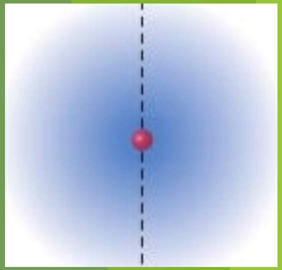
Introduction and Review

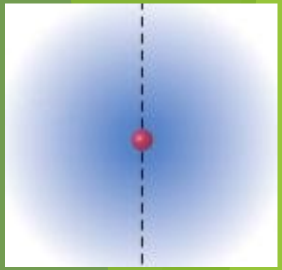
Organic Chemistry, 5th Edition
L. G. Wade, Jr.

ORGANIC CHEMISTRY



STUDY OF CARBON-CONTAINING COMPOUNDS

Classification of Matter



CLASSIFICATION OF MATTER

FIRE AGE - BASED ON COMBUSTION

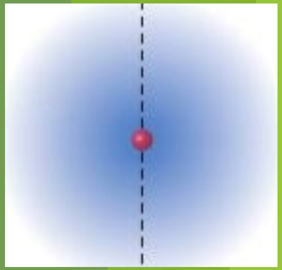
COMBUSTIBLES - FUELS FROM ANIMALS AND PLANTS

OIL, WOOD, FAT

NON-COMBUSTIBLES -DIDNÕT BURN; PUT OUT FIRES

SAND, WATER, ROCKS

BERZILIUS' DEFINITIONS



ORGANIC COMPOUNDS

CHARACTERISTIC PRODUCTS OF LIVING ORGANISMS

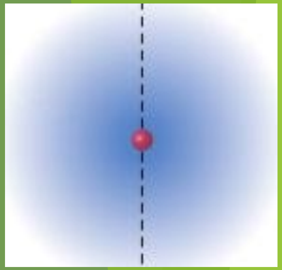
SUBSTANCES LIKE SUGAR AND OLIVE OIL

INORGANIC COMPOUNDS

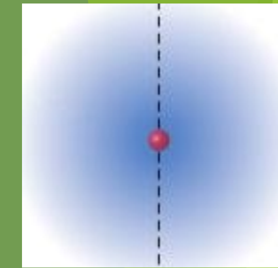
PRODUCTS FROM NON-LIVING ENVIRONMENT

SUBSTANCES LIKE WATER AND IRON

Vital Force Theory



INORGANIC MATERIALS COULD BE CONVERTED TO ORGANIC MATERIALS IN THE PRESENCE OF A VITAL FORCE FOUND ONLY IN LIVING BODIES.



Woehler's urea synthesis 1828

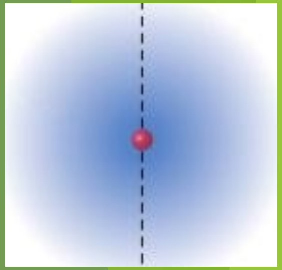
Ammonium isocyanate + heat ------> urea

NH_4CNO

NH_2CONH_2

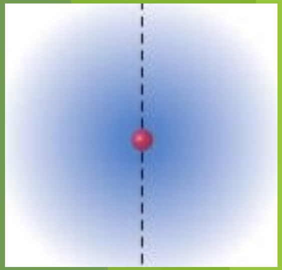
"I have been able to make urea without aid of kidney of man or dog.

Post 1828



- Over 18,000 million compounds have been synthesized
- Pharmaceuticals
- Biochemicals
- Plastics
- Agrichemicals
- Paints

Why so many organic?

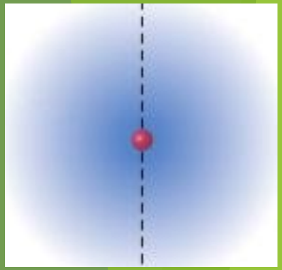


FORMS COVALENT BONDS WITH NON-METALS

H O N X P S Se

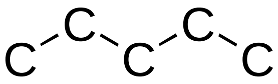
FORMS COVALENT BONDS WITH MANY METALS

Li Mg Al Cd Fe

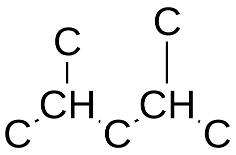


AND

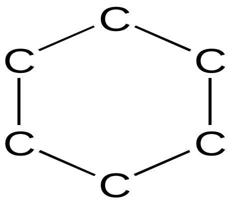
WITH ITSELF



CHAINS



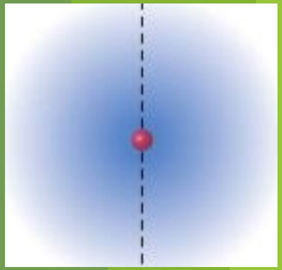
CHAINS WITH BRANCHES



RINGS

No limit

Atomic Structure

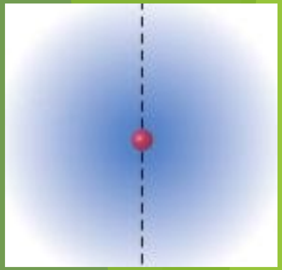


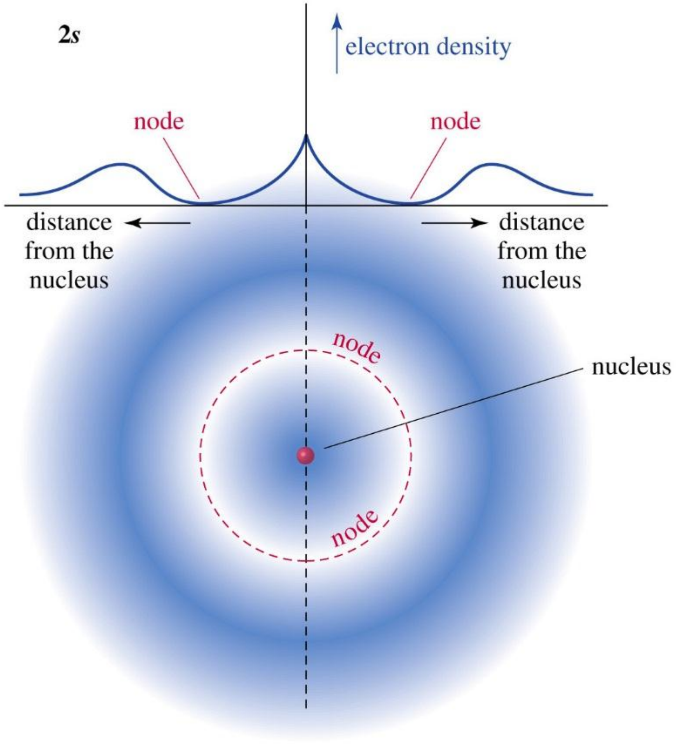
- protons, neutrons, and electrons
- isotopes

$$^{12}_{6}\mathbf{C} \qquad ^{14}_{6}\mathbf{C}$$

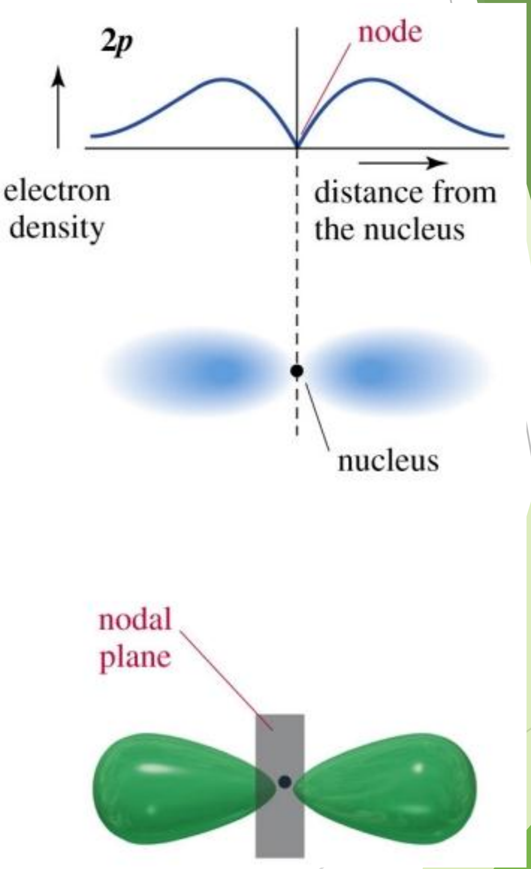
=>

Atomic Orbitals





2*s* orbital (spherical)



2*p* orbital

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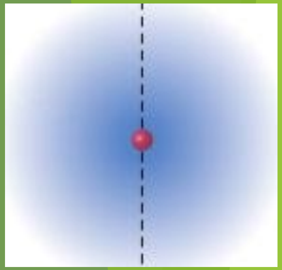
Electronic Configurations



- Aufbau principle: Place electrons in lowest energy orbital first.
- Hund's rule: Equal energy orbitals are half-filled, then filled.

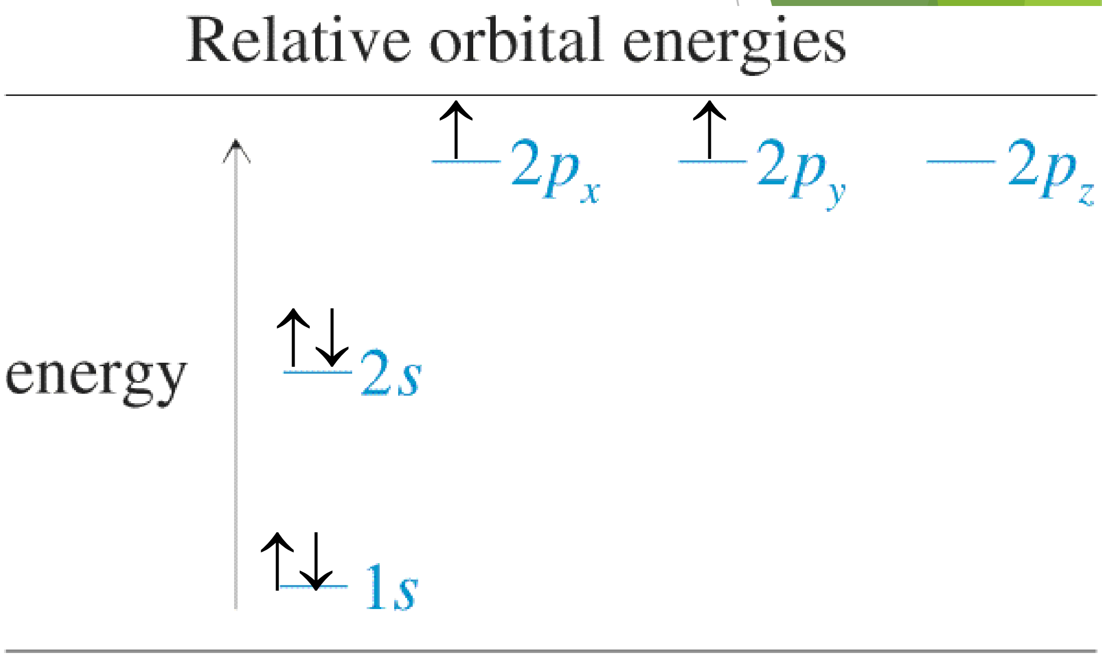


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Table 1-1

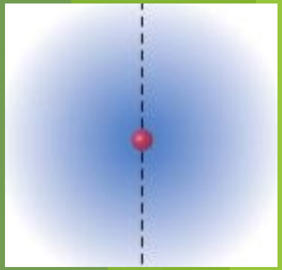
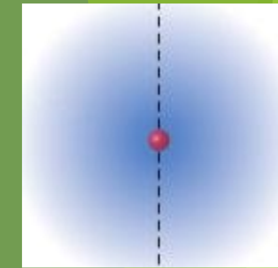


TABLE 1-1 Electronic Configurations of the Elements of the First and Second Rows

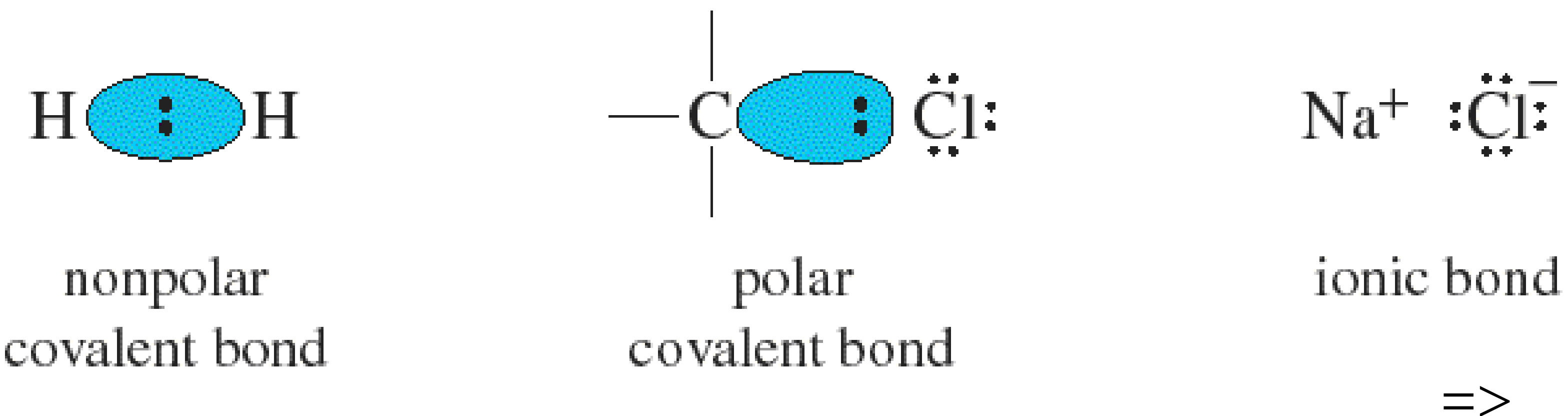
Element	*Configuration*	*Valence Electrons*
H	$1s^1$	1
He	$1s^2$	2
Li	$1s^2\,2s^1$	1
Be	$1s^2\,2s^2$	2
B	$1s^2\,2s^2\,2p_x^1$	3
C	$1s^2\,2s^2\,2p_x^1\,2p_y^1$	4
N	$1s^2\,2s^2\,2p_x^1\,2p_y^1\,2p_z^1$	5
O	$1s^2\,2s^2\,2p_x^2\,2p_y^1\,2p_z^1$	6
F	$1s^2\,2s^2\,2p_x^2\,2p_y^2\,2p_z^1$	7
Ne	$1s^2\,2s^2\,2p_x^2\,2p_y^2\,2p_z^2$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

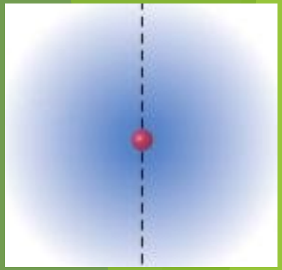
=>

Bond Formation



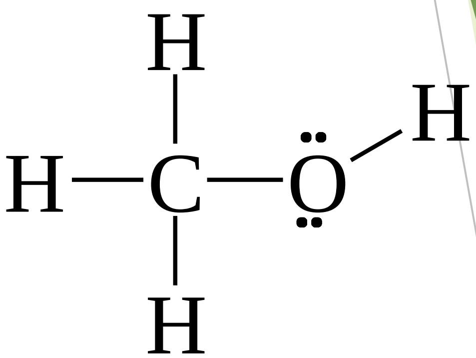
- Ionic bonding: electrons are transferred.
- Covalent bonding: electron pair is shared.





Lewis Structures

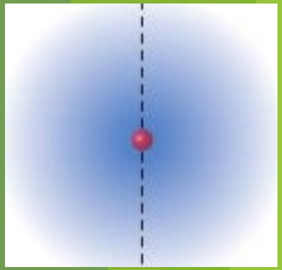
- Bonding electrons
- Nonbonding electrons or lone pairs



Satisfy the octet rule! =>

The **octet rule** is a chemical **rule** of thumb that reflects observation that atoms of main-group elements tend to combine in such a way that each atom has eight electrons in its valence shell, giving it the same electronic configuration as a noble gas.

TIPS



- Neutral atoms

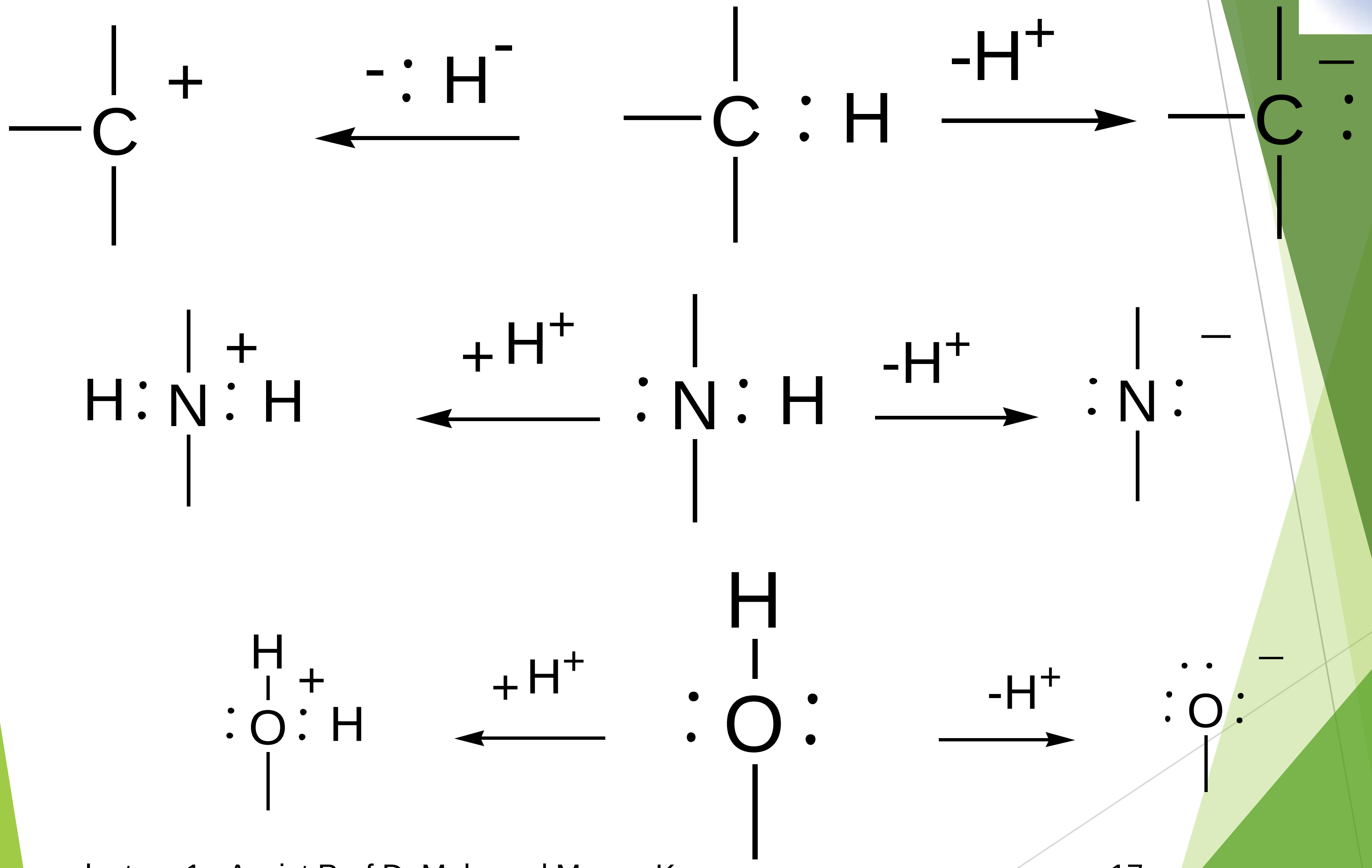
 Carbon 4 bonds (double bonds count as 2 triple bonds count as 3) and NO lone pairs.

 Nitrogen 3 bonds and one lone pair

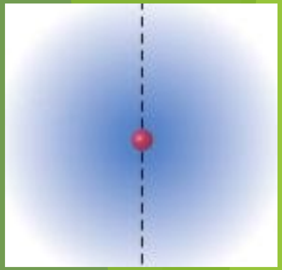
 Oxygen 2 bonds and two lone pairs

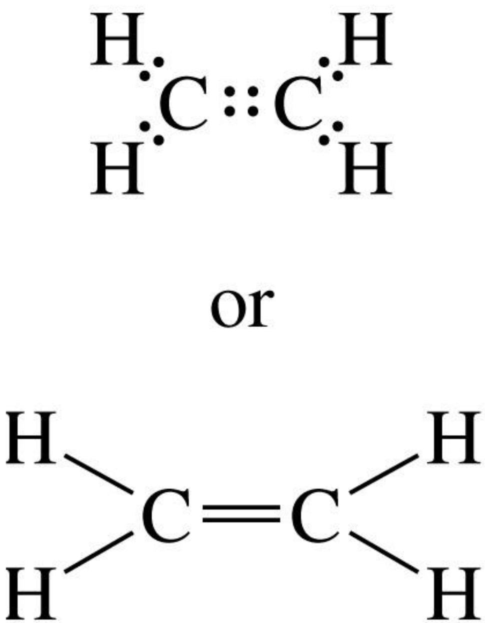
 BORON 3 bonds BUT no lone pairs

TIPS2

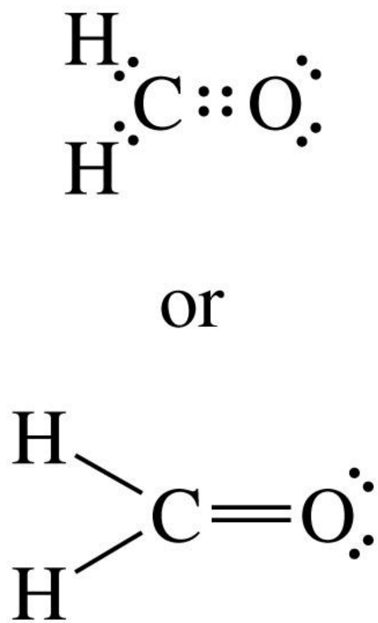


Multiple Bonding

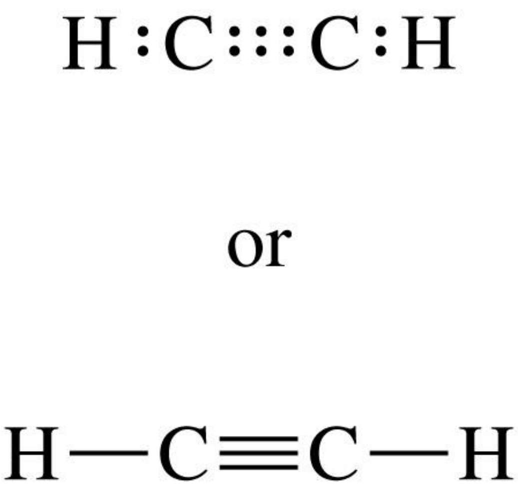




ethylene

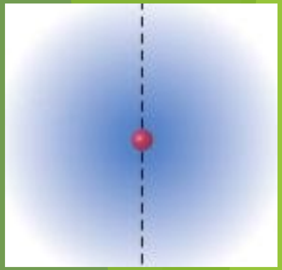


formaldehyde



acetylene

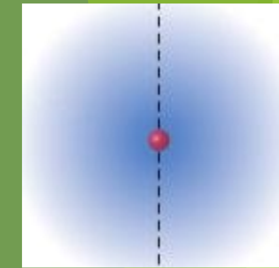
=>



EXAMPLES

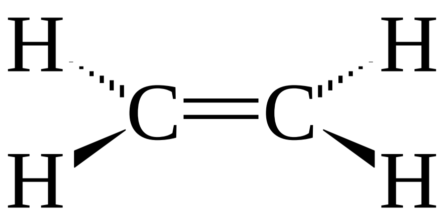
CO_2 SO_2 C_2H_3N

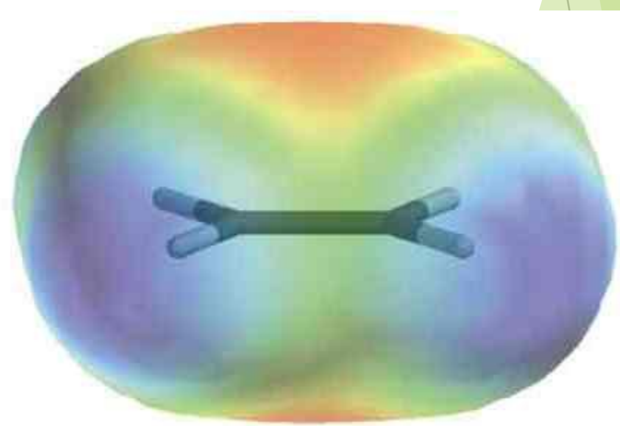
C_3H_6O isomer problem



Dipole Moment

- Amount of electrical charge x bond length.
- Charge separation shown by electrostatic potential map (EPM).
- Red indicates a partially negative region and blue indicates a partially positive region.





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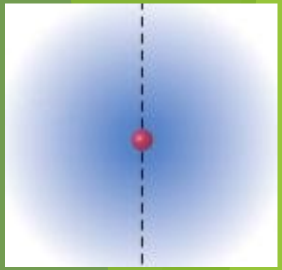
Electronegativity and Bond Polarity

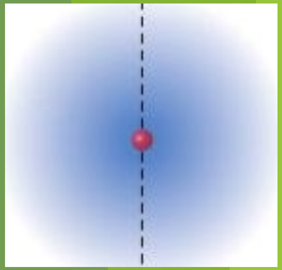


Greater ΔEN means greater polarity

H 2.2						
Li 1.0	Be 1.6	B 1.8	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

=>

EXAMPLES OF BOND POLARITY



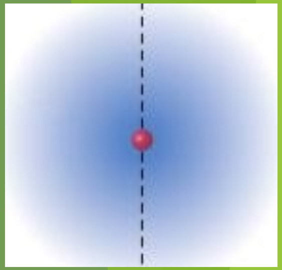
C------Br

C-------Li

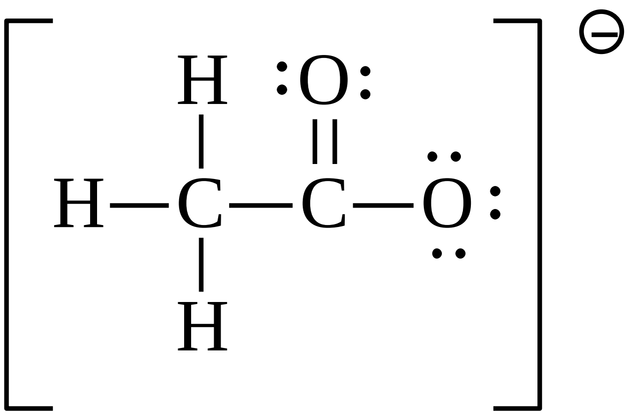
Br--------Cl

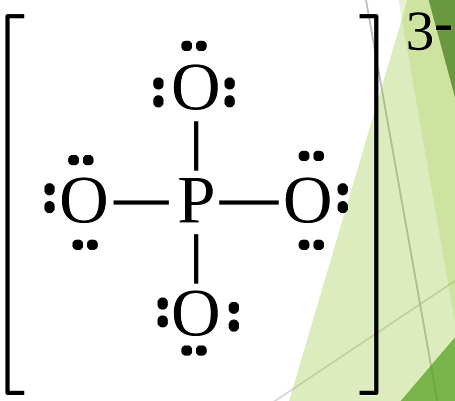
C-------N

Calculating Formal Charge



- For each atom in a valid Lewis structure:
- Count the number of valence electrons
- Subtract all its nonbonding electrons
- Subtract half of its bonding electrons





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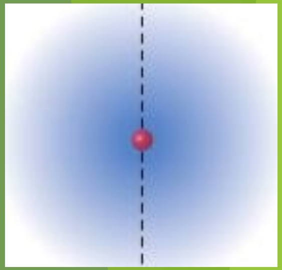
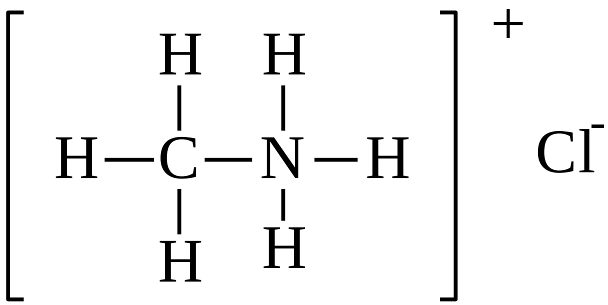
Ionic Structures

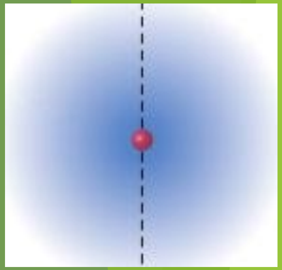


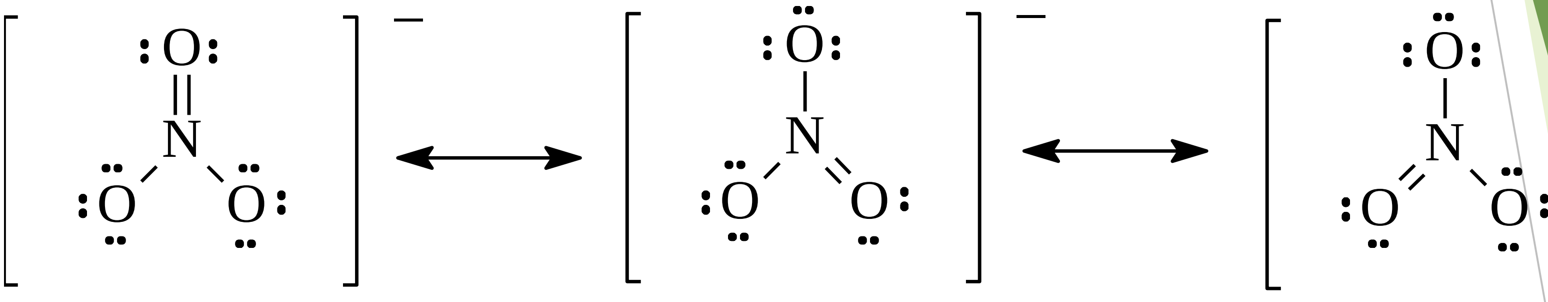


$$Na\cancel{-}O-CH_3 \quad \text{or} \quad Na^{+} \quad {}^{-}O-CH_3$$

=>

Resonance - More than one Lewis Diagram





- Consider writing Lewis structure for NO_3^{-2}
- The real structure is a resonance hybrid.
- All the bond lengths are the same.
- Each oxygen has a -1/3 electrical charge.

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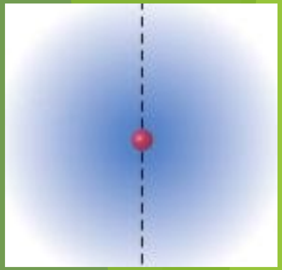
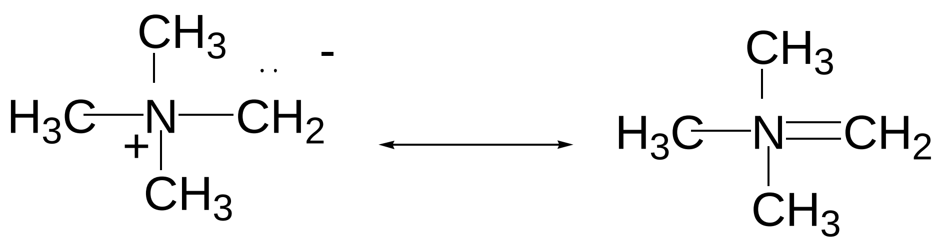


Resonance Rules

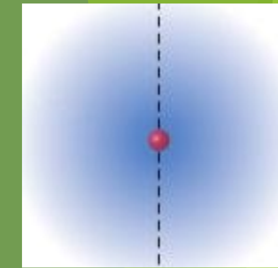
Must be legitimate Lewis structures



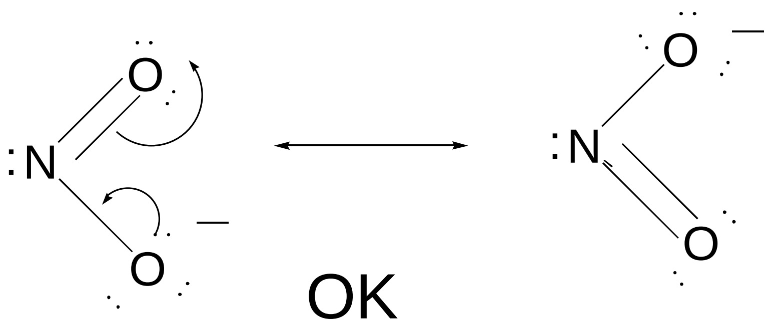
NO NO

Pentavalent nitrogen atom!!

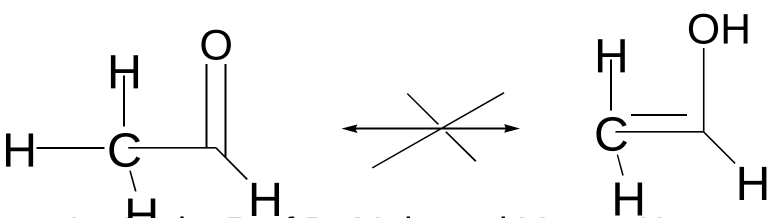
Resonance structures?



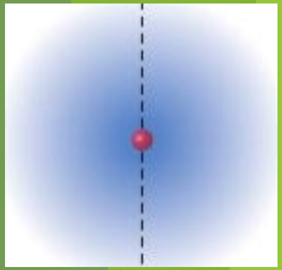
Only electrons can be moved (usually lone pairs or pi electrons).



OK



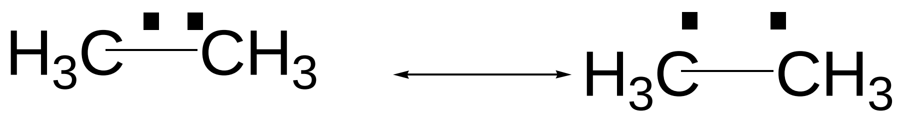
NO NO



Nuclei positions and bond angles remain the same.

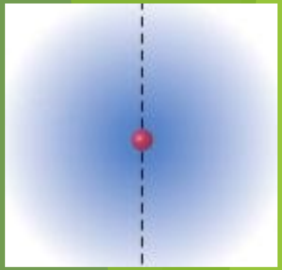
C=C-C+ ⟷ +C-C=C

The number of unpaired electrons remains the same

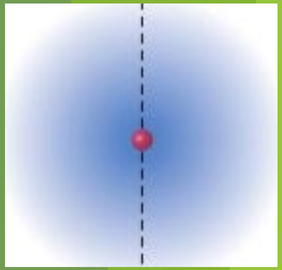


NO NO

DELOCALIZATION OF CHARGE USUALLY IS STABILIZING



Delocalization of charge results in fractional charges at alternate atoms

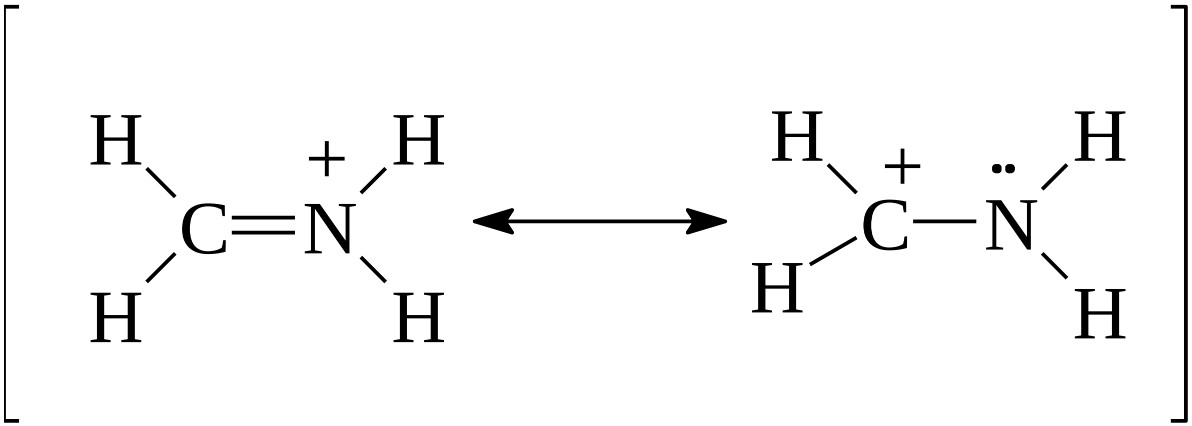


Major Resonance Form

- has as many octets as possible.
- has as many bonds as possible.
- has the negative charge on the most electronegative atom.
- has as little charge separation as possible.

Example=>

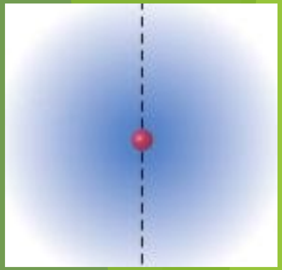
Major Contributor?



major

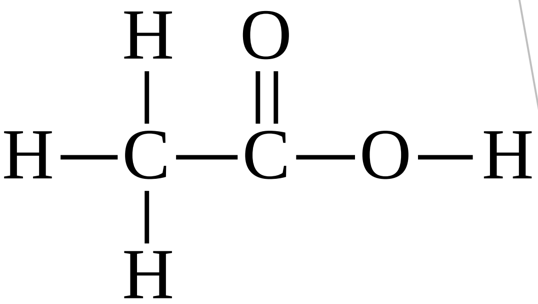
minor,
carbon does
not have octet.

=>

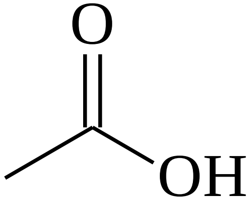


Chemical Formulas

- Full structural formula (no lone pairs shown)



- Line-angle formula



- Condensed structural formula

CH_3COOH

- Molecular formula
  - $C_2H_4O_2$
- Empirical formula
  - CH_2O

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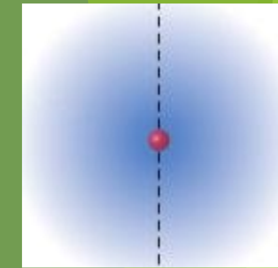
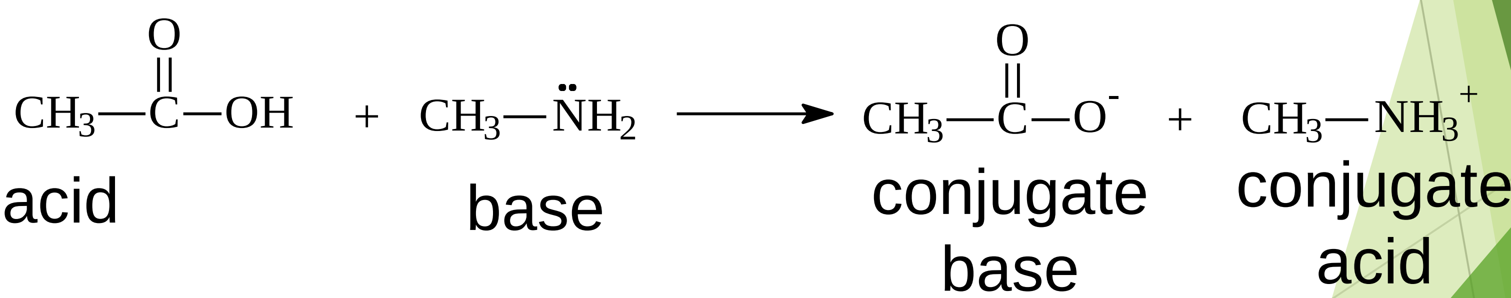


BrØn~~s~~ted-Lowry Acids and Bases

- Acids can donate a proton.
- Bases can accept a proton.
- Conjugate acid-base pairs.



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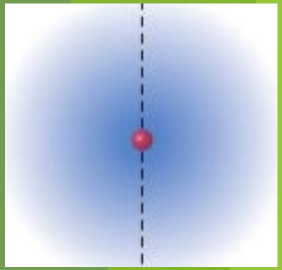
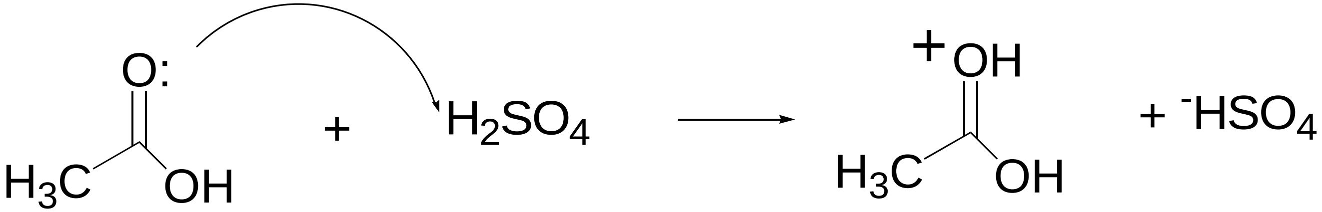
EXAMPLES



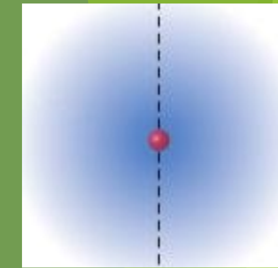
BASE — CONJ ACID

$$CH_3CO_2H + :NH_3 \longrightarrow CH_3CO_2^- + NH_4^+$$

ACID — CONJ BASE

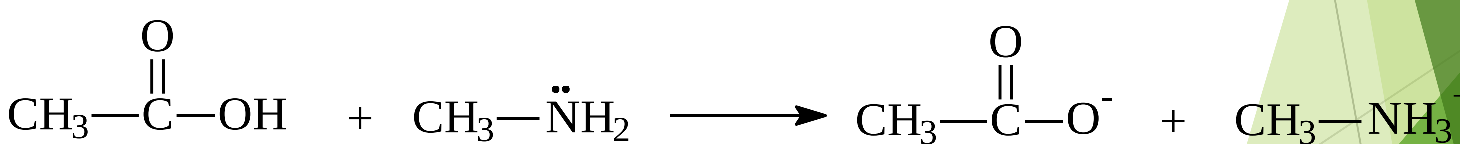


Amphoterism - ability to behave as an acid or base



Acid and Base Strength

- Acid dissociation constant, K_a
- Base dissociation constant, K_b
- For conjugate pairs, $(K_a)(K_b) = K_w$
- Spontaneous acid-base reactions proceed from stronger to weaker.



pK_a 4.74 pK_b 3.36 pK_b 9.26 pK_a 10.64

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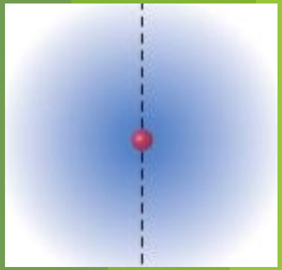


EXAMPLES

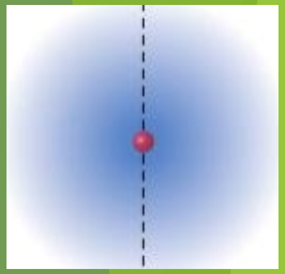
Will NaOH neutralize phenol (C_6H_5OH)?

$$NaOH + C_6H_5OH \longrightarrow HOH + C_6H_5ONa$$

pKa = 10   pKa = 15.7   YES!!

Stronger acid   Weaker acid

$$^{-}OH + C_6H_5OH \longrightarrow HOH + C_6H_5O^{-}$$

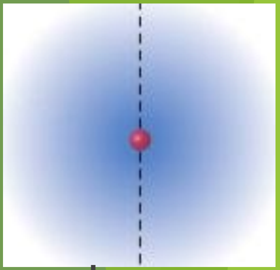


Determining Relative Acidity

- Electronegativity
- Size
- Resonance stabilization of conjugate base

=>

Electronegativity



As the bond to H becomes more polarized, H becomes more positive and the bond is easier to break.

Electronegativity	C	<	N	<	O	<	F
Stability	$^{-}CH_3$	<	$^{-}NH_2$	<	^{-}OH	<	^{-}F
Acidity	$H—CH_3$	<	$H—NH_2$	<	$H—OH$	<	$H—F$
Basicity	$^{-}CH_3$	>	$^{-}NH_2$	>	^{-}OH	>	^{-}F

electronegativity increases $\longrightarrow$

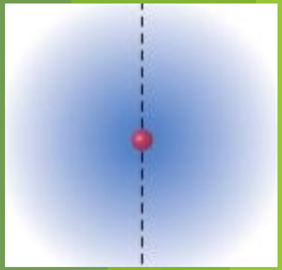
acidity increases $\longrightarrow$

$\longleftarrow$ basicity increases

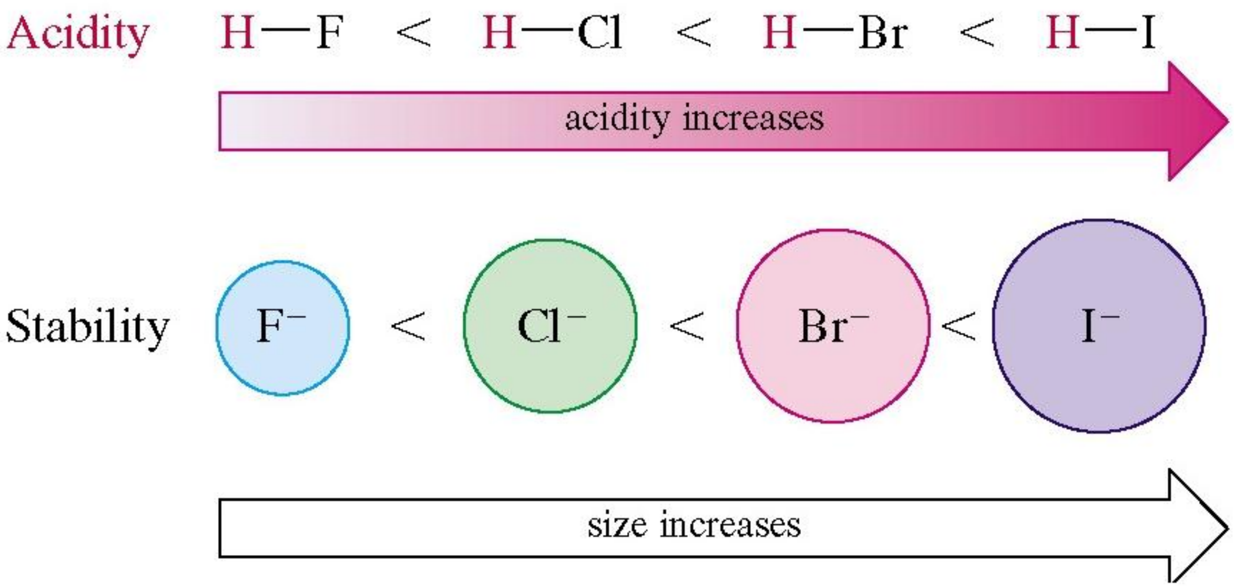
=>

lec

Size



- As size increases, the H is more loosely held and the bond is easier to break.
- A larger size also stabilizes the anion.



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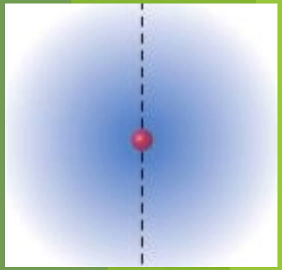
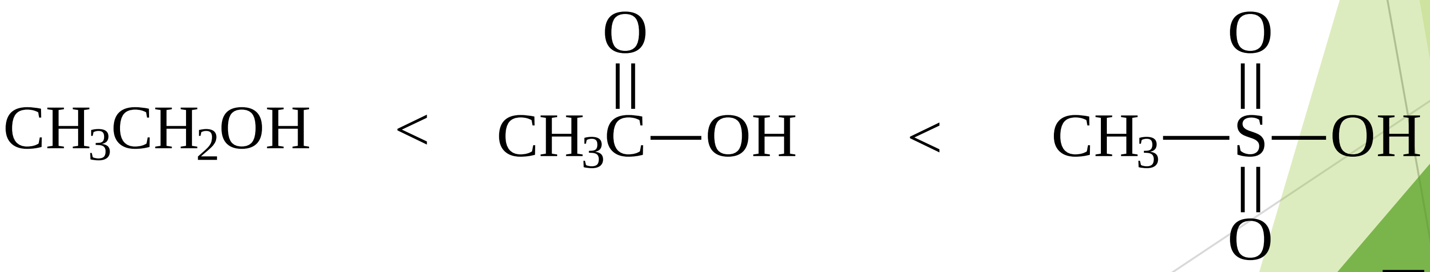


Resonance

- Delocalization of the negative charge on the conjugate base will stabilize the anion, so the substance is a stronger acid.
- More resonance structures usually mean greater stabilization.



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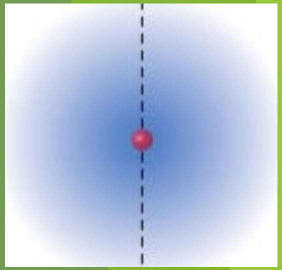
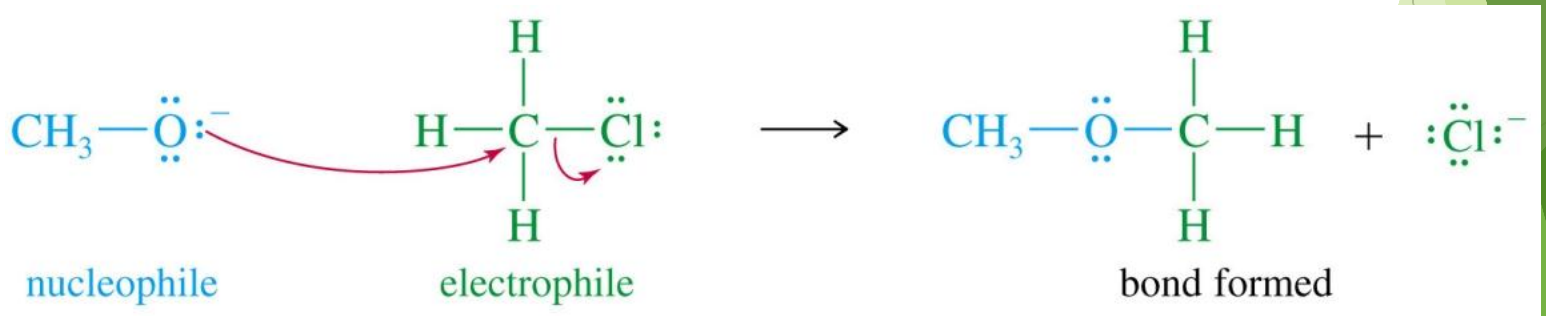
Lewis Acids and Bases



- Acids accept electron pairs = electrophile
- Bases donate electron pairs = nucleophile

$$CH_2{=}CH_2 \quad + \quad BF_3 \longrightarrow {}^{-}BF_3{-}CH_2{-}CH_2^{+}$$

nucleophile electrophile



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