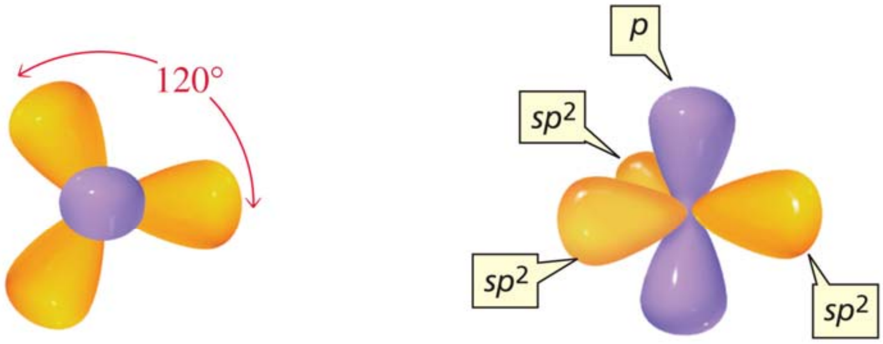
1.8 Double and Triple Bonds

1. Double and triple bonds are far more reactive than single bonds.
2. A C=C bond is not twice as strong as a C-C bond and a C≡C bond is not three times as strong as a single bond.
3. Double bonds lead to a planar shape. Triple bonds lead to a linear shape.

sp^2 hybrid orbitals – one of the p orbitals is not hybridized and three hybridized orbitals form.

p orbital occupies the region above and below the plane occupied by the sp^2 hybrid orbitals.

The sp^2 hybrid orbitals arrange themselves at 120° angles in the plane.



top view side view

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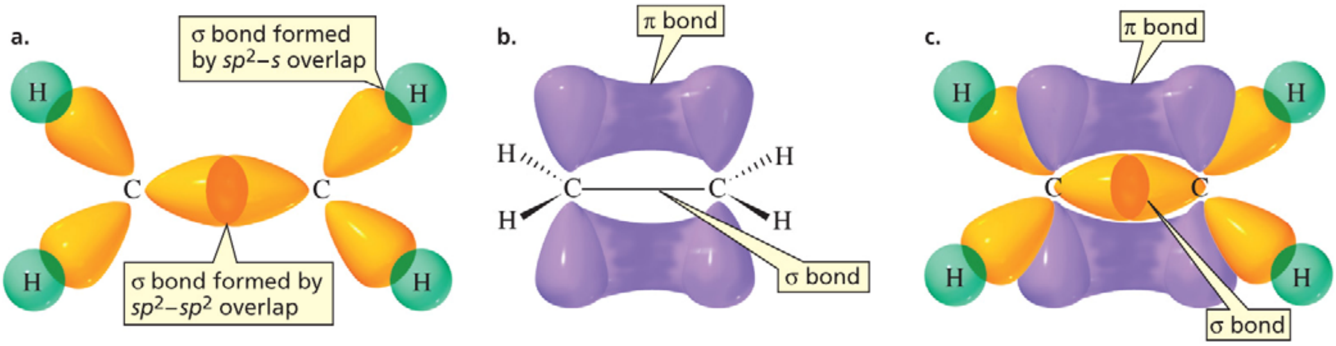
$CH_2=CH_2$

The sp^2 hybrid orbitals of one carbon form **σ bonds** with ether hydrogen atoms or the other sp^2 hybridized carbon atom.

The bond resulting from overlap of p orbitals is called a **pi (π) bond**.

Orbital overlap occurs above and below the bond axis.



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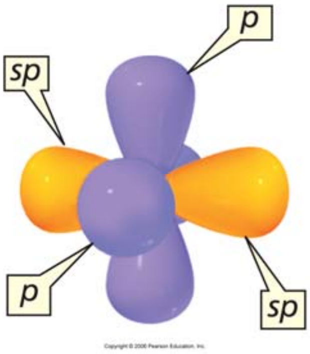


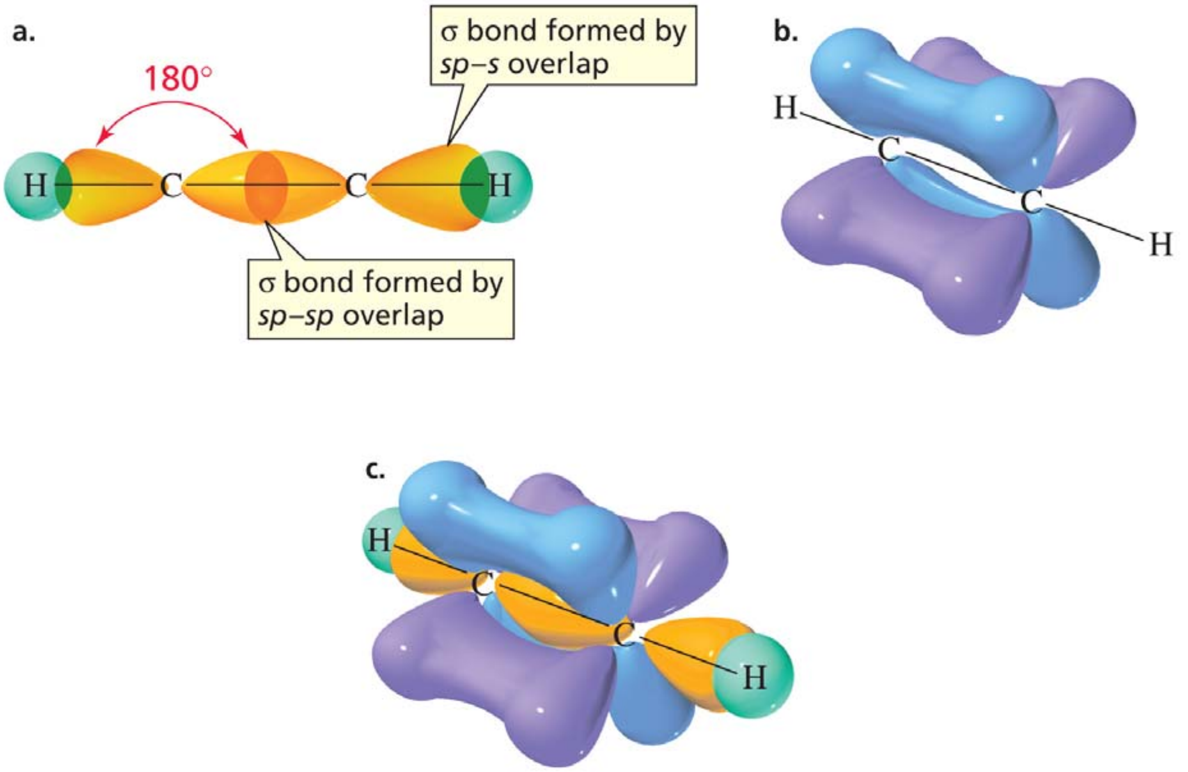
sp hybrid orbitals – two of the p orbitals are not hybridized and two hybridized orbitals form.

The two p orbitals of an sp-hybridized carbon share a common plane and the two sp hybrid orbitals occupy the perpendicular axis.

CH≡CH

Two sp hybrid orbitals of one carbon form σ bonds with a hydrogen and the other sp-hybridized carbon atom. The overlap of the remaining p orbitals gives the double part and triple part of C≡C bond.

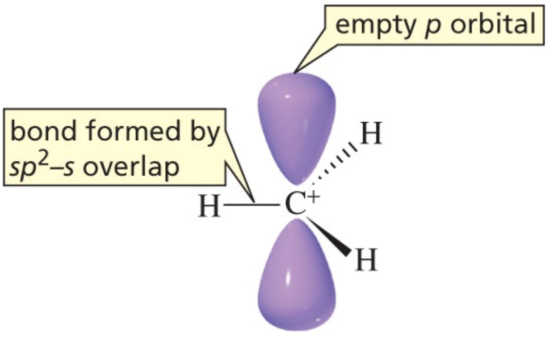
All the atoms are collinear, making the bond angle 180°.



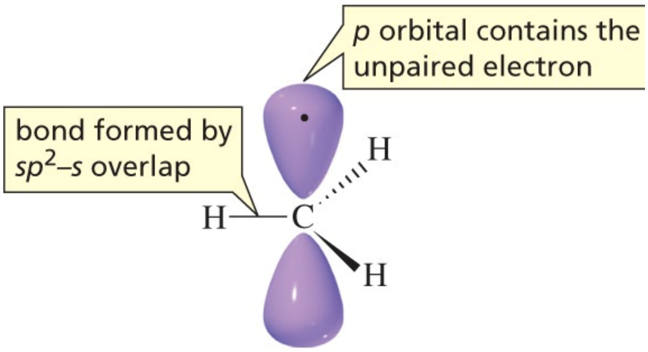
The shapes of all of the hybrid orbitals are similar, but the amount of s character increases from sp^3 to sp^2 to sp.

Molecule	Hybridization	Bond angle	Geometry	Bond length	Bond strength
CH_3-CH_3	sp^3	109.5	Tetrahedral	154 pm	340 kJ/mol (σ)
CH_2=CH_2	sp^2	120	Planar	133 pm	610 kJ/mol ($\sigma + \pi$)
CH≡CH	sp	180	Linear	120 pm	830 kJ/mol ($\sigma + 2\pi$)

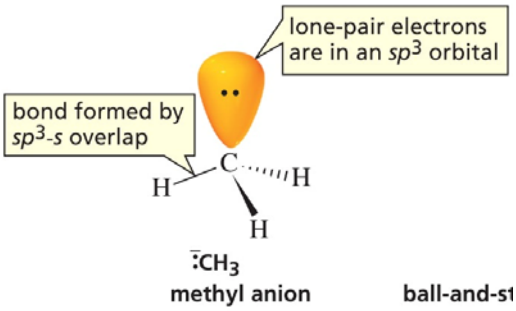
The hybridized orbitals of methyl cation, radical, and anion.



$^+CH_3$
methyl cation



$\cdot CH_3$
methyl radical



1.9 Polar Covalent Bonds: Electronegativity

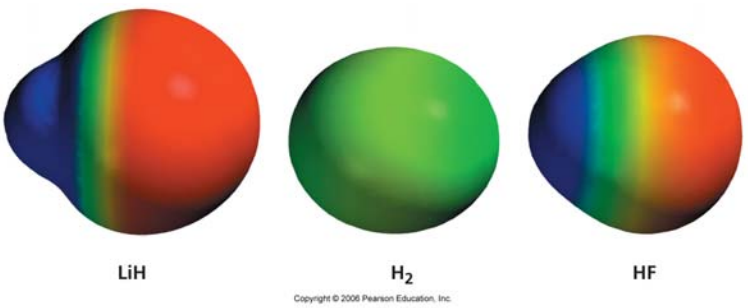
Ionic bonding: electron is transferred from one atom to another resulting in the formation of oppositely charged ions that are held together by electrostatic attractions.

Covalent bonding: two bonding electrons are equally shared by the two equivalent atoms.

Polar covalent bonding: neither truly ionic nor truly covalent but somewhere between the two extremes – the shared electrons are attracted more strongly by one atom than by the other.

Bond polarity is due to difference in **electronegativity**.

Electrostatic Potential Maps

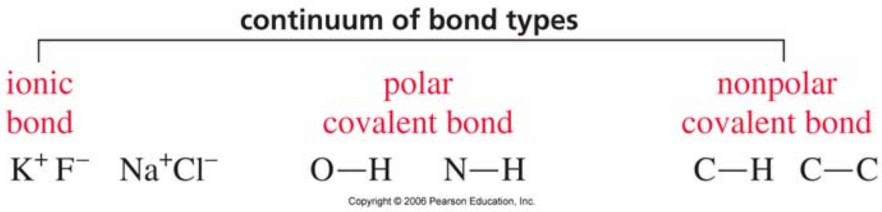


The colors indicate the distribution of charge in the molecule. Red is for electron rich areas and blue is for electron deficient areas. Green signifies no charge

Electronegativity: the intrinsic ability of an atom to attract electrons in a covalent bond. A bond between atoms with similar electronegativities is covalent.

A bond between atoms whose electronegativities differ by less than 2 unit is polar covalent.

A bond between atoms whose electronegativities differ by 2 units or more is largely ionic.



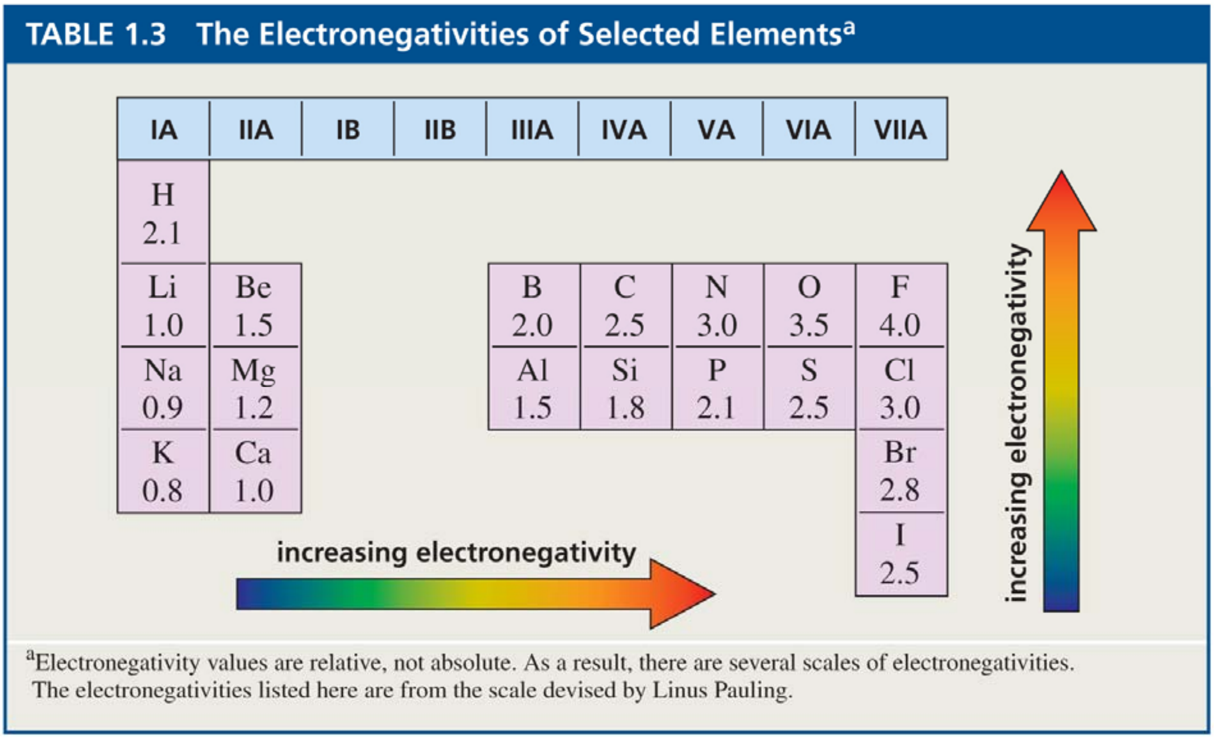


TABLE 1.3 The Electronegativities of Selected Elements[a]

IA	IIA	IB	IIB	IIIA	IVA	VA	VIA	VIIA
H 2.1								
Li 1.0	Be 1.5			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
K 0.8	Ca 1.0							Br 2.8
								I 2.5

[a] Electronegativity values are relative, not absolute. As a result, there are several scales of electronegativities. The electronegativities listed here are from the scale devised by Linus Pauling.

In polar covalent bond, use the notation of crossed arrow, partial positive charge (δ^+), and partial negative charge (δ^-).

Inductive effect: the shifting of electrons in a bond in response to the electronegativity of nearby atoms

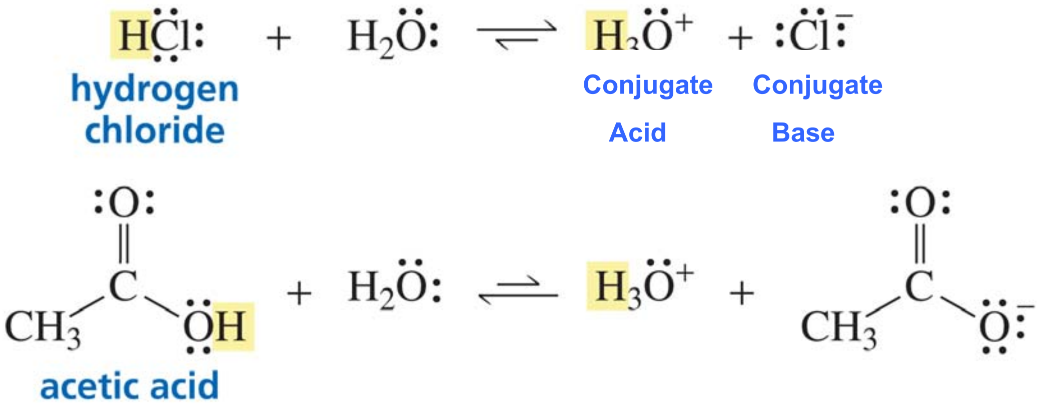
1.10 Acids and Bases: The Bronsted-Lowry Definition

Acidity and basicity are related to electronegativity and bond polarity.

Bronsted-Lowry definition

Donate or accept a hydrogen ion (H^+) – proton

Conjugate acid and conjugate base



Strength of Acids

The exact strength of a given acid in water solution can be expressed by its acidity constant (ionization constant) **K_a**.

$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad pK_a = -\log K_a$$

Mineral acids (H_2SO_4, HNO_3, and HCl) have K_a's in the range 10^2 to 10^9, while many organic acids have K_a's in the range 10^{-5} to 10^{-15}.

$$CH_3CO_2H + {}^-OH \longrightarrow CH_3CO_2^- + H_2O \qquad K = \frac{[CH_3CO_2^-]}{[CH_3CO_2H][{}^-OH]} = 10^{10.98}$$

$pK_a = 4.76$ $\qquad$ $pK_a = 15.74$

Organic acids

(1) those with acidic hydrogens attached to **oxygen atoms** (MeOH, CH_3CO_2H)

(2) those where the acidic hydrogen atom is attached to a **carbon atom** (Acetone)

Organic bases

Those containing an atom (nitrogen or oxygen) with a lone pair of electrons that can bond to H^+.

1.11 Acids and Bases: The Lewis Definition

Lewis acid: a substance that has a vacant valence orbital and can thus accept an electron pair.

Lewis base: a substance that donates an electron pair.

The donated pair of electrons is shared between Lewis acid and base in a newly formed covalent bond