

Organic Chemistry I

Dr. Alex Roche

Organic chemistry is the chemistry of Carbon and its compounds.

Organic molecules constitute the essence of life (fats, sugars, proteins, DNA), and also permeate our everyday lives (cotton, polyester, toothpaste, plastics, etc).

Chemistry's top two commercial fields are organic dominated: Pharmaceuticals and Polymers.

Organic chemistry is also easy - IF: don't fall behind
 do the problems
 understand, not memorize

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Structure of the Atom

Atoms consist of: Protons (+ve)
 Neutrons (neutral)
 Electrons (-ve)

Protons and neutrons are in the nucleus and have similar masses (1800x that of an electron).

Atoms with the same number of *protons* but different *neutrons* are called ISOTOPES.

E.g. ^{12}C (major isotope)
 ^{13}C (~1%, used in carbon NMR)
 ^{14}C (radioactive, used in Carbon dating)

Almost all the mass of an atom is in the nucleus, but it is the electrons that are involved in the chemical bonding and reactions of an atom.

Electronic Structure of the Atom

Electrons display *wave-particle duality*.

Electrons are located in orbitals around a nucleus, but the Heisenberg Uncertainty Principle tells us that we cannot pinpoint exactly where the electron is.

So we use the term ELECTRON DENSITY, which is the *probability* of finding the electron in a particular part of the orbital.

ORBITAL: is an allowed energy state for an electron, with an associated probability function that defines the distribution of electron density in space.

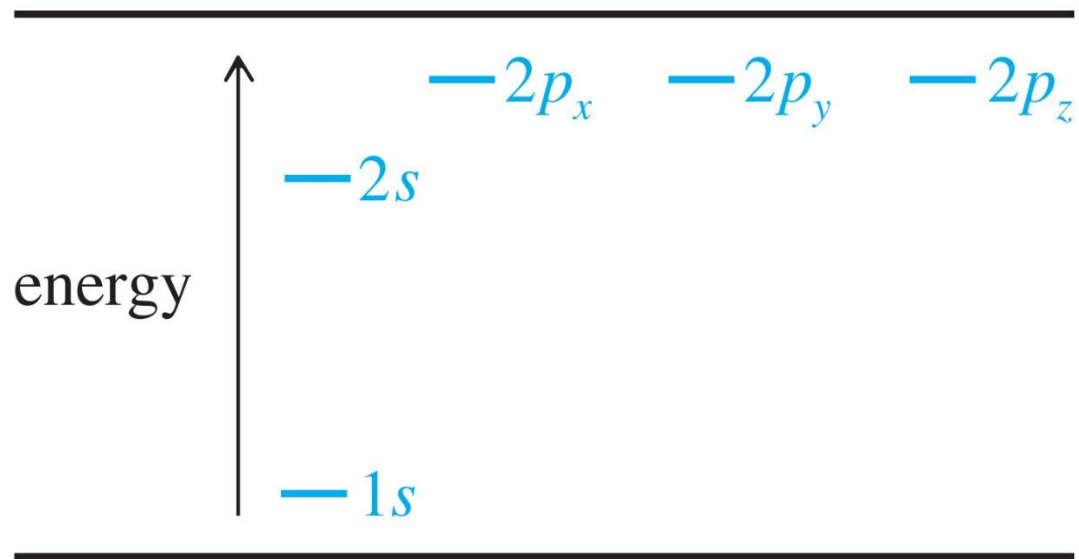
Atomic Orbitals

These are different shells at differing distances away from the nucleus. Each has a principal quantum number (n).

As n increases, Shells are further from the nucleus
 Higher energy
 Can hold more electrons

n=1 can hold 2 electrons, n=2 can hold 8 electrons.

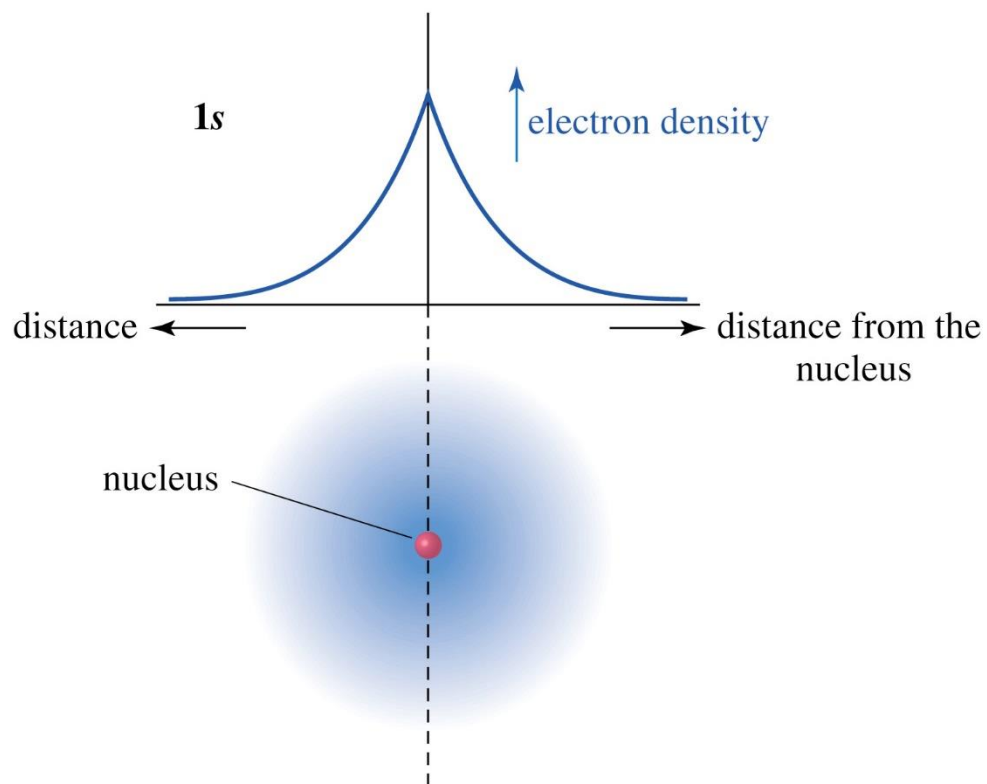
Relative orbital energies



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First Electron Shell
Contains the 1s orbital.

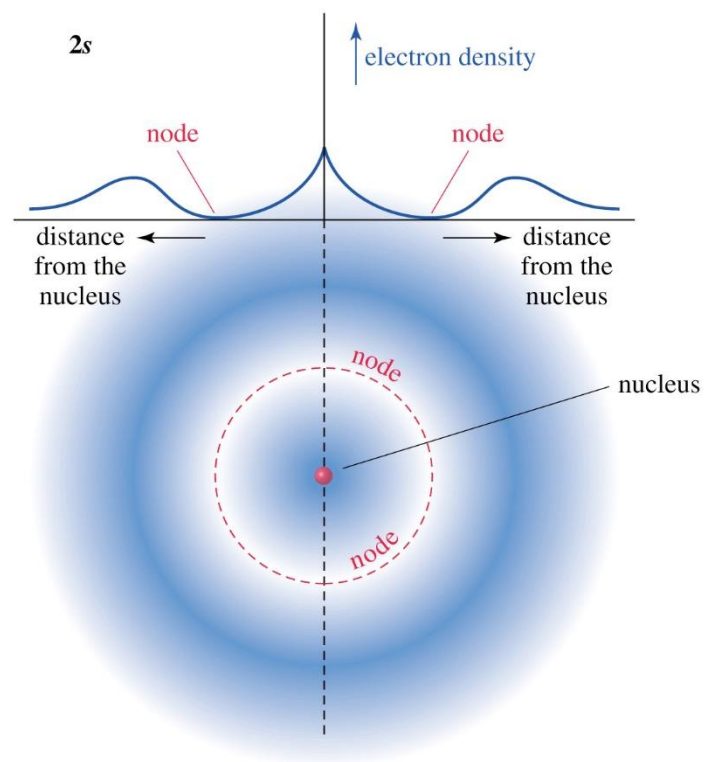
An s orbital is *spherical*, so the electron density is only a function of the distance from the nucleus.



Second Electron Shell

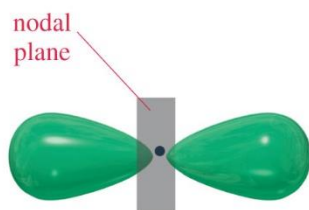
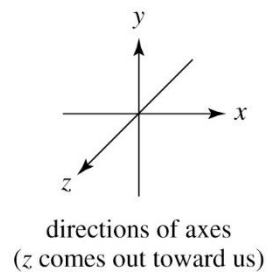
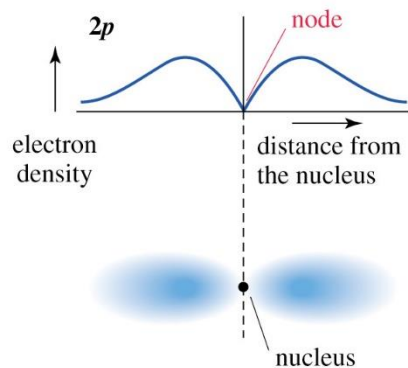
Contains the 2s and the 2p orbitals.

2s is also spherically symmetrical, but is not a simple exponential function.

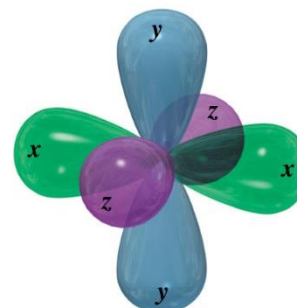


Most of the electron density is **further** away, past a NODE (region of zero electron density).

The second shell also contains three 2p atomic orbitals.



the 2p_x orbital

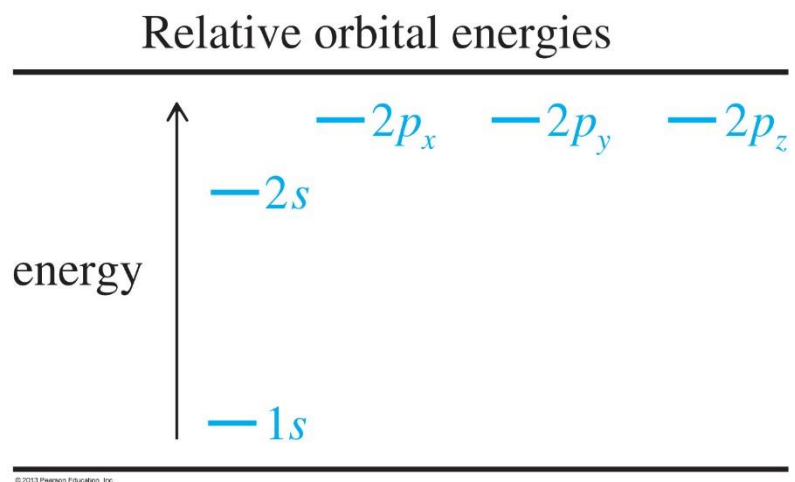


the 2p_x, 2p_y, and 2p_z orbitals superimposed at 90° angles

These are oriented in the three spatial directions. (2p_x, 2p_y, 2p_z).

Orbitals of the **same** energy are said to be DEGENERATE.

2p orbitals are slightly *higher* in energy than 2s orbitals because the average location of the electron is *further from the nucleus*.



The **Pauli Exclusion Principle** tells us each orbital can hold a maximum of 2 electrons, provided the spins are paired.

The first shell (one 1s orbital) can hold 2 electrons.

The second shell (one 2s and three 2p orbitals) can hold 8 electrons.

The third shell (one 3s, three 3p and five 3d orbitals) can hold 18 electrons.

Electronic Configuration of Atoms

The Aufbau Principle tells us how to 'build up' a ground state (most stable) configuration, which is to fill the orbitals in order, until the correct number of electrons has been added.

Hund's rule states that when there are two or more *degenerate* orbitals available, electrons would rather go into *different* orbitals rather than the *same* one.

Element	Configuration	Valence Electrons
H	$1s^1$	1
He	$1s^2$	2
Li	$1s^2 2s^1$	1
Be	$1s^2 2s^2$	2
B	$1s^2 2s^2 2p_x^1$	3
C	$1s^2 2s^2 2p_x^1 2p_y^1$	4
N	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$	5
O	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$	6
F	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$	7
Ne	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$	8

The *valence electrons* are those in the outermost shell. (Periodic group number is the number of valence electrons).

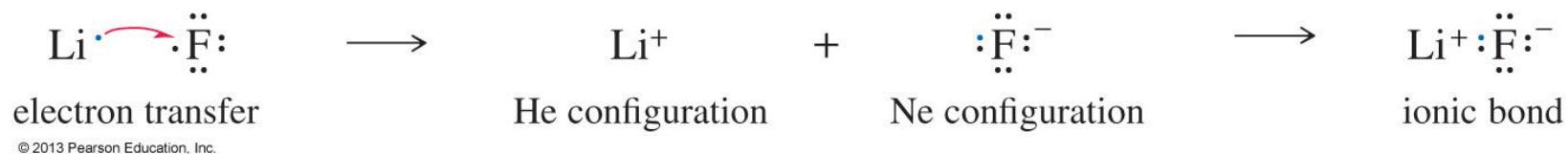
Bonding

Atoms transfer or share electrons in such a way as to attain a filled shell of electrons – The OCTET rule.

A filled shell is also known as a noble gas configuration.

Ionic Bonding

The *transfer* of one or more electrons from one atom to another.



Covalent Bonding

The electrons are *shared*, not transferred.



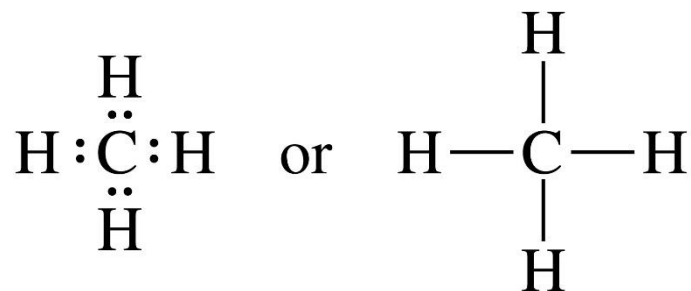
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Covalent is the **most important** bonding in Organic Chemistry.

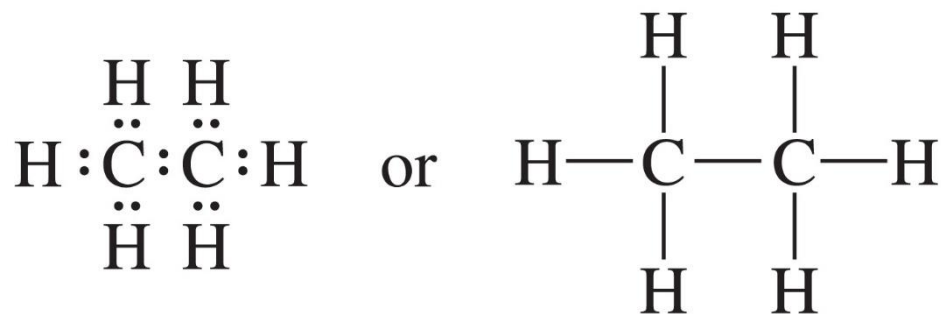
Lewis Structures

Each electron is represented by a dot.

A pair of electrons by two dots, or a dash.



methane



ethane

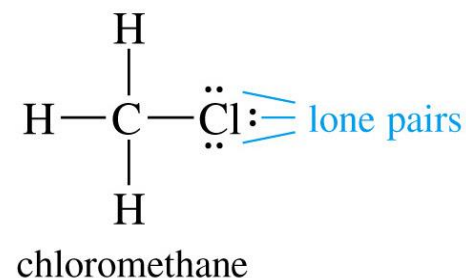
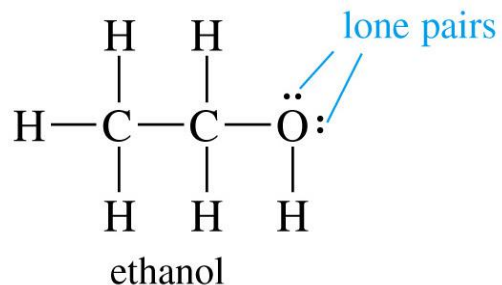
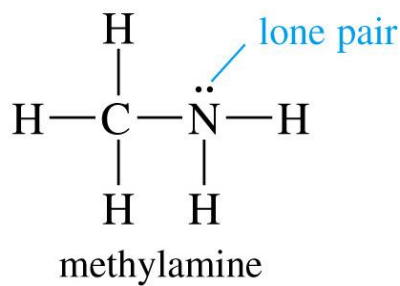
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Each carbon is surrounded by 8 electrons

Each hydrogen is surrounded by 2 electrons.

Nonbonding pairs of electrons

Also known as *lone pairs*.



Lone pairs often dictate a molecule's reactivity.

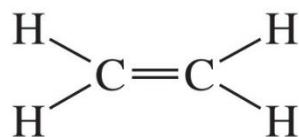
Multiple Bonds

The sharing of **one** pair of electrons is a **single** bond.

The sharing of two pairs gives a double bond.

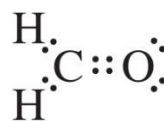


or

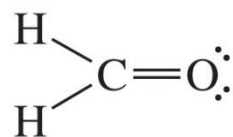


ethylene

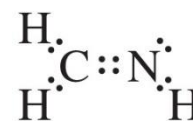
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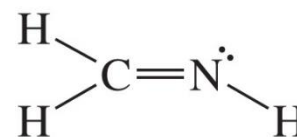
or



formaldehyde



or



formaldimine

The sharing of three pairs gives a triple bond.

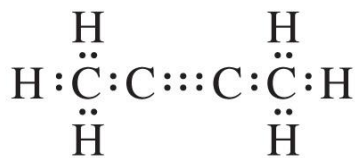


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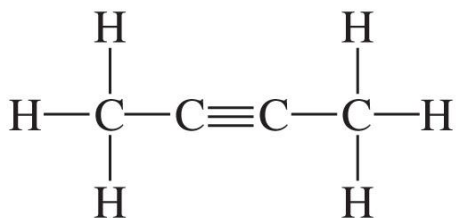


acetylene

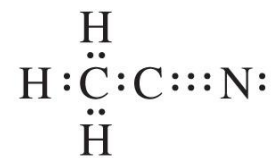
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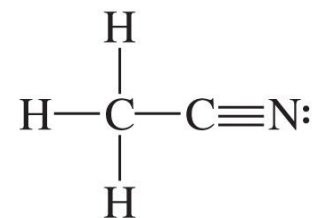
or



dimethylacetylene



or



acetonitrile

In **neutral** organic compounds:

Carbon forms four bonds

Nitrogen forms three bonds (and a lone pair)

Oxygen forms two bonds (2 lone pairs)

Hydrogen forms 1 bond.

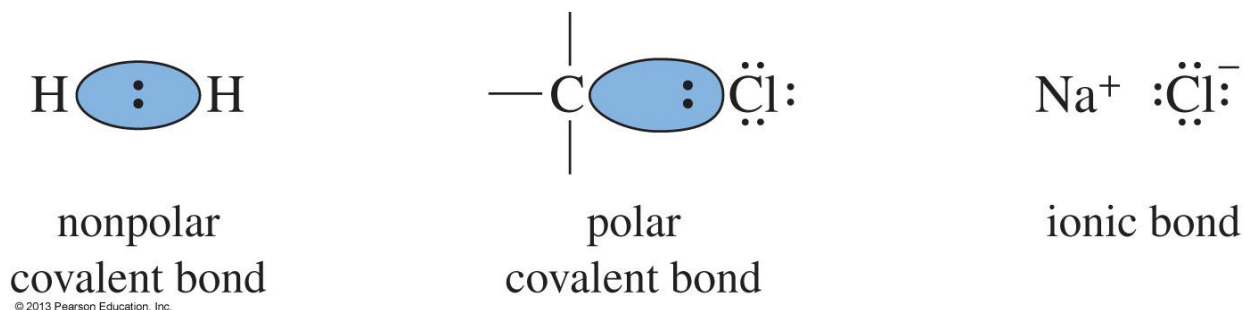
The number of bonds an atom normally forms is called the **VALENCY**.

E.g. Nitrogen is trivalent.

Bond Polarity

A covalent bond, where the electrons are shared *equally* is called a **non-polar** bond. (E.g. H-H)

Bonds between **different** atoms usually result in the electrons being attracted to one atom more strongly than the other. Such an unequal sharing of the pair of bonding electrons results in a POLAR bond.



This competition for electron density is scaled by ELECTRONEGATIVITY values.

Elements with **higher** electronegativity values have **greater attraction** for bonding electrons.

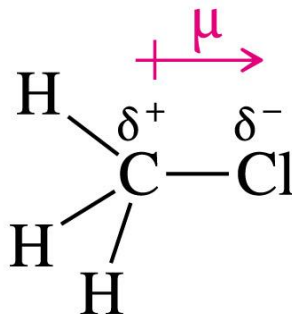
H 2.2							
Li 1.0	Be 1.6	B 2.0	C 2.5	N 3.0	O 3.4	F 4.0	
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2	
K 0.8						Br 3.0	
						I 2.7	

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Notice: EN increases left to right, and down to up.

Chloromethane

When chlorine is bonded to carbon, the bonding electrons are attracted **more strongly** to chlorine.



chloromethane

This results in a small partial positive charge on the carbon, and an equal but opposite partial negative charge on the chlorine.

Bond polarity is measured by Dipole Moment (μ).

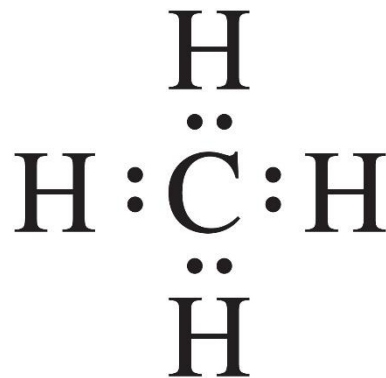
(Generally the C-H bond is considered non-polar).

Formal Charges

Formal charges is a way of keeping count of electrons, but the charges may or may not be 'real'.
(Partial charges δ^+ are 'real').

$$\text{Formal Charge} = (\text{group number}) - (\text{nonbonding } e\text{'s}) - \frac{1}{2}(\text{shared } e\text{'s})$$

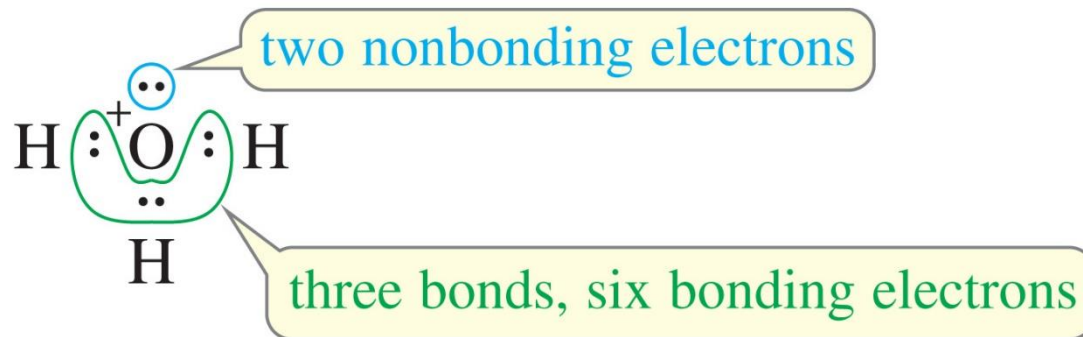
E.g. methane, CH_4



Hydrogens: $FC = 1 - 0 - \frac{1}{2}(2) = 0$

Carbon : $FC = 4 - 0 - \frac{1}{2}(8) = 0$ (whenever C has 4 bonds, it is neutral).

Hydronium Ion, H_3O^+



Hydrogens: Each have one bond and are neutral. $FC = 0$

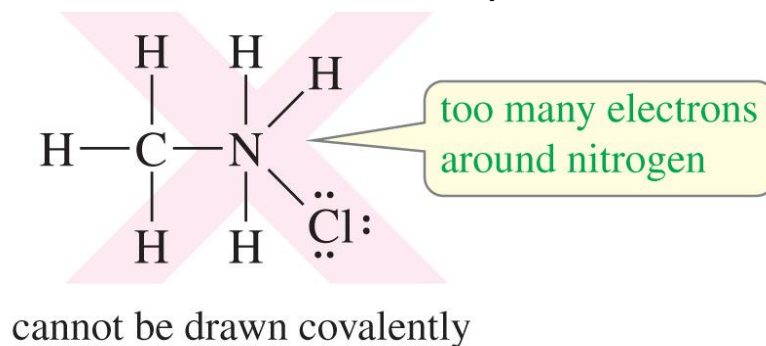
Oxygen: $FC = 6 - 2 - \frac{1}{2}(6) = 1$

Oxygen has a formal charge of +1.

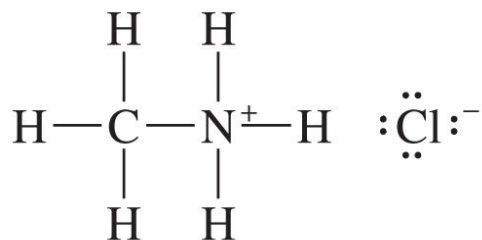
Ionic Structures

Some organic compounds **do contain** ionic bonds.

Methyl ammonium chloride (CH_3NH_3Cl) does NOT contain solely covalent bonds.

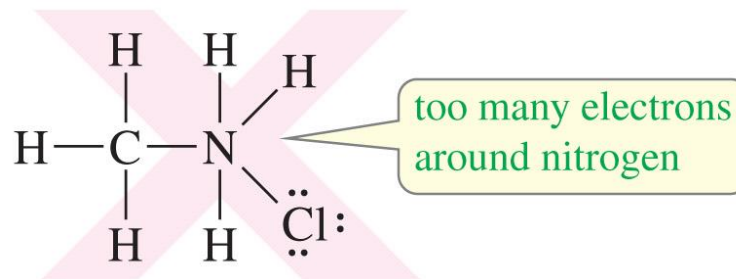


The covalent structure would require 5 bonds (10 e's) around Nitrogen. Chloride must be bonded ionically to the methylammonium cation.



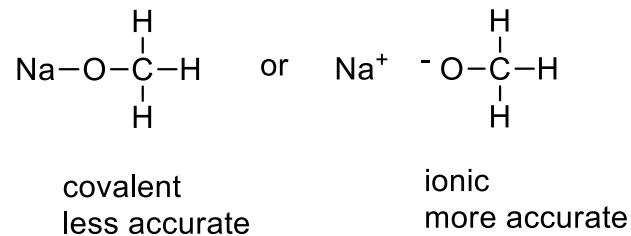
methylammonium chloride

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cannot be drawn covalently

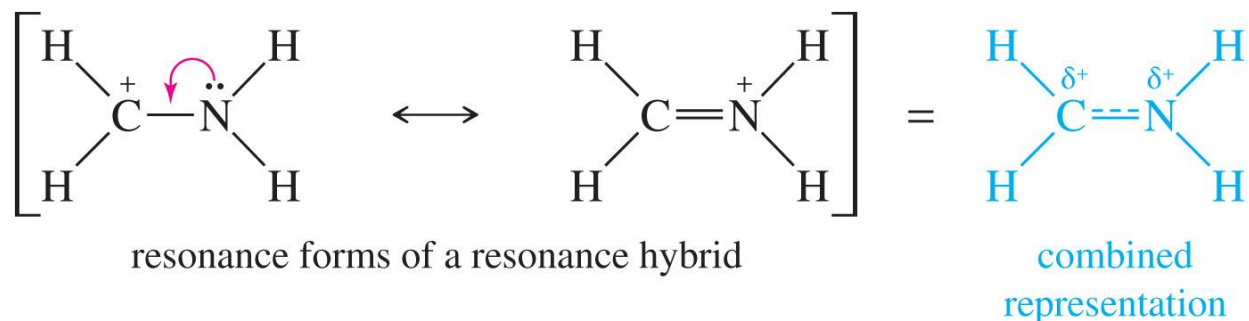
However, some molecules can be written *either* ionically or covalently.



Differences in electronegativity decide which structure is the more accurate description.

Resonance Structures

The structures of some compounds are not sufficiently described by a *single* Lewis structure. E.g. $[\text{CH}_2\text{NH}_2]^+$



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Carbon FC =	+1	0
Nitrogen FC =	0	+1

When two or more valence structures are possible, differing only in location of electrons, the molecule will generally show properties of both structures.
(The atoms must stay in the same location).

These different structures are called **RESONANCE** structures.

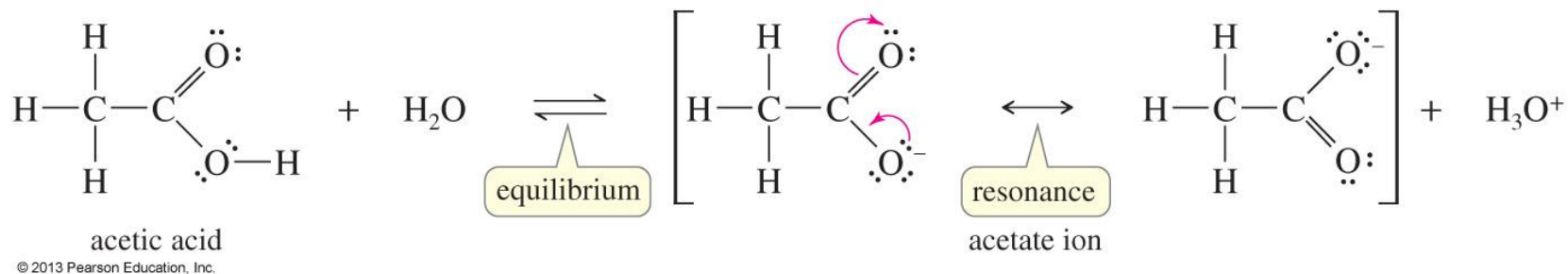
The real structure is a combination of the resonance forms, and is called a resonance **HYBRID**.

The spreading out of the positive charge over two or more atoms makes the overall structure more stable. (Charge delocalisation).

$[\text{CH}_2\text{NH}_2]^+$ is said to be a **resonance stabilized** cation.

The concept of resonance stabilization is very important in organic chemistry.

Consider the deprotonation of acetic acid.



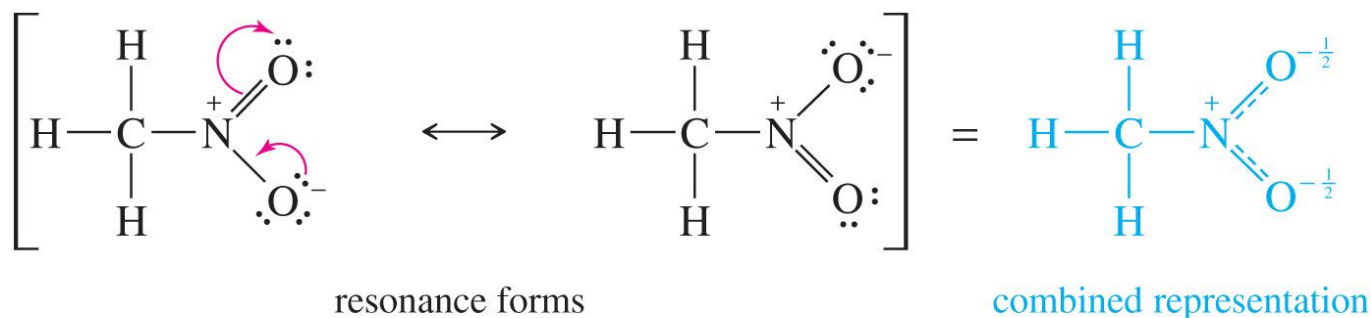
Acetate ion has the negative charge delocalised over 2 oxygen atoms. Each O bears ½ a negative charge. The carbon oxygen bond order is 1½.

Individual structures **do not** exist, and the molecule **does not** oscillate between the two extremes.

Arrows in Chemistry

	Reaction
	Equilibrium
	Resonance
	Two electron movement
	One electron movement

Uncharged molecules can also have resonance forms, with equal +ve and -ve formal charges, like Nitromethane (CH_3NO_2).



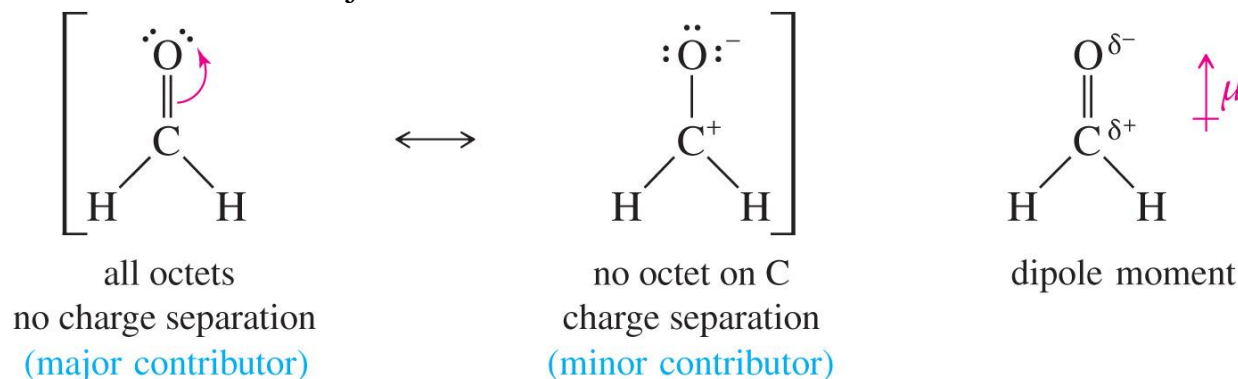
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Major and Minor Contributors

Certain resonance structures are more stable than others (i.e. of lower energy).

These are said to be **major** contributors, whereas higher energy structures are **minor** contributors.

The real structure will resemble the major contributor **more** than it does the minor contributor.



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Consider formaldehyde, even though the minor contributor is of higher energy than its double bonded counterpart, its contribution helps explain the polarization of the double bond.

Resonance Structure Rules:

- 1) All resonance structures must be valid Lewis structures
- 2) Only the placement of electrons can be changed (atoms cannot be moved)
- 3) The number of unpaired (not lone pairs) electrons must stay the same
- 4) The major resonance contributor is the one of lowest energy
- 5) Resonance stabilization is best when delocalising a charge over 2 or more atoms.

General points:

Normally lone pairs or multiple bond electrons are the most common to move for resonance structures.

Good contributors will have all octets satisfied, as many bonds as possible, and as little charge separation as possible.

Negative charges are most stable on more electronegative elements.

Structural Formulas

There are several shorthand notations used by chemists:

Lewis; Condensed Structural and Line Angle Formula

Chemists need to be familiar with all, and often use them interchangeably.

Condensed Structural Formula

These are generally written without lines indicating bonds, or showing lone pairs, and parentheses are used for identical groups.

Compound	Lewis Structure	Condensed Structural Formula
ethane	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	CH_3CH_3
isobutane	$\begin{array}{c} \text{H} \quad \quad \text{H} \quad \quad \text{H} \\ \quad \quad \quad \quad \\ \text{H}-\text{C}-\quad \text{C}-\quad \text{C}-\text{H} \\ \quad \quad \quad \quad \\ \text{H} \quad \text{H}-\text{C}-\text{H} \quad \text{H} \\ \quad \quad \\ \quad \quad \text{H} \end{array}$	$(\text{CH}_3)_3\text{CH}$
<i>n</i> -hexane	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$
diethyl ether	$\begin{array}{c} \text{H} \quad \text{H} \quad \quad \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \quad \\ \text{H}-\text{C}-\text{C}-\ddot{\text{O}}-\text{C}-\text{C}-\text{H} \\ \quad \quad \quad \quad \quad \\ \text{H} \quad \text{H} \quad \quad \quad \text{H} \quad \text{H} \end{array}$	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ or $\text{CH}_3\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$ or $(\text{CH}_3\text{CH}_2)_2\text{O}$

Often, but not always, multiple bonds will be included.

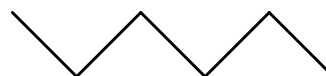
Compound	Lewis Structure	Condensed Structural Formula
but-2-ene	$ \begin{array}{ccccccc} & \text{H} & \text{H} & & \text{H} & & \\ & & & & & & \\ \text{H} & - \text{C} & - \text{C} & = & \text{C} & - \text{C} & - \text{H} \\ & & & & & & \\ & \text{H} & & & \text{H} & \text{H} & \end{array} $	$\text{CH}_3\text{CHCHCH}_3$ or $\text{CH}_3\text{CH}=\text{CHCH}_3$
acetonitrile	$ \begin{array}{c} \text{H} \\ \\ \text{H} - \text{C} - \text{C} \equiv \text{N} : \\ \\ \text{H} \end{array} $	CH_3CN or $\text{CH}_3\text{C} \equiv \text{N}$
acetaldehyde	$ \begin{array}{c} \text{H} \quad \ddot{\text{O}} \\ \quad \\ \text{H} - \text{C} - \text{C} - \text{H} \\ \\ \text{H} \end{array} $	CH_3CHO or $\text{CH}_3\overset{\text{O}}{\parallel}{\text{C}}\text{H}$
acetone	$ \begin{array}{c} \text{H} \quad \ddot{\text{O}} \quad \text{H} \\ \quad \quad \\ \text{H} - \text{C} - \text{C} - \text{C} - \text{H} \\ \quad \quad \\ \text{H} \quad \quad \text{H} \end{array} $	CH_3COCH_3 or $\text{CH}_3\overset{\text{O}}{\parallel}{\text{C}}\text{CH}_3$
acetic acid	$ \begin{array}{c} \text{H} \quad \ddot{\text{O}} \\ \quad \\ \text{H} - \text{C} - \text{C} - \ddot{\text{O}} - \text{H} \\ \\ \text{H} \end{array} $	CH_3COOH or $\text{CH}_3\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ or $\text{CH}_3\text{CO}_2\text{H}$

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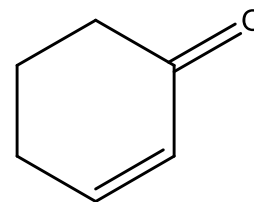
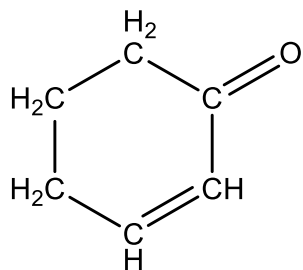
Line Angle Formulae (Stick Figures)

Bonds are represented by lines, carbon atoms are assumed to be present at the *start* and *finish* of a line. Nitrogen, oxygen and halogens are labeled, but hydrogens are only shown when bonded to a drawn atom. Each atom is assumed to have sufficient hydrogen atoms around it to make it *neutral*.

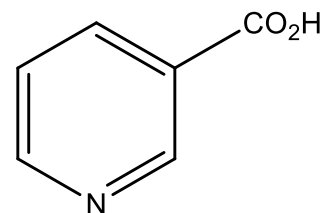
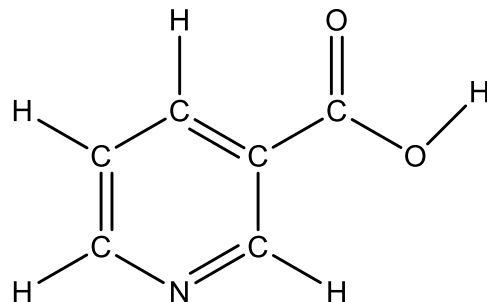
Hexane



Cyclohex-2-enone



Nicotinic Acid



Acids and Bases

Three different definitions: *Arrhenius*
 Bronsted-Lowry
 Lewis

Arrhenius Definition (pre-1900)

An acid is a substance that dissociates in water to give H_3O^+ ions.

(Stronger acids like H_2SO_4 were assumed to dissociate more than weaker acids like $\text{CH}_3\text{CO}_2\text{H}$).



A base is a substance that dissociates in water to give OH^- ions.



pH values

The acidity of an aqueous solution is determined by the concentration of H_3O^+ ions.

Water Autoprotolysis Constant, $K_w = 1.00 \times 10^{-14}$ at 25°C

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-]$$

In a neutral solution, $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7} \text{ M}$

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+]$$

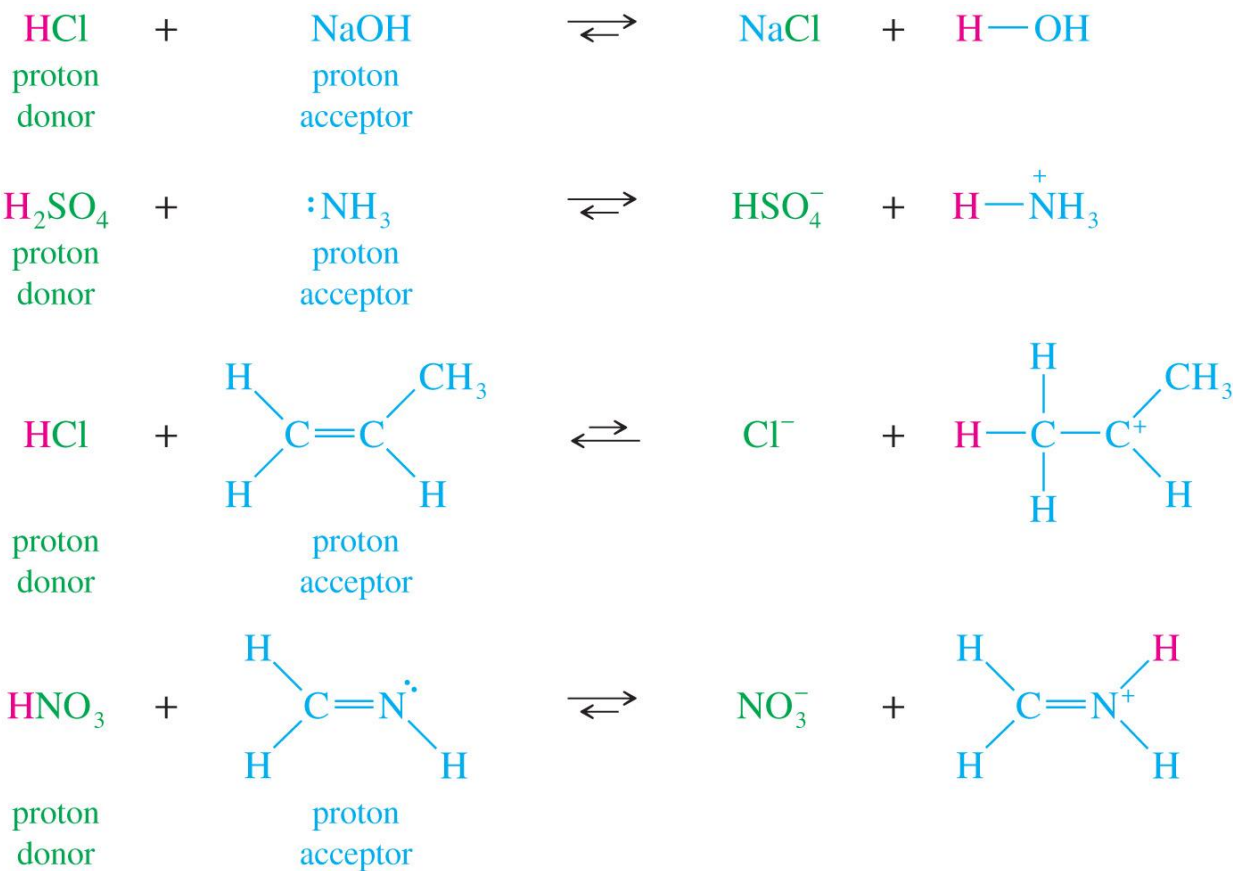
So a neutral pH is 7.

Acidic Solutions have $[\text{H}_3\text{O}^+] > 10^{-7} \text{ M}$; so $\text{pH} < 7$; Basic Solutions have $[\text{H}_3\text{O}^+] < 10^{-7} \text{ M}$; so $\text{pH} > 7$.

Bronsted-Lowry Definition

An acid is a species that can *donate a proton*.

A base is a species that can *accept a proton*.



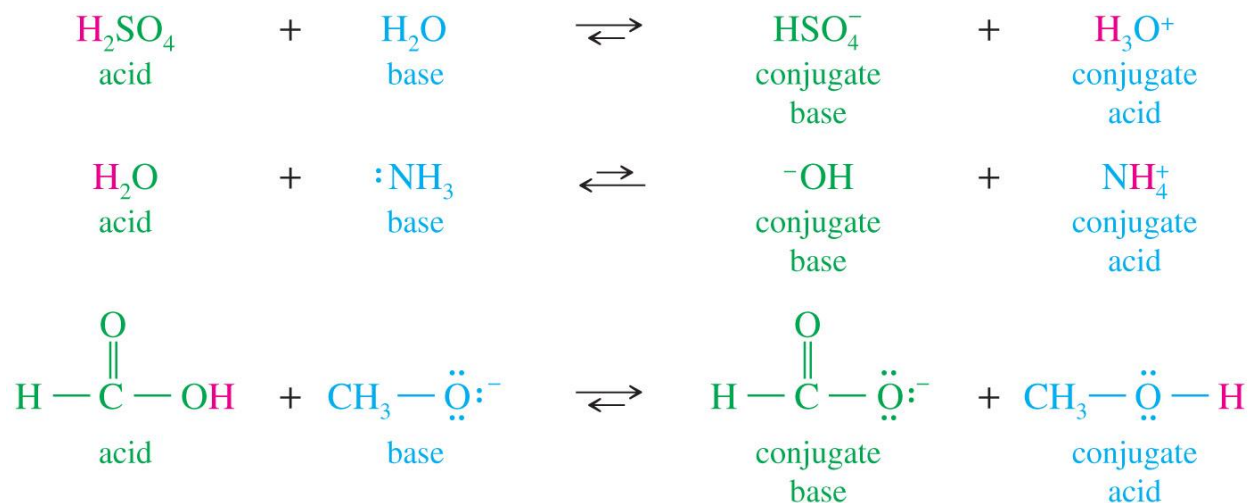
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Bronsted-Lowry definition is **broad**er than the Arrhenius definition.

Conjugate Acids and Bases

When a base accepts a proton, it is capable of returning that proton – it has become an acid. (*Conjugate Acid*)

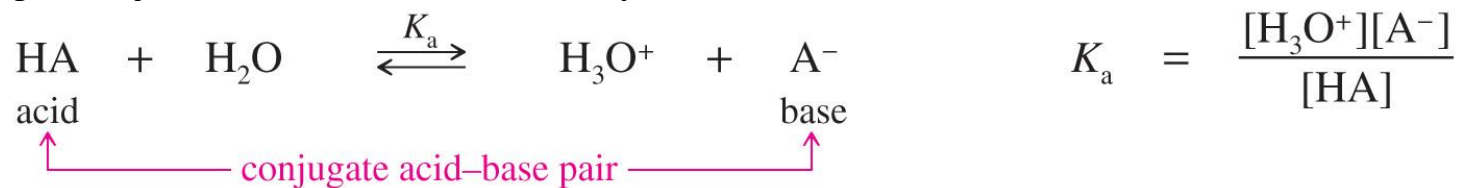
When an acid donates a proton, it is capable of receiving it back – it has become a base. (*Conjugate Base*)



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Acid Strength

This is expressed just as for the Arrhenius acids, by the extent of ionization in water.



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The **stronger** the acid, the **larger** the K_a .

Typical values:

Strong Acid (H ₂ SO ₄)	K _a = 1	pK _a = 0
Organic Acid (CH ₃ CO ₂ H)	K _a = 10 ⁻⁴	pK _a = 4
Organic Compound (CH ₄)	K _a = 10 ⁻⁴⁰	pK _a = 40

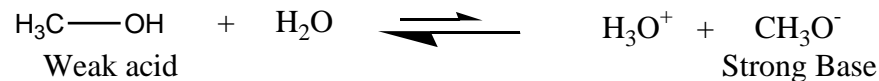
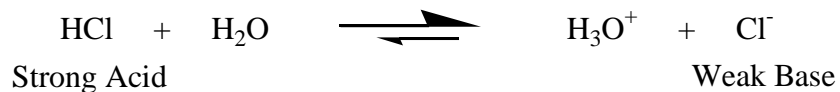
$$\text{pK}_a = -\log_{10} K_a$$

(Stronger the acid, lower the pK_a)

Base Strength

Acid strength is related to base strength of its conjugate base.

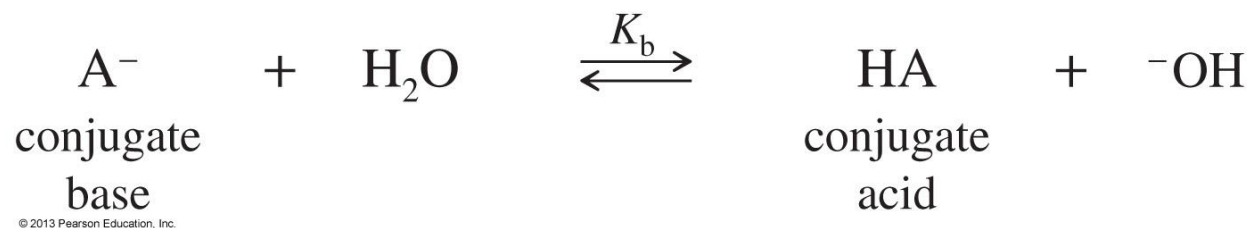
For an acid to be *strong*, its conjugate base must be *weak* (i.e. stable).



For an acid to be *weak*, its conjugate base must be *strong*.

In general, in the reaction between an acid and base, the equilibrium favors the weaker acid or base.

Base strength is measured in a similar way to acid strength, via equilibrium constants of hydrolysis.



$$K_b = \frac{[\text{HA}][\text{}^-\text{OH}]}{[\text{A}^-]} \qquad \text{p}K_b = -\log_{10} K_b$$

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Acid strength is related to the basicity of its conjugate base by the following:

$$(K_a)(K_b) = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \frac{[\text{HA}][\text{}^-\text{OH}]}{[\text{A}^-]} = [\text{H}_3\text{O}^+][\text{}^-\text{OH}] = 1.0 \times 10^{-14}$$

water ion-product constant

$$(K_a)(K_b) = 10^{-14}$$

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So, if K_a is large, K_b must be small.

The stronger the acid, the weaker the conjugate base.

Structural Effects on Acidity

By considering the stability of the conjugate base, we can predict how strong an acid a compound might be.

More stable anions tend to be weaker bases, and thus their conjugate acids are stronger acids.

Factors that influence stability of conjugate bases (anions) are:

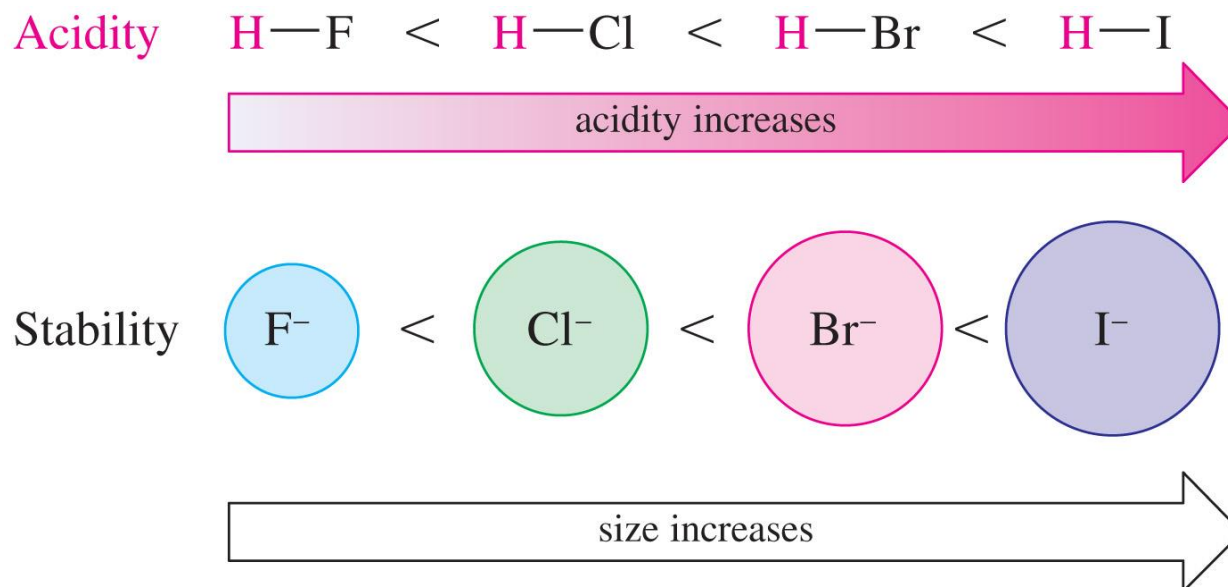
Size

Electronegativity

Resonance.

Size

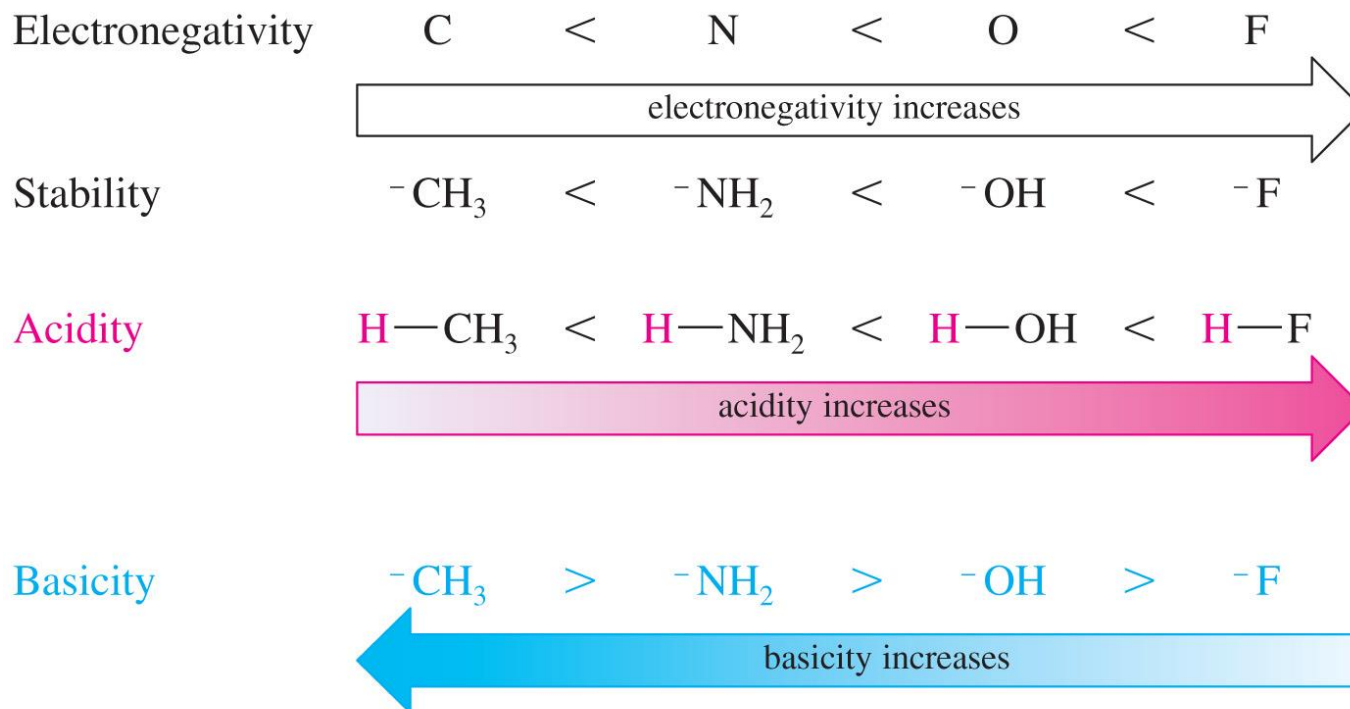
An anion is more stable if the negative charge is spread out over a larger distance in space.



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Electronegativity

More electronegative elements bear negative charge more efficiently.

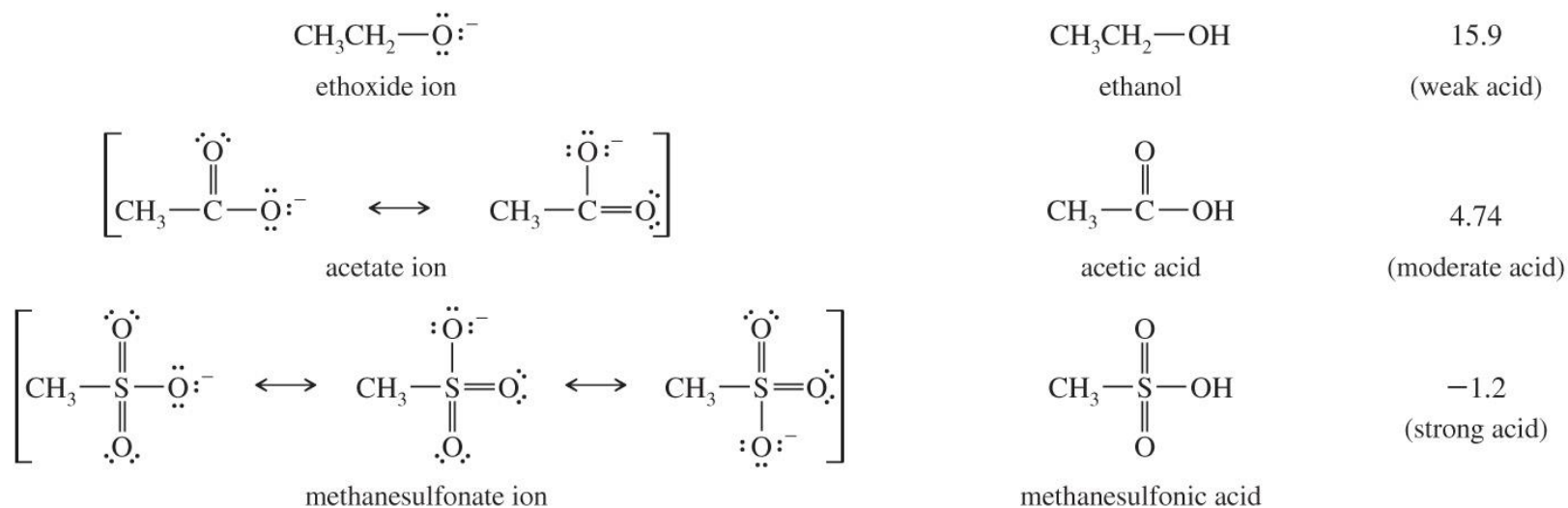


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Resonance

If the negative charge of the conjugate base can be spread over 2 or more atoms, resonance stabilization will make the base weaker (i.e. more stable).

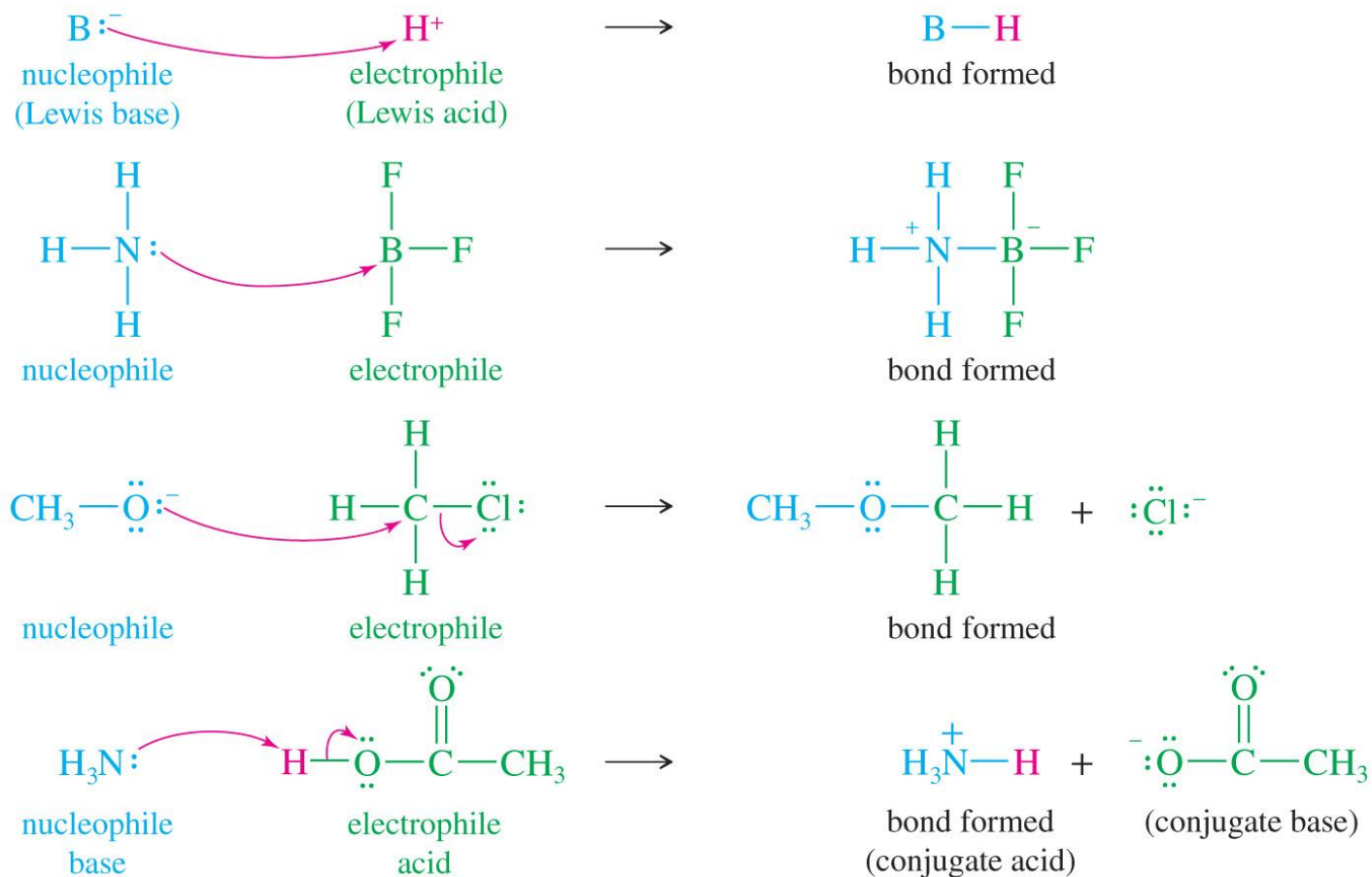
Typically, if resonance stabilization is available to an anion, this is the dominating factor.



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Lewis Acids and Bases

For a broader definition, instead of considering the proton transfer, consider the *movement of electrons*, and the bond formation.



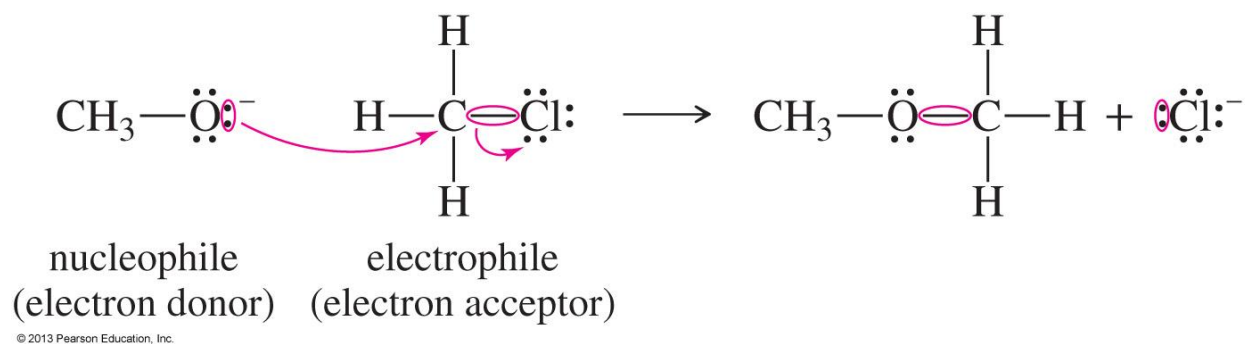
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Lewis acid is an *electron pair* acceptor.
Lewis base is an *electron pair* donor.

Since a Lewis acid is a species that accepts electrons, it is termed an ELECTROPHILE ('lover of electrons')

A Lewis base is a species that donates electrons to a nucleus with an empty (or easily vacated) orbital, and is termed a NUCLEOPHILE.

The departing species is called a LEAVING GROUP.



(Remember, the curly arrows mean movement of 2 electrons).

Curly arrows go **from** the nucleophile **to** the electrophile.