Chapter 9 - Chemical Bonding

2 – Polyatomic Ions and Formal Charge

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Writing Lewis Structurs for Polyatomic Ions

Polyatomic ions have either extra electrons (anions) or less electrons (cations).

Writing Lewis structures for polyatomic ions needs proper steps or one can lose track of the number of electrons in the ion. We call this electronic bookkeeping.

Follow the steps below to get started.

1) Count ALL the valence electrons. Make sure to add electrons if anion and subtract if cation.
2) Find the central atom in the polyatomic ion and place it in the center with all the other atoms around it in a symmetrical manner. Join all terminal atoms to the central with one single bond. (*Subract electrons used from total*)
3) Use the shortcut to think if any terminal atoms and central atom can form multiple bonds (double or triple). If yes, then form the bonds. (*Subract electrons used from left over electrons*).
4) Add the lone electron on the terminal atom that has octet. (*Subract electrons used from left over electrons*).
5) See how many electrons are left after step 4. If structure looks symmetrical and it can be done, then divide all the remaining electrons equally on all the terminal atoms.

NOTE: You will have to remember that some elements e.g., S and P can have expanded shells.

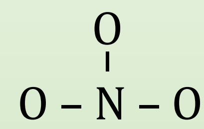
Solved Problem: Writing Lewis structure for polyatomic ions

What is the Lewis structure of NO_3^-?

1) Add all the valence electrons.

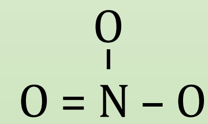
N – 1 x 5 = 5 e^-
O – 3 x 6 = 18 e^-
Anion 1 = 1 e^-
Total e = 24 e^-

2) Draw skeletal structure with central atom being the least electronegative. Subtract 2 for each bond in the skeletal structure.



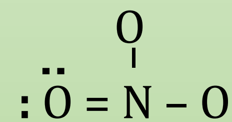
24 e^-
\- 6 e^-
18 e^-

3) Oxygen can have two bonds and nitrogen can have four. Add one double bond to complete electron octets for one oxygen.



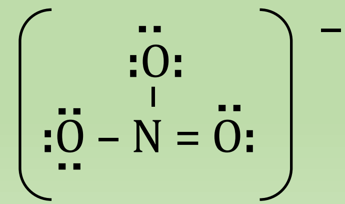
18 e^-
\- 2 e^-
16 e^-

4) Place lone electrons on one oxygen that has the double bond as that has the octet.



16 e^-
\- 4 e^-
12 e^-

5) Divide the 12 remaining electrons on the remaining two oxygens.



24 e^-

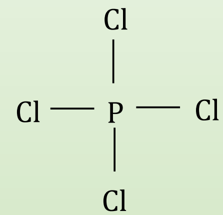
Solved Problem: Writing Lewis structure for polyatomic ions

What is the Lewis structure of PCl_4^+?

1) Add all the valence electrons.

$$\begin{array}{l} P - 1 \times 5 = 5\ e^- \\ Cl - 4 \times 7 = 28\ e^- \\ \text{Cation } -1 = -1\ e^- \\ \hline \text{Total e} = 32\ e^- \end{array}$$

2) Draw skeletal structure with central atom being the least electronegative. Subtract 2 for each bond in the skeletal structure.

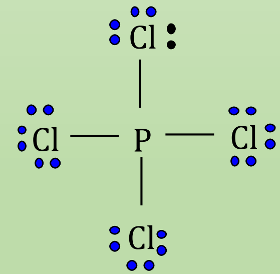


$$\begin{array}{r} 32\ e^- \\ -8\ e^- \\ \hline 24\ e^- \end{array}$$

3) Phosphorous can have 5 bonds but chlorine cannot have more than one bond if it is a terminal atom.

$24\ e^-/4 = 6\ e^-$

4) Divide the remaining 24 electrons equally on the four chlorines.



$32\ e^-$

Formal Charge

The electron surplus or deficit, assigned to an atom, in a Lewis structure.

Formal Charge = valence electrons - Number of bonding electrons/2 (OR *number of bonds*) - nonbonding electrons

Valence electrons (VE) are the electrons in the valence shell. They can be determined easily by seeing which group the element belongs to. (N is group V and has 5 valence electrons etc.).

Number of Bonding Electrons (BE) are the number of electrons bonded on the atom. Since each bond has 2 electrons, one belonging to each atom, just counting the number of bonds will give you the nummber bonding electrons on that atom.

Non-bonding electrons are the **lone electrons (LE)** on the atom left after all electrons have bonded.

NOTE: In general FC are +1, -1 and 0. It is very rare to have -2 or + 2.

Finally, formal charges are not "real" charges. They are assigned for determining where the electrons are on in molecules and ions.

Formal Charge – Example

Formal Charge (FC) =

valence electrons (VE)

\- bonding electrons (BE)

\- Lone electrons (LE)

Example: H_2O = $H:\underset{\cdot\cdot}{\ddot{O}}:H$

	H	O
VE	1	6
-BE	-1	-2
-LE	-0	-4
FC	0	0
TOTAL CHARGE = 2(0) + (0) = **0**		

Both hydrogens are same in water, so you don't have to calculate FC twice, but just make sure you account for them when you calculate the final charge.

<u>Stable compounds</u> are ones that have no formal charge.

In <u>polyatomic ions</u> the addition of all formal charges will result in the charge on the polyatomic ion.

In case of trying to determine which structure is more stable, then the structure in which fewer atoms have formal charge is more stable.

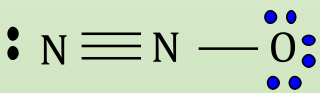
Solved Problem: Determining formal charge

Determine the formal charge on each atom in the following molecules.

N_2O and H_2SO_4

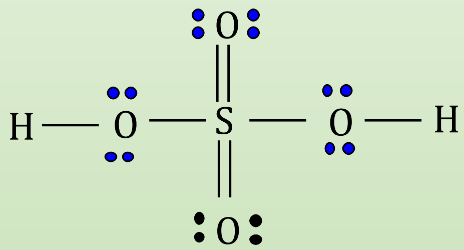
First draw the Lewis structures of all molecules. If this is wrong, then all else will be wrong.

My shorthand: FC = formal charge; VE = valence electrons; BE = bonding electrons; LE = lone electrons



	N	N	O
VE	5	5	6
-BE	-3	-4	-1
-LE	-2	-0	-6
FC	0	+1	-1

TOTAL CHARGE = (0) + (+1) + (-1) = **0**



	H	-O-	=O	S
VE	1	6	6	6
-BE	-1	-2	-2	-6
-LE	-0	-4	-4	-0
FC	0	0	0	0

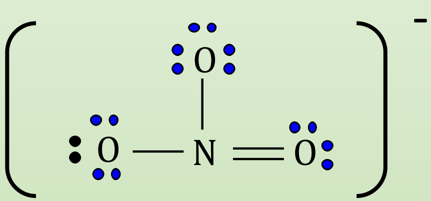
TOTAL CHARGE = 2(0) + 2(0) + 2(0) + (-0) = 0

Solved Problem: Determining formal charge

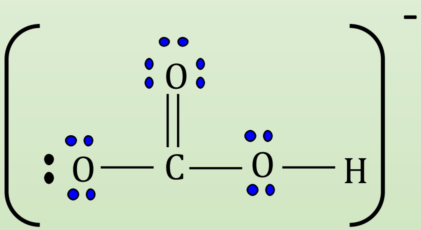
Determine the formal charge on each atom in the following polyatomic ions.

NO_3^-, HCO_3^-

First draw the Lewis structures of all molecules. If this is wrong, then all else will be wrong.



	-O	N	=O
VE	6	5	6
-BE	-1	-4	-2
-LE	-6	-0	-4
FC	-1	+1	-0
TOTAL CHARGE = 2(-1) + (+1) + (0) = **-1**			



	-O	C	=O	-O-	H
VE	6	4	6	6	1
-BE	-1	-4	-2	-2	-1
-LE	-6	-0	-4	-4	-0
FC	-1	0	0	0	0
TOTAL CHARGE = (-1) + (0) + (0) + (0) + (0) = **-1**					

Formal Charge - Stability

- A Lewis structure with *no* formal charges is usually better than one with formal charges.
- Small number of formal charges are generally better than large formal charges.
- Negative formal charges should be on the more electronegative atom(s).

Solved Problem: Determining the more stable structure

Write the correct structure of H_2CO using formal charges to support your answer

H C O H

or

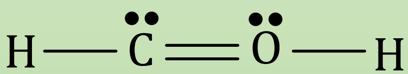
H

C O

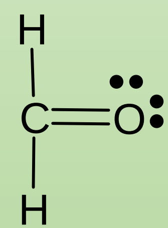
H

?

Answer:



	C	O
VE	4	6
-BE	-3	-3
-LE	-2	-2
FC	-1	+1



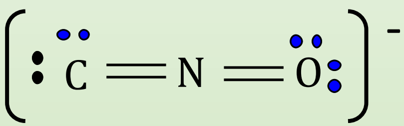
This structure is best because of **0** formal charges.

	C	O
VE	4	6
-BE	-4	-2
-LE	0	-4
FC	0	0

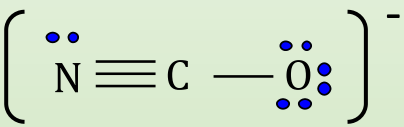
Solved Problem: Determining probable structure using formal charge

Calculate the formal charge for the two ions below and determine which of the following structures is likely to exist.

My shorthand: FC = formal charge; VE = valence electrons; BE = bonding electrons; LE = lone electrons



	C	N	O
VE	4	5	6
-BE	-2	-4	-2
-LE	-4	-0	-4
FC	-2	+1	0
TOTAL CHARGE = (-2) + (+1) + (0) = **-1**			



	N	C	O
VE	5	4	6
-BE	-3	-4	-1
-LE	-2	-0	-6
FC	0	0	-1
TOTAL CHARGE = (-0) + (+0) + (-1) = **-1**			

In the first structure more atoms have FC, whereas in the second structure only one atom has a FC, hence the second structure is more stable.

Formal Charge – Easy Way

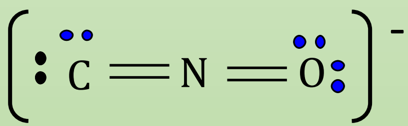
Most elements in their octet states have a 0 FC. For example: oxygen should have FC of 0 when it has two bonds.

Elements that have one more bond than octet have a +1 formal charge. Oxygen with three bonds will be +1.

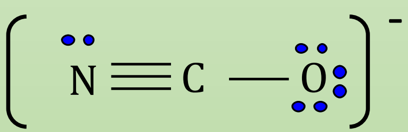
Elements that have one less bond than octet have a -1 FC. Oxygen with one bond will be -1.

Solved Problem: Using short cut to determine FC

Use the short cut to determine the formal charges in the atoms below



C has two less bonds – -2 FC
N has one extra bond - +1 FC
O has correct bonds – 0 FC



N has correct bonds - 0 FC
C has correct bonds – 0 FC
O has one less bond – -1 FC

Bond Strength and Bond Length

Bond strength is determined by how much energy it takes to break a bond. The greater the overlap of electrons the stronger the bond.

bond strength single < double < triple (strongest)

Bond length is also determined by the degree of overlap of electrons. The more the electrons overlap the shorter the bond.

bond length single > double > triple (shortest)

	N–N	N=N	N≡N
Bond Strength	163 kJ/mol	418 kJ/mol	941 kJ/mol
Bond Length	1.47 Å	1.24 Å	1.10 Å

Key Points

- Lewis structures of polyatomic ions.
- Formal charge
- Bond length
- Bond strength