Molecules Module – Lecture 2: Lewis Structures

Learning Objective	Openstax 2e Chapter
Writing Lewis Structures	7.3
Formal Charges	7.4
Resonance	7.4
Octet Rule Exceptions	7.3

Suggested Practice Problems

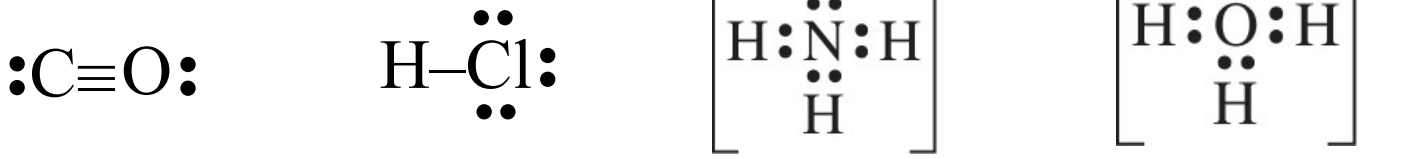
Chapter 7 Exercises – Questions: 23, 27, 29, 31, 35, 37, 39, 45, 47, 51, 53, 55

Answers can be found in the Chapter 7 Answer Key

Writing Lewis Structures

Reminder of some of the essential features of Lewis structures:

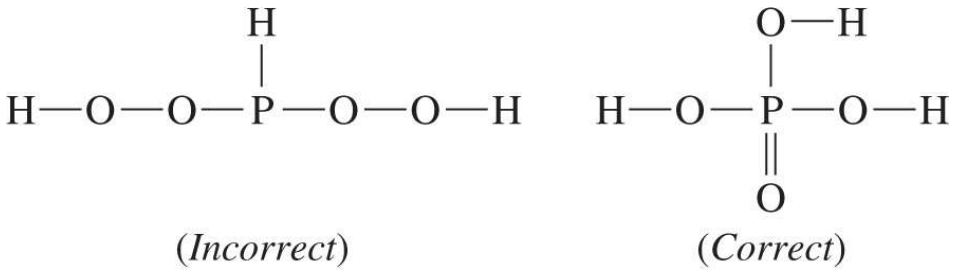
- All valence electrons of atoms must appear in the Lewis structure
- Usually, all the electrons in a Lewis structure are paired (diamagnetic molecules)
- Usually, each atom acquires an outer-shell octet of electrons, especially for period 2 (row 2) [for Hydrogen, a full outer-shell is 2 electrons]
- Sometimes, multiple covalent bonds may be needed to complete octets (Readily formed by C, N, O, S, and P)



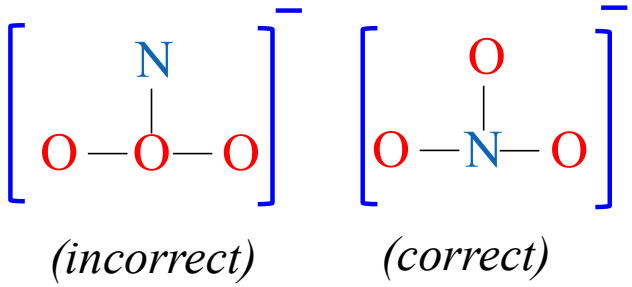
Skeletal Structures

Atoms in the structure are arranged in the order in which they are bonded to one another.

- Distinguish between **central** (bonded to 2 or more atoms) and **terminal** (bonded to just one other atom) atoms.
  - H and F are always terminal atoms
  - Central atoms are usually those with the lowest electronegativity
  - Carbon atoms are always central atoms
- Molecules and polyatomic ions generally have compact and symmetrical structures (except for the very large number of chain-like organic molecules).



Phosphoric acid, H_3PO_4

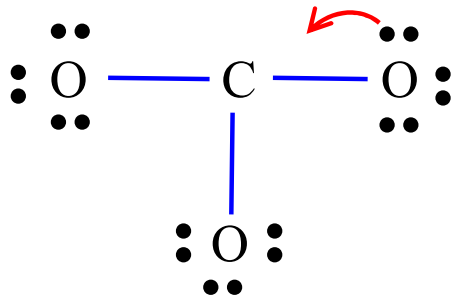


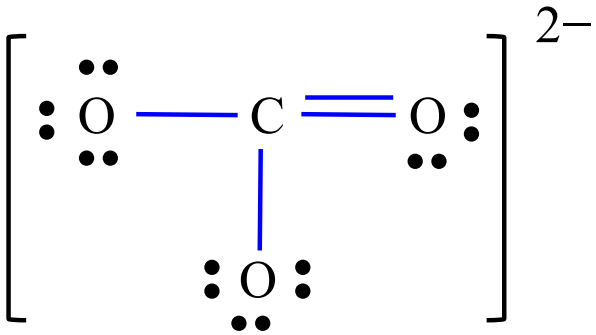
Nitrate ion, NO_3^-

A Strategy for Writing Lewis Structures

Draw a Lewis structure for carbonate ion, CO_3^{2-}

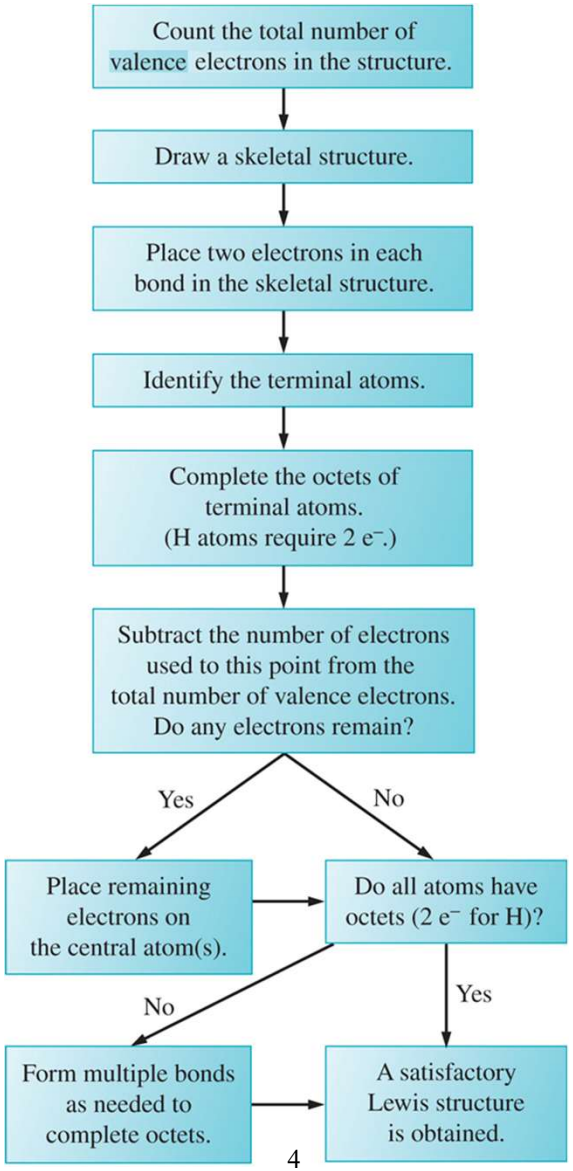
Total # V.E.= 4+6 × 3+2=24





"All valence electrons present?" Yes

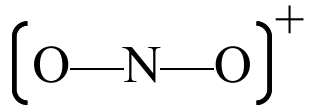
"Do all atoms have octets?"
No, C doesn't have octet
- so form a multiple bond

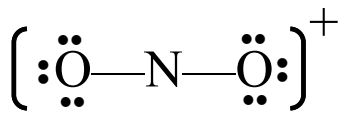


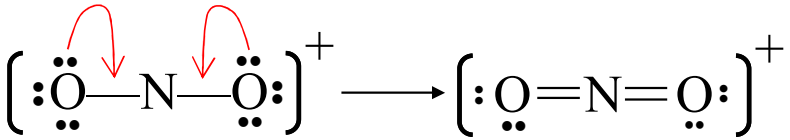
Example:

Write a Lewis Structure for nitronium ion, NO_2^+

Total # of valence e^- = 5 + 6 x 2 – 1 = 16







Is there any other Lewis structure possible?

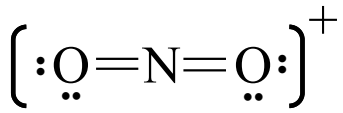
Formal Charge (FC) on an atom

FCs arise when atoms have not contributed equal # of electrons to the covalent bonds joining them.

$$FC = \#_{\text{valence } e^-\text{ for a free atom}} - \#_{\text{lone pair } e^-} - \frac{1}{2}\#_{\text{bond pair } e^-}$$

Subtract # of electrons assigned to atom, including in bonds, in a Lewis structure

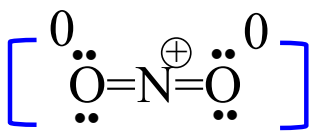
or FC = # valence e- for atom – 2 x # lone pairs – # bonds



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

$$FC(N) = 5 - 0 - 4 = +1$$

formal charge of each atom →

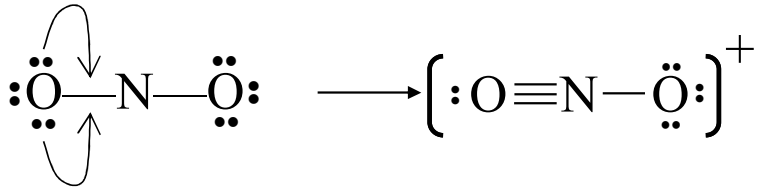


+ ← overall charge of the cation

Example 1

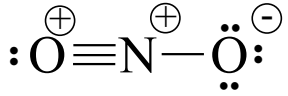
When more than one possible Lewis structure exists, FC are used to ascertain the most satisfactory one.

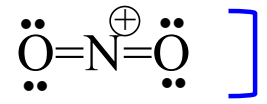
Calculate formal charge for the alternative Lewis structure of NO_2^+



$FC(O\equiv) = 6 - 2 - 3 = +1$ $\qquad$ $FC(N) = 5 - 0 - 4 = +1$

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

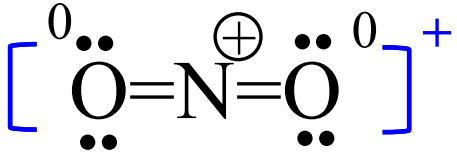


Why is this less preferred than the previous structure? 

Which Lewis structure is plausible?

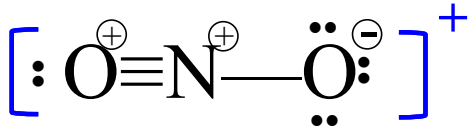
Follow general rules based on formal charges (FC)

1. Sum of FC is the overall charge of the molecule or polyatomic ion.
2. Where FC are required, they should be as small as possible.
3. Negative FC usually appears on most electronegative elements, and positive FC on the least electronegative atoms.
4. FC of same sign on adjacent atoms is unlikely.



(best)

Conforms to all rules

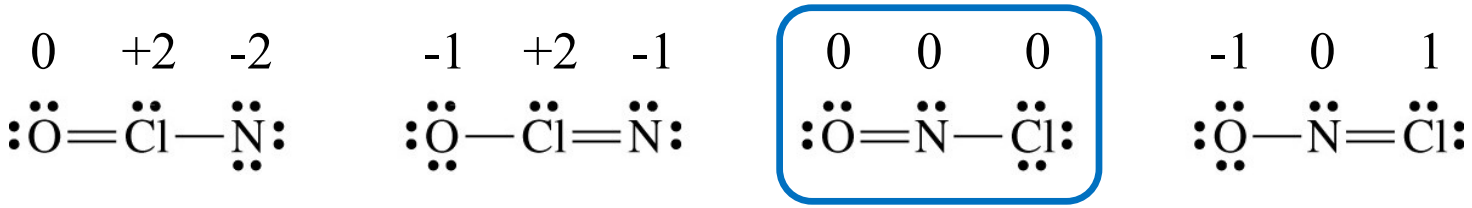


(unlikely)

Only conforms to the first 2 rules

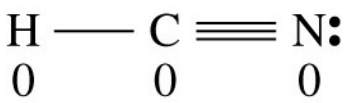
Example 2

Use formal charges to determine the “best” Lewis structure among several possible for nitrosyl chloride (NOCl).



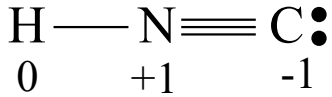
However, it does not mean that only the best Lewis structure can exist. Other unlikely Lewis structures can be real as well.

Hydrogen cyanide



Best

Hydrogen isocyanide



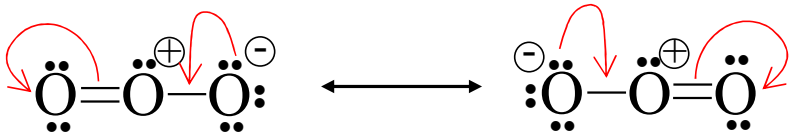
High energy molecule found in interstellar medium

Resonance

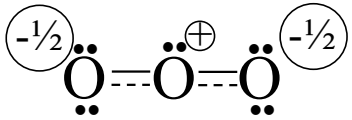
The situation in which two or more plausible Lewis structures contribute to the "correct" structure.

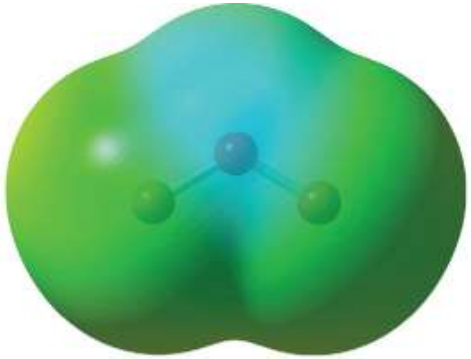
Two possible Lewis structures exist for ozone, O_3 :

Experimental evidence indicates that the two oxygen-to-oxygen bonds are the same with 127.8 pm length (intermediate between single and double bonds).



The true structure is a <u>resonance hybrid</u> of plausible contributing structures.





Electrostatic potential map of ozone (revisit later)

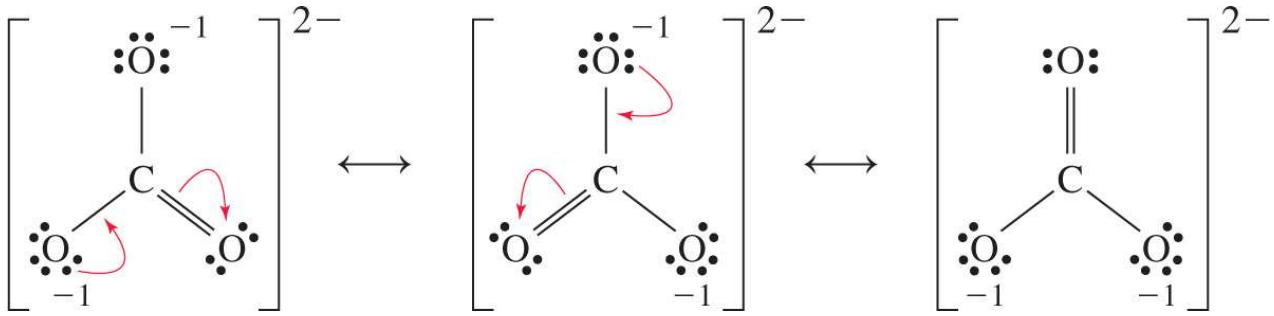
Resonance

The situation in which two or more plausible Lewis structures contribute to the "correct" structure.

Acceptable contributing structures to a resonance hybrid:

- Must all have the same skeletal structure (the atomic positions cannot change)
- They can differ only in how electrons are distributed within the structure.

Resonance structures of carbonate ion, CO_3^{2-} :

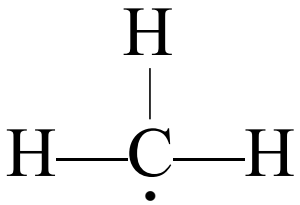


The three C-O bonds are equivalent.
The ion has the same hybrid structure all the time

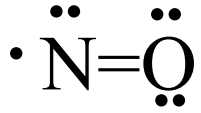
Exceptions to the Octet Rule

Case 1: Odd-Electron Species

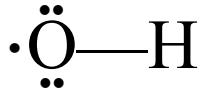
- Molecules with an odd number of electrons must have an unpaired electron somewhere in the structure. Lewis theory deals with electron pairs and does not tell us where to put the unpaired electron.
- These molecules are known as free radicals and are highly reactive.



Methyl radical



Nitrogen monoxide (Unpaired electron is placed on N to get a structure free of FC)

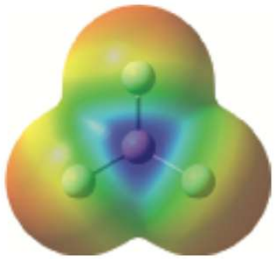


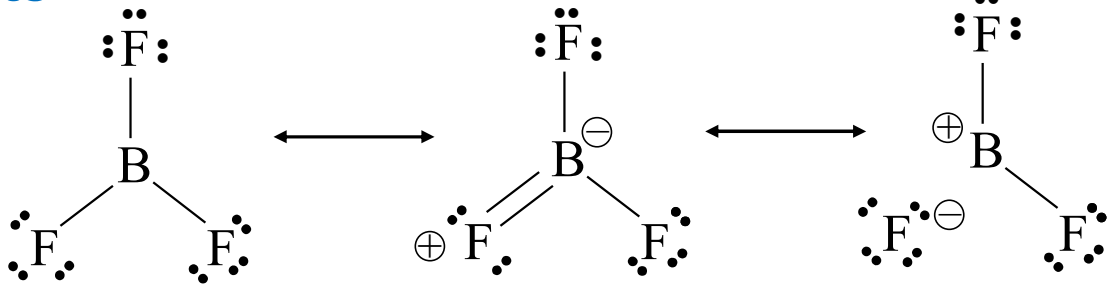
Hydroxyl radical

Exceptions to the Octet Rule

Case 2: Incomplete Octets

Boron trifluoride, BF_3





B has incomplete octet

Positive FC on the most electronegative atom

F has a much higher electronegativity than B

(best) (unlikely)

- **Usually, we complete octets and then minimize formal charges, however, in this case that gives a +ve charge on F and a –ve charge on a neighbouring B, which is extremely against electronegativities**
- **In this extreme case, EN wins over completing octets and structure with 0 formal charges is best**
- **Note the electrostatic potential map agrees with the left-most structure and not with the other two**

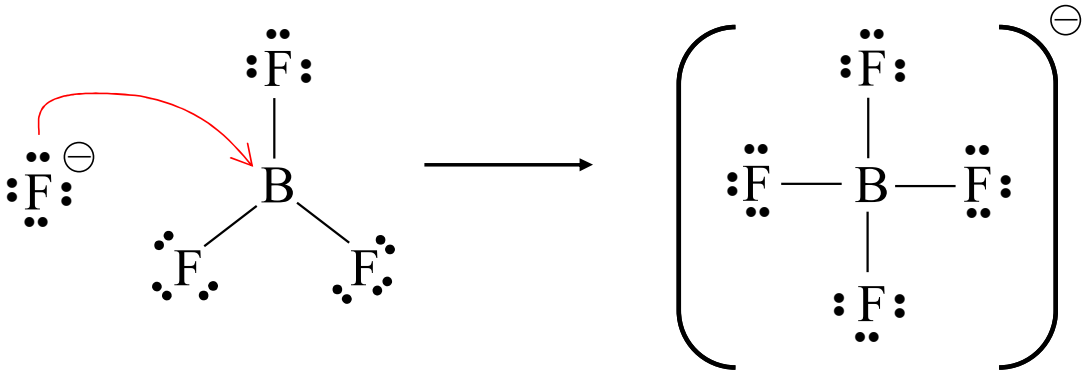
Exceptions to the Octet Rule

Case 2: Incomplete Octets

Boron trifluoride, BF_3

BF_3 chemical behaviour is consistent with central B atom not having a complete octet, but "wanting" one.

BF_3 has a strong tendency to form a coordinate covalent bond with species capable of donating electron pair to B.

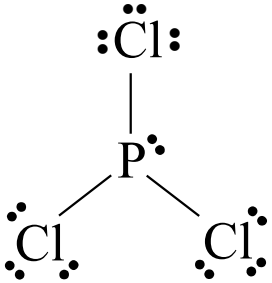


Exceptions to the Octet Rule

Case 3: Expanded Valence Shells

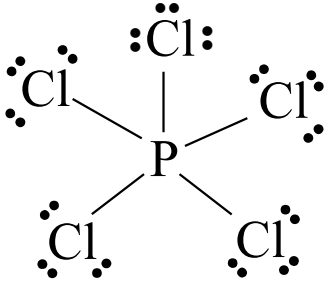
- Nonmetals of 3rd period and beyond can form stable molecules with more than 8 (e.g., 10 or 12) electrons around the central atom.
- Usually occurs when a nonmetal atom is bonded to highly electronegative atoms

PCl_3



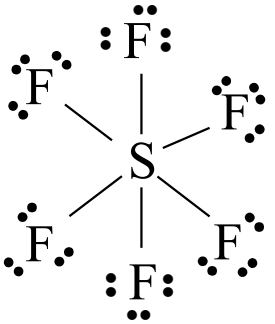
octet

PCl_5



expanded valence shell

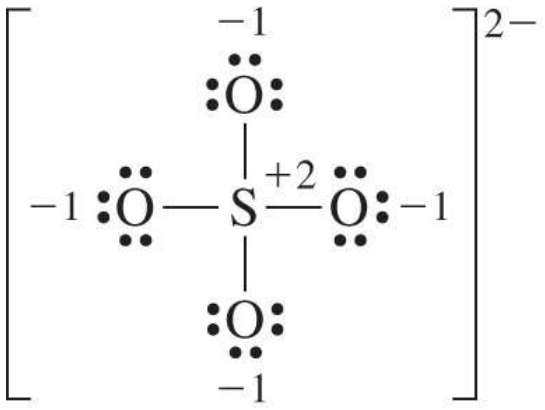
SF_6



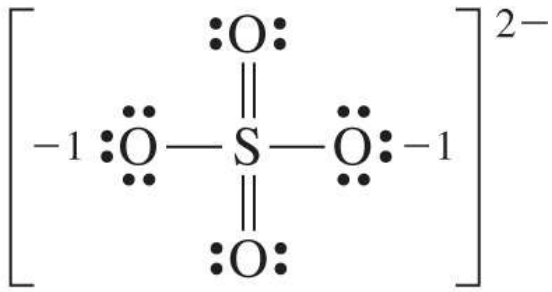
expanded valence shell

Example 3

Draw Lewis structure of sulfate ion, SO_4^{2-}



Normal octet



Expanded valence shell

Better structure because it

1. **reduces formal charges.**
2. **agrees with experimental evidence.**

Draw resonance structures and calculate formal charges.