Unit 3

Molecular Structure

Slide Color Codes

All Lectures			Section Only	
Required	Required	OK to Skip	Useful	Not Examable

Blueprint question

How do you choose a solvent or dispersant for an important clean-up?

https://www.chemistryworld.com/earth/explainer-why-are-chemical-dispersants-used-in-oil-spills/1017322.article

Learning Objectives (Part 1)

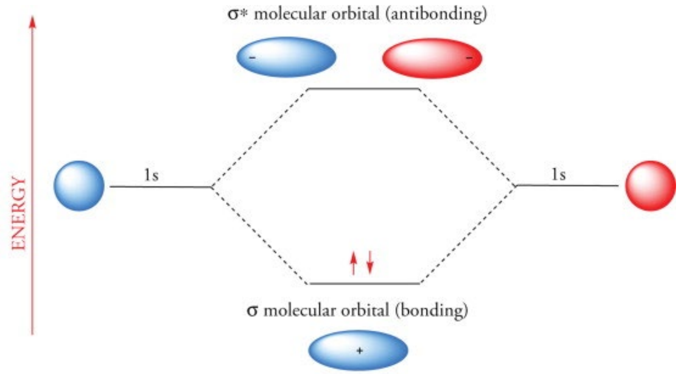
After mastering this unit you will be able to:

- Draw Lewis structures for a given chemical formula, or use the features of a Lewis structure to identify the unknown elements or chemical formula of a molecule.
- Draw resonance structures, or identify valid resonance structures, for a given molecule.

Bonding Theories

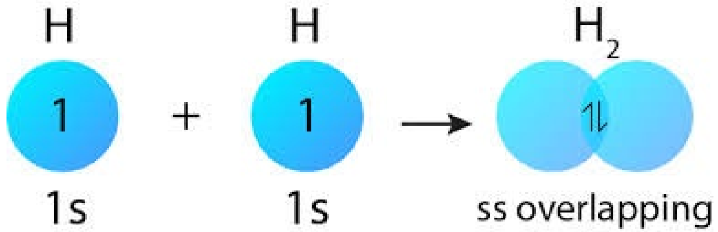
- **Molecular Orbital Theory** (exact)

-Correct quantum mechanical description with orbitals extending over entire molecule



- **Valence Bond Theory** (not quite exact)

-Localized electron picture with bonds formed by the overlap of singly occupied atomic orbitals

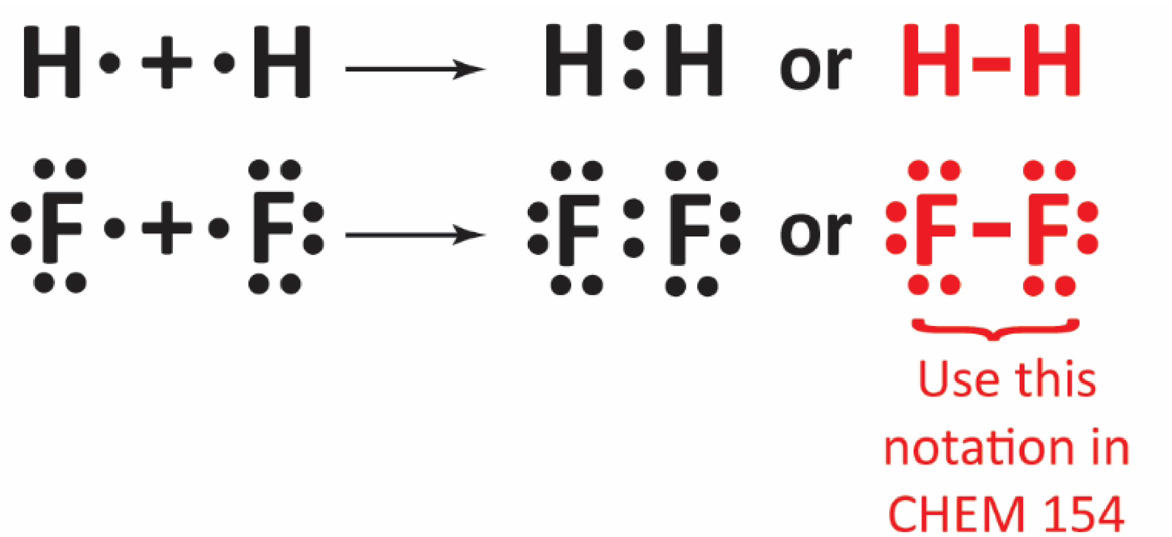


- **Lewis Theory** (approximate; CHEM 154 uses Lewis theory)

- Localized electron picture using rules based upon counting electrons

Representation of Covalent Bonds

- A **Lewis structure** shows how valence electrons are shared in a molecule.
- Valence electrons that form a bond are called **bonding pairs**.
- Valence electrons that do NOT form a bond are called **lone pairs**.



Lewis Structures

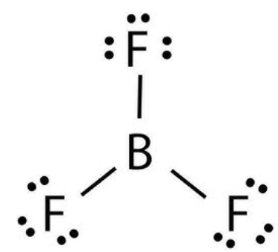
- **Octet Rule**

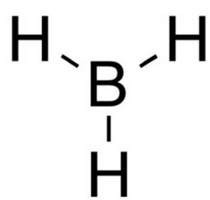
In forming chemical bonds, main group elements gain, lose, or share electrons to achieve a configuration in which they are surrounded by 8 valence electrons.

- **Duet Rule**

For hydrogen only, surrounded by 2 electrons.

- **Exceptions can happen:**





e.g. Boron

Boron trifluoride (BF_3) and borane (BH_3) with three valence electrons, forms three covalent bonds, resulting in only six electrons around the boron atom.

Drawing Lewis Structures – Formal charge

- **Formal charge:** Formal charge is the difference between the number of valence electrons and the number of electrons surrounding an atom in a particular Lewis structure.

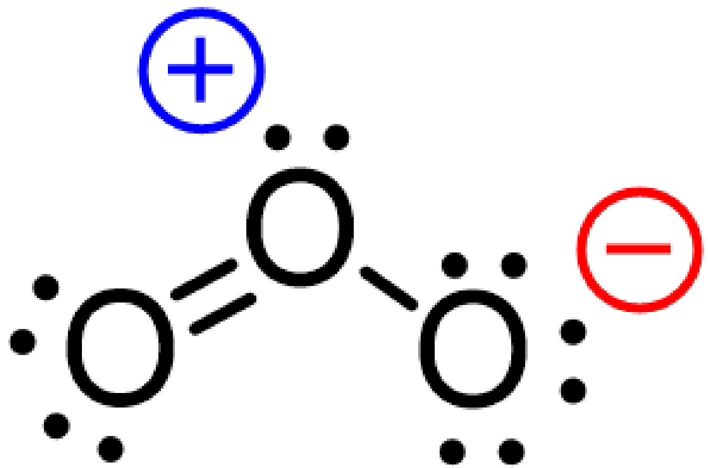
$$FC = VE - LPE - 1/2(BE)$$

VE = number of valence electrons
LPE = number of lone pair electrons
BE = number of bonding electrons

- The overall molecular charge is the SUM of the formal charges.

Example

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



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

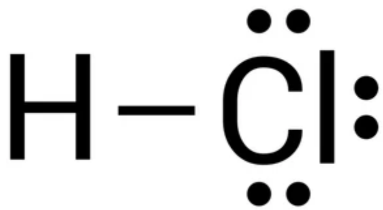
Oxidation State (Oxidation Number)

- Oxidation state of an atom is equal to the total number of electrons which have been removed from an element (producing a positive oxidation state) or added to an element (producing a negative oxidation state) to reach its present state.
- Oxidation involves an increase in oxidation state
- Reduction involves a decrease in oxidation state
- The more electronegative element in a substance is assigned a negative oxidation state. The less electronegative element is assigned a positive oxidation state.

$$\overset{+1}{\mathrm{Na}}\,\overset{-1}{\mathrm{Cl}} \qquad \overset{-4}{\mathrm{C}}\,\overset{+1}{\mathrm{H}}_4 \qquad \overset{0}{\mathrm{Cl}}_2$$

Electron Bookkeeping and Reality

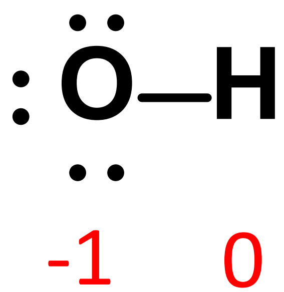
- Several different methods are used in chemistry for electron bookkeeping, each with their own particular application and philosophy. The table below contrasts formal charges and oxidation states with reality for the molecule HCl.

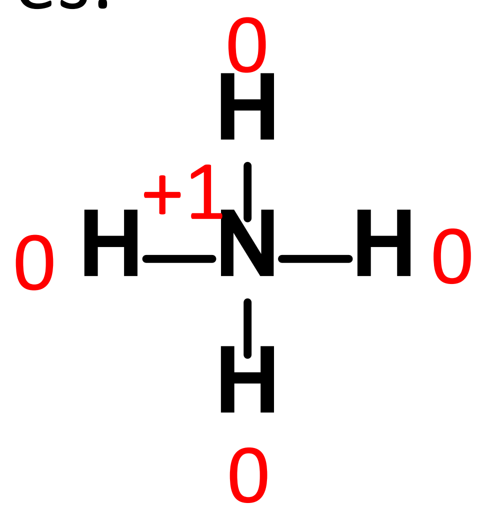


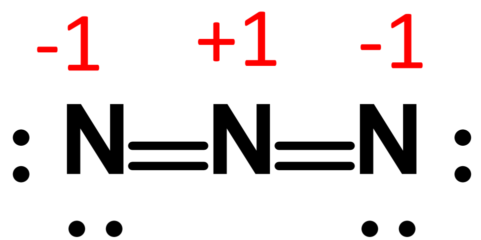
Method	Charge on H	Charge on Cl	Description
Formal Charge	**0**	**0**	Bonding e^- shared equally
Oxidation State	**+1**	**-1**	Bonding e^- to atom with highest EN
Reality	δ^+	δ^-	Polarized bonds with fractional charges

Worksheet Question #1

Calculate the formal charge of each atom in the following structures:







$$\text{formal charge on N atom} = 5 - 0 - \frac{1}{2} \times 8 = +1$$

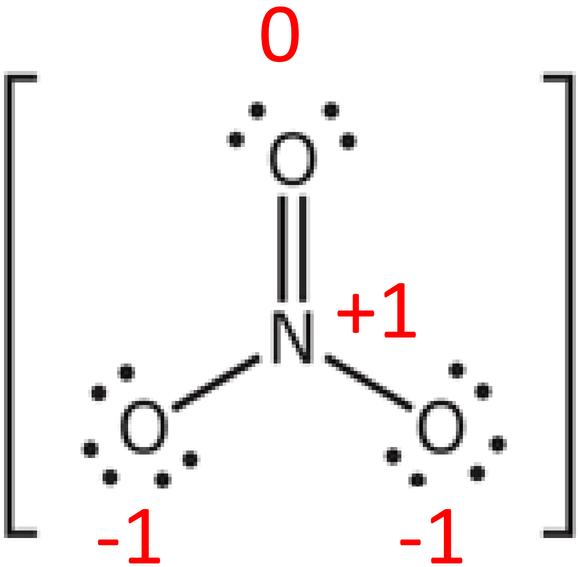
$$\text{formal charge on each H atom} = 1 - 0 - \frac{1}{2} \times 2 = 0$$

The overall molecular charge is NOT given in these structures. It is the SUM of the formal charges!

Clicker Question

What is the **formal charge** on the central N atom in the following molecule?

A) +2
B) +1
C) 0
D) -1
E) -2



nitrate ion

Drawing Lewis Structures

1. Count the number of valence electrons (#ve$^-$) in the molecule or ion
2. Draw the skeletal structure of the molecule
   a) The least electronegative atom is generally the central atom
   b) Hydrogen is ALWAYS a terminal atom
   c) Unless told otherwise, do NOT form rings
3. Place two electrons in each bond of the skeletal structure (represented by single lines)

Drawing Lewis Structures

4. Place the remaining valence electrons not accounted for in Step 3 as lone pairs on individual atoms until the octet rule is satisfied
5. Form multiple bonds as needed to complete octets and account for all valence electrons
6. Label the formal charges (FCs)
    - The sum of FCs is equal to the overall molecular charge.

Remember

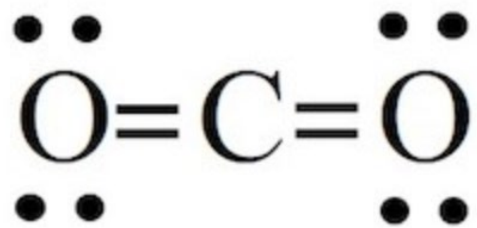
- Hydrogen atoms are always terminal
- The most stable Lewis structure is the one with the least non-zero formal charges
- The most stable Lewis structure is the one that, when possible, places the negative charge on the most electronegative atom and the positive charge on the least electronegative atom

Lewis Structure Tips

- ***Carbon*** – always has 4 bonds and no lone pairs
- ***Hydrogen*** – always has 1 bond
- ***Oxygen*** – 2 bonds + 2 lone pairs if FC = 0
  – 1 bond + 3 lone pairs if FC = -1
  – 3 bonds + 1 lone pair if FC = +1 (rare)
- ***Nitrogen*** – 3 bonds + 1 lone pair if FC = 0
  – 4 bonds + 0 lone pairs if FC = +1
- These patterns also apply to other elements in the same groups (unless hypervalency is used).

Exercise

Draw the Lewis structure of CO_2



Tutorials

CHEM C126: Mon, Tues, Thurs, Fri: 5-6pm

MCLD 3002: Mon 5-6pm

MCLD 2012: Thurs 5-6pm

Remember that these rooms will only hold so many students, so arrive on time. Tutorials will be working through Worksheet questions and attendance is NOT mandatory, but recommended if you have questions.

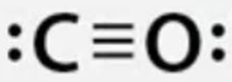
Tutorials start next week: Sept 22, 2025

Office hours

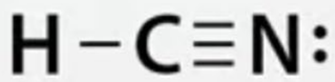
- Office Hours (Starting Sept. 16)
  - Tuesday, 2:10 – 2:50 PM
  - Friday, 10:00 – 10:50 AM
- Location: Chemistry D348
- Email: kcchou@chem.ubc.ca
- Office hours on Friday, September 19 are canceled due to a scheduling conflict with a thesis defense.


Hebb Bldg
Abdul Ladha Science Student Centre
Volkoff Ln
Chemistry Building
X
UBC Department of Chemistry
Chemistry Physics Bldg
East Mall
UBC Science Advising
University Blvd
Musqueam Post
East Mall
UBC Bookstore
Book store
University Blvd
University Blvd
Networks of Centres of Excellence Campus...
artha Piper Plaza
Michael Smith Laboratories

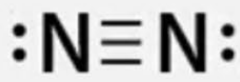
Common Lewis Structures



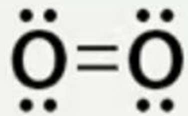
Carbon monoxide



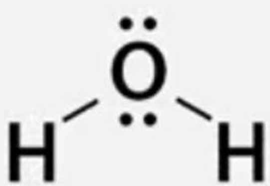
Hydrogen cyanide



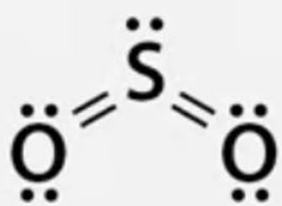
Nitrogen



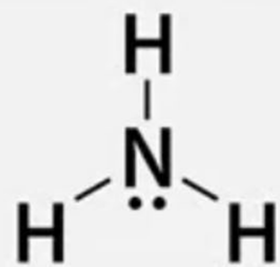
Oxygen



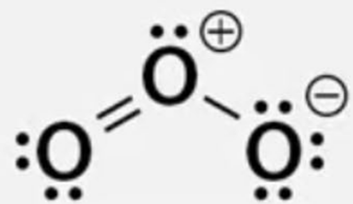
Water



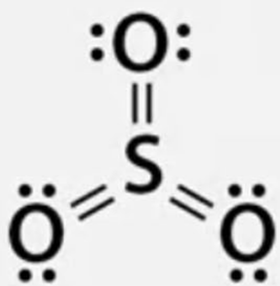
Sulfur dioxide



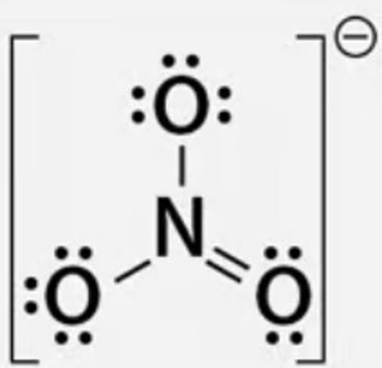
Ammonia



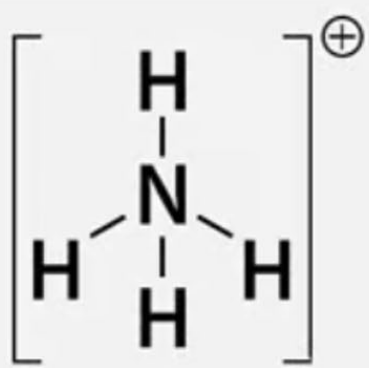
Ozone



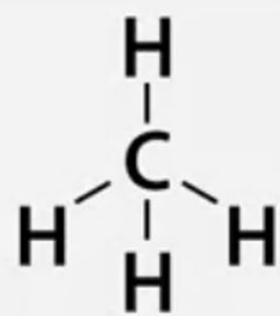
Sulfur trioxide



Nitrate



Ammonium



Methane

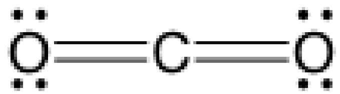
Evaluating Lewis structures - what's best?

1. Do all atoms have full octets?
2. Are formal charges **minimized**?
   - Can't always make them zero, but we want to minimize them
   - Minimize total number of formal charges – charge separation takes energy
   - The one with minimized total formal charges the **best** Lewis structure
3. Put charges on right atoms
   - Negative charges on most electronegative atoms
   - Positive charges on least electronegative atoms

Clicker Question: CO_2

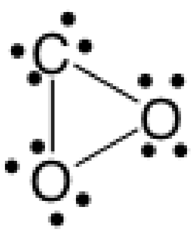
Which of the following represents the **best** Lewis structure for CO_2?

A

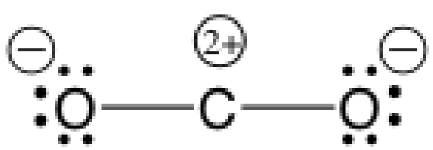


B

C



D

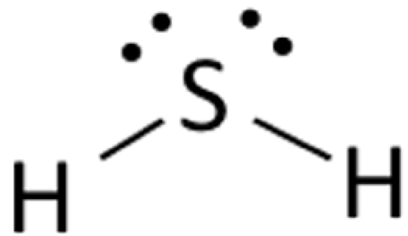


Worksheet Question #2

Draw the best Lewis structure for the following molecules:

a) H_2S

b) N_2O



Worksheet Question #2b – Clicker

In the N_2O structure you drew, the central atom is:

A) Nitrogen

B) Oxygen

C) It is a ring structure without a central atom.

Electronegativity: O = 3.44 vs N = 3.04

Worksheet Question #2b – Clicker

For N_2O, which would represent the BEST Lewis structure for the molecule?

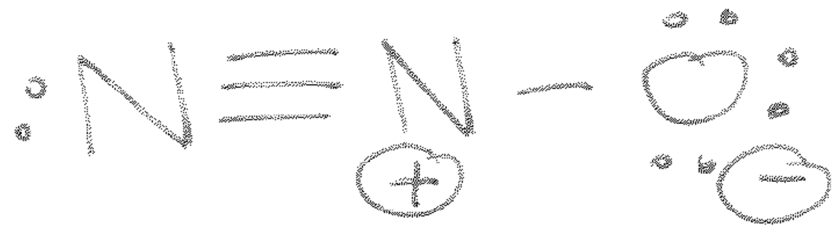
A) Structure I, because the <u>negative charge</u> is on the <u>more electronegative atom</u>

B) Structure II, because the negative charge is on the more electronegative atom

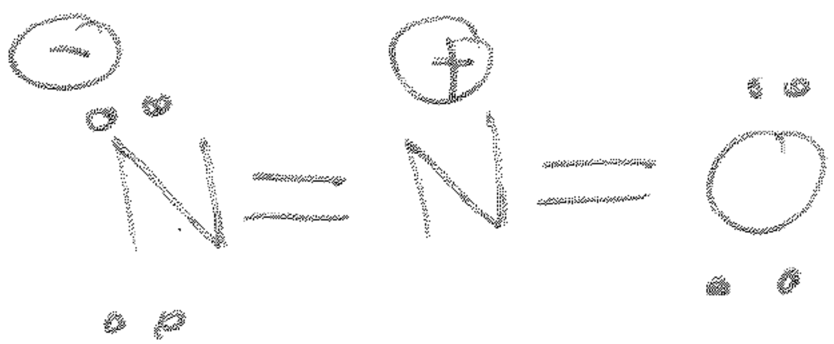
C) Structure I, because it has a (stronger) nitrogen-nitrogen triple bond

D) Structure II, because it has two double bonds

Structure I



Structure II



Worksheet Question #2b – Clicker

For N_2O, the Lewis structure you drew has a Nitrogen-nitrogen bond order of…

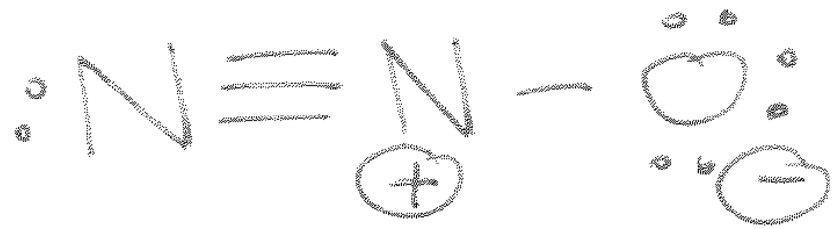
A) 0

B) 1

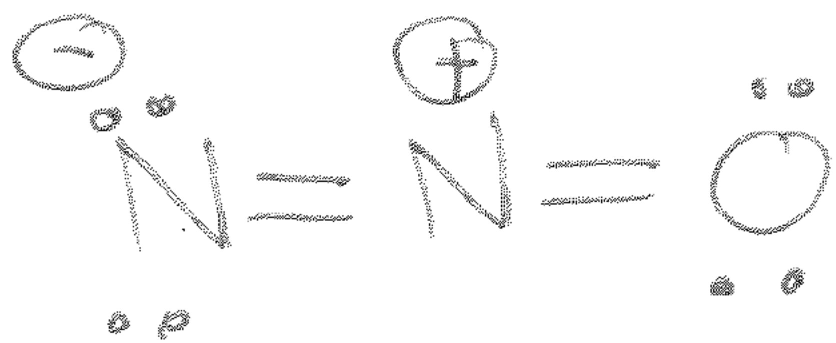
C) 2

D) 3

Structure I



Structure II

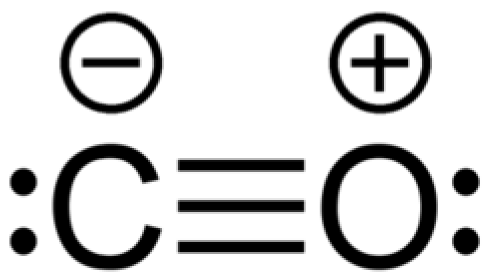


Worksheet Question #2

Draw the best Lewis structure for the following molecules:

c) CN^-

d) CO



Worksheet Question #2c – Clicker

For CN^-, the negative formal charge is located on…

A) The carbon atom

B) The nitrogen atom

C) Both the carbon and nitrogen atoms

D) Neither of the carbon and nitrogen atoms

Worksheet Question #2d (Clicker)

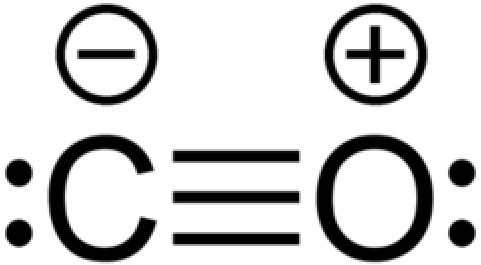
The carbon-oxygen bond order in the best Lewis structure for CO is…

A) 1

B) 2

C) 3

D) 4



Worksheet Question #2d (Clicker)

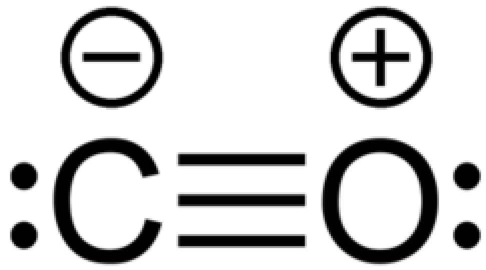
The best Lewis structure for CO has…

A) A positive formal charge on oxygen

B) A carbon-oxygen double bond

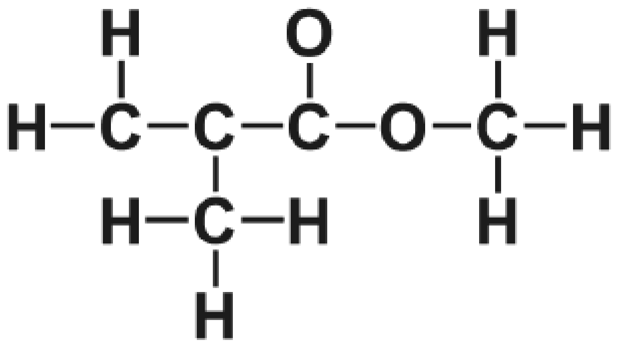
C) A positive formal charge on carbon

D) A carbon-oxygen single bond



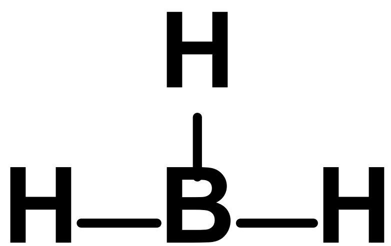
Worksheet Question #7 – GOOD QUESTION

Poly(methyl methacrylate) (PMMA) is a polymer commonly known as acrylic glass and commercially sold under the tradename Plexiglas®. PMMA is synthesized by the polymerization of methyl methacrylate (MMA). The skeletal structure (showing atom connectivity) of MMA is shown below. Draw multiple bonds and lone pairs as necessary to show the best Lewis structure of MMA.



Exceptions to the Octet Rule

Incomplete Octet: Elements in Group 13 sometimes follow a “sextet” rule. In other words they have only three electron groups surrounding them:



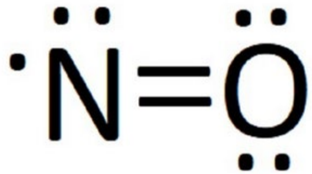
Group

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
11 Na 22.99	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.9	23 V 50.941	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.7	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.8
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc "(98)"	44 Ru 101.07	45 Rh 102.9	46 Pd 106.4	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.33	57 La* 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.2	83 Bi 208.98	84 Po "(209)"	85 At "(210)'	86 Rn "(222)"
87 Fr 223	88 Ra 226.03	89 Ac# 227.03	104 Rf	105 Db {261}	106 Sg	107 Bh	108 Hs	109 Mt									
		*	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm 145	62 Sm 150.4	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.5	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97	
		#	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 260	

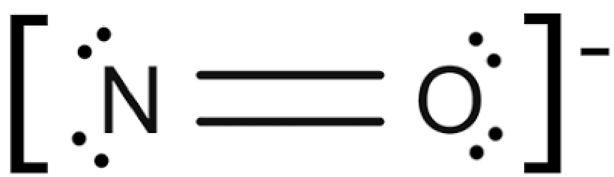
Exceptions to the Octet Rule

- <u>**Radical**</u> **species:** Molecules with an <u>odd number of electrons</u> will have an <u>unpaired</u> electron. These species are called radicals.

Example: NO



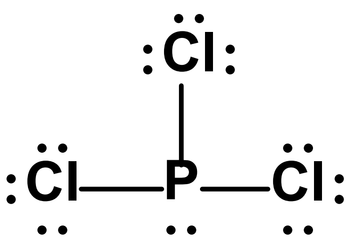
VE = 5 + 6 = 11 (unstable)

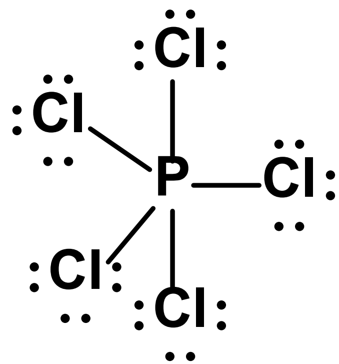


VE = 5 + 6 +1 = 12 (stable)

Exceptions to the Octet Rule

- **Hypervalence** (expanded octets): Elements on the third row of the periodic table and below can expand their octets. For example, although phosphorus obeys the octet rule in PCl_3, it has an expanded octet in PCl_5.





Group

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
11 Na 22.99	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.9	23 V 50.941	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.7	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.8
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc "(98)"	44 Ru 101.07	45 Rh 102.9	46 Pd 106.4	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.33	57 La* 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.2	83 Bi 208.98	84 Po "(209)"	85 At "(210)'	86 Rn "(222)"
87 Fr 223	88 Ra 226.03	89 Ac# 227.03	104 Rf	105 Db {261}	106 Sg	107 Bh	108 Hs	109 Mt									
		*	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm 145	62 Sm 150.4	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.5	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97	
		#	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 260	

Hypervalence

Group

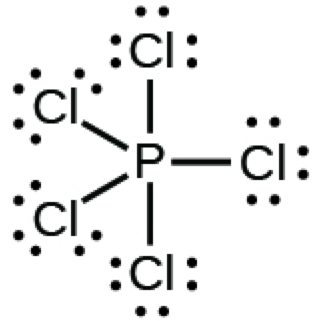
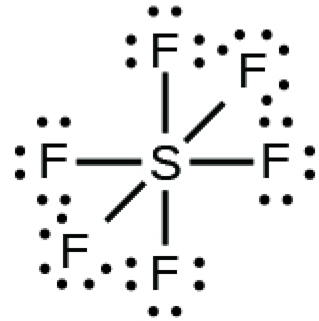
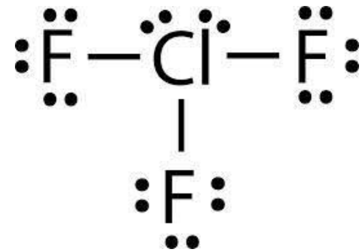
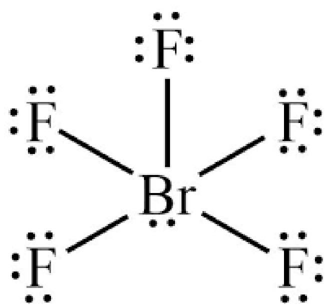
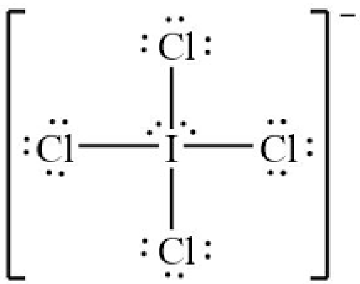
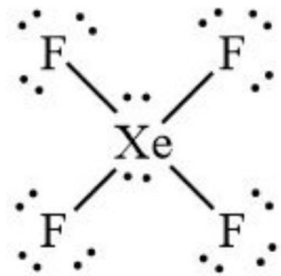
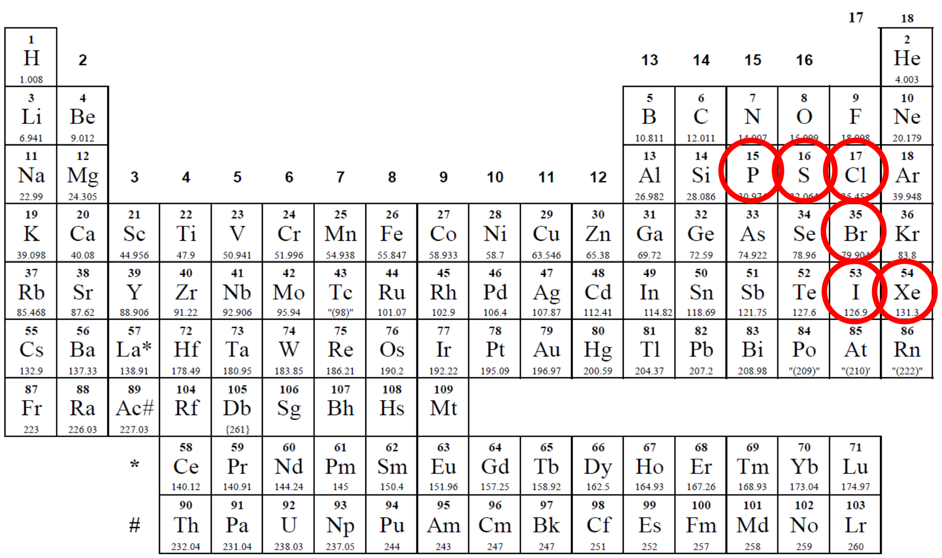
1	13	14	15	16	17	18	
H						He	Maximum duet
	B	C	N	O	F	Ne	Maximum octet, B may have 6 electrons (sextet)
	Al	Si	P	S	Cl	Ar	If central atom, can exceed octet
	Ga	Ge	As	Se	Br	Kr	If central atom, can exceed octet
	In	Sn	Sb	Te	I	Xe	If central atom, can exceed octet
	Tl	Pb	Bi	Po	At	Rn	If central atom, can exceed octet

Hypervalence Rules

- The octet rule will NOT be exceeded unless necessary to form bonds with more than four atoms or to minimize formal charges.
- Only atoms in the third row (period) of the periodic table and below can be hypervalent.
- Terminal atoms are not hypervalent.

Hypervalence

- **Examples:**

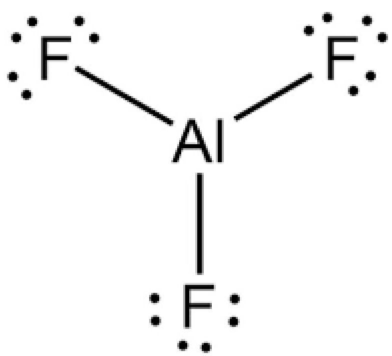








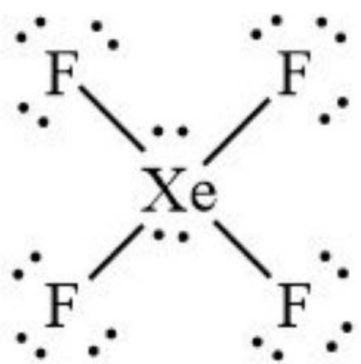
Worksheet Question #8

Draw the best Lewis structure of

a) AlF_3

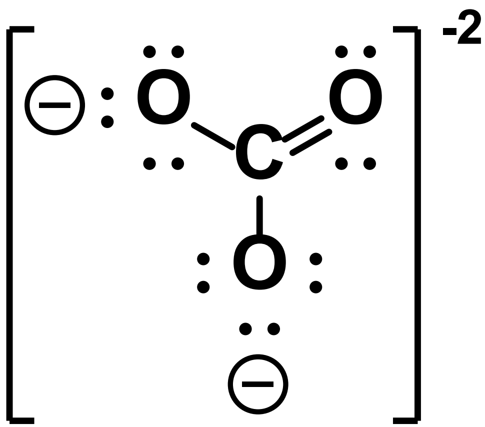
b) XeF_4



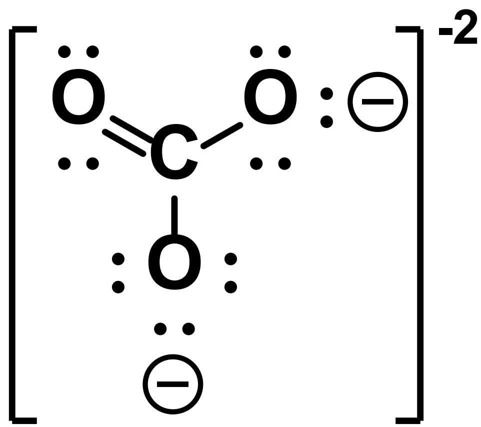


Worksheet Question #11 (Clicker Question)

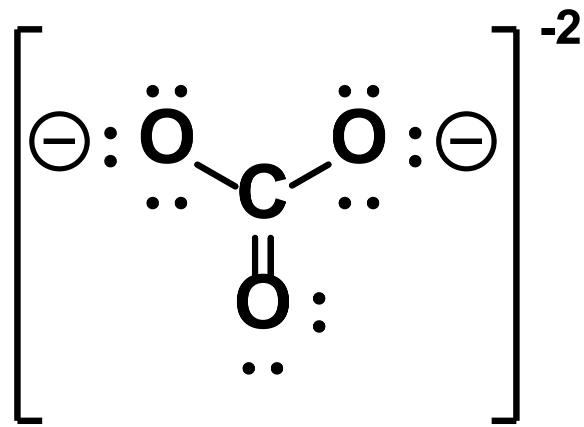
Which Lewis structure resembles the structure of $CO_3{}^{2-}$ you drew?



a.



b.



c.

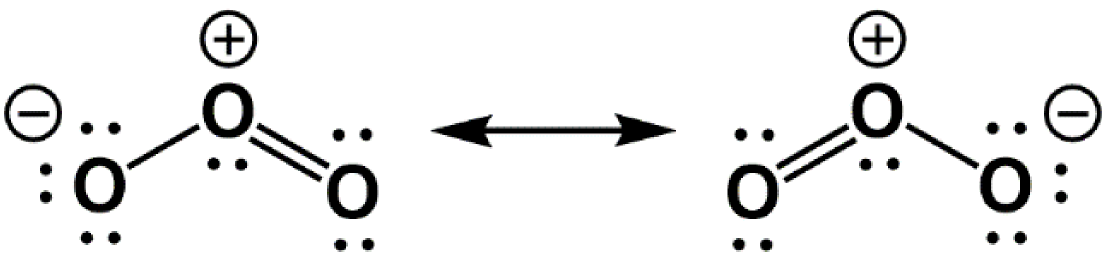
d. All of the above

e. None of the above

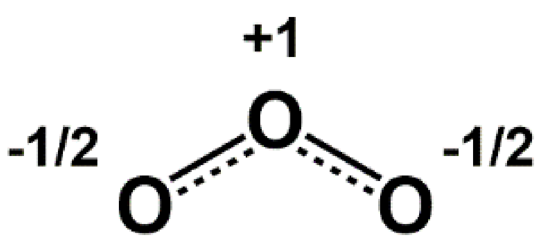
ANS: the double bond can be located on any of the three carbon-oxygen bonds, resulting in three distinct resonance.

Resonance structures

- **Resonance** occurs when **the same arrangement of atoms** produces more than one Lewis structure. This indicates a delocalized bond (extending beyond two atoms) is present. These structures contribute to the resonance hybrid (the actual molecular structure).



- **Resonance hybrid** is the “true” structure of a molecule that cannot be described by a single Lewis structure.



(bond order = 3/2)

It is NOT a Lewis structure.

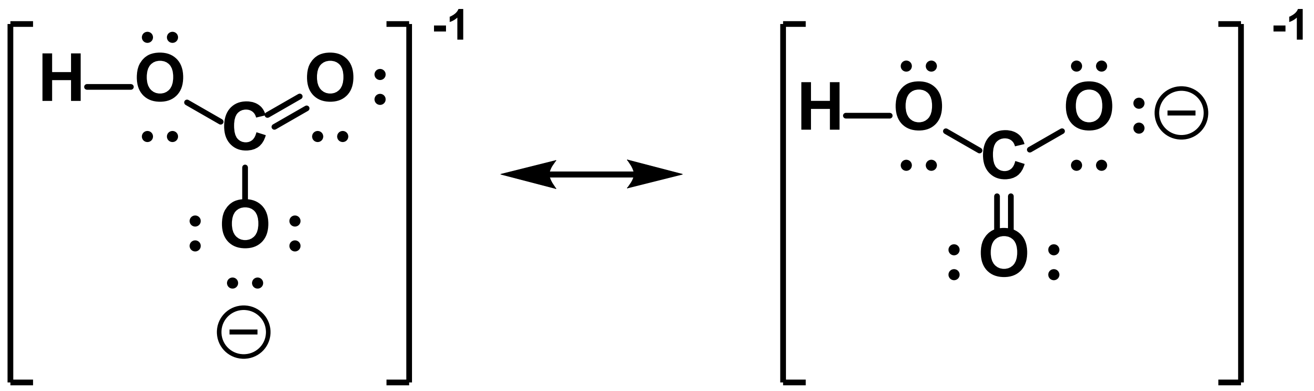
Drawing Resonance Structures

- Only **electrons** can be moved – nuclei NEVER move in resonance structures
- Total number of electrons in system is constant, total charge in system is constant
- All structures should be proper Lewis structures
- *Look for lone pair and double-bond electrons. These move in resonance structures.*

Clicker Question

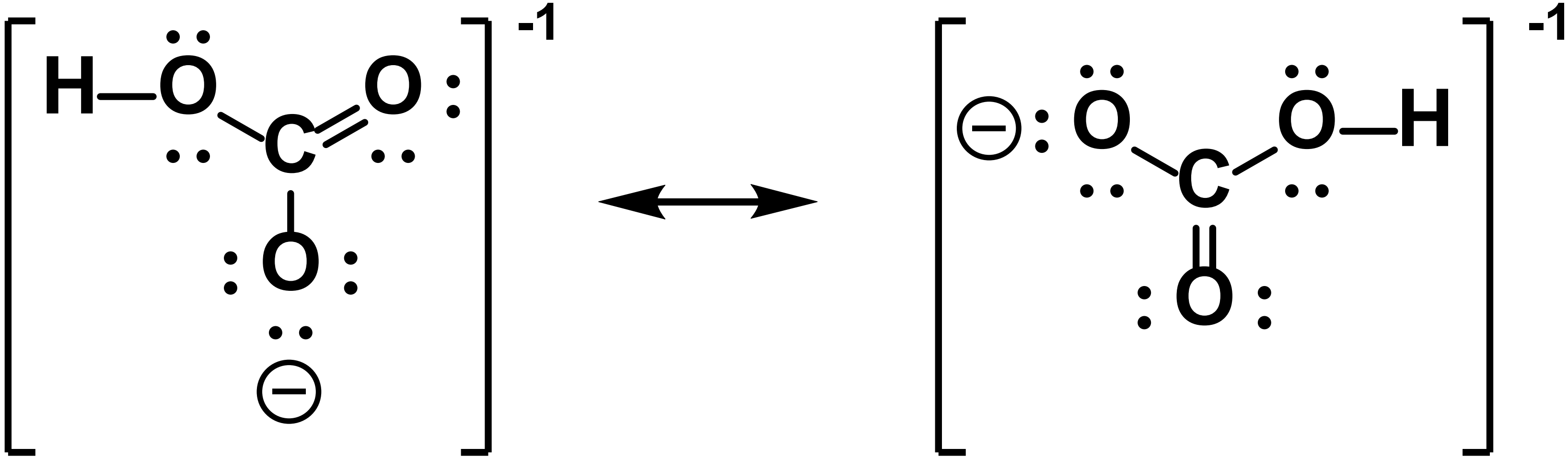
- True of False: Are the following structures contributing to the same resonance hybrid of the $[HCO_3]^-$ anion?

a. True
b. False



Clicker Question

True of False: Are the following structures contributing to the same resonance hybrid of the $[HCO_3]^-$ anion?

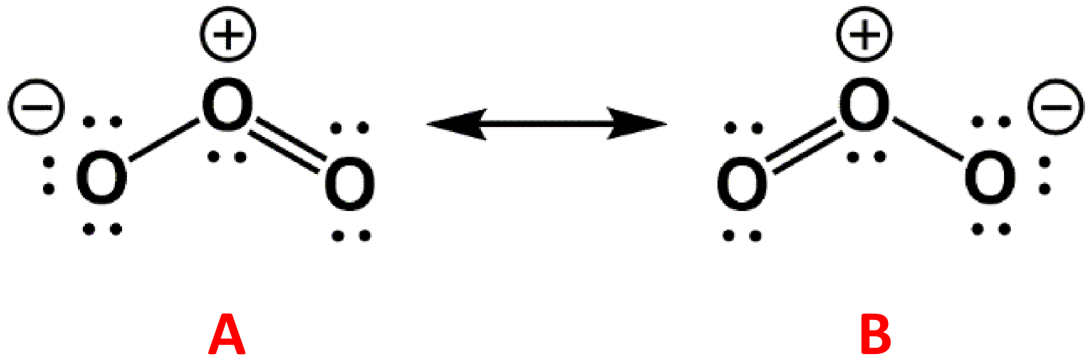


a. True

b. False

Atoms do NOT move between resonance structures. Only the electrons!

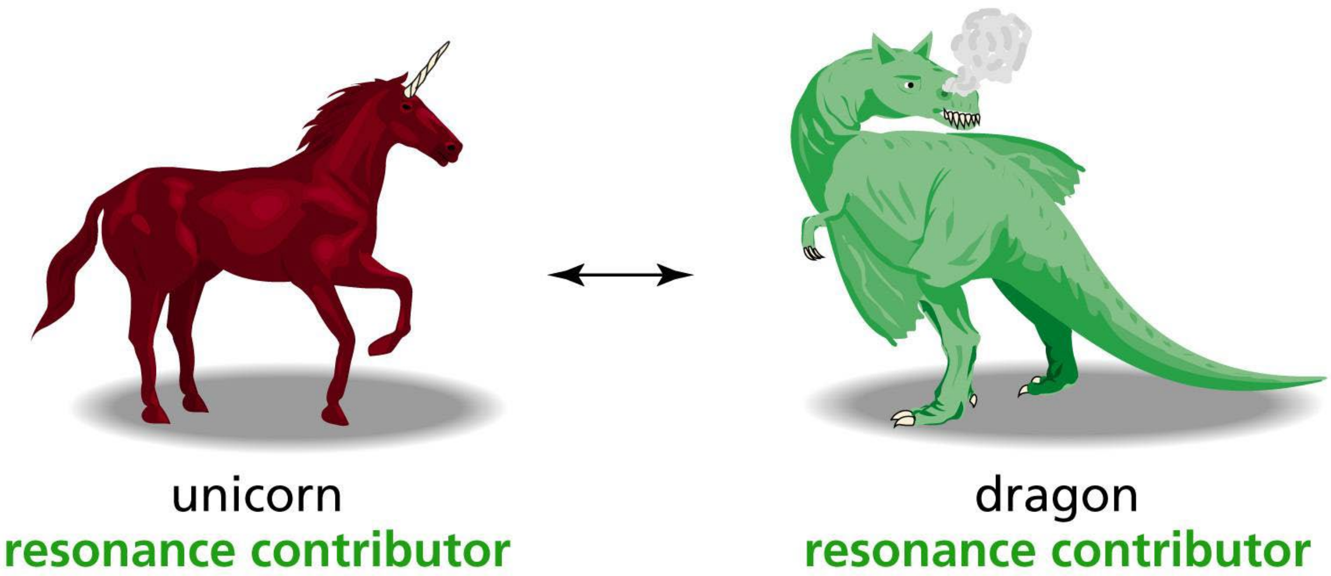
Clicker Question



An engineer is able to characterize a 1 M solution of ozone by observing the O-O bonds in the molecule. What will they observe?

a) An equal mixture (1:1) of molecules A and B
b) An equilibrium mixture of molecules A and B
c) Molecules quickly converting between A and B
d) None of molecules A or B will be observed

An analogy…



A rhinoceros isn't a unicorn some of the time and a dragon some of the time – it's a rhinoceros **ALL** the time!

Clicker Question

What is the best description of “resonance structures”?

A) a series of Lewis structures that interconvert between each other because they are of the same energy

B) a series of Lewis structures that show how the electrons move around in the molecule without changing it

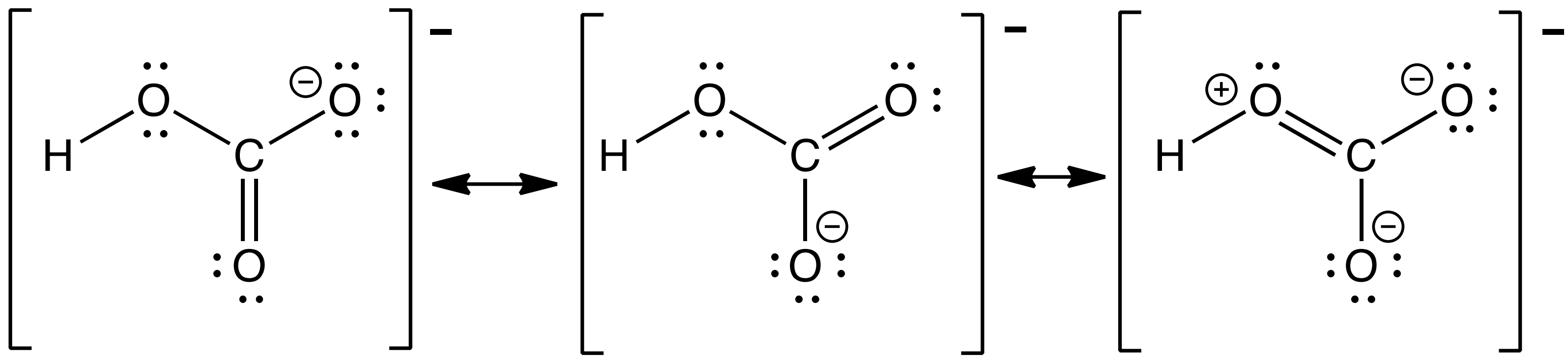
C) a series of Lewis structures that each partially represent the true nature of the bonding in a molecule

D) a series of Lewis structures that are present in equal proportions in a solution

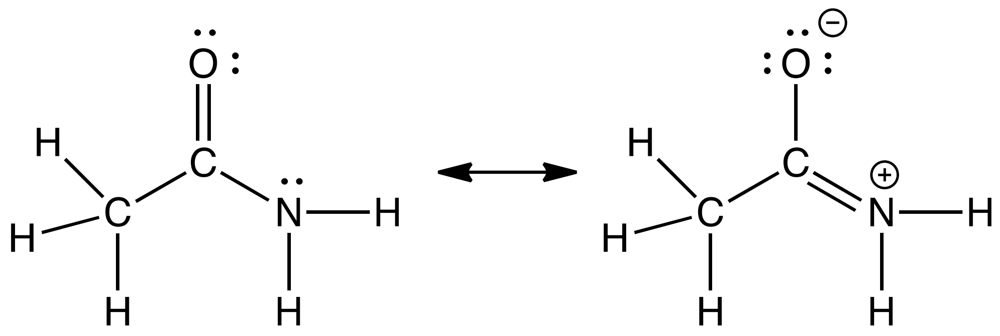
Stability of Resonance Contributors

- Resonance contributors may not all have the same stability. *Better* (more stable) Lewis structures will make a stronger contribution to structure of the resonance hybrid.

Ex: Bicarbonate

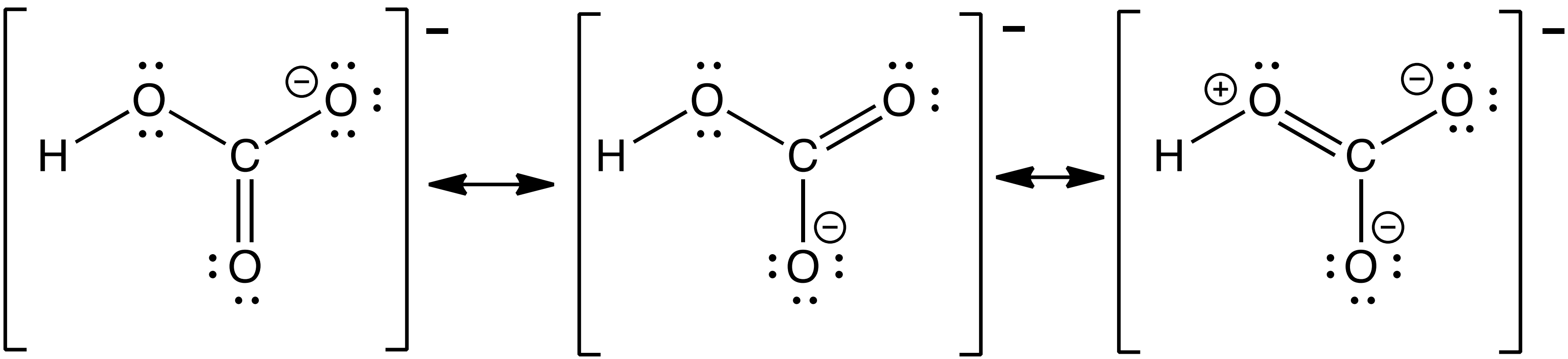


Acetamide



Clicker Question

Which resonance structure(s) would be the greatest contributor(s) to the resonance hybrid?



1 **2** **3**

A) 1 + 2

B) 1 only

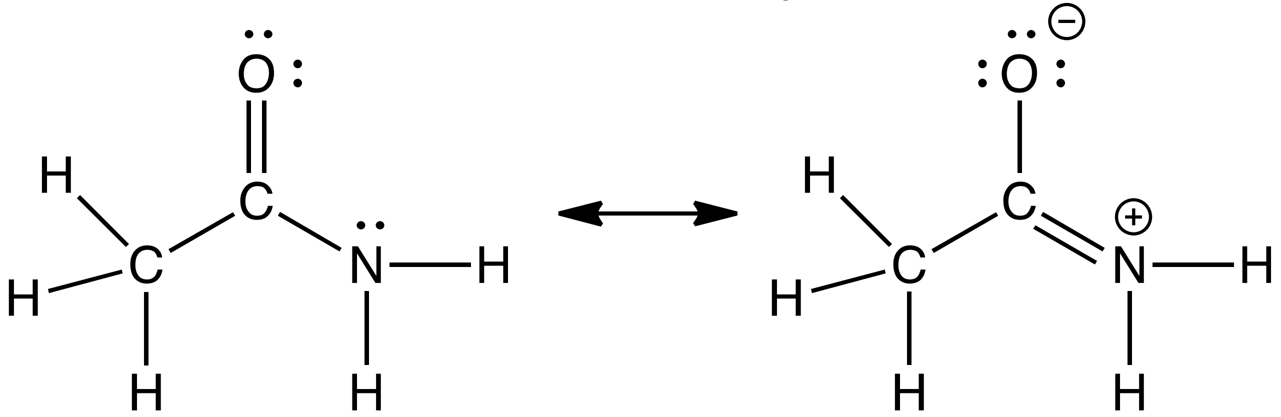
C) 2 only

D) 3 only

E) All are equal contributors

Clicker Question

Which resonance structure(s) would be the greatest contributor(s) to the resonance hybrid?



1 **2**

A) 1 only

B) 2 only

C) 1 + 2

D) Both are equal contributors

Hypervalency and resonance

In CHEM 154, if multiple **hypervalent** resonance structures are possible, only those having positive or zero formal charges on the central atom are considered valid.

Do NOT put a negative formal charge on the central atom unless you absolutely have to (i.e. there are no better resonance structures).

In CHEM 154, you should NEVER put a double bond on a terminal halogen (group 17).