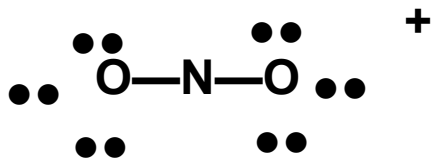
Lewis structures for polyatomic ions

$[NO_2]^+$

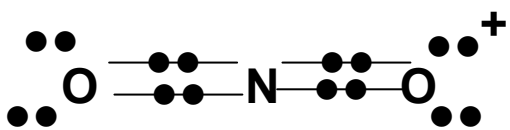
Total number of valence electrons: 5 (N) + 2x6(O) -1 (charge) = 16

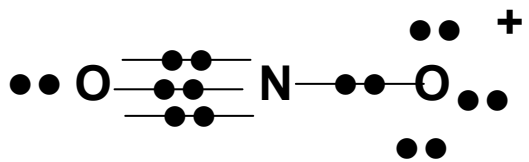
O—N—O

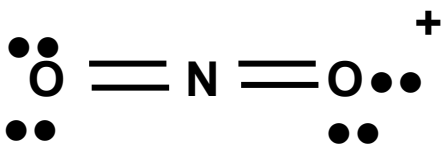
16-2x2=12 assign 12 electrons



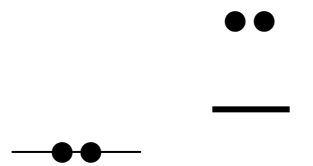
Complete octet for N using multiple bonds







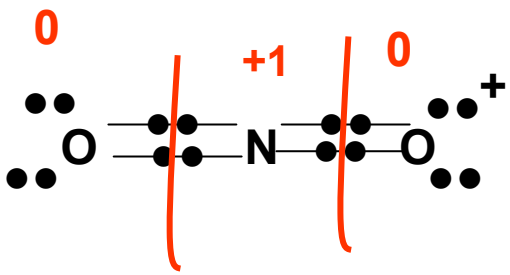
Which one?



Formal Charge (FC) – apparent charge in Lewis structure

FC= number of valence electrons in free atom –number of electrons assigned for this atom in the Lewis structure

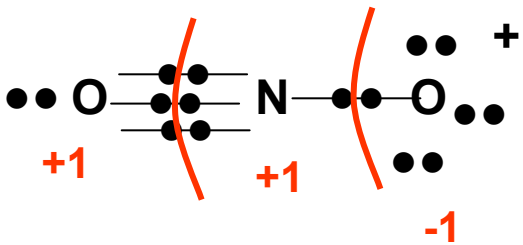
How to assign electrons in the Lewis structure?
½(number of electrons from the bonds around) + number of electrons in lone pairs around the atom



FC (N) = 5 -4(bonds) = +1

FC (O) = 6-2(bonds) – 4(lone pairs) = 0

Net charge =FC(O) + FC (N) + FC(O)= 0+ 0 +1 =+1

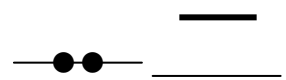


FC (N) = 5 -4 = +1

FC(O_1) = 6-3-2 = +1

FC(O_2) = 6-1-6 = -1

Net charge= +1 +1 -1= +1

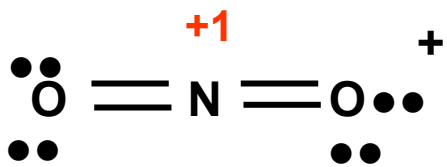


Rules for Formal Charges (FC)

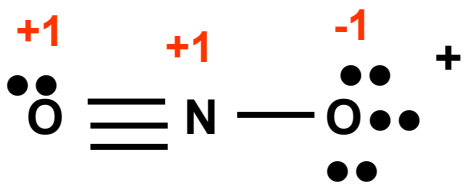
1. The FC must be as small as possible

2. Negative FC should be on the atoms with larger electronegativity

3. Adjacent atoms should not have charges of the same sign



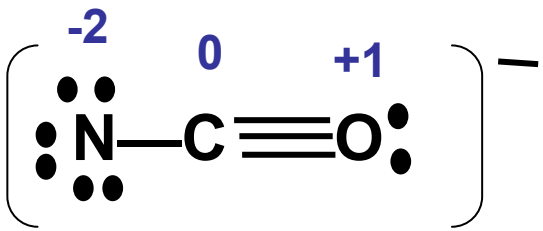
Most plausible structure (2 double bonds, 4 lone pairs)

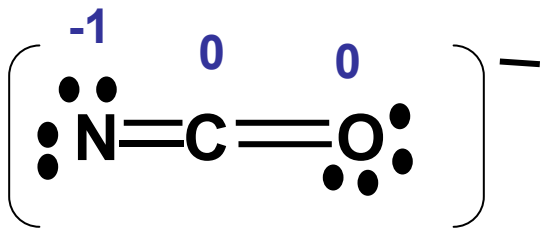


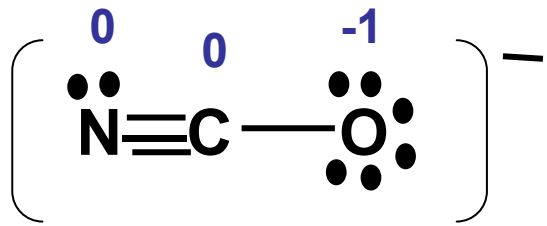
Less plausible structure (single and triple bonds, 4 lone pairs)

Formal Charge

- The most stable structure has:
- the lowest possible formal charge on each atom,
  - the most negative formal charge is on the most electronegative atoms.



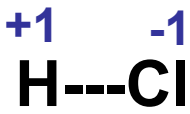




Most stable

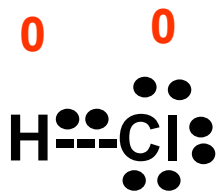
Oxidation numbers, formal charges and actual partial charges

Oxidation numbers



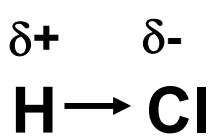
Overestimate the role of electronegativity

formal charges

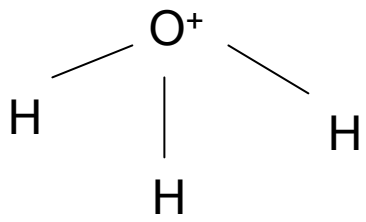


Ignore the role of electronegativity

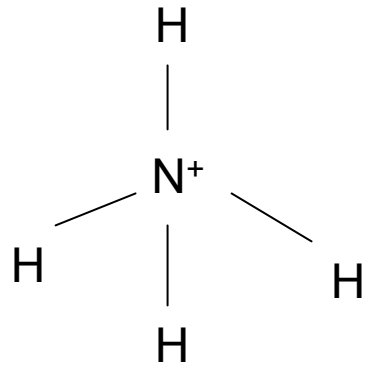
actual partial charges



Lewis structure for the hydronium ion

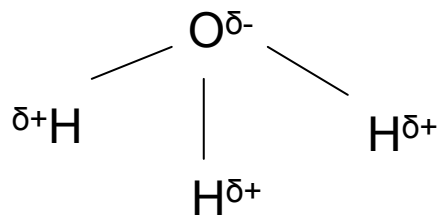


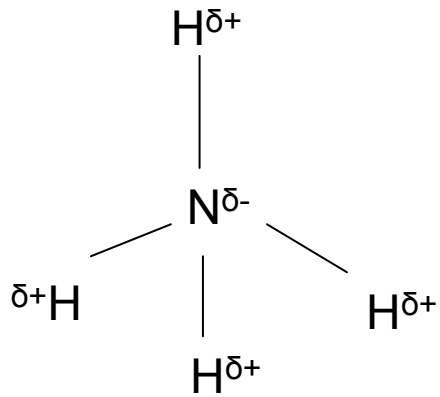
Lewis structure for the ammonium ion



In fact

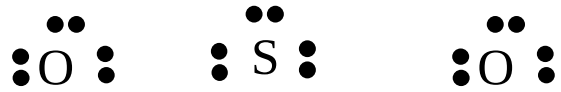
Partial real charges





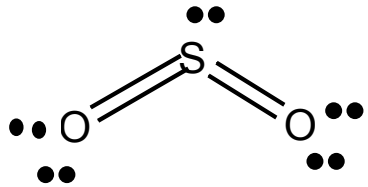
Resonance Structures

Draw Lewis Structure for SO_2 : 3x6=18e

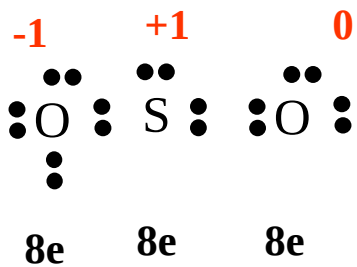


Check octet rule

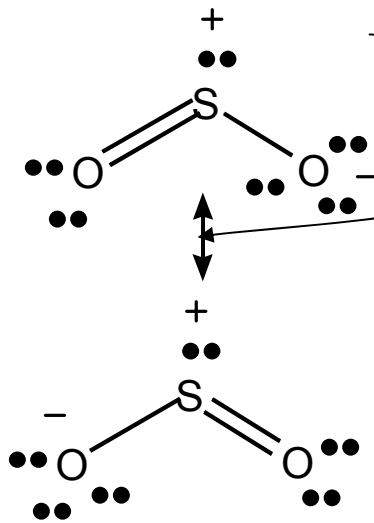
Octet rule not satisfied

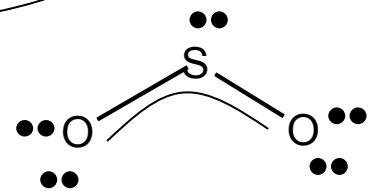


Sign of resonance

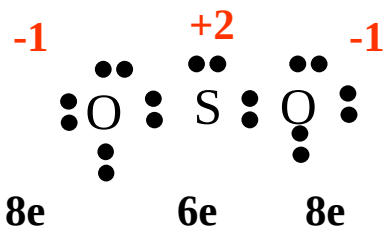


Octet rule satisfied

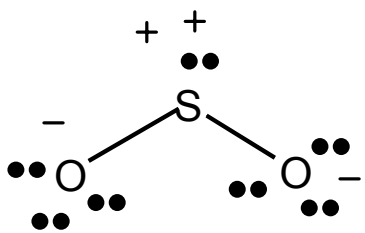




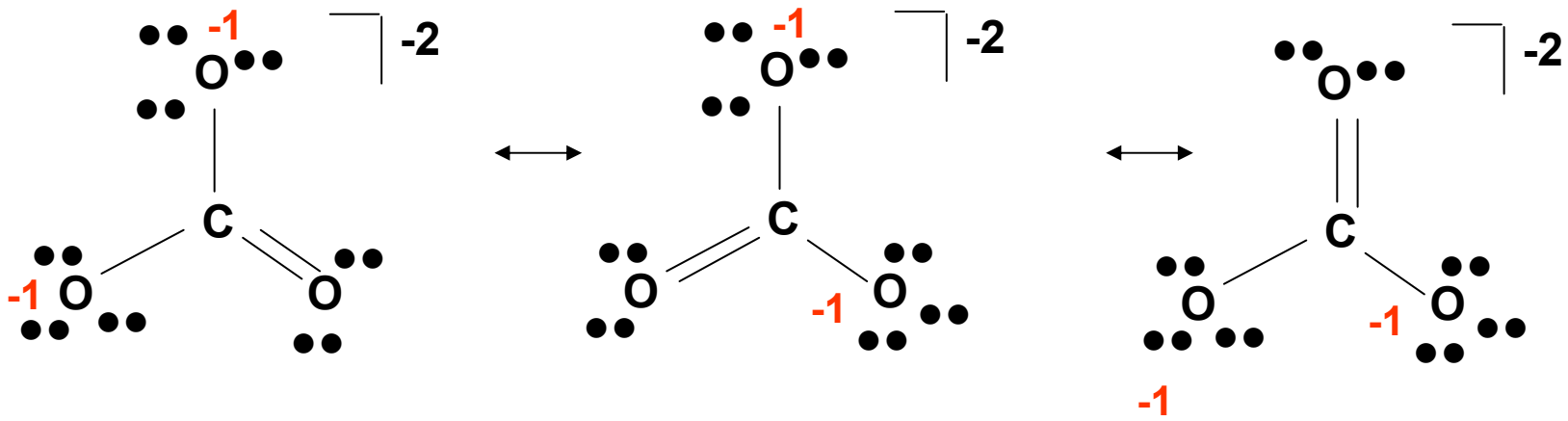
Resonance structure



Octet rule not satisfied



CO_3^{2-}



All C-O bonds are of the same length: slightly shorter than typical single C-O bond and longer than typical C=O double bond

Real charge (2-) is evenly distributed over the oxygen atoms

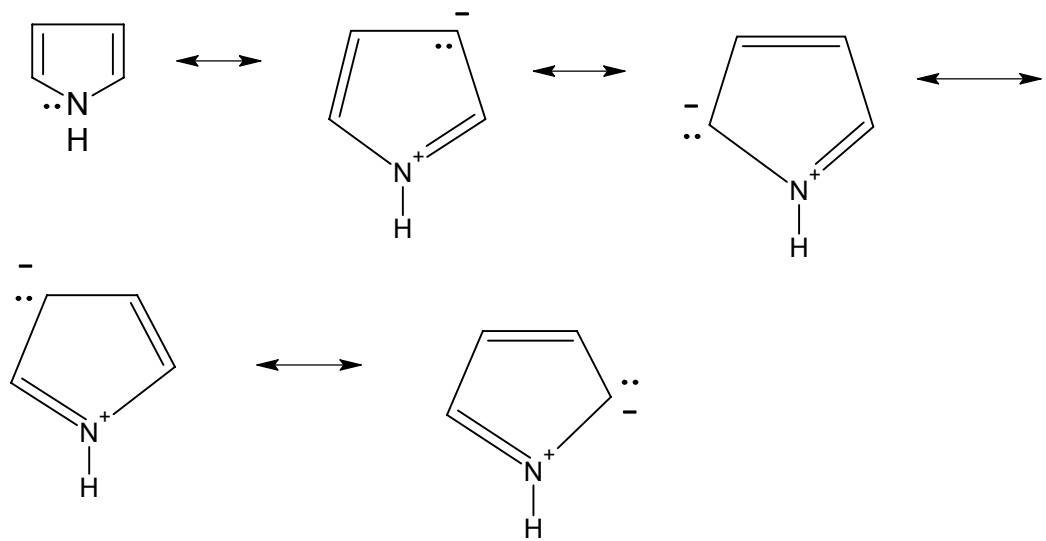
The electron pair of the C=O double bond is also evenly distributed or DELOCALIZED over the system.

Delocalization of electrons STABILIZES the system.

Thus, presence of resonance structures indicates stability

Resonance structures in organic chemistry

Resonance of pyrrole



The more resonance Lewis structures we could draw- the more stable the compound.

Exceptions to the Octet Rule

There are three classes of exceptions to the octet rule:

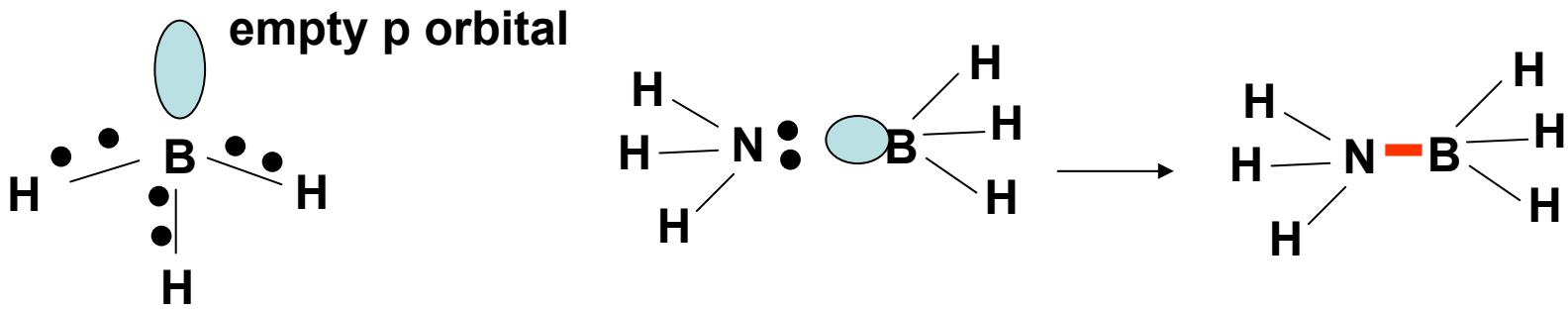
- Molecules with an odd number of electrons;
- Molecules in which one atom has less than an octet;
- Molecules in which one atom has more than an octet.

Odd Number of Electrons

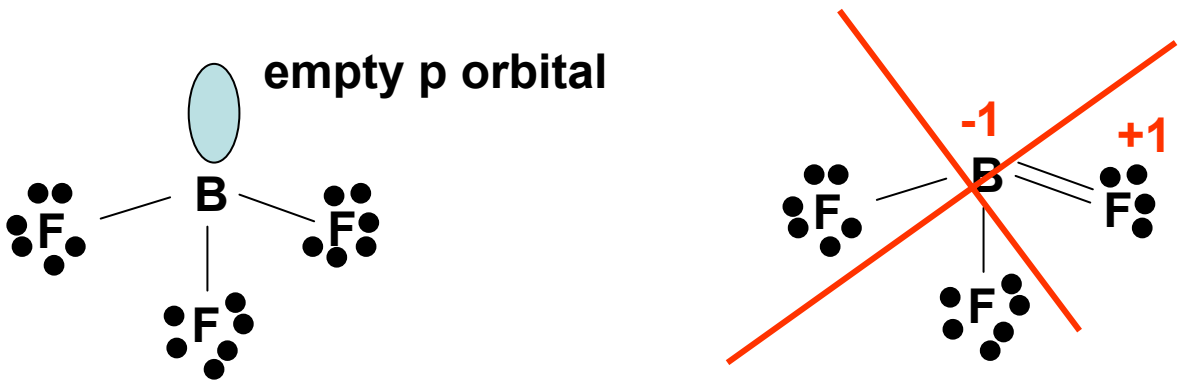
- Few examples. Generally molecules such as ClO_2, NO, and NO_2 have an odd number of electrons.

Less than an Octet

- Relatively rare.
- Molecules with less than an octet are typical for compounds of Groups 1A, 2A, and 3A (electron deficient).



- Formal charges indicate that the Lewis structure with an incomplete octet is more important than the ones with double bonds.



In organic chemistry, carbon violates the octet rule.

Carbon might be electron deficient : carbocations

CH_3^+

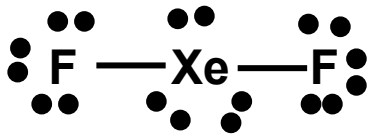
C^+ is electronic analog of B

More than an Octet

- **This is the largest class of exceptions.**
- **Atoms starting from the 3rd period can accommodate more than an octet.**
- **The vacant *d*-orbitals are low enough in energy to participate in bonding and accept the extra electron density.**

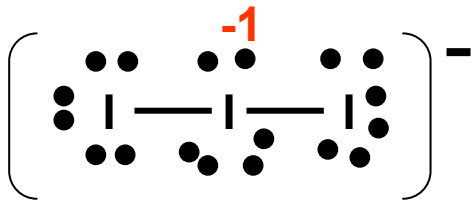
XeF_2, I_3^-, AsF_6^-

2(7e) + 8e = 22e,
11e pairs



Xe has 10 e around
– expanded octet

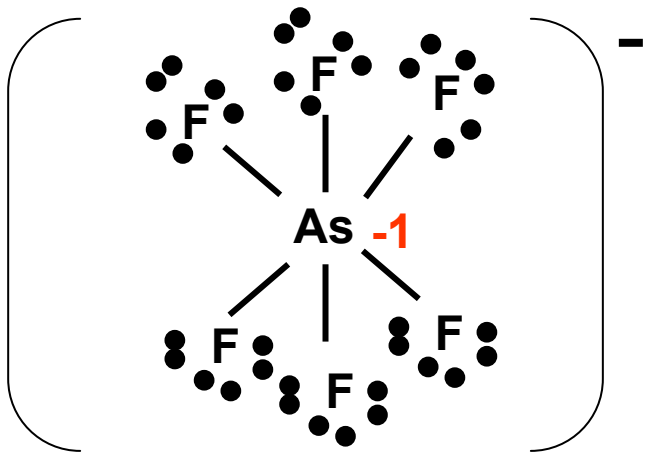
3(7e)+1 = 22e, 11e pairs



Central I has 10 e around
– expanded octet

6(7e) + 5e +1= 48e
24 e pairs

As has 12e around



Mini-quiz

1. {0.2} Count the number of valence electrons

2. {0.2} Draw the skeletal structure

3. {0.2} Draw the most plausible Lewis structure(s). Show resonance structures if exist.

4. {0.2} write formal charges on atoms

5. {0.2} write the number of lone pairs in the system

For the following structures:

N_2O

NO_2^-