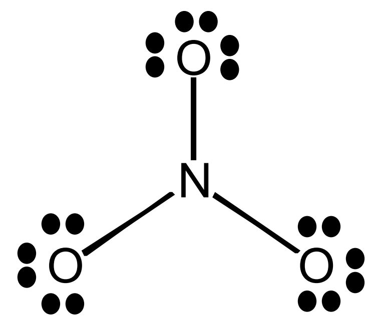
9.8 Resonance and Formal Charge

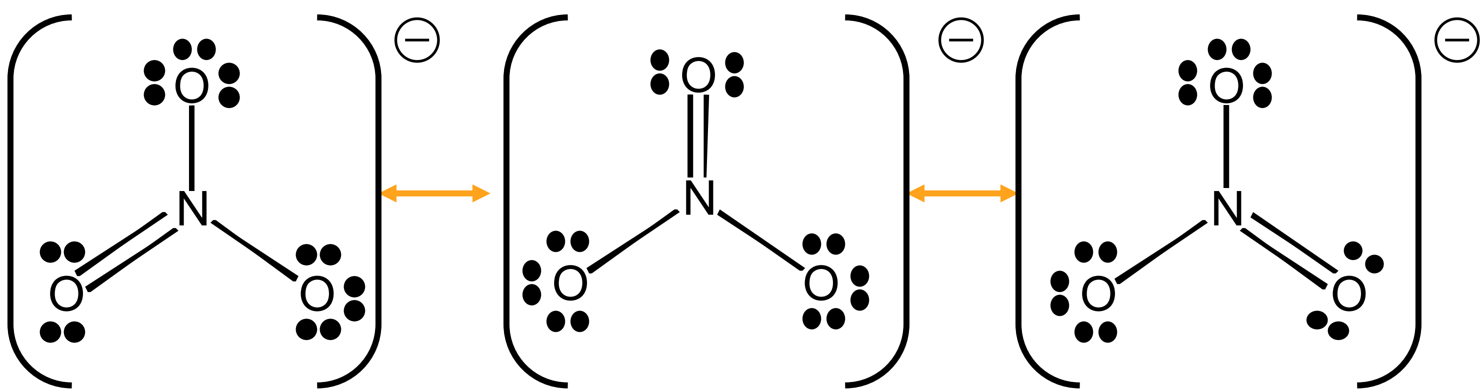
- Sometimes a molecule must be represented by two or more equivalent Lewis structures, called **resonance structures**:
- Example: ozone, O_3:

- Resonance structures have the same placement of atoms, and only differ in the locations of bonds and lone pairs.
- The resonance structures of a compound are **not** interconverting, but rather show different contributions to the true structure, which is a **hybrid** of the resonance structures.

Another example of Resonance Structures:

The nitrate ion, NO_3^-:





- Average N–O bond is a 1 ⅓ bond

Formal Charge

- The resonance structures of a molecule are not always equivalent. **Formal charges** can help us determine which one is best.
- Formal charge is the charge that an atom would have if one electron in a bond was assigned to each atom.

- To calculate the formal charge of an atom:

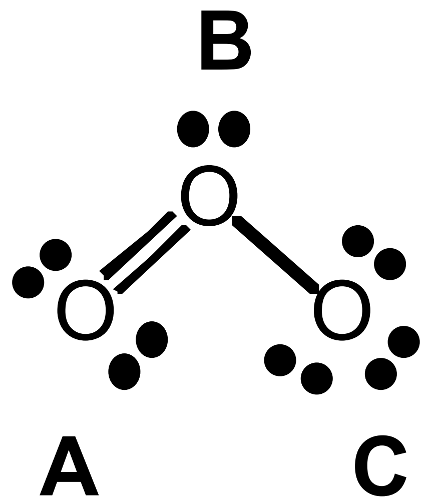
Formal Charge =

$$\text{\# of valence electrons} - \left[\text{\# of unshared electrons} + \tfrac{1}{2}\,\text{\# of shared electrons}\right]$$

- The sum of the formal charges of all of the atoms in a molecule must equal **zero** (or the charge for a polyatomic ion)

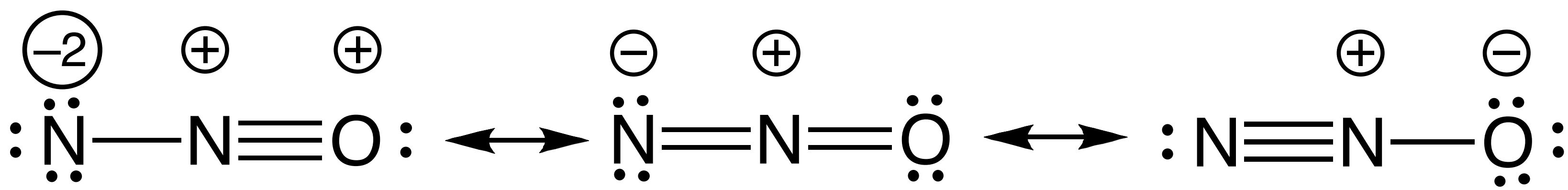
Formal Charge (contd.)

- Example: Assign formal charges to each atom in ozone.



Choosing the Best Lewis Structure:

- The resonance structures of a molecule may not all be equivalent:



- The best Lewis structure has:

1. Minimal formal charges (ideally all zero).
2. If formal charges are unavoidable, a negative formal charge should go on the most electronegative atom.

9.9 **Exceptions to the Octet Rule**

(1) Molecules with too few electrons:

- *e.g.* BH_3 (6 valence electrons)

Exceptions to the Octet Rule **(contd.)**

(2) **Radicals** – substances with an odd number of electrons.

- *e.g.* NO (11 valence electrons)

Exceptions to the Octet Rule **(contd.)**

(3) Expanded octets:

- Atoms in the third period (P, S, etc…) or below can be surrounded by more than eight electrons.
- Elements in the second period (C, N, O etc…) **never** have an expanded octet.
- Examples: PF_5, SF_6

Expanded Octets (contd.)

- Some molecules with an expanded octet will have one or more lone pairs on the central atom.

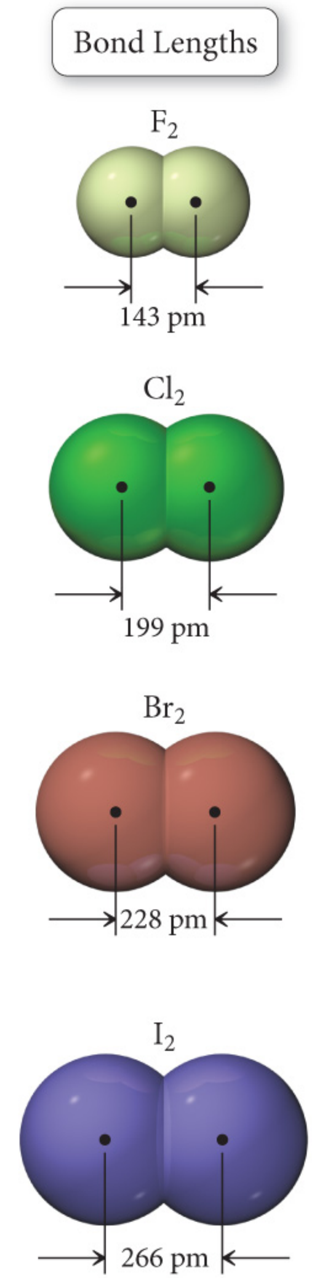
  e.g. BrF_5:

9.10: Bond Lengths and Strengths

- A **bond length** is the distance between the two nuclei in a chemical bond.
- Bond lengths increase as the atoms become larger, *e.g.* $F_2 < Cl_2 < Br_2 < I_2$
- Shorter bonds are usually **stronger** and longer bonds **weaker** (p.413).

Bond	Bond Length (pm)	Bond Strength (kJ/mol)
N—F	139	272
N—Cl	191	200
N—Br	214	243
N—I	222	159

- The **bond energy (BE)** is the energy required to break a chemical bond:



Bond Energy (contd.)

- As the **bond order** increases from single to double to triple, more electrons are involved in the bonding, so the bond becomes shorter and stronger.
  - BE increases: single < double < triple

Bond	Bond Length (pm)	Bond Strength (kJ/mol)
C≡C	120 pm	837 kJ/mol
C═C	134 pm	611 kJ/mol
C—C	154 pm	347 kJ mol

Bond Energies and ΔH_{rxn}

ΔH for a reaction can be considered to be the difference between the bond energies of the reactants and those of the products.

- If the products have stronger bonds than the reactants, the reaction will be **exothermic**.
- If the products have weaker bonds than the reactants, the reaction will be **endothermic**.
- **Fuels** are substances with relatively weak bonds that can be converted to products with stronger bonds, releasing energy.
- Bond energies can be used to calculate ΔH_{rxn} for reactions in the gas phase:

$$\Delta H_{rxn} = \Sigma\ \mathrm{BE}(\text{bonds broken in reactants}) - \Sigma\ \mathrm{BE}(\text{bonds formed in products})$$

Example: Use bond energies to calculate ΔH_{rxn} for:

$$CH_4\,(g) + Cl_2\,(g) \rightarrow CH_3Cl\,(g) + HCl\,(g)$$

Figure 9.12 Estimating the Enthalpy Change of a Reaction from Bond Energies

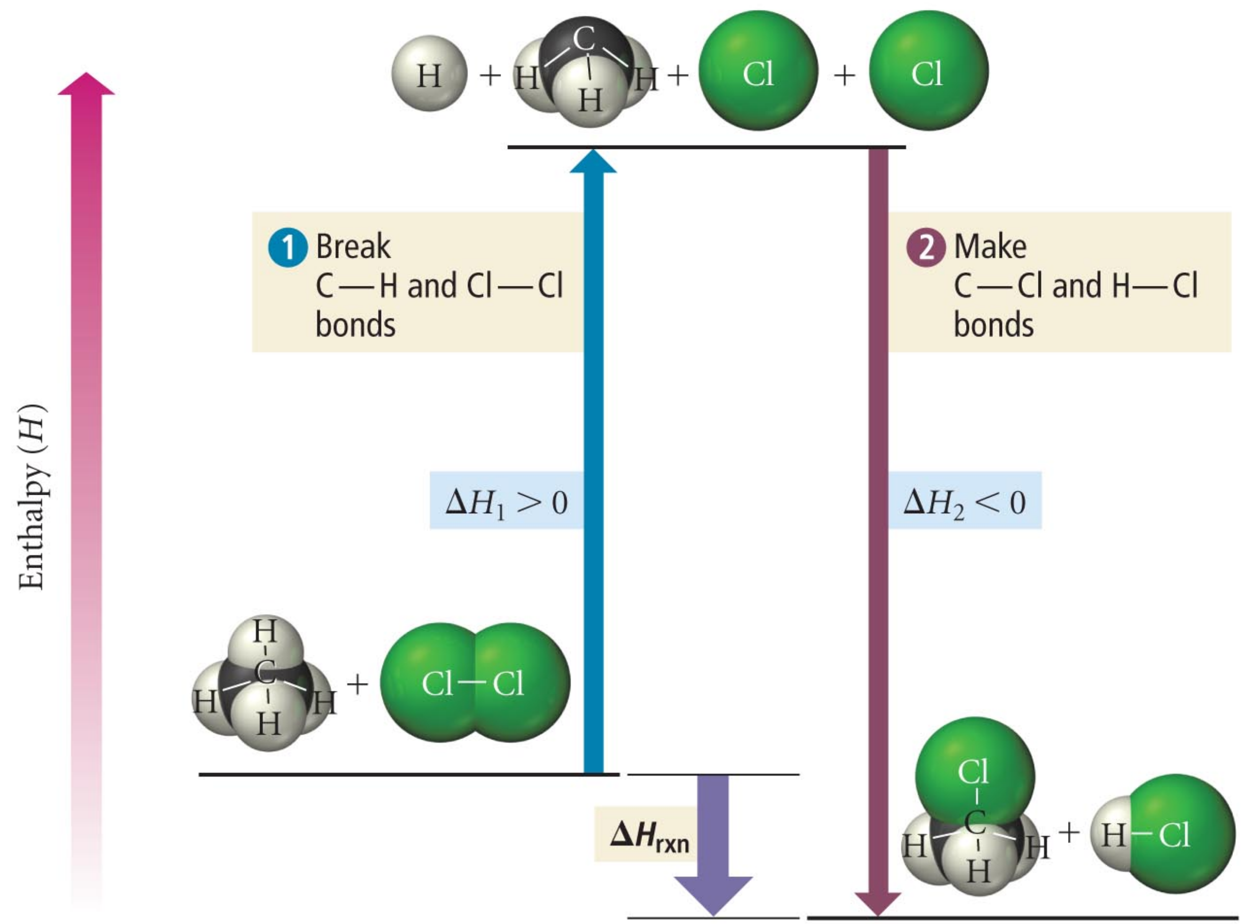


TABLE 9.3 Average Bond Energies

Bond	Bond Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)
H—H	436	N—N	163	Br—F	237
H—C	414	N=N	418	Br—Cl	218
H—N	389	N≡N	946	Br—Br	193
H—O	464	N—O	222	I—Cl	208
H—S	368	N=O	590	I—Br	175
H—F	565	N—F	272	I—I	151
H—Cl	431	N—Cl	200	Si—H	323
H—Br	364	N—Br	243	Si—Si	226
H—I	297	N—I	159	Si—C	301
C—C	347	O—O	142	S—O	265
C=C	611	O=O	498	Si=O	368
C≡C	837	O—F	190	S=O	523
C—N	305	O—Cl	203	Si—Cl	464
C=N	615	O—I	234	S=S	418
C≡N	891	F—F	159	S—F	327
C—O	360	Cl—F	253	S—Cl	253
C=O	736*	Cl—Cl	243	S—Br	218
C≡O	1072			S—S	266
C—Cl	339				

*799 in CO_2

Example: Use bond energies to calculate ΔH_{rxn} for:

$$CH_4\ (g) + Cl_2\ (g) \rightarrow CH_3Cl\ (g) + HCl\ (g)$$

Example: Use bond energies to calculate ΔH_{rxn} for:

$CH_4\ (g)\ +\ Cl_2\ (g)\ \rightarrow\ CH_3Cl\ (g)\ +\ HCl\ (g)$

Including **all** bonds: