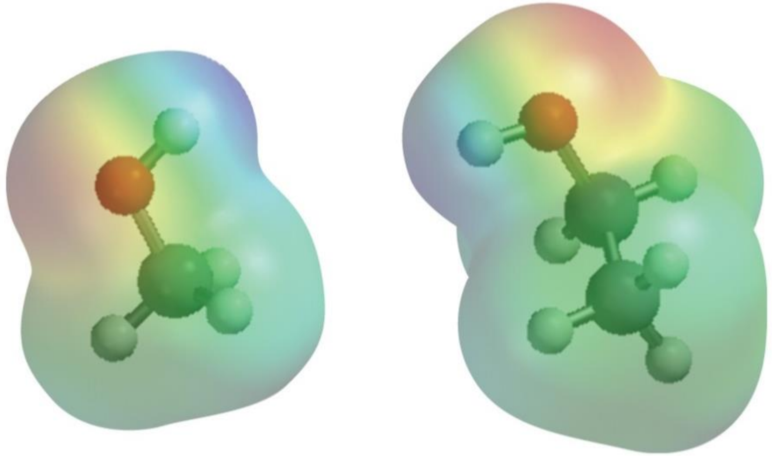
GENERAL CHEMISTRY I



Chapter 8
Basic Concepts of Chemical Bonding

Contents

What is a chemical bond?

- A **chemical bond** is the connection of different elements through the sharing, transferring or pooling of electrons.

Why do atoms bond?

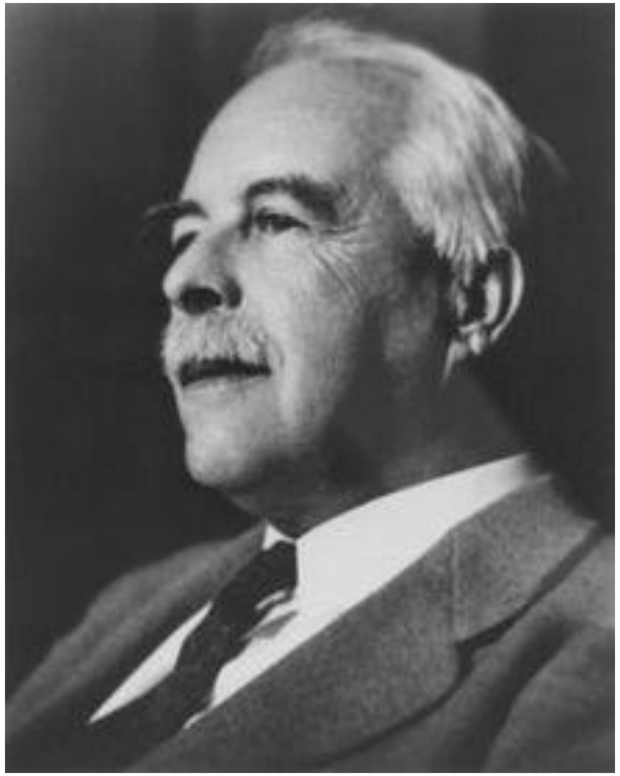
- ionic bonding **lowers** the potential energy between positive and negative ions
- covalent bonds form is to follow the **Octet rule**, in which the element is then surrounded by 8 valence electrons

How do atoms bond?

- An **ionic bond** involves the **transferring** of an electron from one element to another element.
- A **covalent bond** involves the **sharing** of electron(s) between elements.
- A **metallic "bond"** isn't really a bond. Think of electrons as being **loosely connected or "pooling"** on the surface of many metals.

8-1 Lewis Symbols and the Octet Rule

- Valence e^- play a fundamental role in chemical bonding.
- e^- transfer leads to *ionic bonds*.
- Sharing of e^- leads to *covalent bonds*.
- e^- are transferred of shared to give each atom a noble gas configuration
  - *the octet.*

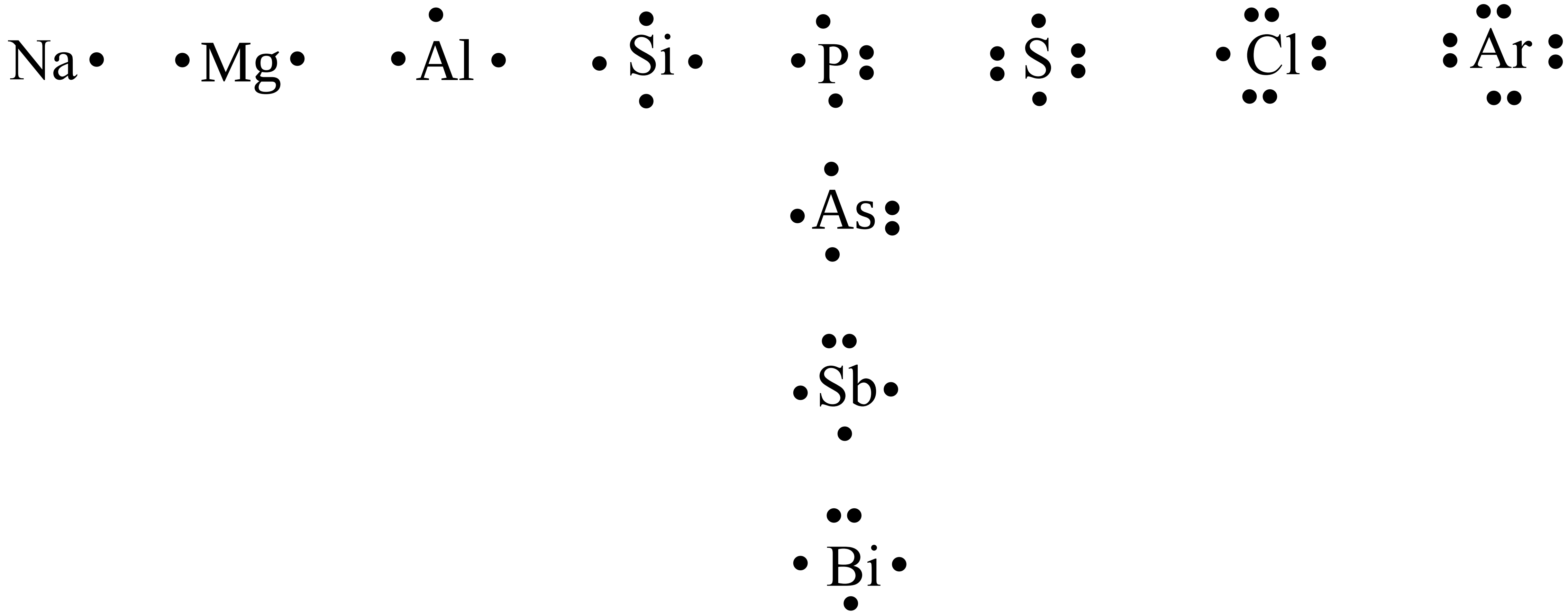


Gilbert Newton Lewis

(1875 – 1946)

Lewis Symbols

- A chemical symbol represents the nucleus and the *core* e^-.
- Dots around the symbol represent *valence* e^-.



The Octet Rule

- Atoms tend to gain, lose, or share electrons until they are surrounded by eight valence electrons.

Table 8.1 Lewis Symbols

Group	Element	Electron Configuration	Lewis Symbol	Element	Electron Configuration	Lewis Symbol
1A	Li	$[He]2s^1$	Li·	Na	$[Ne]3s^1$	Na·
2A	Be	$[He]2s^2$	·Be·	Mg	$[Ne]3s^2$	·Mg·
3A	B	$[He]2s^22p^1$	·Ḃ·	Al	$[Ne]3s^23p^1$	·Ȧl·
4A	C	$[He]2s^22p^2$	·Ċ̣·	Si	$[Ne]3s^23p^2$	·Ṩi·
5A	N	$[He]2s^22p^3$	·Ṇ̇:	P	$[Ne]3s^23p^3$	·Ṗ̣:
6A	O	$[He]2s^22p^4$	:Ọ̇:	S	$[Ne]3s^23p^4$	:Ṩ:
7A	F	$[He]2s^22p^5$	·F̤̈:	Cl	$[Ne]3s^23p^5$	·C̤̈l:
8A	Ne	$[He]2s^22p^6$	:N̤̈e:	Ar	$[Ne]3s^23p^6$	:Ä̤r:

8-2 Ionic Bonding

$$Na(s) + \tfrac{1}{2}Cl_2(g) \longrightarrow NaCl(s) \qquad \Delta H_f^\circ = -410.9\,\text{kJ}$$

$$Na\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \longrightarrow Na^+ + [:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:]^-$$

$$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g) \qquad \Delta H_{\text{lattice}} = +788\,\text{kJ/mol}$$

Table 8.2 Lattice Energies for Some Ionic Compounds

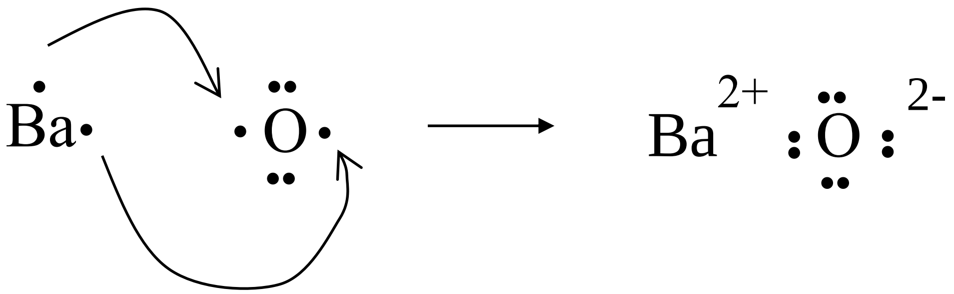
Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	$MgCl_2$	2326
LiCl	834	$SrCl_2$	2127
LiI	730		
NaF	910	MgO	3795
NaCl	788	CaO	3414
NaBr	732	SrO	3217
NaI	682		
KF	808	ScN	7547
KCl	701		
KBr	671		
CsCl	657		
CsI	600		

EXAMPLE

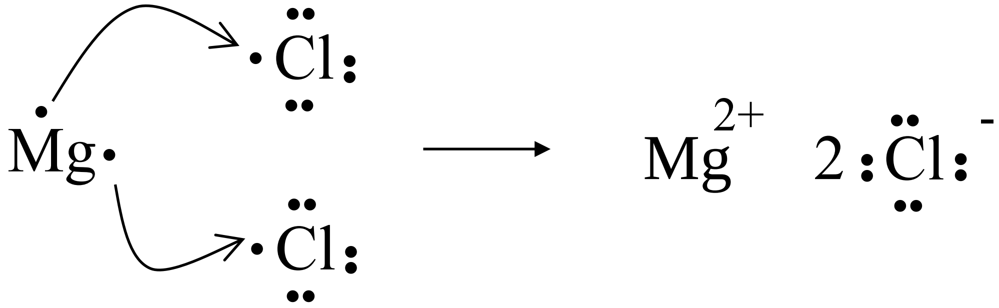
Writing Lewis Structures of Ionic Compounds.

Write Lewis structures for the following compounds: (a) BaO; (b) $MgCl_2$; (c) aluminum oxide.

BaO

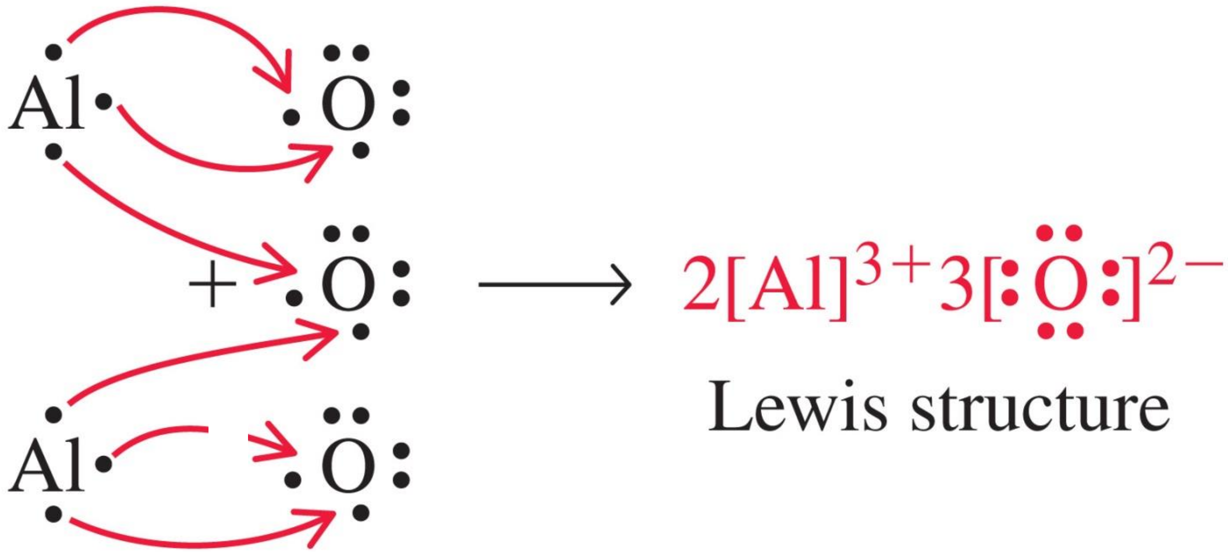


$MgCl_2$

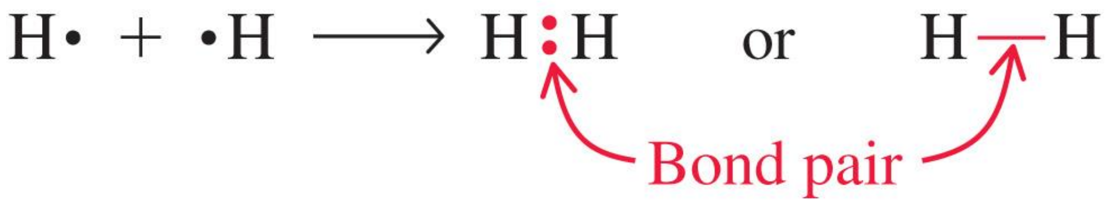


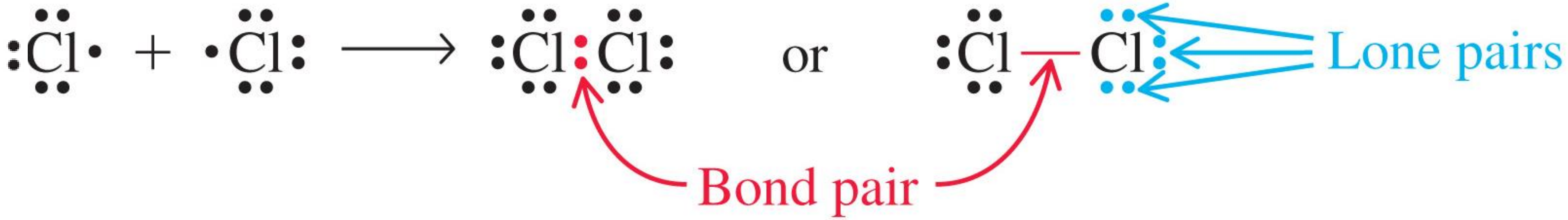
EXAMPLE

Al_2O_3



8-3 Covalent Bonding





water

dichlorine oxide

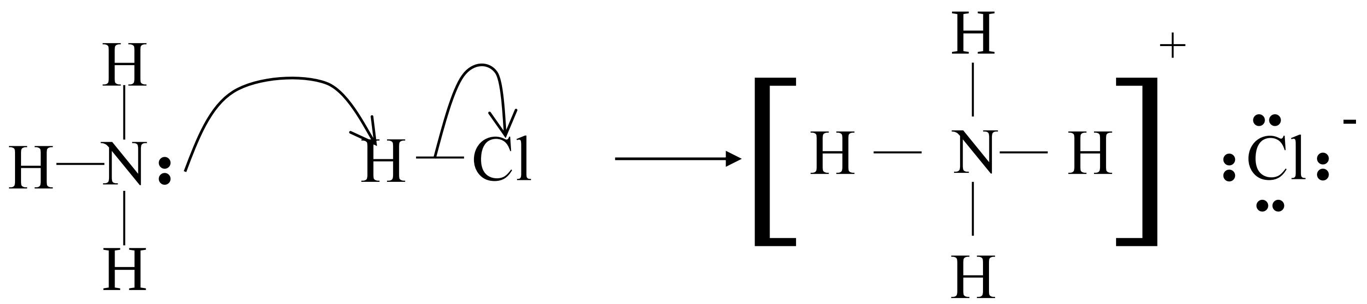
__2__ bond pairs

__2__ lone pairs

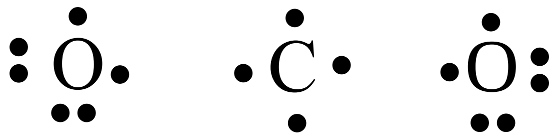
__2__ bond pairs

__8__ lone pairs

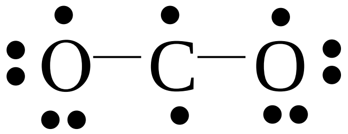
Coordinate Covalent Bonds



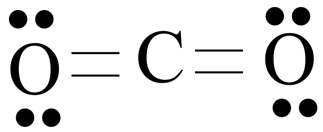
Multiple Covalent Bonds



6 valence e^- on O
4 valence e^- on C



7 e^- on O
6 e^- on C

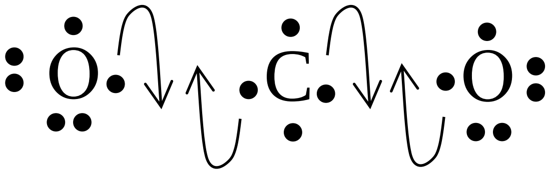


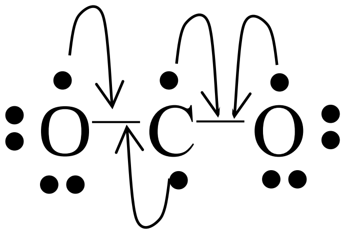
8 e^- on O
8 e^- on C

Satisfies the octet rule

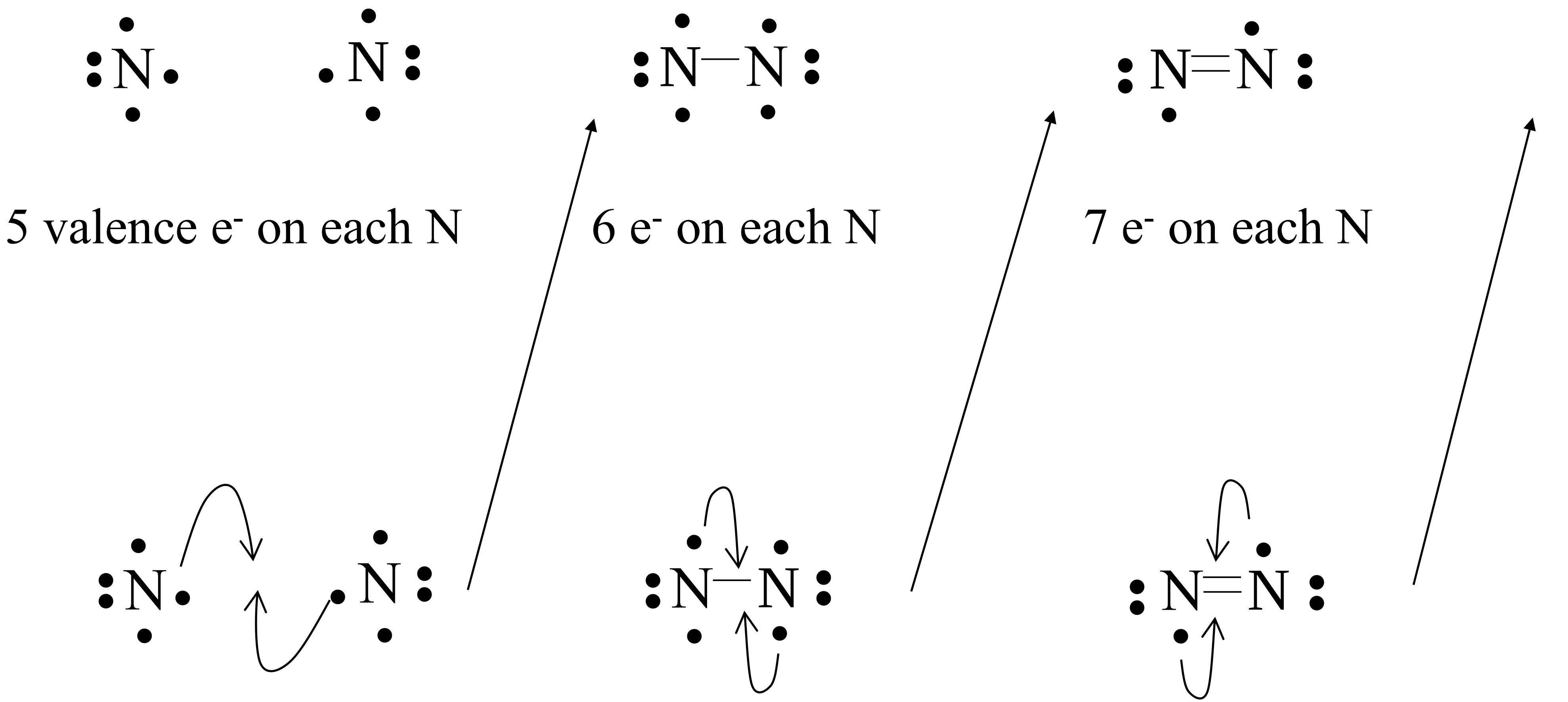
4 bond pairs (2 double bonds)

4 lone pairs





Multiple Covalent Bonds



Satisfies the octet rule

3 bond pairs

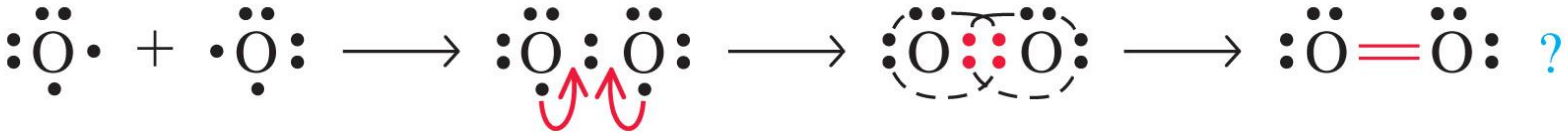
(one triple bond)

2 lone pairs

Quiz

Octet rule: https://forms.office.com/r/NbPSPDqkjR

Paramagnetism of Oxygen



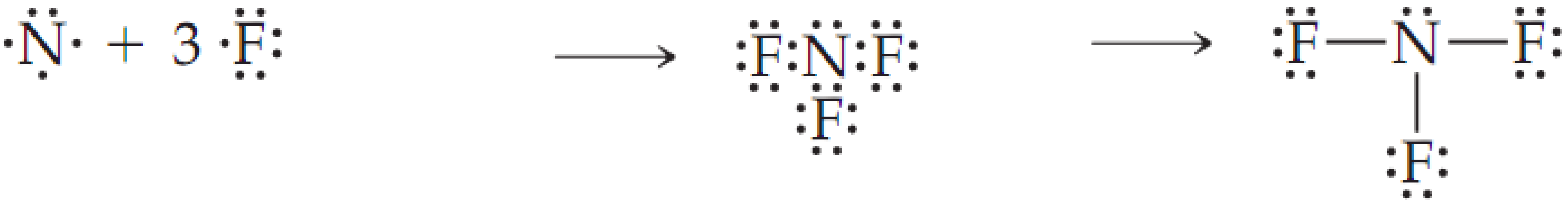
The Lewis structure of O_2 gives a misleading impression. It shows that all the electrons in oxygen are paired, so oxygen should be *diamagnetic*.

Yet oxygen **is** paramagnetic as it is attracted into a strong magnetic field (Oxygen has a weak magnetic property)

The correct explanation comes from **Molecular Orbital theory**.

EXAMPLE

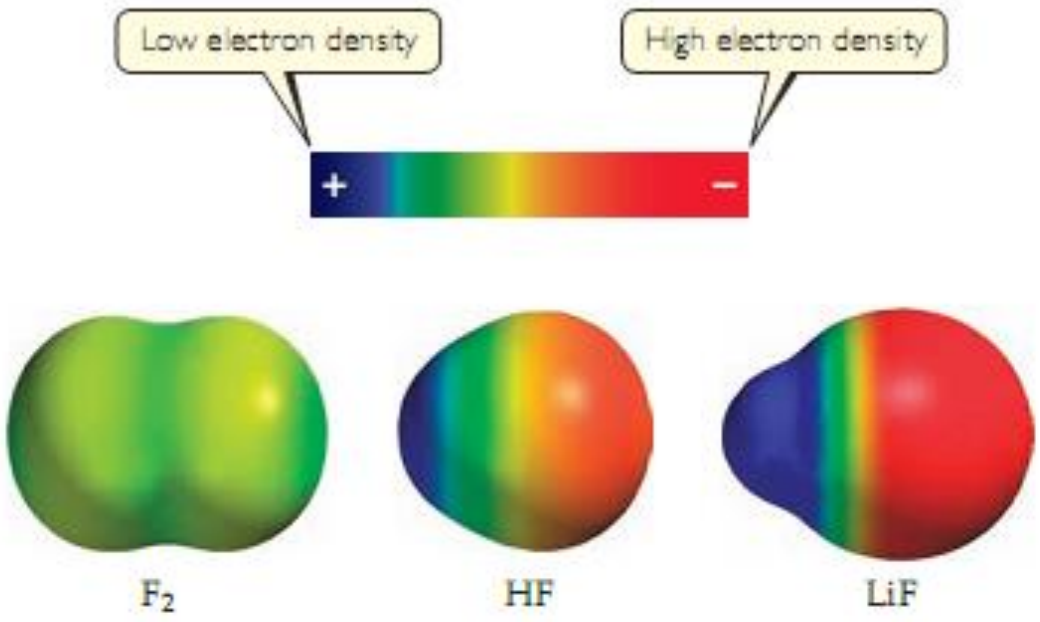
Given the Lewis symbols for nitrogen N and fluorine F , predict the formula of the stable binary compound (a compound composed of two elements) formed when nitrogen reacts with fluorine and draw its Lewis structure.

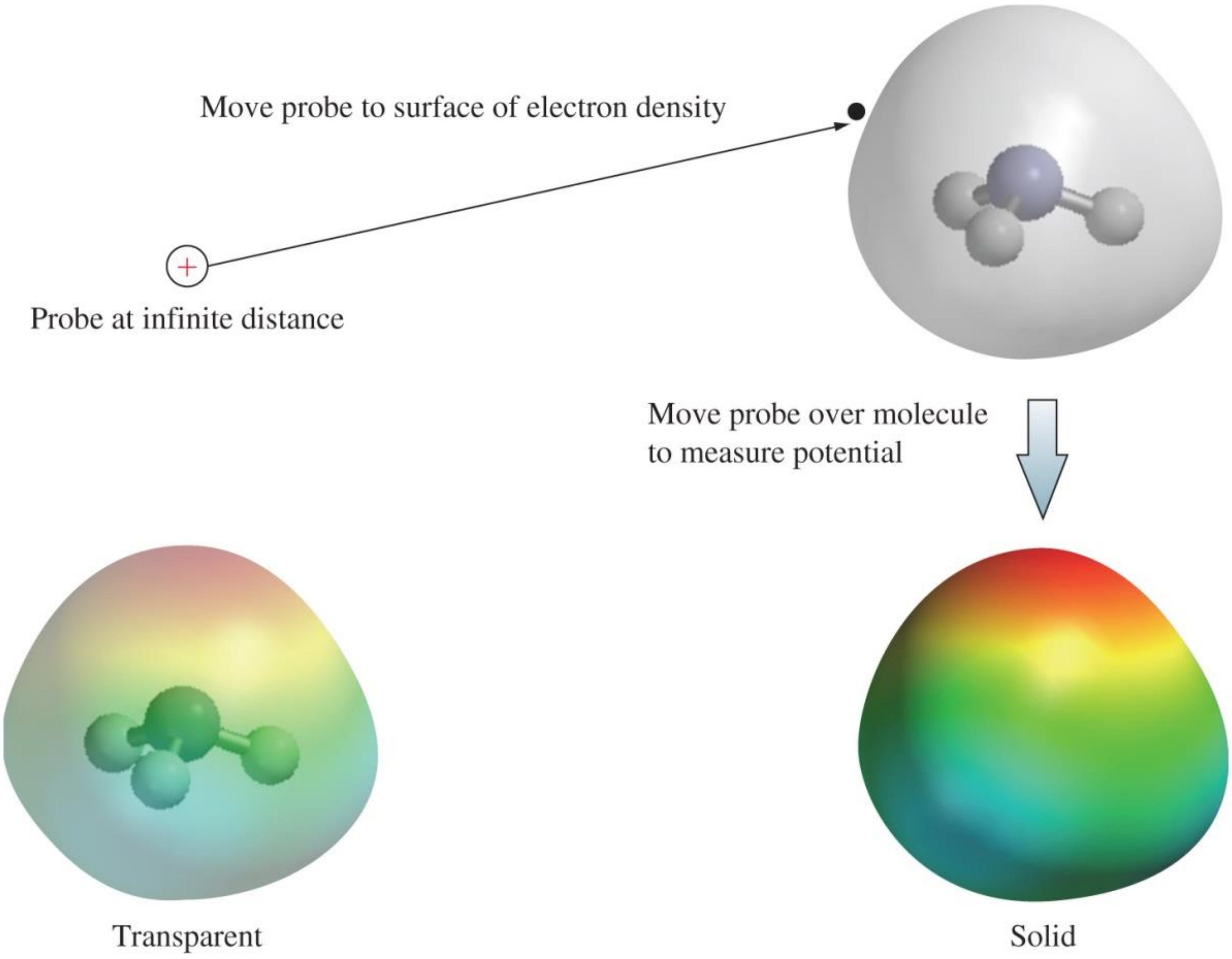


Nitrogen must share a pair of electrons with three fluorine atoms to complete its octet

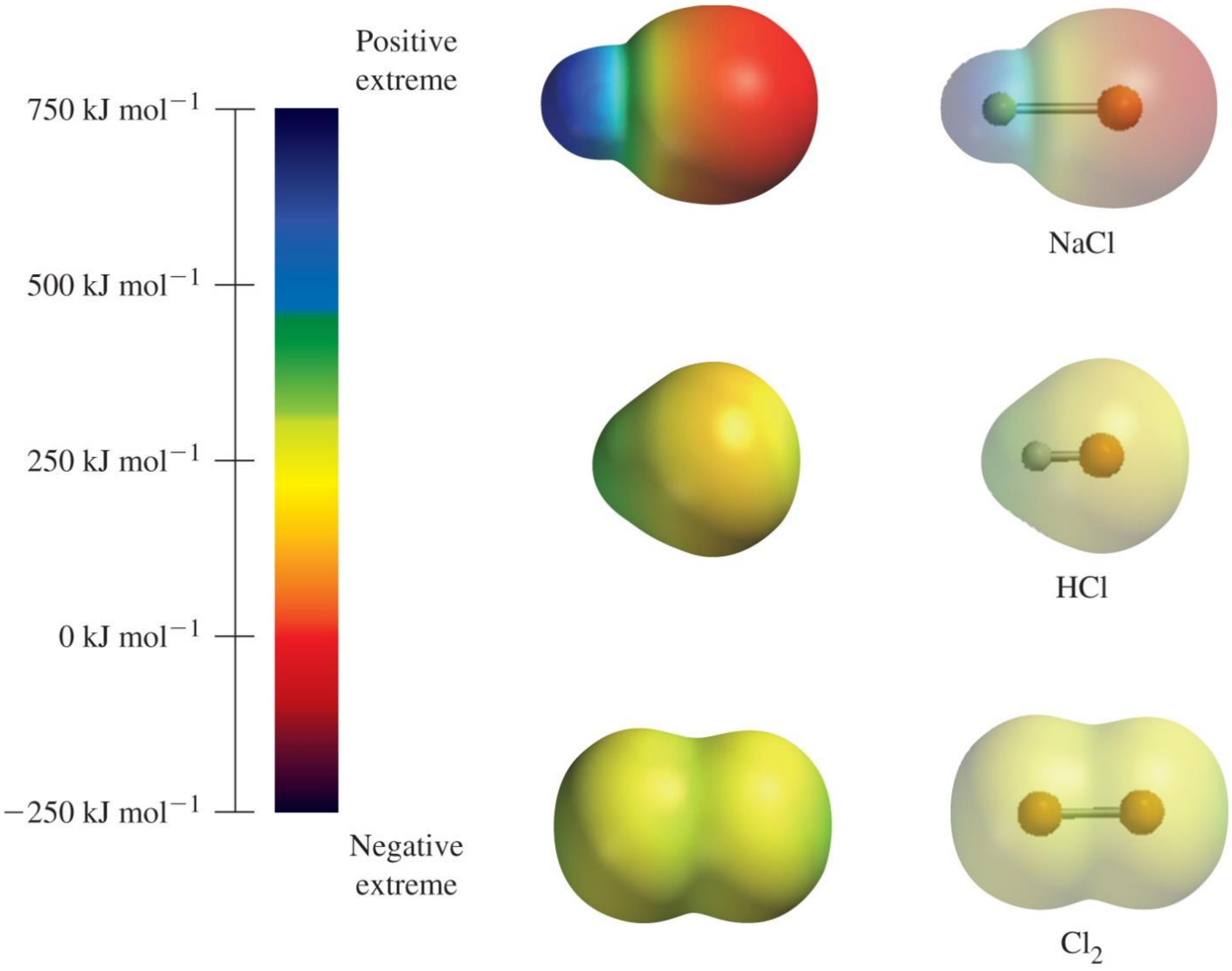
8-4 Bond Polarity and Electronegativity

- **Bond polarity** is a measure of how equally or unequally the electrons in any covalent bond are shared.
  - In a **nonpolar covalent bond,** the electrons are shared equally, as in Cl_2 and N_2.
  - In a **polar covalent bond**, one of the atoms exerts a greater attraction for the bonding electrons than the other.




Move probe to surface of electron density
Probe at infinite distance
Move probe over molecule
to measure potential
Transparent
Solid

Polar Molecules



Electronegativity

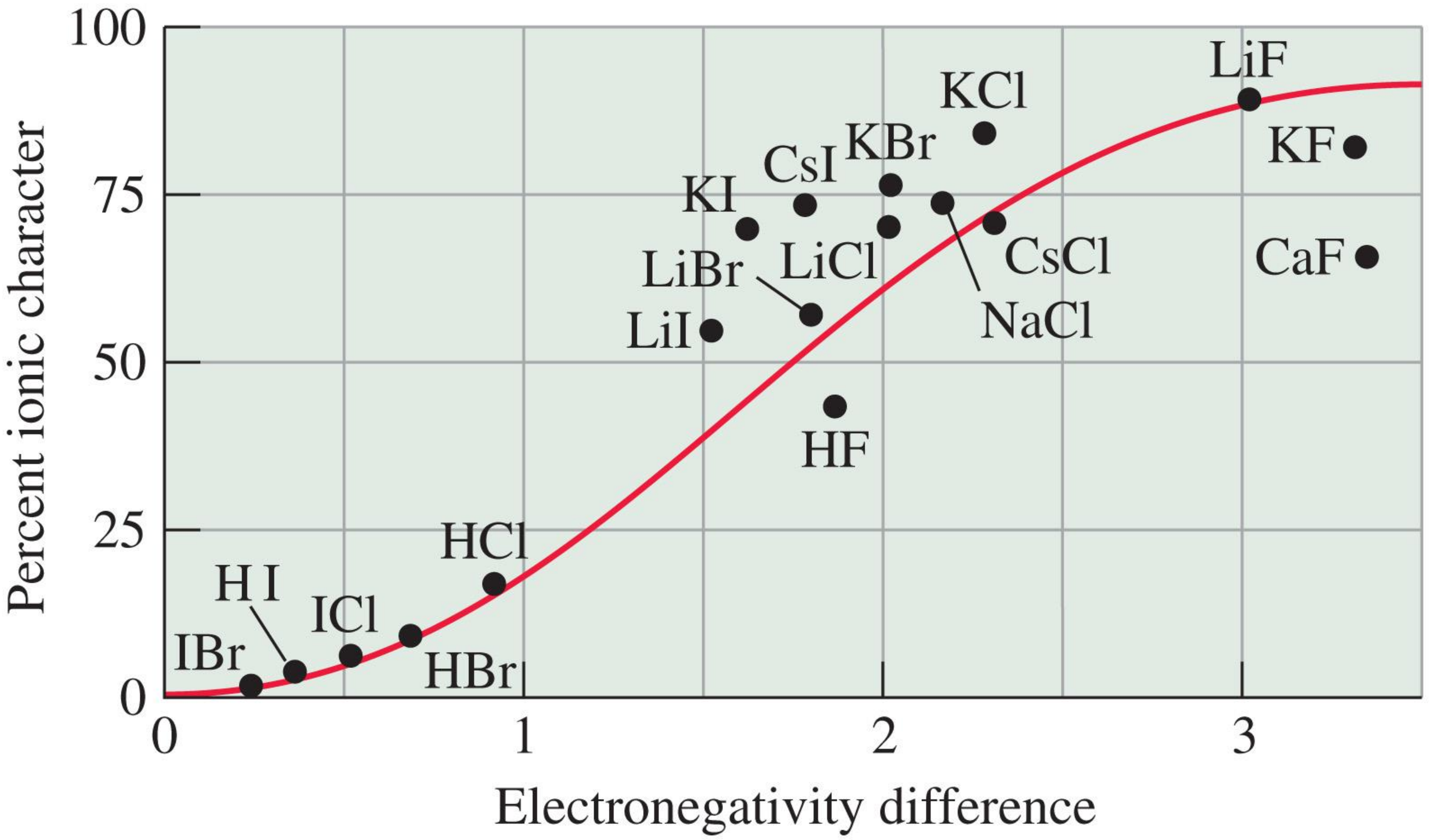
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
H 2.1																
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.8	Ba 0.9	La* 1.1	Hf 1.3	Ta 1.5	W 2.4	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac† 1.1														

- below 1.0
- 1.0–1.4
- 1.5–1.9
- 2.0–2.4
- 2.5–2.9
- 3.0–4.0

*Lanthanides: 1.1–1.3

†Actinides: 1.3–1.5

Percent Ionic Character



EXAMPLE

In each case, which bond is more polar? B-Cl or C-Cl. Indicate in each case which atom has the partial negative charge.

The chlorine atom is common to both bonds. ➔ we just need to compare the electronegativities of B and C.

B is to the left of C in the periodic table, we predict that boron has the lower electronegativity.

Cl is on the right side of the table, has high electronegativity.

➔ The B-Cl bond is more polar;

➔ The chlorine atom carries the partial negative charge because it has a higher electronegativity

8-5 Drawing Lewis Structures

- *All* the valence e^- of atoms must appear.
- *Usually*, the e^- are paired.
- *Usually*, each atom requires an octet.
  - H only requires 2 e^-.
- Multiple bonds may be needed.
  - Readily formed by C, N, O, S, and P.

Skeletal Structure

Identify central and terminal atoms:

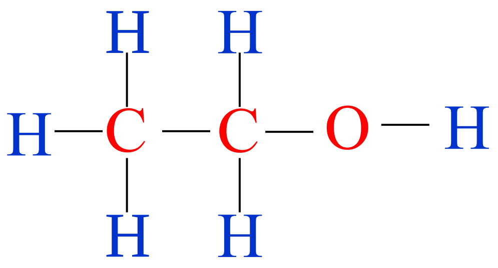
- Hydrogen atoms are always terminal atoms.

  (H can only accommodate two electrons)

- Central atoms are generally those with the lowest electronegativity.

  (H and O are common exceptions to rule 2)

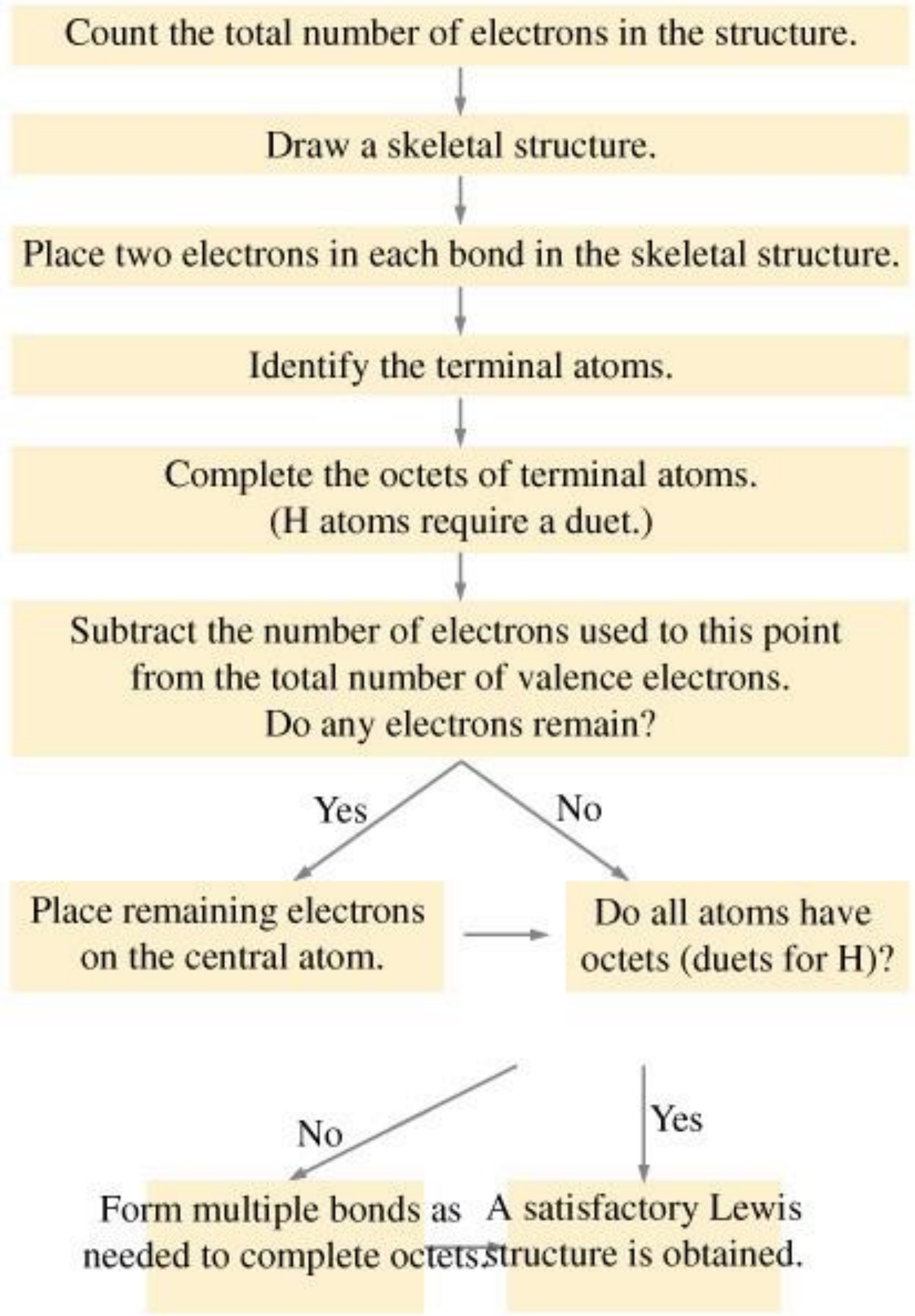
- Carbon atoms are always central atoms.



- Generally structures are compact and symmetrical.

  (Organic compounds are not always compact nor symmetrical)

Strategy for Writing Lewis Structures



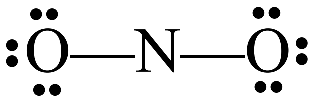
EXAMPLE

Writing a Lewis Structure for a Polyatomic Ion. Write the Lewis structure for the nitronium ion, NO_2^+.

Step 1: Total valence e^- = 5 + 6 + 6 – 1 = 16 e^-

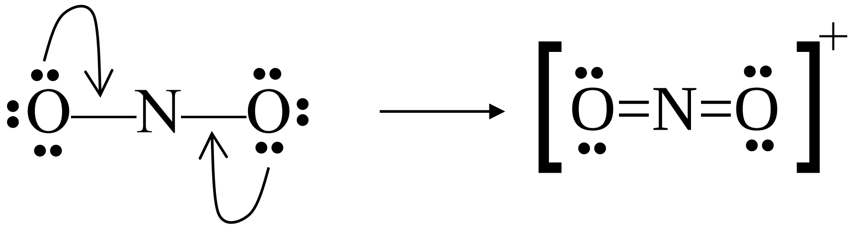
Step 2: Identify the central and terminal atoms

Step 3: Plausible structure: O—N—O

Step 4: Add e^- to terminal atoms: 

Step 5: Determine e^- left over: 16 – 4 – 12 = 0

Step 6: Use multiple bonds to satisfy octets.



Formal Charge

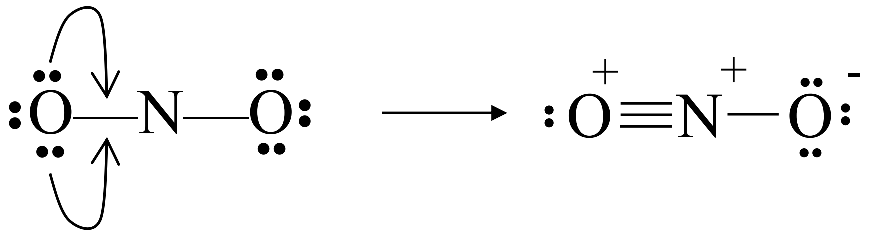
$$FC = \#_{\text{valence } e\text{-}} - \#_{\text{lone pair } e\text{-}} - \frac{1}{2}\#_{\text{bond pair } e\text{-}}$$

$$\ddot{\underset{\cdot\cdot}{O}}=\overset{+}{N}=\ddot{\underset{\cdot\cdot}{O}}$$

$$FC(O) = 6 - 4 - \frac{1}{2}(4) = 0$$

$$FC(N) = 5 - 0 - \frac{1}{2}(8) = +1$$

Alternative Lewis Structure



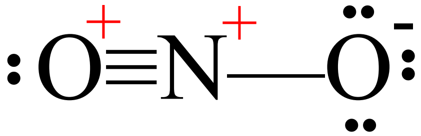
$$FC(O\equiv) = 6 - 2 - \frac{1}{2}(6) = +1$$

$$FC(N) = 5 - 0 - \frac{1}{2}(8) = +1$$

$$FC(O—) = 6 - 6 - \frac{1}{2}(2) = -1$$

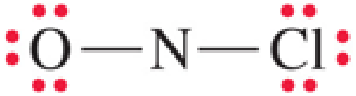
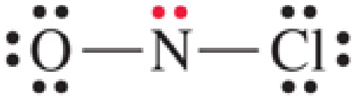
Alternative Lewis Structures

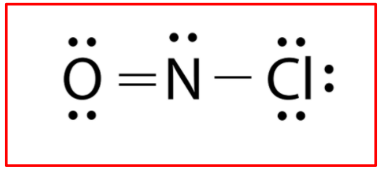
- Sum of FC is the overall charge.
- FC should be as small as possible.
- Negative FC usually on most electronegative elements.
- FC of same sign on adjacent atoms is unlikely.

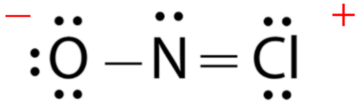


EXAMPLE

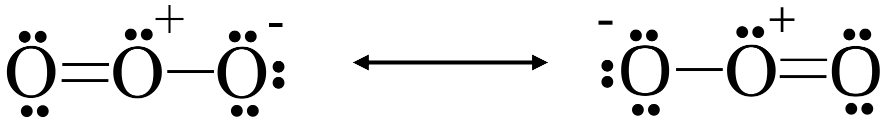
Using the Formal Charge in Writing Lewis Structures. Write the most plausible Lewis structure of nitrosyl chloride, NOCl, one of the oxidizing agents present in *aqua regia*.

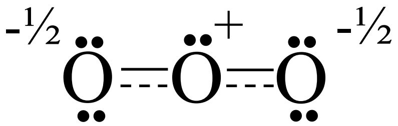
- Nitrogen is less electronegative than oxygen or chlorine, it is the central atom
- Total valence electrons: $5_{(N)} + 6_{(O)} + 7_{(Cl)} = 18$
- Assign four electrons 
- Assign twelve more electrons 
- Assign the last two electrons 
- A lone pair of electrons on a terminal atom must be used to form a bonding pair with N.

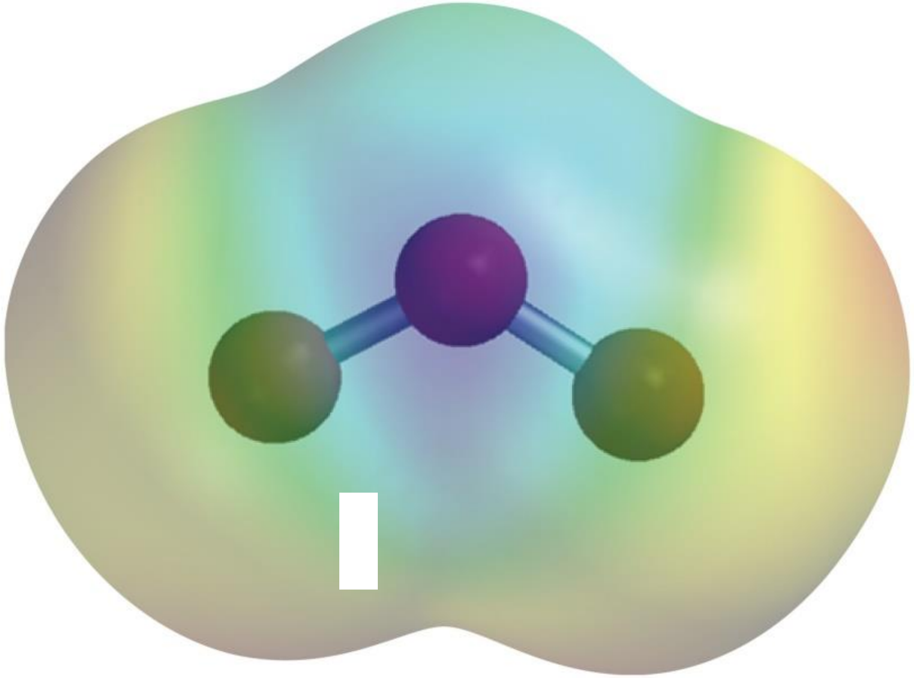




8-6 Resonance Structures

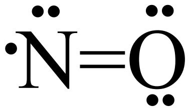


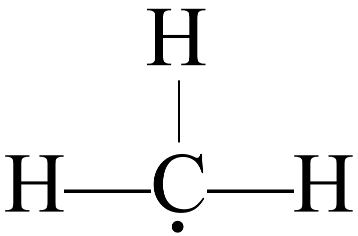


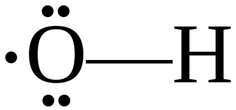


8-7 Exceptions to the Octet Rule

- Odd e^- species.

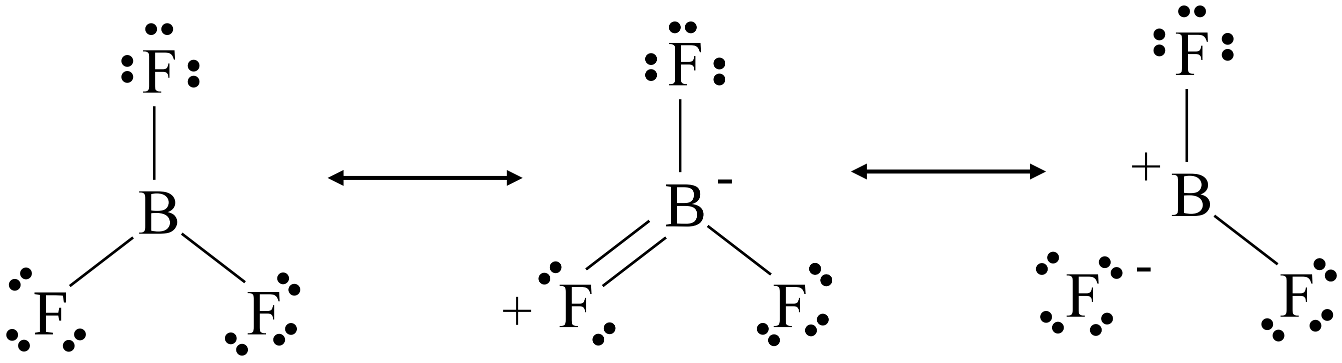






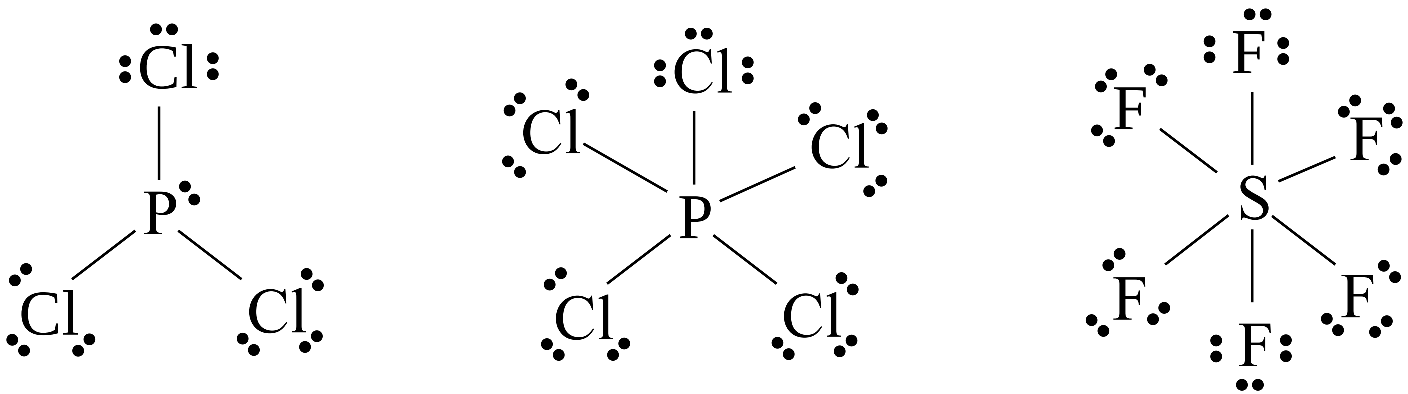
Exceptions to the Octet Rule

- Incomplete octets.



Exceptions to the Octet Rule

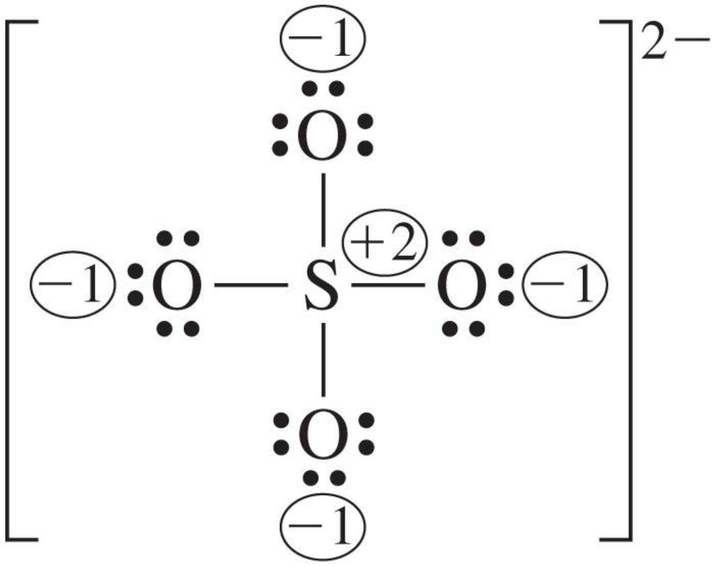
- Expanded octets.



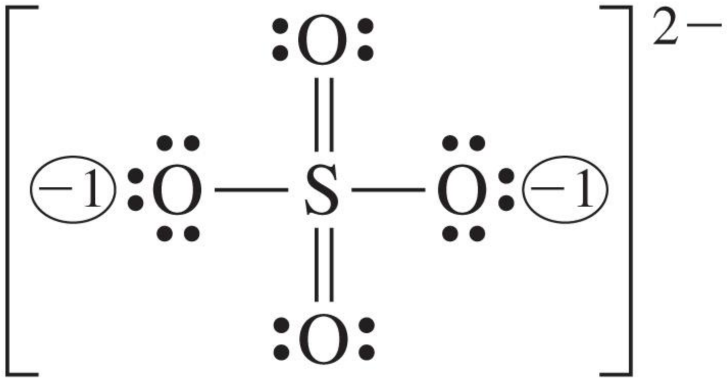
Expanded Valence Shell

- The octet rule can be 'expanded' by some elements by utilizing the d-orbitals found in the 3rd principal energy level and beyond (**period 3 and below**)
- There are **more than eight electrons** around one atom.
- **Sulfur, phosphorus, silicon, and chlorine** are common examples of elements that form an expanded octet.

Expanded Valence Shell



Normal octet



Expanded valence shell

Terminology

- Bond length – distance between nuclei.
- Bond angle – angle between adjacent bonds.
- VSEPR Theory
  - Electron pairs repel each other whether they are in chemical bonds (bond pairs) or unshared (lone pairs). Electron pairs assume orientations about an atom to minimize repulsions.
- Electron group geometry – distribution of e^- pairs.
- Molecular geometry – distribution of nuclei.

8-8 Strengths and Lengths of Covalent Bonds

- Bond Order
  - Single bond, order = 1
  - Double bond, order = 2
- Bond Length
  - Distance between two nuclei
- Higher bond order
  - Shorter bond
  - Stronger bond

TABLE 10.2 Some Average Bond Lengths[a]

Bond	Bond Length, pm	Bond	Bond Length, pm	Bond	Bond Length, pm
H—H	74.14	C—C	154	N—N	145
H—C	110	C=C	134	N=N	123
H—N	100	C≡C	120	N≡N	109.8
H—O	97	C—N	147	N—O	136
H—S	132	C=N	128	N=O	120
H—F	91.7	C≡N	116	O—O	145
H—C1	127.4	C—O	143	O=O	121
H—Br	141.4	C=O	120	F—F	143
H—I	160.9	C—C1	178	C1—C1	199
				Br—Br	228
				I—I	266

[a]Most values (C—H, N—H, C—H, and so on) are averaged over a number of species containing the indicated bond and may vary by a fe picometers. Where a diatomic molecule exists, the value given is the actual bond le gth in that molecule (H_2, N_2, HF, and so on) and is known more precisely.

Bond Energies

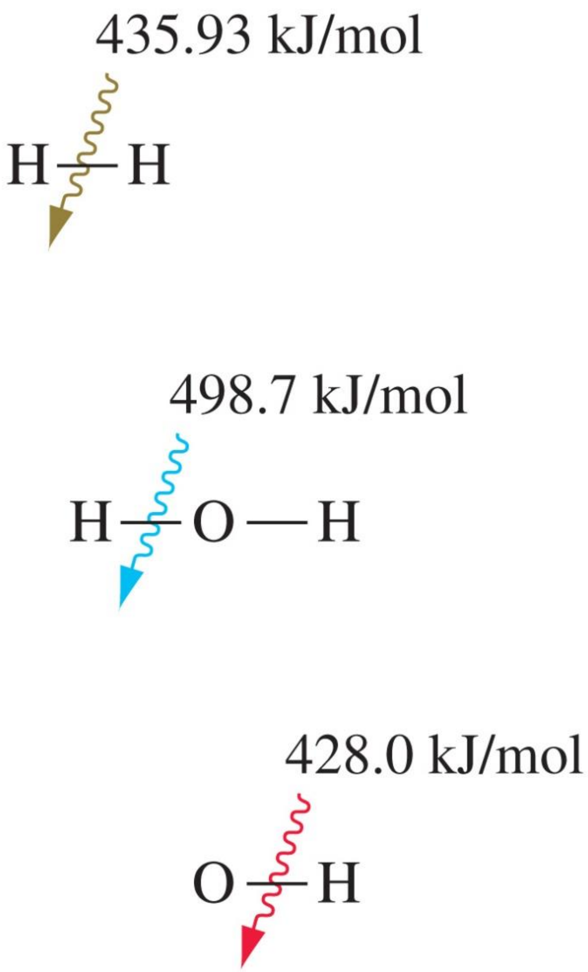


TABLE 10.3 Some Average Bond Energies[a]

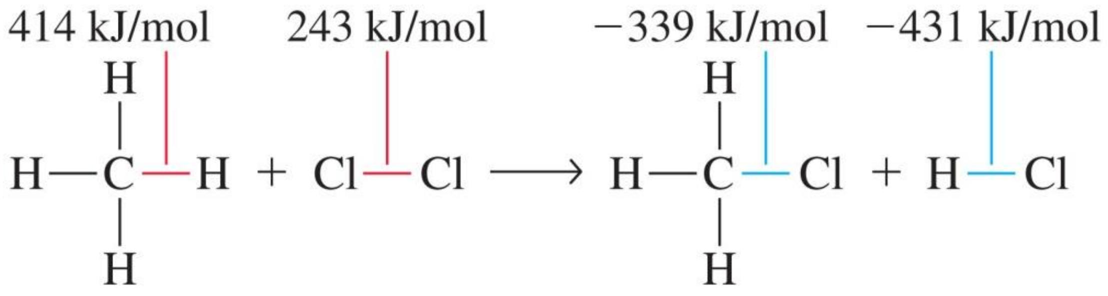
Bond	Bond Energy, kJ/mol	Bond	Bond Energy kJ/mol	Bond	Bond Energy kJ/mol
H—H	436	C—C	347	N—N	163
H—C	414	C=C	611	N=N	418
H—N	389	C≡C	837	N≡N	946
H—O	464	C—N	305	N—O	222
H—S	368	C=N	615	N=O	590
H—F	565	C≡N	891	O—O	142
H—C1	431	C—O	360	O=O	498
H—Br	364	C=O	736[b]	F—F	159
H—I	297	C—C1	339	C1—C1	243
				Br—Br	193
				I—I	151

[a] Although all data are listed with about the same precision (three significant figures), some values are actually known more precisely. Specifically, the values for the diatomic molecules H_2, HF, HCl, HBr, HI, N_2 (N≡N), O_2 (O=O), F_2, Cl_2, Br_2, and I_2 are actually bond-dissociation energies, rather than average bond energies.

[b] The value for the C=O bonds in CO_2 is 799 kJ/mol.

EXAMPLE

Calculating an Enthalpy of Reaction from Bond Energies. The reaction of methane (CH_4) and chlorine produces a mixture of products called chloromethanes. One of these is monochloromethane, CH_3Cl, used in the preparation of silicones. Calculate ΔH for the reaction.



$$\Delta H_{rxn} = \Sigma\, \Delta H(\text{product bonds}) - \Sigma \Delta H(\text{reactant bonds})$$

$$= \Sigma\, \Delta H \text{ bonds formed} - \Sigma\, \Delta H \text{ bonds broken}$$

$$= -\,(339\text{kJ/mol} + 431\text{kJ/mol1}) - [-(414\text{kJ/mol} + 243\text{kJ/mol})$$

$$= -770 \text{ kJ/mol} + 657 \text{ kJ/mol} = -113 \text{ kJ/mol}$$

Key terms

Bond energy: năng lượng liên kết

Bond length: chiều dài liên kết

Bond pair of electron: cặp điện tử liên kết

Bond polarity: tính phân cực của liên kết

Covalent bond: liên kết cộng hóa trị

Diamagnetism: nghịch từ

Double bond: liên kết đôi

Electronegativity: độ âm điện

Formal charge: điện tích hình thức

Ionic bond: liên kết ion

Lewis structure: cấu trúc Lewis

Lone pair of electron: cặp điện tử không liên kết

Metalic bond: liên kết kim loại

Octet rule: quy tắc bát tử

Paramagnetism: thuận từ

Polar covalent bond: liên kết cộng hóa trị phân cực

Polar molecule: phân tử phân cực

Resonance structure: cấu trúc cộng hưởng

Single bond: liên kết đơn

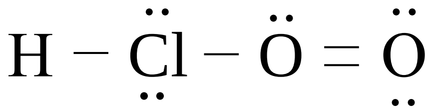
Skeletal structure: Cấu trúc khung xương

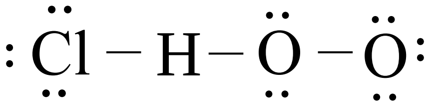
Triple bond: liên kết ba

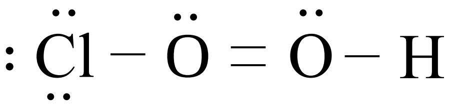
Valence electron: điện tử hóa trị

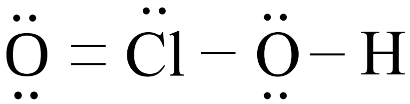
Quiz

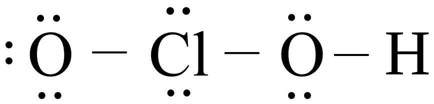
- Regardless of the formal charge, write all possible Lewis structures of HClO2

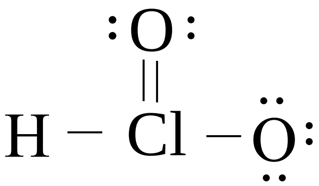
A. 

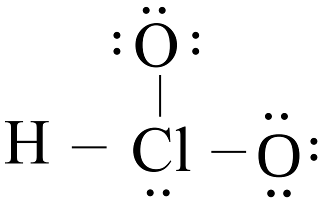
B. 

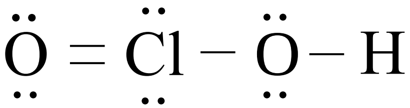
C. 

D. 

E. 

F. 

G. 

H. 

- Use formal charge to determine the most plausible Lewis structure of $HClO_2$
- Compare the bond lengths of O = Cl and O – Cl in $HClO_2$
- Compare the bond strengths of O = Cl and O – Cl in $HClO_2$