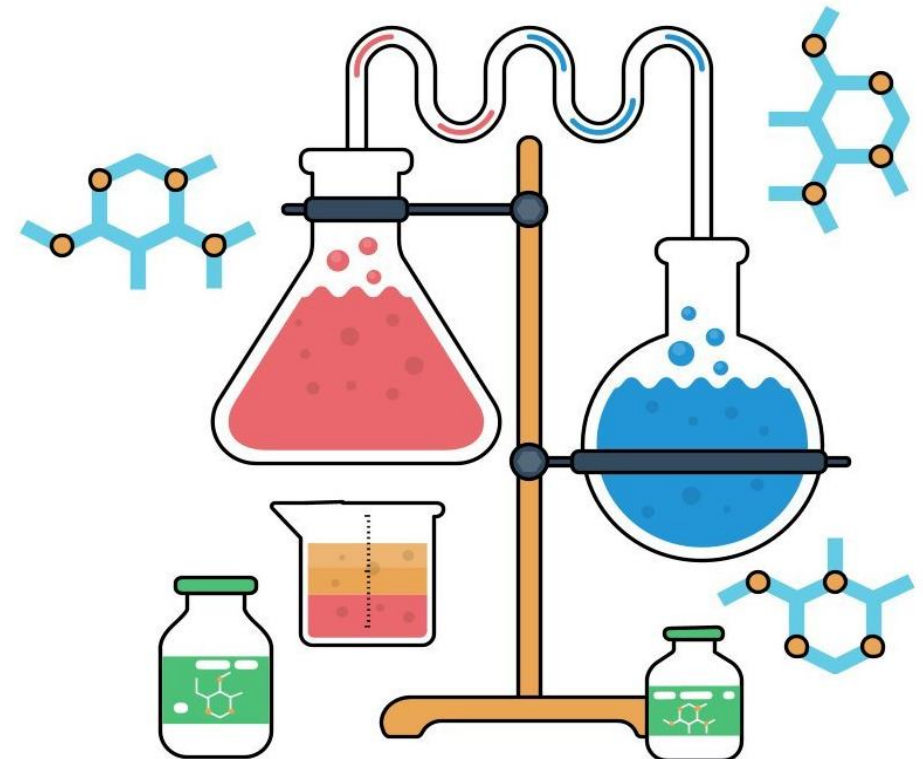




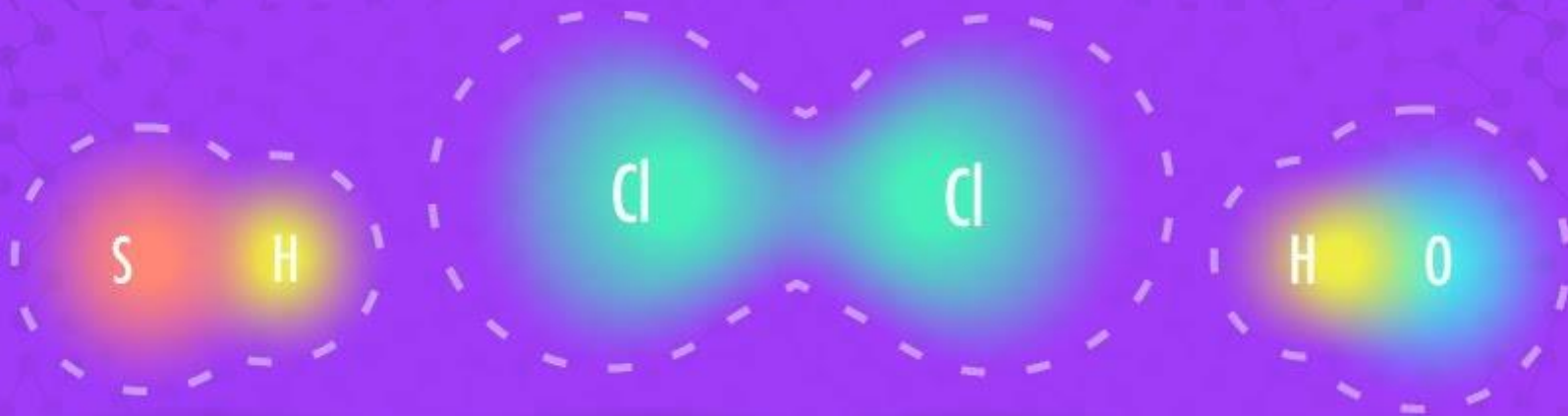
CHE 205

General Chemistry

Dr. Sara El Moussawi



Chapter II: Bonding : General Concepts



Chapter 2

Bonding: General Concepts

Chapter outline

1. Types of Chemical Bonds
2. Electronegativity
3. Bond Polarity and Dipole Moments
4. Ions: Electron Configurations and Sizes
5. The Localized Electron Bonding Model
6. Lewis Structures
7. Exceptions to the Octet Rule
8. Resonance structures
9. Formal charge
10. Molecular Structure: The VSEPR Model
11. Valence Bond Theory: Hybridization of Atomic Orbitals

The Localized Electron Bonding Model

Localized electron (LE) model: A model used to describe covalent bonds within a molecule.

The model assumes that a molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms.

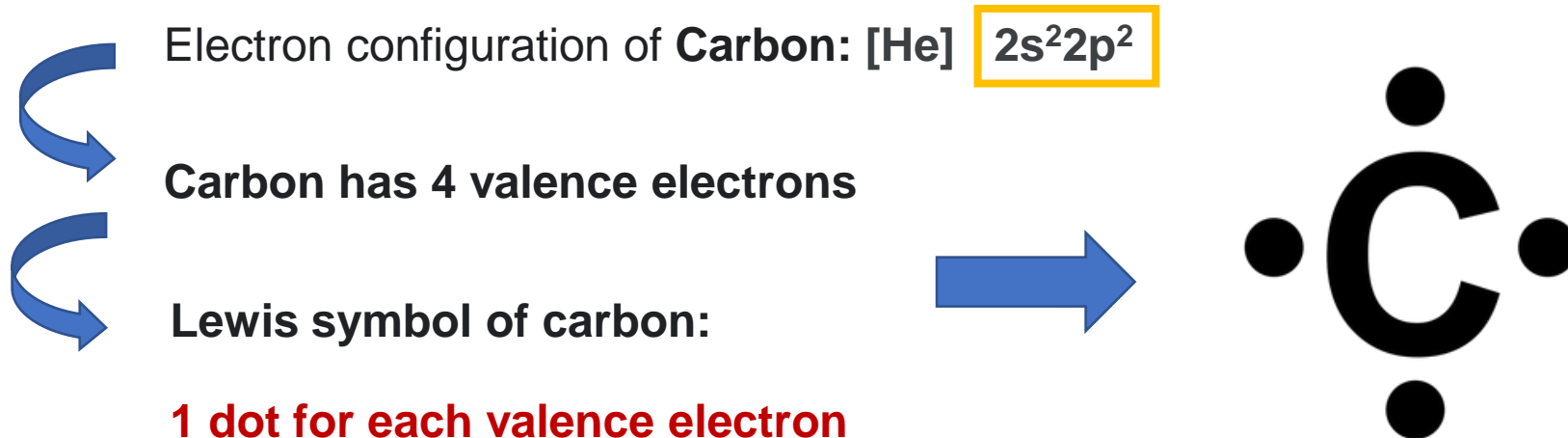
The LE model has three parts:

1. **Lewis structures:** Description of the valence electron arrangement in the molecule
2. **Valence Shell Electron-Pair Repulsion (VSEPR) model:** Prediction of the geometry of the molecule.
3. **Valence Bond Theory:** Description of the **type of atomic orbitals** used by the atoms to share electrons or hold lone pairs.

Lewis Structures

Lewis structures: Simple visualize of the valence electron arrangement in an atom

- In ionic compounds, electrons are transferred from a metal to a nonmetal and the resulting ions typically have noble gas electron configurations.
- In writing **Lewis structures**, the rule is that **only the valence electrons are included**.
- **Using dots to represent electrons**



Lewis Structures

- In a **Lewis symbol**, the valence electrons of main-group elements are represented as dots surrounding the symbol for the element.
- Each dot represents a valence electron. The dots are placed around the element's symbol with a **maximum of two dots per side**. We can draw Lewis symbols for all of the row 2 elements.

Place one dot on each side and then begin pairing up electrons



Main-group elements: **the 4 sides** of an element correspond to valence electrons in the **s and p subshell**.

- Atoms with **eight valence electrons** are stable with full outer level and identified as having **an octet (eight dots)**.
- For helium:** the two dots in the Lewis symbol are always paired; referred to **as a duet**.

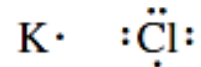


n = 1 quantum level fills with only two electrons.

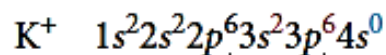
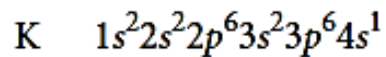
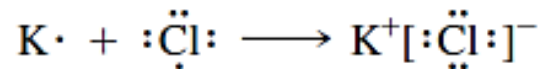
Lewis Structures

Remember: stable compound seeks to **achieve noble gas electron configurations**
→ **to obtain octet or duet in Lewis structure**

- **Lewis structure for ionic compounds:** electrons are transferred from a metal to a nonmetal and the resulting ions typically have noble gas electron configurations
- **Example:** Potassium and chlorine, which have the following Lewis symbols:



When potassium and chlorine bond, potassium transfers its valence electron to chlorine.



Octet in previous level

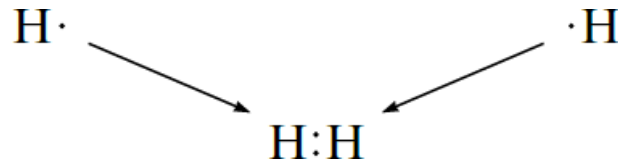
No dots are shown on the K⁺ ion because it has no valence electrons.

Lewis symbol of an **anion is usually written within brackets** with the charge in the upper right-hand corner.

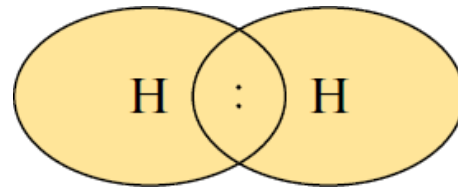
The transfer of the electron gives **chlorine an octet** (shown as eight dots around chlorine) and leaves **potassium** without any valence electrons but with an **octet in the previous principal energy level**

Lewis Structures

- **Lewis structures for molecules with covalent bonds**, involving elements in the first and second periods. The principle of achieving a noble gas electron configuration applies to these elements as follows:
- **Hydrogen** forms stable molecules where it shares two electrons. That is, it follows a **duet rule**.



By sharing electrons, each hydrogen in H_2 , in effect, has two electrons; that is, each hydrogen has a filled valence shell.

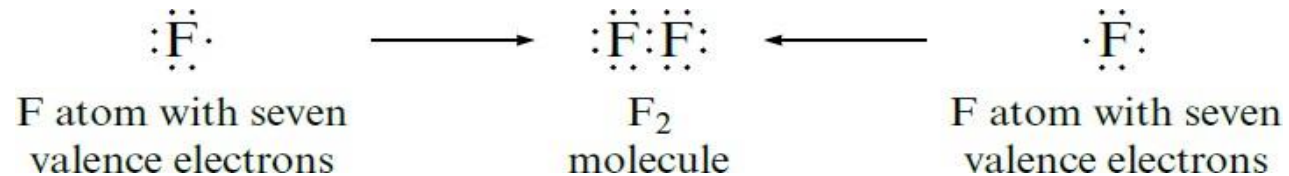


- **Helium does not form bonds** because its valence **orbital is already filled**: $1s^2$ $\text{He}:$

Lewis Structures

- The second-row nonmetals, carbon through fluorine, form stable molecules when they are surrounded by enough electrons to fill the valence orbitals, that is, the 2s and the three 2p orbitals.
- Since eight electrons are required to fill these orbitals, these elements typically obey the **octet rule**; they are surrounded by **eight electrons**.

An example is the **F₂ molecule**, which has the following **Lewis structure**:



- **Each fluorine atom in F₂ is surrounded by eight electrons.**
 - **Bonding pair:** Two electrons shared between atoms.
 - **lone pairs:** Electron pairs that are not involved in bonding. Each fluorine atom also has three lone pairs
- **Neon does not form bonds** because **it already has an octet** of valence electrons (2s²2p⁶) $\cdot\ddot{\text{Ne}}\cdot$

Lewis Structures

Steps for writing Lewis structures of molecules

(formed of atoms from the first two periods):

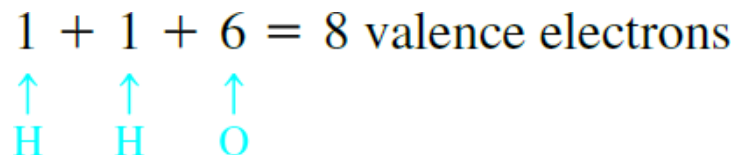
1. Sum the valence electrons from all the atoms.
2. Write the correct skeletal structure of a molecule:
 - hydrogen atoms are always terminal
 - Place the more electronegative elements in terminal positions
 - Place the element of single atom at the center position and it should be less electronegative (other than hydrogen).
3. Use a pair of electrons to form a bond between each pair of bound atoms.
4. Arrange the remaining electrons to satisfy the duet rule for hydrogen and the octet rule for the second-row elements.
5. If any atoms lack an octet, form double or triple bonds as necessary to give them octets.

Lewis Structures

Steps for writing Lewis structures of molecules
(formed of atoms from the first two periods):

Example: Water molecule (H₂O)

1. We sum the *valence* electrons for H₂O



2. Write the correct skeletal structure of a molecule: **H—O—H**

3. Use a pair of electrons to form a bond between each pair of bound atoms.

A line instead of a pair of dots is used to indicate each pair of bonding electrons.

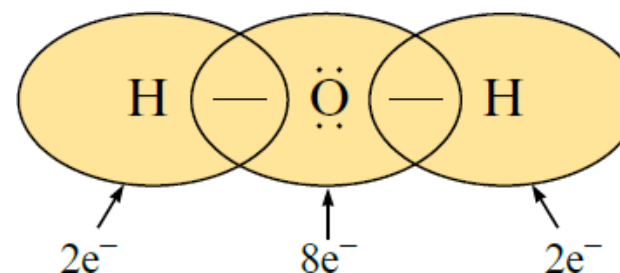
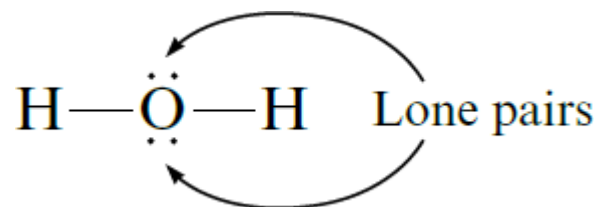
Lewis Structures

Steps for writing Lewis structures of molecules

(formed of atoms from the first two periods):

4. Arrange the remaining electrons to satisfy the duet rule for hydrogen and the octet rule for the second-row elements. Since four electrons have been used in forming the two bonds, four electrons (8 - 4) remain to be distributed.
- Hydrogen is satisfied with two electrons (duet rule), but oxygen needs eight electrons to have a noble gas configuration (octet rule).
- Thus, the remaining four electrons are added to oxygen as two lone pairs.

Dots are used to represent the lone pairs



Lewis Structures

Steps for writing Lewis structures of molecules

(formed of atoms from the first two periods):

- **Example: Carbon dioxide (CO₂)**

1. Summing the valence electrons: $4 + 6 + 6 = 16$

$\begin{array}{ccc} \uparrow & \uparrow & \uparrow \\ \text{C} & \text{O} & \text{O} \end{array}$

2. Write the correct skeletal structure of a molecule



3. Use a pair of electrons to form a bond between each pair of bound atoms.

4. The remaining electrons are distributed to satisfy octet rule. In this case we have 12 electrons (16 - 4) remaining after the bonds are drawn.

- We have 6 pairs of electrons to distribute.

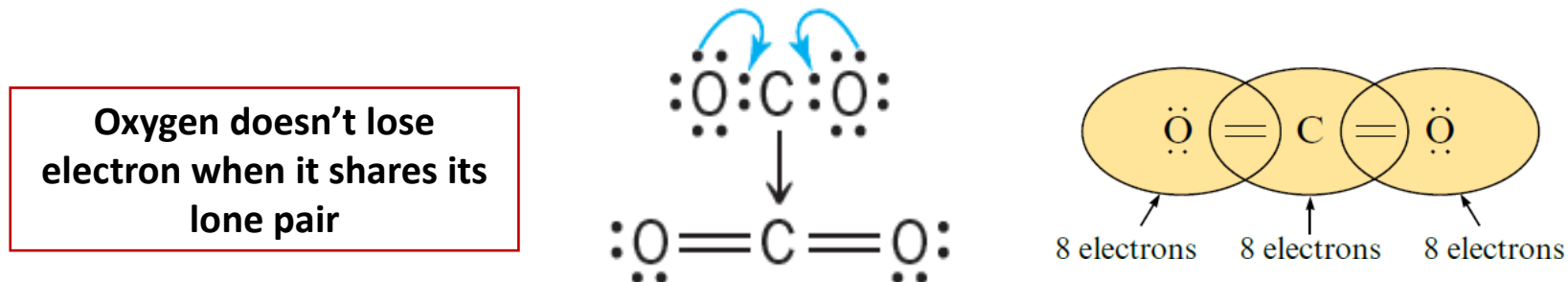
Lewis Structures

Steps for writing Lewis structures of molecules (formed of atoms from the first two periods):

- **Example: Carbon dioxide (CO₂)**

5. If any atoms lack an octet, form double or triple bonds as necessary to give them octets.

Carbon lacks an octet in this case. Move lone pairs from the oxygen atoms to bonding regions to form double bonds.



- Each atom is surrounded by 8 electrons, and the total number of electrons is 16, as required.
- This is the correct Lewis structure for carbon dioxide, which has two double bonds and four lone pairs.

Lewis Structures

- Cyanide ion (CN^-)

Number of ve-: CN^-

$$4 + 5 + 1 = 10$$

Cyanide Lewis structure: $[:\text{C}\equiv\text{N}:]^-$

- When drawing the **Lewis structure** of a **polyatomic ion**, the **charge** of the ion is reflected in the **number of total valence electrons**

Exercise:

Give the Lewis structure for each of the following.

a. HF

b. N_2

c. NH_3

d. CH_4

e. CF_4

f. NO^+

Lewis Structures

Solution:

	Total Valence Electrons	Draw Single Bonds	Calculate Number of Electrons Remaining	Use Remaining Electrons to Achieve Noble Gas Configurations	Check Number of Electrons
a. HF	$1 + 7 = 8$	H—F	6	H—F̈:	H, 2 F, 8
b. N ₂	$5 + 5 = 10$	N—N	8	:N≡N:	N, 8
c. NH ₃	$5 + 3(1) = 8$	$\begin{array}{c} \text{H} - \text{N} - \text{H} \\ \\ \text{H} \end{array}$	2	$\begin{array}{c} \text{H} - \ddot{\text{N}} - \text{H} \\ \\ \text{H} \end{array}$	H, 2 N, 8
d. CH ₄	$4 + 4(1) = 8$	$\begin{array}{c} \text{H} \\ \\ \text{H} - \text{C} - \text{H} \\ \\ \text{H} \end{array}$	0	$\begin{array}{c} \text{H} \\ \\ \text{H} - \text{C} - \text{H} \\ \\ \text{H} \end{array}$	H, 2 C, 8
e. CF ₄	$4 + 4(7) = 32$	$\begin{array}{c} \text{F} \\ \\ \text{F} - \text{C} - \text{F} \\ \\ \text{F} \end{array}$	24	$\begin{array}{c} \text{:}\ddot{\text{F}}\text{:} \\ \\ \text{:}\ddot{\text{F}} - \text{C} - \ddot{\text{F}}\text{:} \\ \\ \text{:}\ddot{\text{F}}\text{:} \end{array}$	F, 8 C, 8
f. NO ⁺	$5 + 6 - 1 = 10$	N—O	8	[:N≡O:] ⁺	N, 8 O, 8

Lewis Structures

Exercise:

Write the Lewis structures that obey the octet rule (duet rule for H) for each of the following molecules:

- a) Carbon monoxide (CO)
- b) Chloroform (CHCl₃)
- c) Nitrate ion (NO₃⁻)
- d) Hydrazine (N₂H₄)

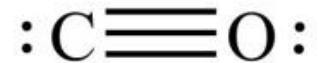
Given electron configurations:

⁶C: 1s²2s²2p², ⁸O: 1s²2s²2p⁴, ¹H: 1s¹, ¹⁷Cl: 1s²2s²2p⁶3s²3p⁵ ⁷N: 1s²2s²2p³

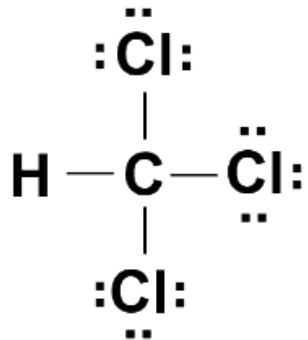
Lewis Structures

Solution:

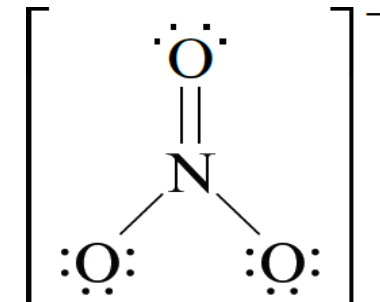
a) Valence electrons of CO = $4 + 6 = 10$



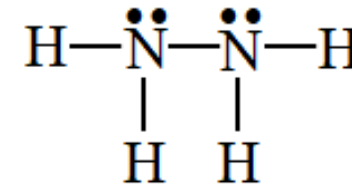
b) Valence electrons of chloroform = $4 + 1 + 3(7) = 26$



c) Valence electrons of nitrate ion = $5 + 3(6) + 1 = 24$



d) Valence electrons of hydrazine = $2(5) + 4 = 14$



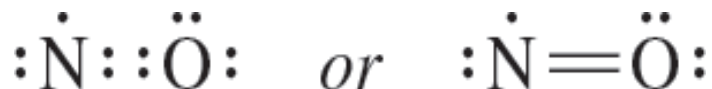
Exceptions to the Octet Rule

1. Odd-Electron Species:

Molecules or ions with an **odd number of electrons**. They are **free radicals**.

Example:

- **Nitrogen monoxide** has 11 electrons
- If we try to write a Lewis structure for nitrogen monoxide, we can't achieve octets for both atoms:



- It is impossible to satisfy octet rule in Lewis structures for free radicals, yet some of these molecules exist in nature.
- They tend to be somewhat unstable and reactive.

Exceptions to the Octet Rule

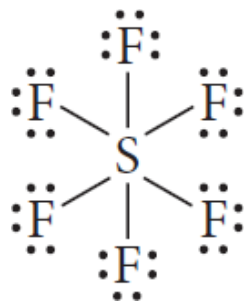
2. Expanded Octets:

Molecules or ions with **more than eight electrons** around an atom.

- Elements in the third row of the periodic table and beyond often exhibit expanded octets of up to 12 (and occasionally 14) electrons.

Example:

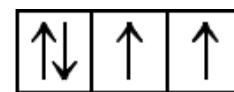
Sulfur hexafluoride:



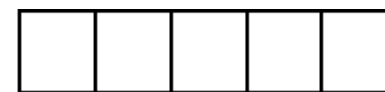
***d* orbitals in these elements are energetically accessible** and can accommodate the extra electrons.



3s



3p



3d

- In SF₆, sulfur has an expanded octet of 12 electrons. This compound exist and is stable.
- Ten- and twelve-electron expanded octets are common in third-period elements and beyond because the ***d* orbitals in these elements are energetically accessible** (they are not much higher in energy than the orbitals occupied by the valence electrons) and can accommodate the extra electrons.
- Expanded octets never occur in second-period elements.*

Exceptions to the Octet Rule

3. Incomplete Octets:

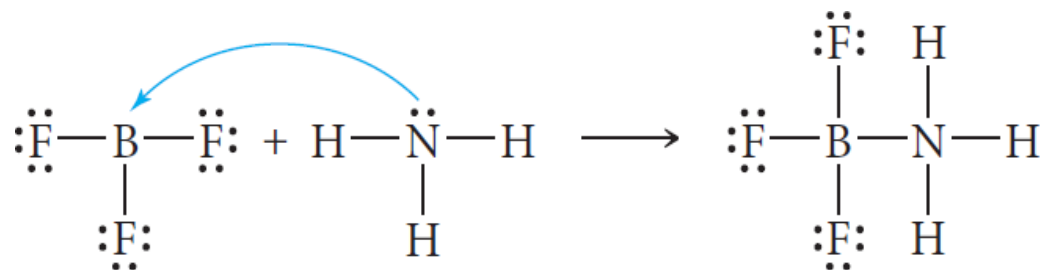
Molecules or ions with fewer than eight electrons around an atom.

Example:

- Boron** forms compounds with only six electrons around it, rather than eight.



- This Lewis structure has octets for all atoms, including boron. However, when we assign formal charges to this structure, we get a negative formal charge on B and a positive formal charge on F (the most electronegative element). BF₃ can complete its octet via a chemical reaction. BF₃ reacts with NH₃ as follows:

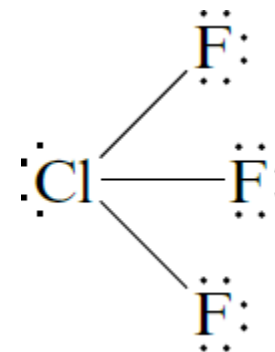


Exceptions to the Octet Rule

Write the Lewis structure for each molecule or ion.

a. ClF_3 **b.** BeCl_2 **c.** ICl_4^-

a. The chlorine atom (third row) accepts the extra electrons.



b. Beryllium is electron-deficient. $:\ddot{\text{Cl}}-\text{Be}-\ddot{\text{Cl}}:$

c. Iodine exceeds the octet rule. $\left[\begin{array}{cc} :\ddot{\text{Cl}} & & :\ddot{\text{Cl}} \\ & \diagdown & / \\ & \text{I} & \\ & / & \diagdown \\ :\ddot{\text{Cl}} & & :\ddot{\text{Cl}} \end{array} \right]^-$

Exceptions to the Octet Rule

Which molecule would you expect to be a free radical?

- (a) CO
- (b) CO₂
- (c) N₂O
- (d) NO₂

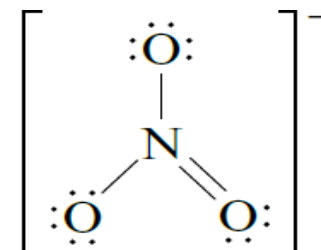
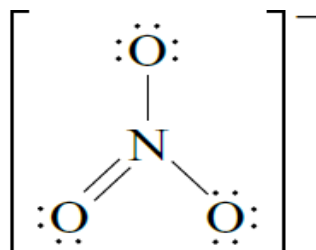
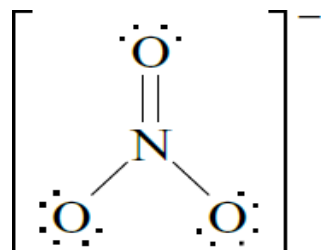
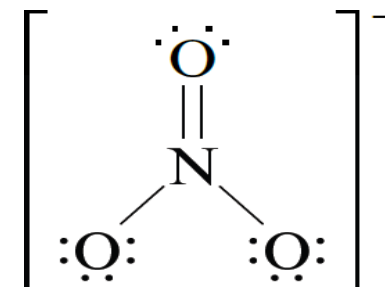
Solution

(d) NO₂ because the sum of the valence electrons of its atoms is an odd number.

Resonance

Consider the Lewis structure for the nitrate ion (NO_3^-):

- There is no reason for choosing a particular oxygen atom to have the double bond.
- There are really three valid Lewis structures:

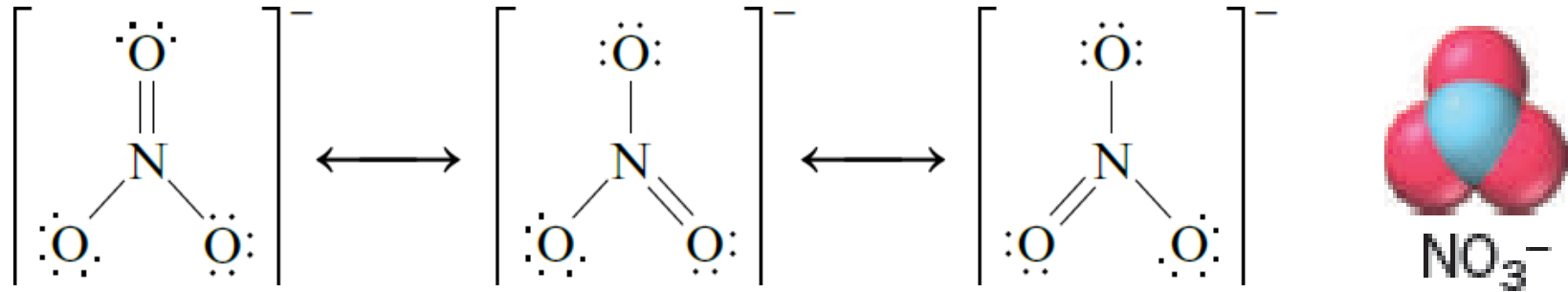


- Is any of these structures a correct description of the bonding in NO_3^- ?

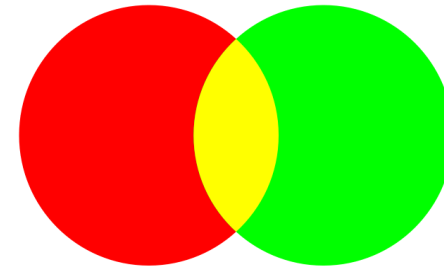
No, because NO_3^- does not have one double and two single bonds, it has three equivalent bonds.

Resonance

The correct description of NO_3^- is not given by any one of the three Lewis structures but it is intermediate between the two resonance structures and is a **resonance hybrid**.

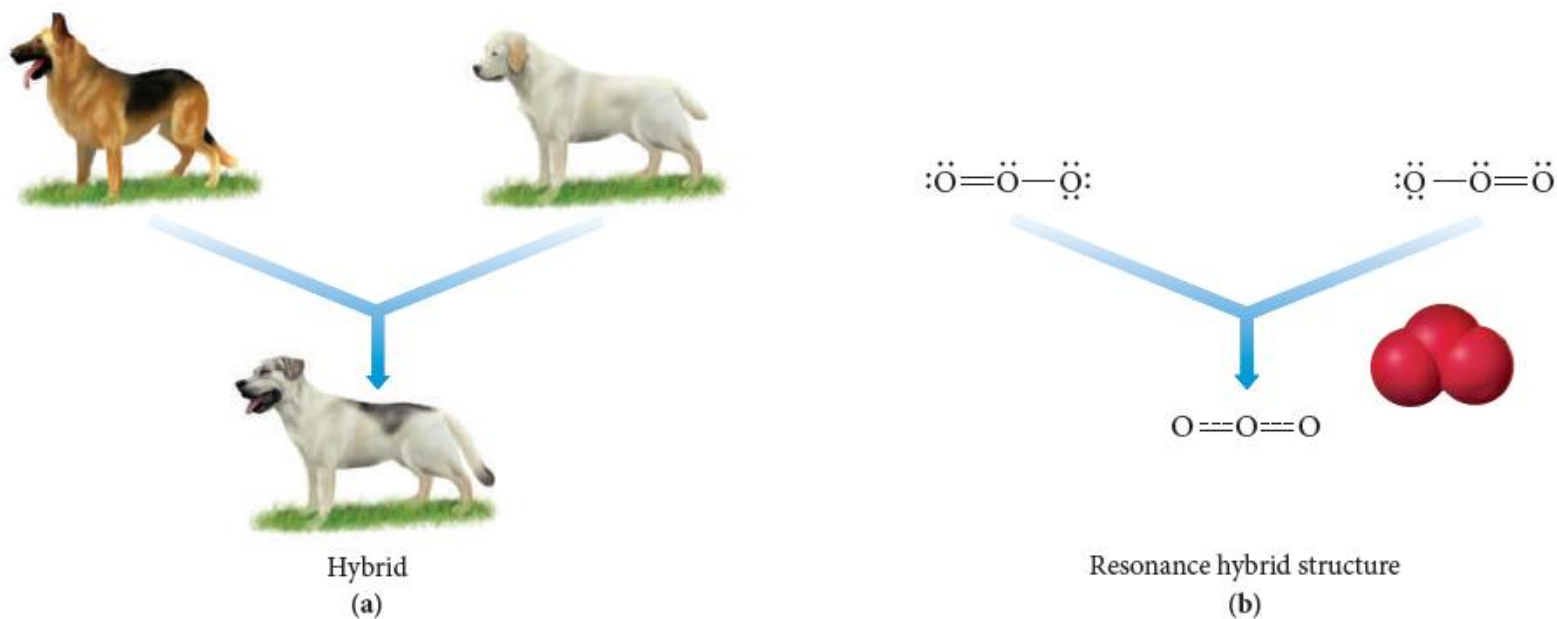


Resonance hybrid is the superimpose of resonance structures. As in color mixing, yellow is the superimpose of red and green; you see the yellow color as yellow and not onetime as red and the other times as green.



Resonance

Consider the **Resonance structures** for the **ozone gas (O_3)** (which protect living things from too much ultraviolet radiation from the sun):



For instant, the offspring of two animals or plants of different varieties is a *hybrid* (intermediate) between the two varieties. Similarly, the structure of a **ozone resonance hybrid is intermediate between the two resonance structures.**

Resonance

Example:

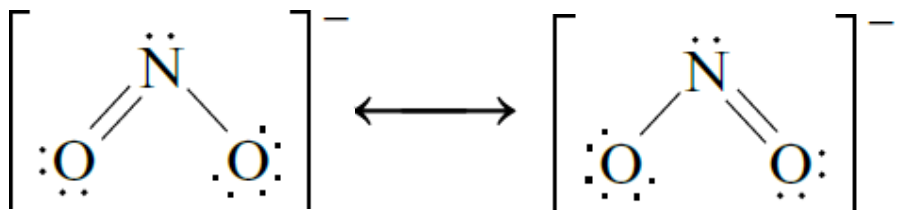
Describe the electron arrangement in the nitrite anion (NO_2^-) using the localized electron model.

Solution:

In NO_2^- : $5 + 2(6) + 1 = 18$ valence electrons.



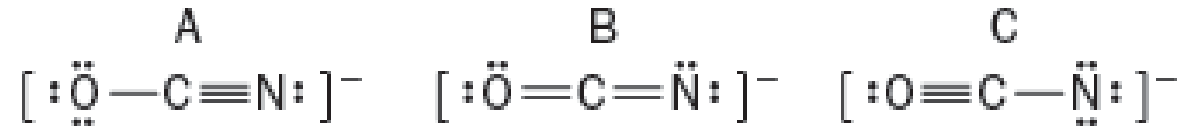
The remaining 14 electrons ($18 - 4$) can be distributed to produce these structures:



The electronic structure of the molecule is correctly represented not by either resonance structure but by the average of the two.

Resonance

- In the examples of resonance hybrids that we have examined so far, the contributing structures have been **equivalent** (or equally valid) Lewis structures.
- **In some cases**, however, we can write resonance **structures that are not equivalent**. Example cyanate ion (OCN⁻):



For reasons we have to determine the **formal charge** of an atom in a molecule, that will determine which resonance structure is somewhat better than the others.

Formal Charge

- Used to decide which of the **nonequivalent Lewis structures** best describes the actual bonding in a specific molecule or polyatomic ion.
- The **formal charge** of an atom in a molecule is the difference between the number of valence electrons on the free atom and the number of valence electrons assigned to the atom in the molecule.

We need to know two things:

1. The number of valence electrons on the **free neutral atom** (which has zero net charge because the number of electrons equals the number of protons).
2. The number of valence electrons “**belonging**” to the atom in a molecule.

$$\text{Formal charge} = \text{(number of valence electrons on free atom)} - \text{(number of valence electrons assigned to the atom in the molecule)}$$

Formal Charge

- The number of **valence electrons assigned** to a given atom is calculated as follows:

$$(\text{Valence electrons})_{\text{assigned}} = (\text{number of lone pair electrons}) + \frac{1}{2} (\text{number of shared electrons})$$

$$\text{Formal charge} = \text{number of valence electrons} - \left(\text{number of lone pair electrons} + \frac{1}{2} \text{number of bonding electrons} \right)$$

Example:

Calculate the formal charge of hydrogen and Fluorine in HF molecule

(When calculating the formal charge we completely ignore the effects of electronegativity)

Formal Charge

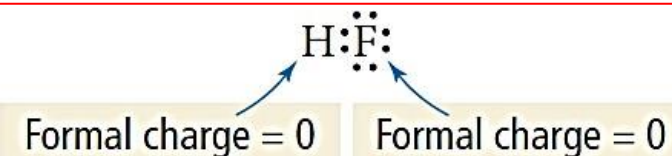
Formal charge = number of valence electrons –
(number of lone pair electrons + $\frac{1}{2}$ number of bonding electrons)

So the formal charge of hydrogen in HF is:

$$\text{Formal charge} = 1 - \left[0 + \frac{1}{2}(2) \right] = 0$$

Number of valence
electrons for H

Number of electrons that H
"owns" in the Lewis structure



Similarly, the formal charge of fluorine in HF is:

$$\text{Formal charge} = 7 - \left[6 + \frac{1}{2}(2) \right] = 0$$

Number of valence electrons for F

Number of electrons that F
"owns" in the Lewis structure

Formal Charge

The concept of formal charge is useful because it can help us **distinguish between competing skeletal structures** and competing resonance structures.

In general, **these four rules apply:**

1. The sum of all formal charges in a neutral molecule must be zero.
2. The sum of all formal charges in an ion must equal the charge of the ion.
3. Small (or zero) formal charges on individual atoms are better than large ones.
4. When formal charge cannot be avoided, negative formal charge should reside on the most electronegative atom.

Formal Charge

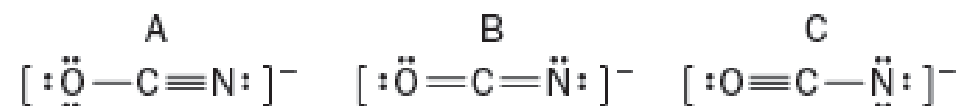
Example: The formal charge of each atom in the structure is calculated below the atoms.

	Structure A			Structure B		
	H	—	C ≡ N:	H	—	N ≡ C:
number of valence e ⁻	1		4 5	1		5 4
-number of lone pair e ⁻	-0		-0 -2	-0		-0 -2
$-\frac{1}{2}$ (number of bonding e ⁻)	$-\frac{1}{2}(2)$		$-\frac{1}{2}(8)$ $-\frac{1}{2}(6)$	$-\frac{1}{2}(2)$		$-\frac{1}{2}(8)$ $-\frac{1}{2}(6)$
Formal charge	0		0 0	0	+1	-1

The sum of the formal charges for each of these structures is zero (as it should be for neutral molecules). However, structure **B** has formal charges on both the N atom and the C atom, while structure **A** has no formal charges on any atom. Furthermore, in structure **B**, the negative formal charge is not on the most electronegative element (nitrogen is more electronegative than carbon). Consequently, **structure A is the better Lewis structure.**

Formal Charge

Example: Assign formal charges to each atom in the resonance forms of the cyanate ion (OCN⁻). Which resonance form is likely to contribute most to the correct structure of OCN⁻?



	A [: $\ddot{\text{O}}$ –C \equiv N:] [–]			B [: $\ddot{\text{O}}$ =C= $\ddot{\text{N}}$:] [–]			C [:O \equiv C– $\ddot{\text{N}}$:] [–]		
Number of valence e [–]	6	4	5	6	4	5	6	4	5
–number of lone pair e [–]	–6	–0	–2	–4	–0	–4	–2	–0	–6
– $\frac{1}{2}$ (number of bonding e [–])	–1	–4	–3	–2	–4	–2	–3	–4	–1
Formal charge	–1	0	0	0	0	–1	+1	0	–2

The sum of all formal charges for each structure is -1, as it should be for a 1⁻ ion. **Structures A and B have the least amount of formal charge** and are therefore preferable over structure C. **Structure A is preferable to B because it has the negative formal charge on the more electronegative atom.** We thus expect structure A to make the biggest contribution to the resonance forms of the cyanate ion.

Review

Lewis Structures: Comments About the Octet Rule

- The **second-row elements C, N, O, and F** should always be assumed to **obey the octet rule**.
- The **second-row elements B and Be** often have fewer than eight electrons around them in their compounds. These **electron-deficient compounds** are very reactive.
- The second-row elements never exceed the octet rule, since their valence orbitals ($2s$ and $2p$) can accommodate only eight electrons.
- **Third-row and heavier elements** often satisfy the octet rule but **can exceed the octet rule** by using their empty valence d orbitals.
- When writing the Lewis structure for a molecule, satisfy the octet rule for the atoms first.
- If electrons remain after the octet rule has been satisfied, then place them on the elements having available d orbitals (elements in Period 3 or beyond) (usually it is the central atom).
- If a molecule has **non-equivalent Lewis structures**, **depend on the formal charge** method in your selection.

Periodic Table of the Elements

1 1A 1A 1 H Hydrogen 1.008	2 2A 2A 4 Be Beryllium 9.012											13 3A 3A 5 B Boron 10.811	14 4A 4A 6 C Carbon 12.011	15 5A 5A 7 N Nitrogen 14.007	16 6A 6A 8 O Oxygen 15.999	17 7A 7A 9 F Fluorine 18.998	18 8A 8A 2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 84.798
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]						

Lanthanide Series	57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.242	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]