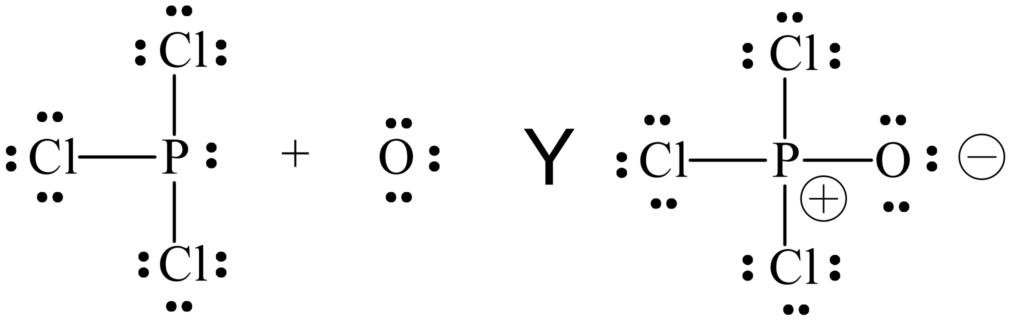
Formal Charge

In terms of "electron bookkeeping" of Lewis models, some bonds are formed by each atom contributing electrons.

no e^- gain or loss

In other cases one atom seems to be donating a pair of electrons to the other.



P “loses” 1e^- by sharing
O “gains” 1e^- by sharing

L Formal charges are the *hypothetical* charges atoms would have if all elements had the same electronegativity.

STEPS FOR ASSIGNING FORMAL CHARGES

1. Write the electron dot structure (Lewis dot model) for the compound or complex ion.

2. Count electrons about each atom by the following method:

   non-bonded pair (:) = 2

   bonded pair (–) = 1

   [Note: *This is not the same as the method used to determine octets in constructing Lewis dot models*.]

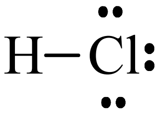
3. Compare the number of electrons counted in this manner with the number of valence electrons the isolated neutral atom would have.

4. If the count is higher than for the neutral atom, assign a negative formal charge equal to the difference. Write the formal charge inside a circle next to the atom (e.g., Ö).

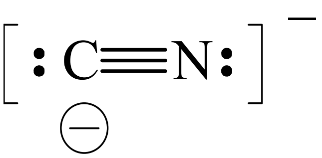
5. If the count is lower than for the neutral atom, assign a positive formal charge equal to the difference. Write the formal charge inside a circle next to the atom (e.g., ¾).

6. The algebraic sum of all positive and negative formal charges for a neutral molecule should be zero. For a complex ion, it should equal the net charge on the ion.

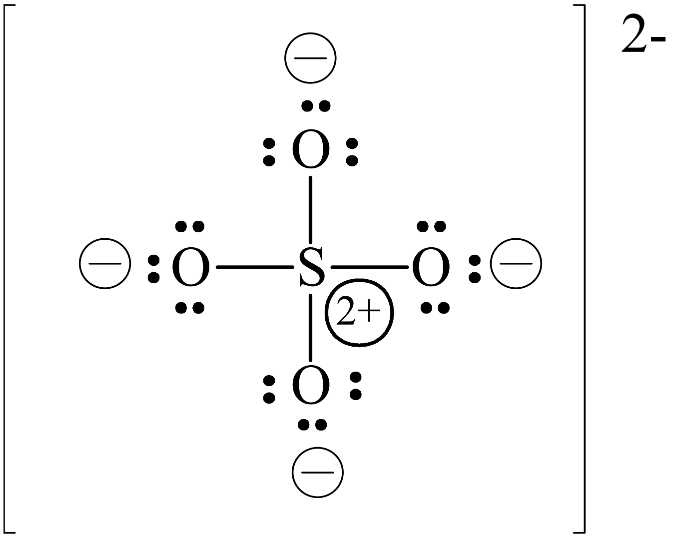
Examples of Formal Charge Assignments



No formal charges



Negative formal charge on carbon



Negative formal charge on O's; 2+ formal charge on S. Charge on the ion is the sum of the formal charges. Negative ion charge resides on oxygen atoms.

Formal Charges for Determining the "Best" Lewis Structure

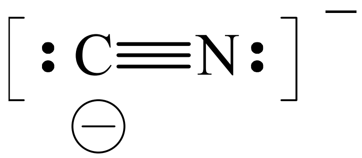
When trying to decide among possible Lewis structures, those most conforming to the following criteria *probably* are most plausible:

1. All atoms have the smallest formal charges.

2. Negative formal charges are assigned to electronegative elements, and positive charges are assigned to electropositive elements.

3. Adjacent atoms do not have the same formal charge, if a structure that avoids this can be drawn.

4. The preceding guidelines do not apply if there is no other plausible model (e.g., CN^-).



$$\left[:\underset{\ominus}{C}{\equiv}N: \right]^-$$

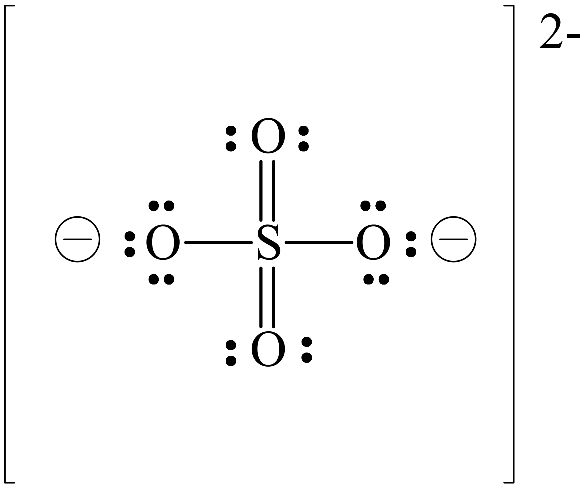
(OK to assign S to carbon, even though nitrogen is more electronegative.)

Arbitrary Hypervalence

L Do not expand valence in an attempt to minimize formal charges if a structure that obeys the octet rule can be drawn.

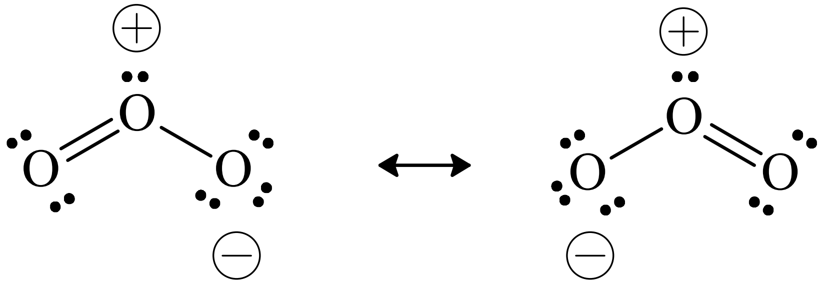
- Drawing hypervalent structures in such cases implies use of *d* orbitals by the central atom, which are generally not available for significant participation in bonding with non-transition elements.

Example: The following structure (shown in many books) is *not* reasonable, even though the formal charges have been minimized.



Resonance

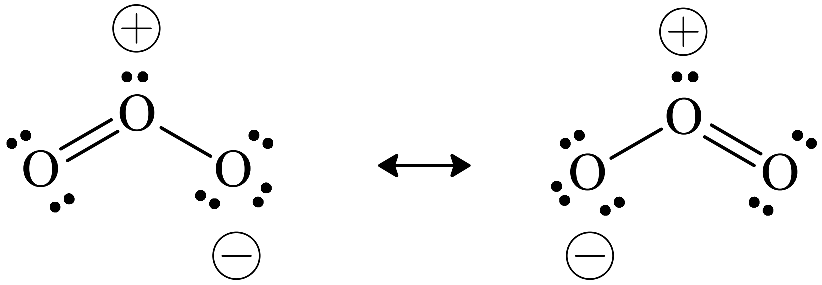
- Structures that cannot be adequately described by a single Lewis structure are sometimes better represented as the average of two or more *hypothetical* extreme models, called **resonance forms** or **canonical forms**.



ozone, $O_3(g)$

- Canonical forms are not real; i.e., they do not represent the true state of the molecule at any time in its lowest overall energy state (ground state).

Resonance Forms with Multiple Bonds



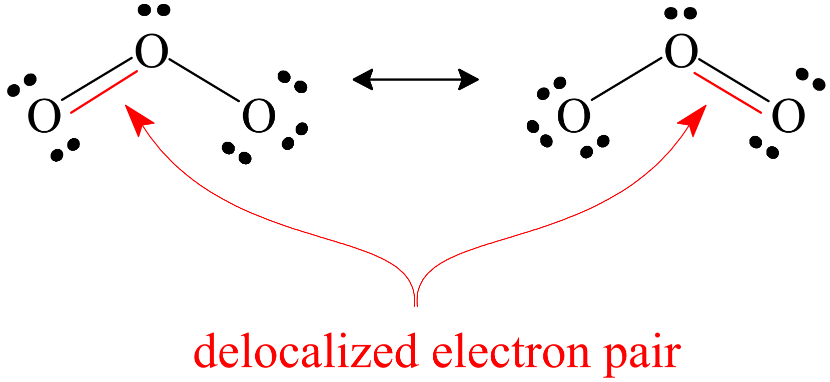
L Molecules represented by resonance forms in which one or more multiple bonds are shown on various atom pairs across the several forms do not have these multiple bonds at any time in their ground states.

- The ozone molecule (O_3) does not have double bonds!

L Electrons used to form "multiple bonds" across several resonance forms are *delocalized* across all the bonds in which they appear over the various resonance forms.

- Delocalized electrons add strength to the bonds.
- Each O-O bond in ozone effectively involves 1½ electron pairs, making an approximate bond order (B.O.) of 1½.

Delocalization and Bond Parameters

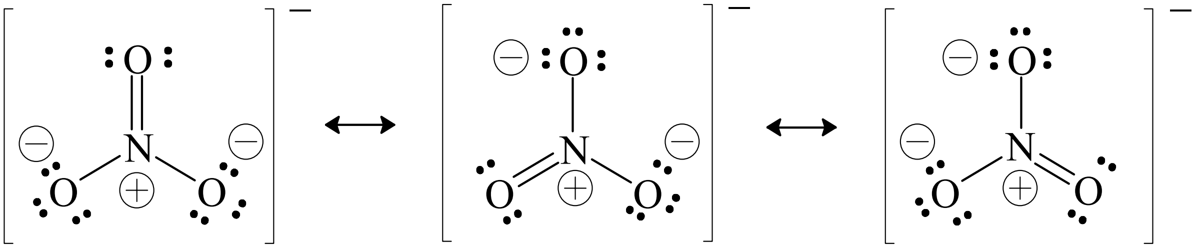


Molecule	O-O B.O.	Length (Å)	*D* (kJ/mol)
H_2O_2	1	1.49	138
O_3	1½	1.28	300
O_2	2	1.21	496

L For resonance hybrids for which all forms contribute equally

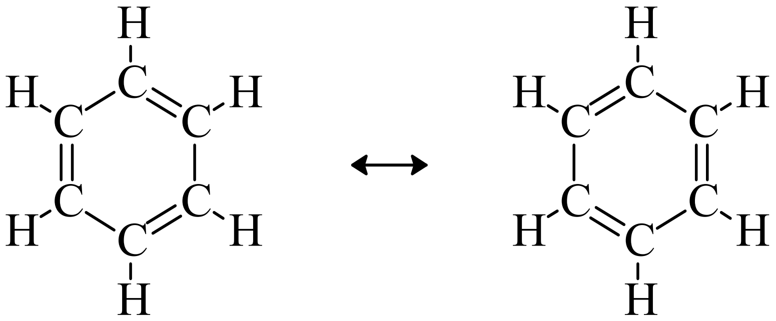
$$\text{B.O.} = \frac{x \text{ bond pairs}}{y \text{ equivalent bonds}}$$

Examples of Resonance Hybrids
Nitrate Ion



N-O B. O. = 1⅓

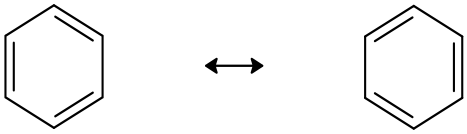
Examples of Resonance Hybrids
Benzene

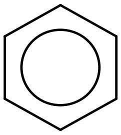


C-C B.O. = 1½

C-C B.O.	$d_{\text{C-C}}$ (Å)
1	1.54
1½	1.40
2	1.34

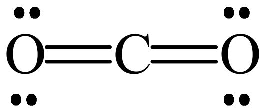
Alternative representations:





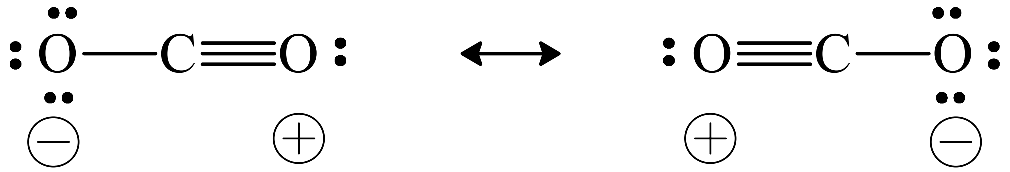
Examples of Resonance Hybrids
Carbon Dioxide

- The CO_2 molecule would seem to be adequately represented by the following Lewis structure:



- The C=O bond in CO_2 is 1.15 D, shorter than a "normal" C=O double bond (1.22 D).

C The shorter bond can be rationalized by including the following two lesser resonance forms:



Guidelines for Drawing Resonance Forms

1. Draw all resonance structures (canonical forms) with exactly the same geometry, the same atom-pair linkages, and the same orientation on the page.

2. Do not move atoms from form to form. Only bonds to the same atoms change from form to form.

3. Where the "octet rule" is observed, all forms obey it. (Do not arbitrarily introduce hypervalent forms.)

4. The number of electron pairs must be the same across all forms.

5. Resonance forms that minimize formal charges, minimize formal charge separations, and avoid placing like formal charges on adjacent atoms are more reasonable and will be greater contributors to the overall description of the molecule.

6. **Remember: Resonance forms are not real states of the molecule.** The average of all the hypothetical resonance forms is *suggestive* of the actual electron distribution across the molecule.