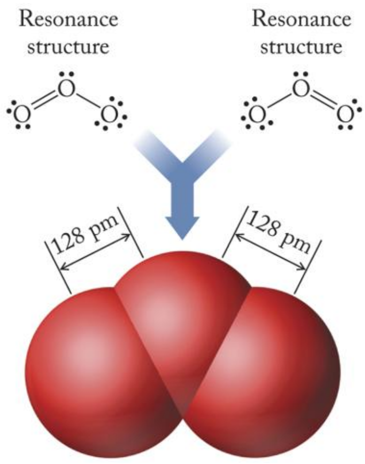
The Concept of "Resonance"

Resonance structures (or hybrids) = some molecules have two or more plausible Lewis structures. The actual structure is "intermediate" or an "average" of all the possibilities.

e.g. O_3

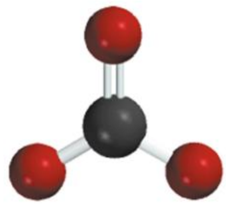
Resonance Structures: Ozone

- There are two plausible Lewis structures for ozone.
- The actual structure for O_3 is the "average" of the two resonance structures.



Resonance Structures: CO_3^{2-}

e.g. what are the resonance structures of the carbonate (CO_3^{2-}) ion?



Formal Charge and Lewis Structures

A way to decide which Lewis Structure, out of several possibilities, that's the most stable and therefore the most likely.

1. For neutral molecules, a Lewis structure in which there are no formal charges is preferable to one in which formal charges are present.
2. Lewis structures with large formal charges are less plausible than those with small formal charges.
3. Among Lewis structures having similar distributions of formal charges, the most plausible structure is the one in which negative formal charges are placed on the more electronegative atoms.

Calculating Formal Charge

formal charge on an atom in a Lewis structure	=	total number of valence electrons in the free atom	-	total number of nonbonding electrons	-	total number of covalent bonds

The sum of the formal charges of the atoms in a molecule or ion must equal the charge on the molecule or ion.

Formal charges are not real charges, but a useful tool to help decide the correct Lewis structure and it's stability.

Formal charges also help to determine which resonance structure is the most stable.

Sample Exercise 8.8

What is the most likely Lewis structure for CO_2?

Choosing the Most Stable Resonance Structure

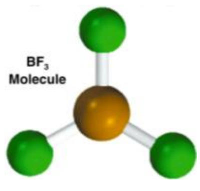
CO_2

N_2O

Exceptions to the Octet Rule

1. The Incomplete Octet (Central atom in Group 3A)

e.g. BF_3



Exceptions to the Octet Rule

2. *Odd-Electron Molecules* – "free radicals" (one unpaired electron = high reactivity)

NO

NO_2

Exceptions to the Octet Rule

3. Expanded Octet – central atom has greater than 8 valence electrons surrounding it. Occurs only with elements in row 3 and higher because they have available d-orbitals

A. Covalent Molecules

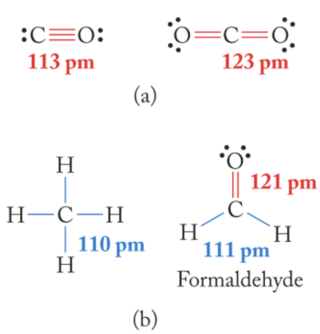
SF_6

Exceptions to the Octet Rule

B. Polyatomic Ions

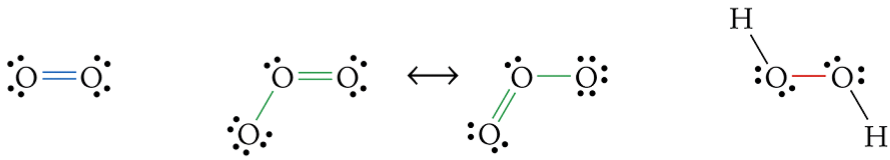
PO_4^{3-} SO_4^{2-}

The Lengths and Strengths of Covalent Bonds: Bond Length vs Bond Order



Bond	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
C-C	1	154	348
C=C	2	134	614
C≡C	3	120	839
C-N	1	143	293
C=C	2	138	615
C≡N	3	116	891

Resonance Structures have an intermediate bond order



121 pm | 128 pm | 148 pm

Bond order = 1.5

Bond order = 2

Bond order = 1

Table of Average Covalent Bond Lengths and Bond Energies – can be used to estimate ΔH_{rxn}

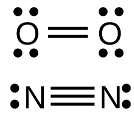
TABLE 8.2 Selected Average Covalent Bond Lengths and Bond Energies

Bond	Bond Length (pm)	Bond Energy (kJ/mol)	Bond	Bond Length (pm)	Bond Energy (kJ/mol)
C—C	154	348	N≡O	106	678
C═C	134	614	O—O	148	146
C≡C	120	839	O═O	121	495
C—N	143	293	O—H	96	463
C═N	138	615	S—O	151	265
C≡N	116	891	S═O	143	523
C—O	143	358	S—S	204	266
C═O	123	743[a]	S—H	134	347
C≡O	113	1072	H—H	75	436
C—H	110	413	H—F	92	567
C—F	133	485	H—Cl	127	431
C—Cl	177	328	H—Br	141	366
N—H	104	388	H—I	161	299
N—N	147	163	F—F	143	155
N═N	124	418	Cl—Cl	200	243
N≡N	110	941	Br—Br	228	193
N—O	136	201	I—I	266	151
N═O	122	607			

[a] The bond energy of the C═O bond in CO_2 is 799 kJ/mol.

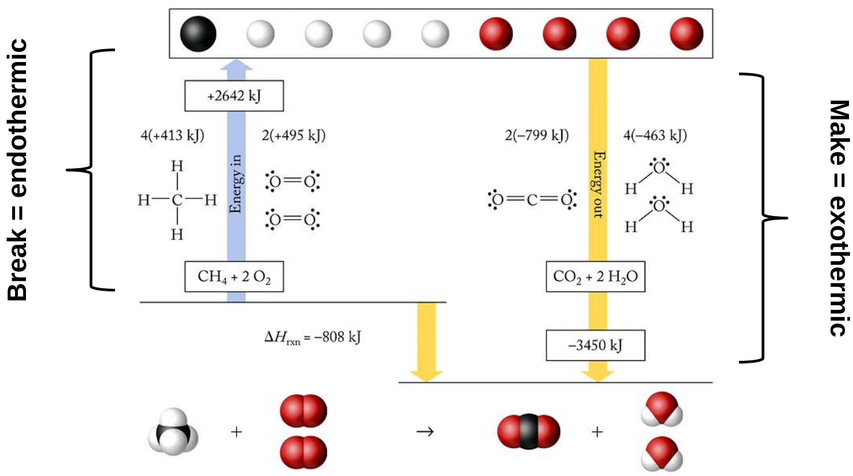
Bond energy = the average energy required to break a particular type of bond.

	Bond Energy
$H_{2\,(g)} \longrightarrow H_{(g)} + H_{(g)}$	$\Delta H^0 = 436$ kJ
$Cl_{2\,(g)} \longrightarrow Cl_{(g)} + Cl_{(g)}$	$\Delta H^0 = 243$ kJ
$HCl_{(g)} \longrightarrow H_{(g)} + Cl_{(g)}$	$\Delta H^0 = 431$ kJ
$O_{2\,(g)} \longrightarrow O_{(g)} + O_{(g)}$	$\Delta H^0 = 495$ kJ
$N_{2\,(g)} \longrightarrow N_{(g)} + N_{(g)}$	$\Delta H^0 = 941$ kJ



ΔH^0 = total energy input – total energy released

= ΣBE(reactants) – ΣBE(products)



e.g. $CH_4 + 2\,O_2 \rightarrow H_2O + 2\,CO_2$

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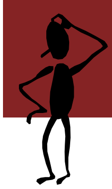
$\Delta H^0 = \sum BE(\text{reactants}) - \sum BE(\text{products})$

Type of bonds broken	Number of bonds broken	Bond energy (kJ/mol)	Energy change (kJ)

Type of bonds formed	Number of bonds formed	Bond energy (kJ/mol)	Energy change (kJ)



Use bond energies to calculate the enthalpy change for: $CH_4 + 2\,O_2 \rightarrow H_2O + 2\,CO_2$

$\Delta H^0 = \sum BE(\text{reactants}) - \sum BE(\text{products})$

Type of bonds broken	Number of bonds broken	Bond energy (kJ/mol)	Energy change (kJ)

Type of bonds formed	Number of bonds formed	Bond energy (kJ/mol)	Energy change (kJ)