Bonding and Lewis Structures

- There are two types of chemical bonds: ionic and covalent. However, some bonds are frequently "in between."

A. Ionic Bonds

- In an ionic bond, at least one electron is *completely* transferred from one atom to another.

- If the ionic compounds are from main-group elements (not the transition elements), the ions have noble-gas configuration in their valence shells.

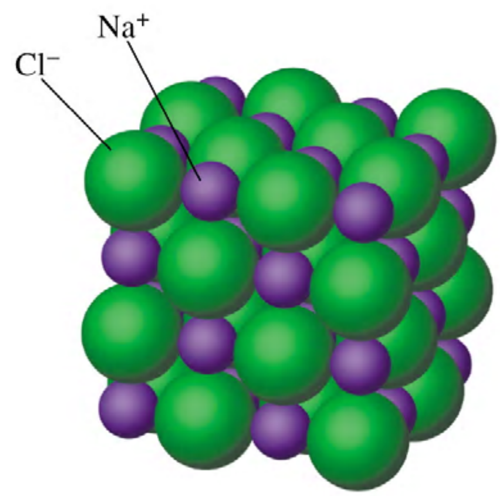
$$Na + Cl \rightarrow Na^+Cl^- \quad (Na^+ = [Ne] \text{ and } Cl^- = [Ar])$$

- Because of the strong electrostatic interactions between the cations and the anions, ionic compounds exist as crystal lattice at room temperature. Melting breaks the lattice.

- The force of attraction between the cation and the anion is dictated by Coulomb's Law

$$\text{Force} = \frac{kQ_1Q_2}{r^2}$$

where the Q values are sizes of the charges on the ions and r is the distance between them.



- Which has a higher melting point, NaCl or LiF?

B. Covalent Bonds

1. Structures

- Unlike ionic bonds, covalent bonding involves the *sharing* of electrons between atoms.
- It is assumed that only electrons in the valence shell are involved in the formation of covalent bonds.
- Suppose we have two H atoms forming molecular hydrogen:

$$\cdot H(g) \quad + \cdot H(g) \quad \rightarrow \quad \overset{H-H}{H_2(g)} \qquad \Delta H = -ve$$

negative

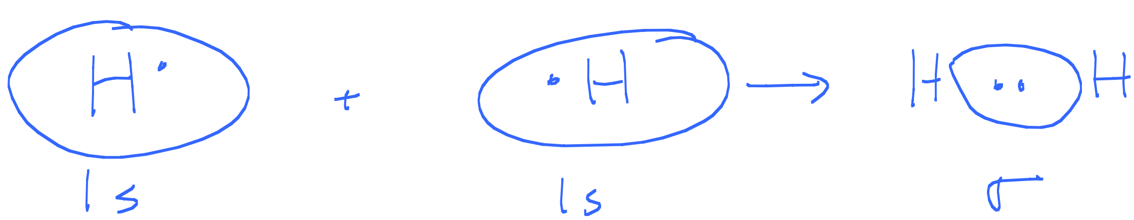
- This is favourable because:
  - o The two electrons in the bond are simultaneously attracted to both nuclei.
  - o The pairing of electrons with opposite spin reduces the energy of the system

- We use electron-dot structures to show electrons and bonds:

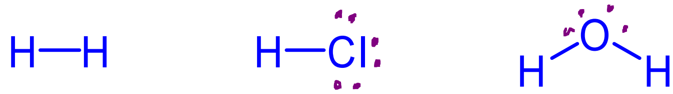
H· + H× ⟶ H·×H

- Each bond contains two electrons (one electron pair).
- In order for bonds to form, *orbital overlap* must occur. In this case, the 1*s* orbital from each H atom overlaps.

more later!



- Since each H atom has the configuration $1s^1$ (one electron in the valence shell), it can only form one bond.

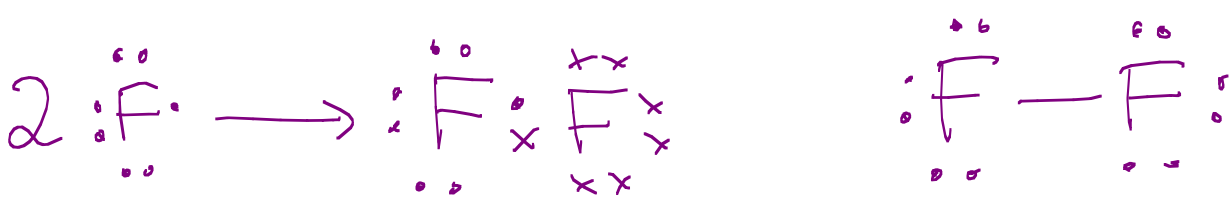


- What if there is more than one electron in the valence shell, for example, with oxygen in water above?

- Such atoms can form more than one bond, but

  - The number of valence electrons surrounding a non-metal should be equal to a noble-gas structure.
  - For principle quantum number n = 2, recall that a full valence shell is $2s^2$ $2p^6$ = 8 electrons = [Ne].
  - So in covalent bonding, elements in the 2nd period need to obey the octet rule (maximum of 8 electrons).

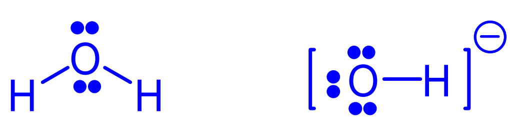
- Example: F has 7 valence electrons ($2s^2$ $2p^5$ = Group 17). If it obtains another electron by bonding with another F, its shell will be completed. (F now surrounded by eight electrons)



- This electron-dot structure is called a Lewis structure. There is one shared bonding pair and three non-bonding (NB) pairs per atom. Each NB pair is "owned" by the atom it resides on.

- Remember, when writing Lewis structures, only the valence electrons are involved and drawn.
    - These ideas apply to the main-group elements. When we examine transition elements, or even elements with higher *n* values, it becomes more complicated.

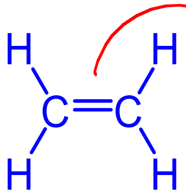
- In the examples below, each O or N is surrounded by eight electrons, thus completing the inert gas shell $2s^2\ 2p^6$.



- Bonded atoms can share more than one pair of electrons. Nonetheless, the octet rule is still obeyed.
    - Two shared pairs = bond order of 2

of course you know the 2 bonds are not the same

$1\sigma + 1\pi$

 represents 

- Three shared pairs = bond order of 3

H—C≡C—H represents 

$1\sigma + 2\pi$

- While there are some exceptions to the octet rule (H, Be, B, etc.), these guidelines are useful. *Yet, practice is essential.*

Writing Lewis Structures

1. Count the total number of valence electrons in the molecule. Remember to add one for each negative charge, and deduct one for each positive charge.
2. Using the concept of a *central atom* bonded to two or more *terminal atoms*, draw a skeleton structure, joining the atoms by single bonds.
3. Count how many single bonds are present. Realizing that each single bond = two electrons, calculate how many of the total valence electrons have not been accounted for.
4. These leftover valence electrons must be distributed in the structure drawn. Count the number of electrons needed fill the octets of all of the atoms (except for H)
   - H always forms a single bond
   - If the number of valence electrons equals that required to fill the octets (except H), distribute the leftover electrons as non-bonding pairs.
   - If the number of leftover electrons is less than the number required, the skeleton must be modified by converting single bonds to multiple bonds.
     - Short two electrons? Convert single to double
     - Short four electrons? Convert two singles to two doubles, or one single to one triple.

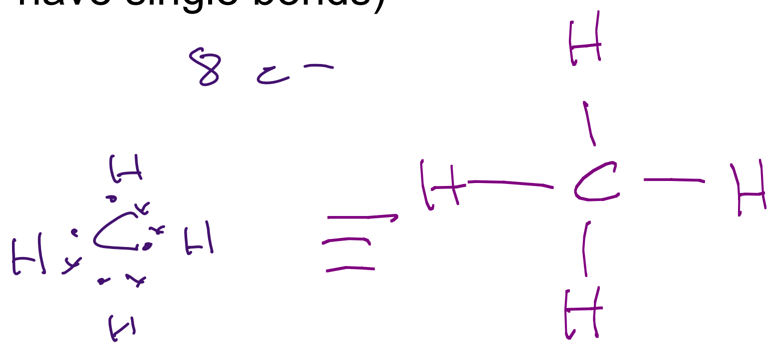
While this may appear complicated, drawing Lewis structures is actually very straightforward.

- Examples: draw Lewis structures for the compounds below (all of these only have single bonds)

Methane, CH_4

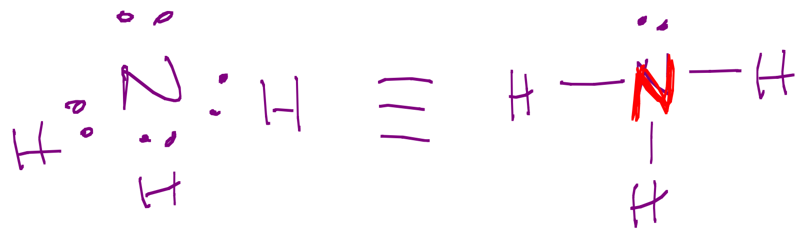
8 e−

$C = 4$ v.e.
$H = 4 \times 1$ v.e
$\overline{}$
8 e−

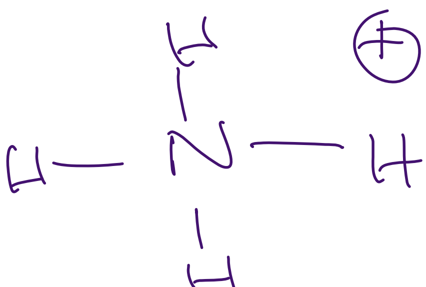


Ammonia, NH_3

$N = 5$ v.e.
$H = 3 \times 1$ v.e
$\overline{}$
8 e−



Ammonium, NH_4^+



$\left.\begin{array}{l} N = 5\ e^- \\ 4H = 4\ e^- \end{array}\right\}$ 9 e−

⊕ subtract 1 e−
$\overline{}$
8 e−

- By adding H^+, we change the NB pair into a bonding pair without changing the electron arrangement. Ammonium is considered to be

Water, H_2O

Lewis says nothing about the shape

more later

Hydronium, H_3O^+

+

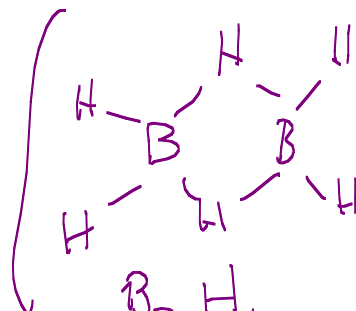
Borane, BH_3

3ve

3×1 / 6e−

6e−

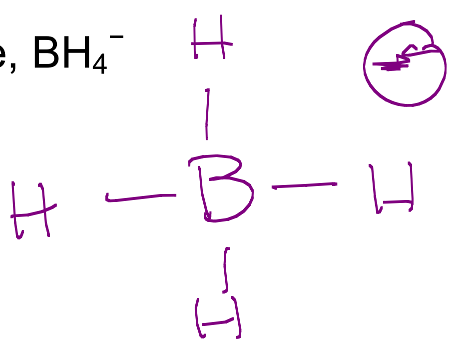
exception



B_2H_6

- This Group 3 element does not obey the octet rule. It is electron-deficient and can have one more pair (or bond).

Borohydride, BH_4^-



F.C. = 3−0−4

= −1

8 ve total

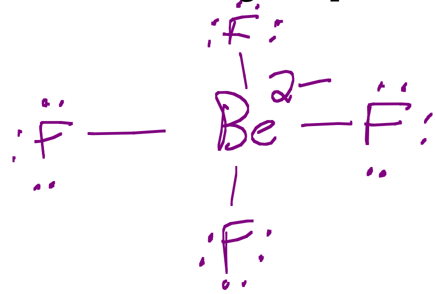
3 × 4 + 1

- The negative charge is balanced by a cation ($NaBH_4$).

Formal Charge (see below)

An odd example: Group 2 compounds are mainly ionic, but Be forms BeF_2, which can add two fluorides to give $[BeF_4]^{2-}$.

not filled



- Examples involving multiple bonds

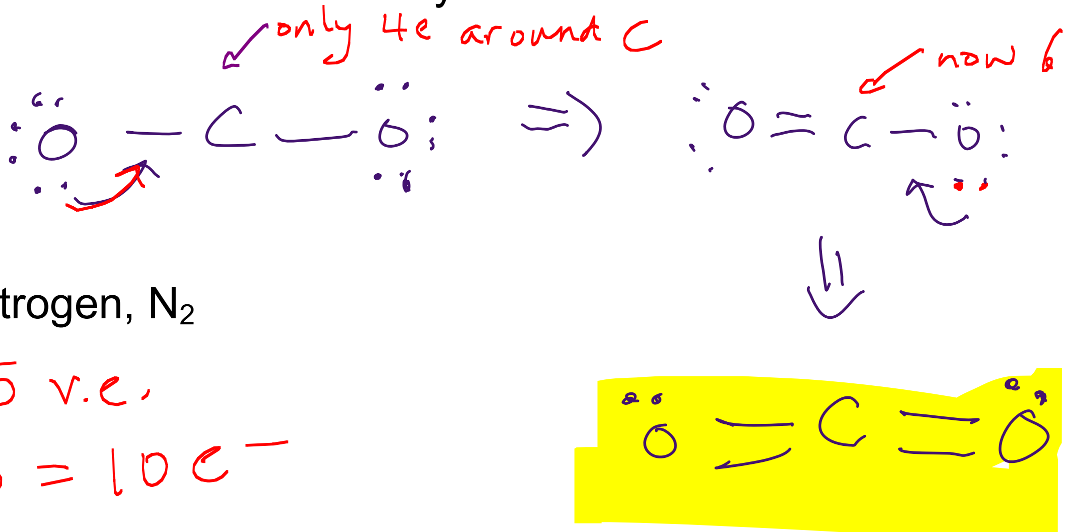
C - 4 e-

Carbon dioxide, CO_2

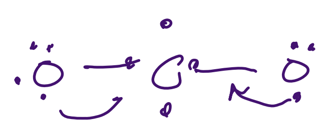
2 O = 2×6 = 12e-

- o Remember, draw single bonds, count how many electrons are needed to fill the octets, and compare that number to how many valence electrons are available.

16e-



All atoms have filled octet

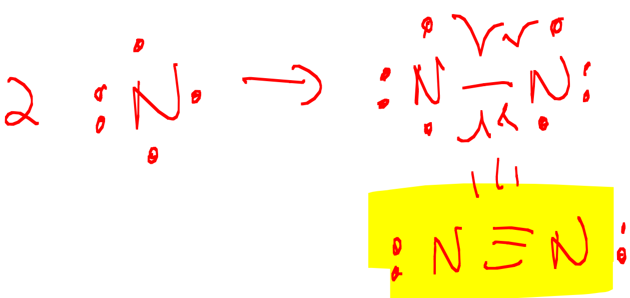


another approach

Nitrogen, N_2

N = 5 v.e.

2×5 = 10 e-



$FC = 6 - (2 + 3)$
$= 1$

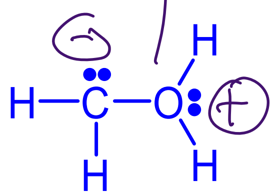
2. Deciding Between Lewis Structures

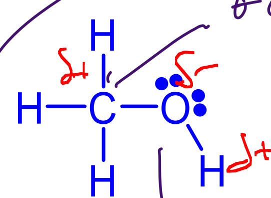
- Sometimes, we cannot decide on the best Lewis structure without additional information. For example, what is the structure of molecule A_2B? Is it A−A−B or is it A−B−A?

- Example: what is the structure methanol, molecular formula CH_4O? Both of these possibilities obey the octet rule:

C

$FC = 4 - (2 + 3)$
$= -1$





$FC = 4 - (0 - 4)$
$= 0$

$FC = 6 - (4 + 2)$
$= 0$

- One way to determine the correct structure is to apply the concept of formal charge.

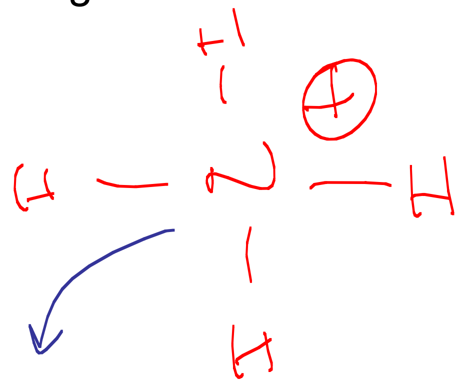
- This is a method of assigning charges to atoms in a molecule by counting the electrons. The structure with the [illegible]

- An atom is assigned a formal charge if the number of electrons *belonging to it* differs from the number around it in its neutral, atomic state (its valence electrons).
    - All non-bonding pairs belong to the atom they are on. Bonding electrons are shared between two atoms, so *half* of the bonding ones belong to the atom of interest.
    - NOTE: the sum of formal charges on the atoms must equal to the total charge on the molecule or ion.

Formal Charge = # valence electrons − number of non-bonded electrons − 1 for each bond

- Example: What is the formal change of the N atom in ammonia and in ammonium?

$F.C. = 5 - 2 - 3 = 0$

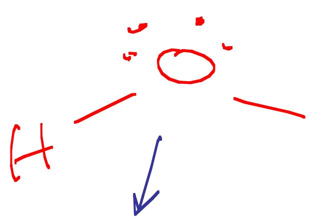


$F.C = 5 - 0 - 4 = +1$

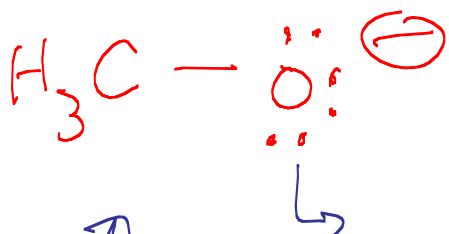
  - In the addition of H^+ to NH_3 to form NH_4^+, the net effect is that N has given away one electron. It is sharing/losing more electrons than usual.

methoxide

- How about water and hydroxide?

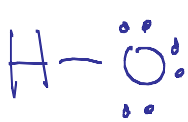


$F.C. = 6 - 4 - 2 = 0$



$F.C. = 6 - 6 - 1 = -1$

  - [illegible]



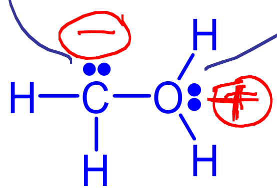
$FC = 6 - 6 - 1 = -1$

$FC = 1 - 0 - 1 = 0$

FC. = 4 − 2 − 3 = −1

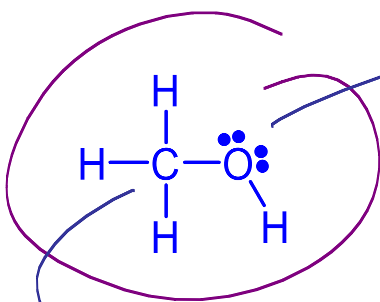
FC = 6 − 2 − 3 = +1

- How does this apply to our methanol problem? The one with the least formal charges is the correct Lewis structure.



2 formal charges

FC = 6 − 4 − 2 = 0

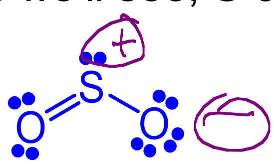


NO FORMAL CHARGES

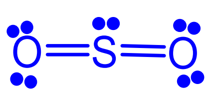
BETTER!

FC = 4 − 0 − 4 = 0

- How about SO_2?
  (As we'll see, S compounds often don't obey the octet rule!)



do these!

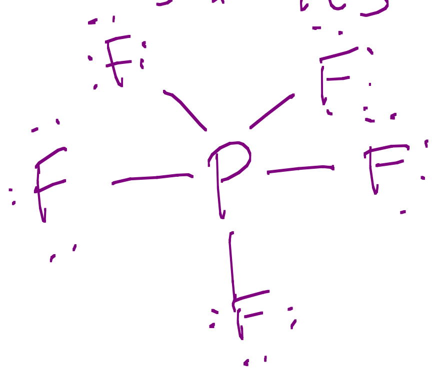


3. Exceptions to the Octet Rule

- The octet rule works for the eight elements on the 2nd period.
- Now consider period-three elements (S, P, etc). These are *not* limited by the octet rule, [illegible] are [illegible] and t[illegible] an arrangement c[illegible] called a [illegible]

$5 + 7 \times 5 = 40$

PF_5

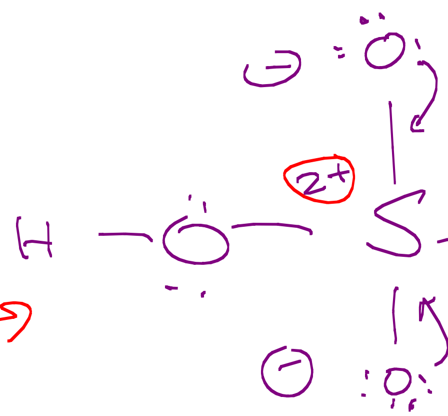


H_2SO_4

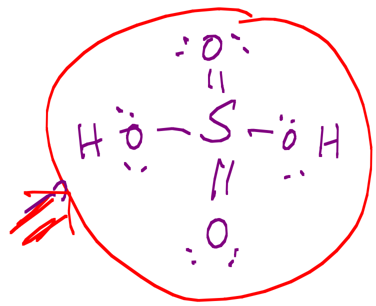
$2 + 6 + 24$

$= 32$

Formal charges



Better



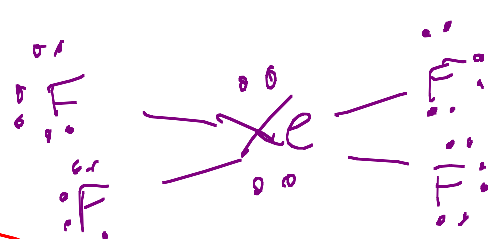
$HClO_4$

$Xe = 8$

$4 \times 7 = 28$

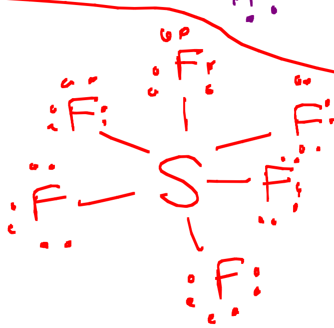
36

XeF_4



$32\ e^-$

SF_6



- Some molecules contain odd numbers of electrons. Clearly, these will have an unpaired electron somewhere in the structure… they are called [illegible] and are very reactive.

$5 \rightarrow 6 = 11e^-$ ODD electron

NO (nitric oxide – most studied molecule in the past decade)

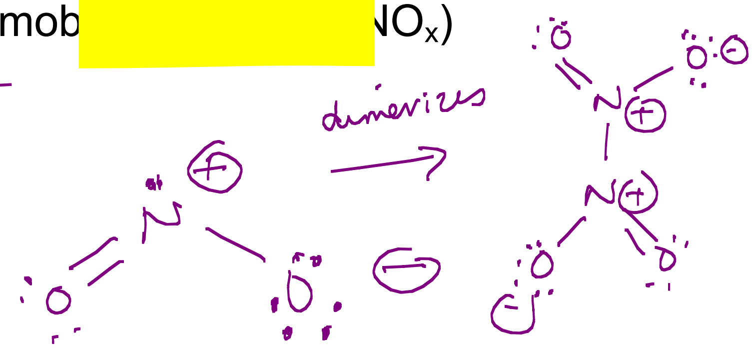
unpaired e^-

No F.C.

Brown haze in summer!

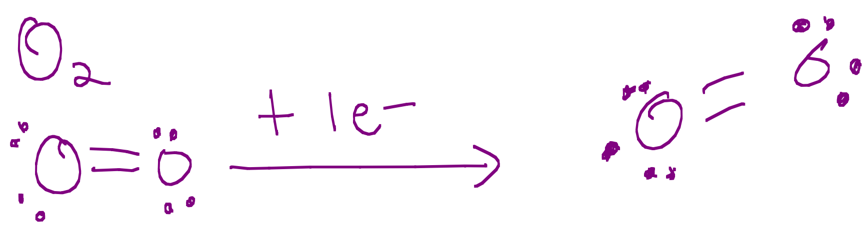
NO_2 (nitrogen dioxide – automob [illegible] NO_x)

$5 + 2(6) = 17e^-$



O_2^- (superoxide – toxic by-product of aerobic metabolism)

O_2



Superoxide

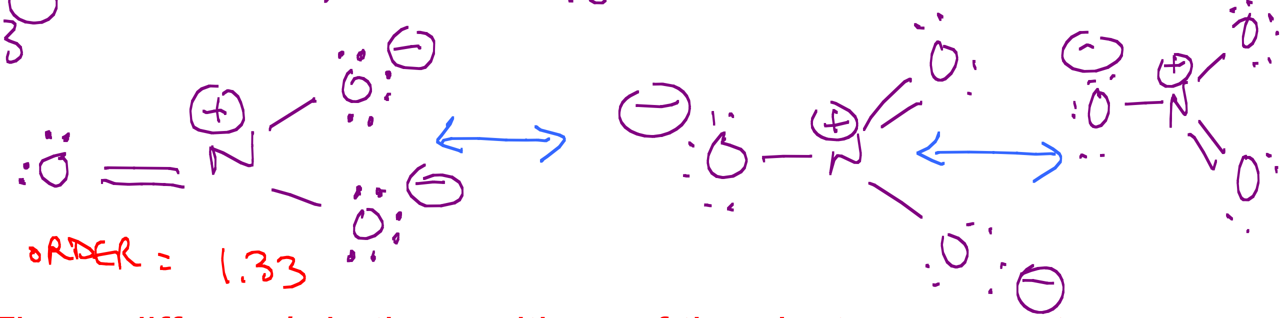
AGING!

"free radicals"

- We can often draw multiple, reasonable Lewis structures that differ *only in the positions* of the electrons. Such structures are called resonance, or contributing structures.

- Consider the nitrate ion. It can be drawn in three equivalent Lewis structures.

NO_3^{-} $5e + 3(6) + 1 = 24e^-$



BOND ORDER = 1.33

- These differ *only* in the positions of the electrons, *not* atoms. In each of these structures, the double bond and the formal negative charges reside on different atoms.

- Which one of these three is the most correct, real-life structure? NONE. The real structure is an "average" of all three. Each one of these contributes to the correct structure.

- The arrow is used exclusively to indicate resonance.

- Notice that this is not the same as an equilibrium arrow.

$\rightleftharpoons$ $\rightleftarrows$

these are for equilibria

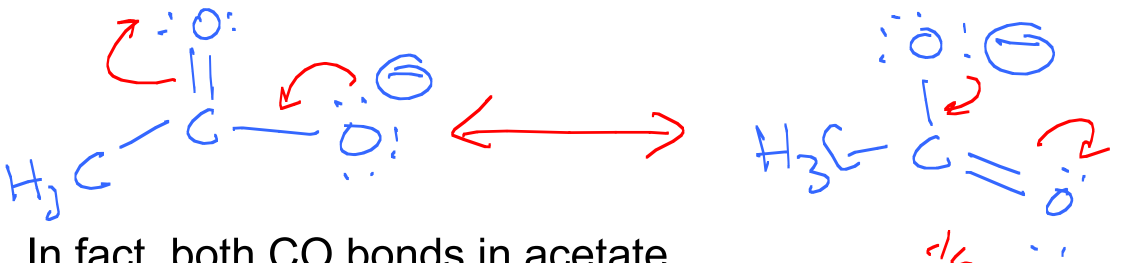
NOT resonance

$H_3C_2O_2^{\ominus}$

BOND ORDER

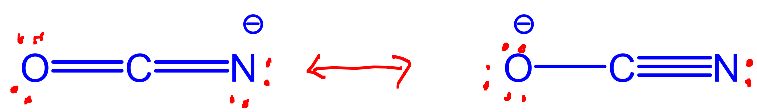
1.5

- Another example is the acetate ion, with two resonance forms



- In fact, both CO bonds in acetate are identical. The actual structure most closely resembles:

- We can also have [illegible]ce structures $OCN^{\ominus}$

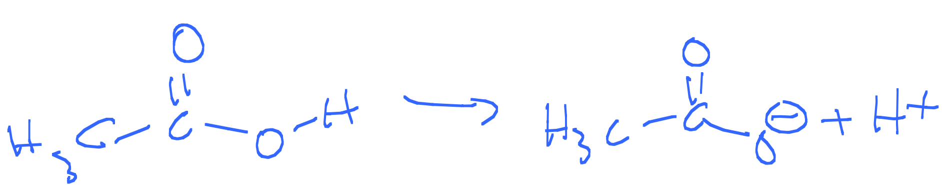


- In general, the existence of resonance is indicative of *increased thermodynamic stability*. This is especially true in the delocalization (spreading out) of charge over a few atoms.

- Stronger acids have conjugate bases that are more stable.

CH_3COOH $pK_a = 5$ $\qquad$ CH_3CH_2OH $pK_a = 16$ $\quad$ $CH_3CH_2O^{\ominus}$

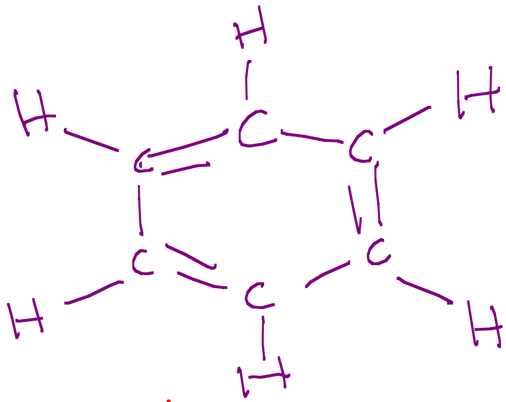
$H^{\oplus}$

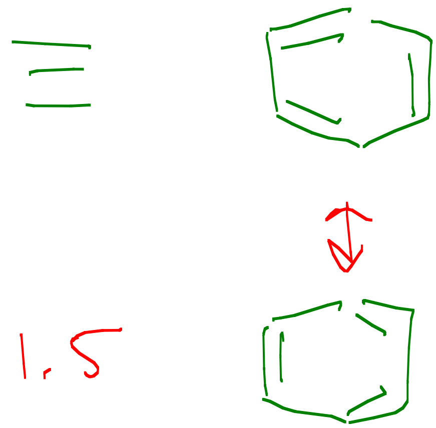


The greater stability of acetate shifts the acid-base equilibrium HA $\rightleftharpoons$ $H^+ + A^-$ to the right.

Resonance

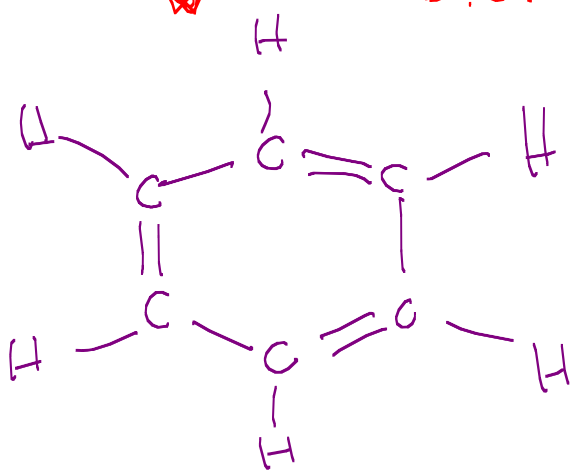
C_6H_6

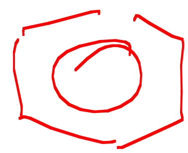




C–C

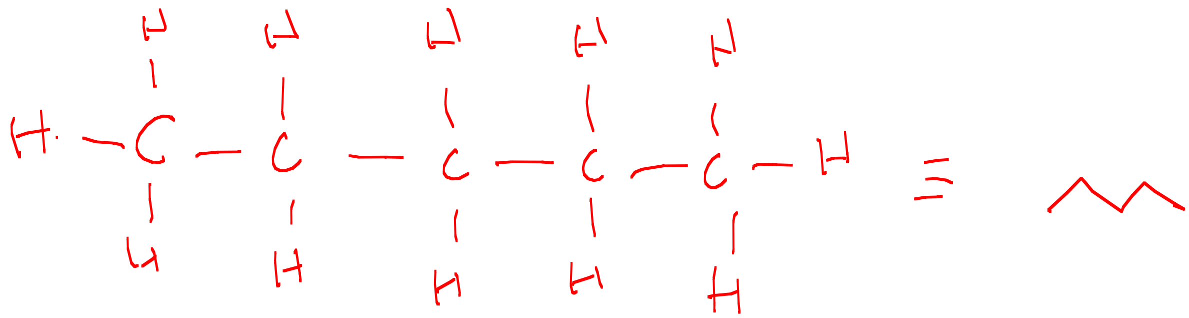
B.O. = 1.5



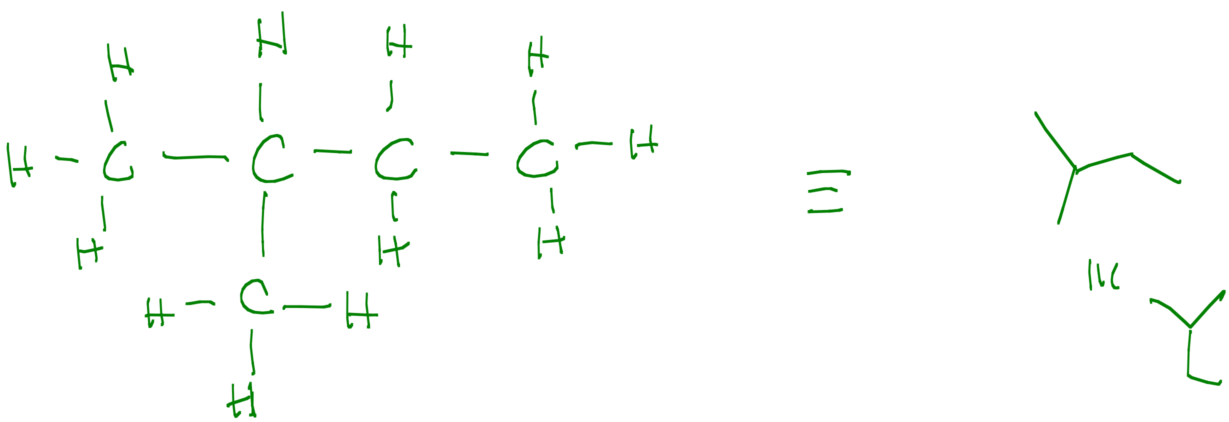


Lewis Structures of C_5H_{12}

1



2



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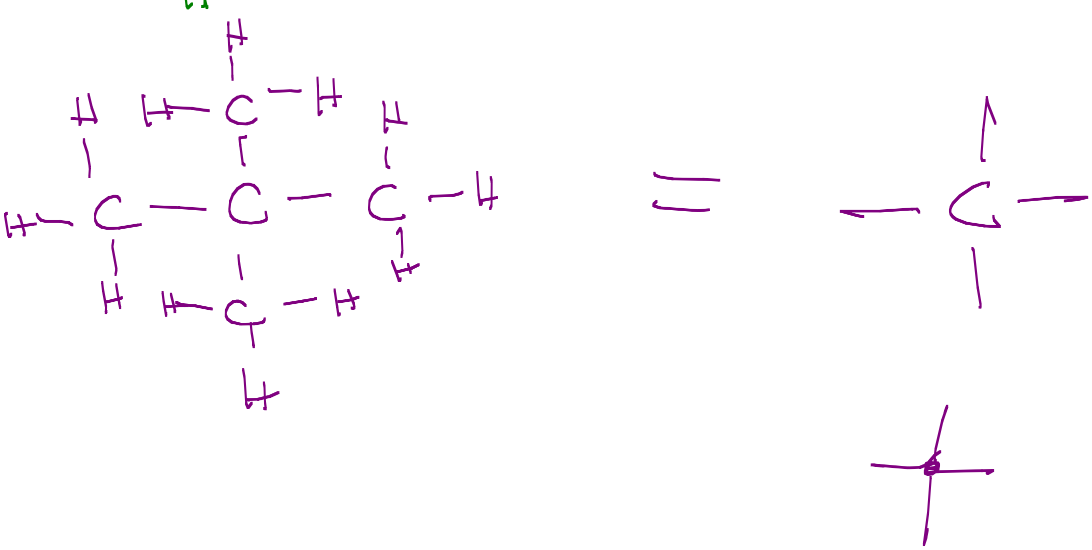

- #21 April 2004. How many resonance structures are possible for the monofluorophosphate (FPO_3^{2-}) anion?

- #23 April 2005. Which of the following have an average bond order of 1.5 in their ground-state Lewis structures?
    1. O_3
    2. CO_2
    3. NO_2^-
    4. CO_3^{2-}