Lewis Theory

1916-1919 - Lewis, Kossel, and Langmuir made several important proposals on bonding which lead to the development of Lewis Bonding Theory

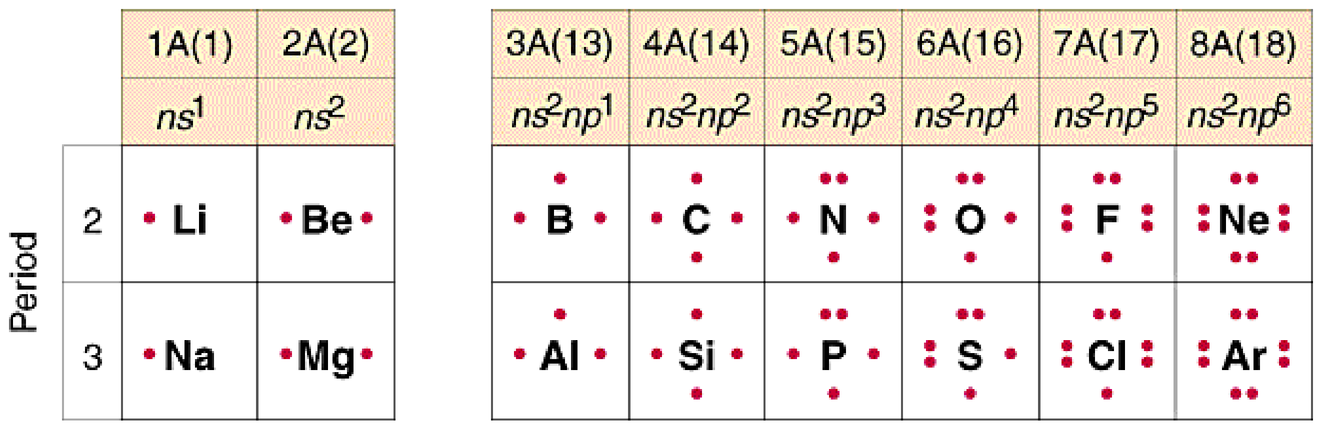
Elements of the theory:

1. Valence electrons play a fundamental role in chemical bonding.
2. ***Ionic bonding*** involves the ***transfer*** of one or more electrons from one atom to another.
3. ***Covalent bonding*** involves ***sharing*** electrons between atoms.
4. Electrons are transferred or shared such that each atom gains an electron configuration of a noble gas (ns^2np^6), i.e. having 8 outer shell (valence) electrons.
5. This arrangement is called the ***octet rule***.
6. Exceptions to the octet rule do exist and will be explored later.

Lewis Symbols represent the resulting structures that accommodate the octet rule.

In a Lewis symbol, an element is surrounded by up to ***8 dots***, where elemental symbol represents the nucleus and the dots represent the valence electrons.

Lewis Symbols:



Lewis Structures for Ionic Compounds

Ionic Bonding results when an electron or electrons are transferred from one atom to another. The transfer results in each attaining an octet or Noble gas electron configuration.

$$\underset{\textstyle Na}{\overset{3s^1}{\downarrow}} \quad + \quad \underset{\textstyle Cl}{\overset{3s^2 3p^5}{\downarrow}} \quad \rightarrow \quad Na^+ \, Cl^-$$

$$Na^+ \, Cl^- \rightarrow \quad 2s^2 2p^6 \rightarrow Na^+ \; [Ne] \qquad\qquad 3s^2 3p^6 \rightarrow Cl^- \; [Ar]$$

See example 11.2 for more info.

Ionic bonds

The strength of an ionic bond is a function of the ***electrostatic forces*** (Coulomb's Law) that exist between the cations and anions that make up the ionic compound.

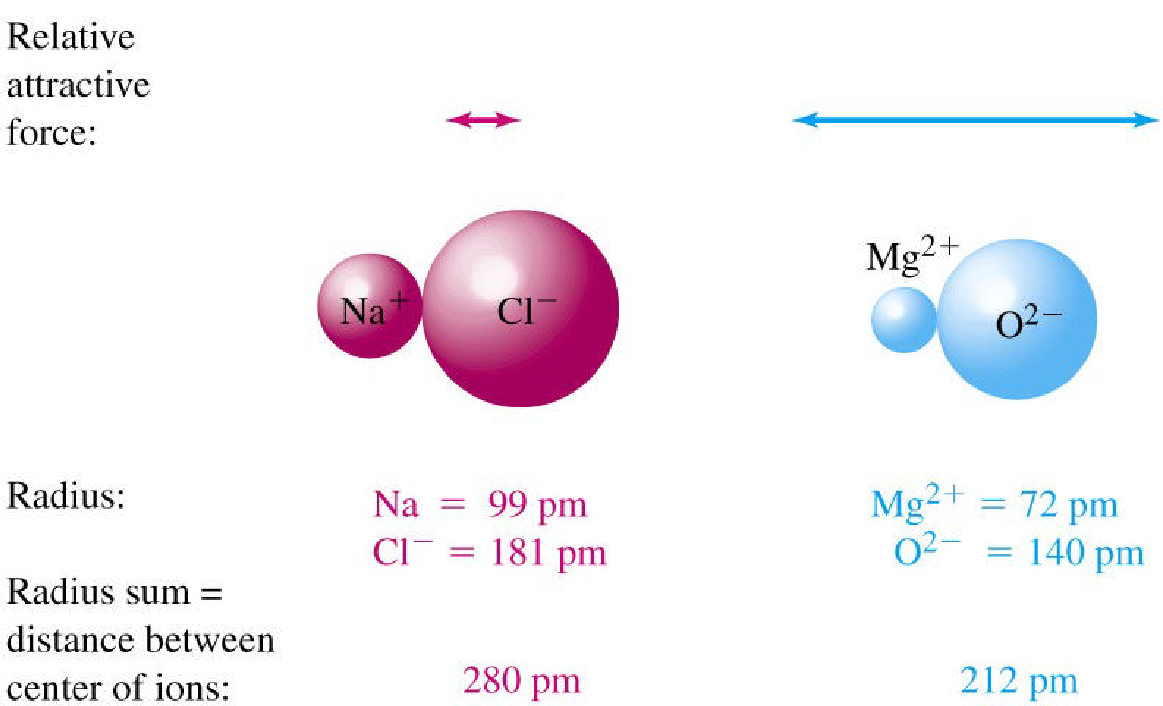
Where:

$$F \sim \frac{n(e+)\, n(e-)}{d^2}$$

n(e+) is the charge on the cation

n(e-) is the charge on the anion

and d is the internuclear distance



Since the charges are greater and the distance between is smaller for MgO, it has a stronger ionic bond than NaCl.

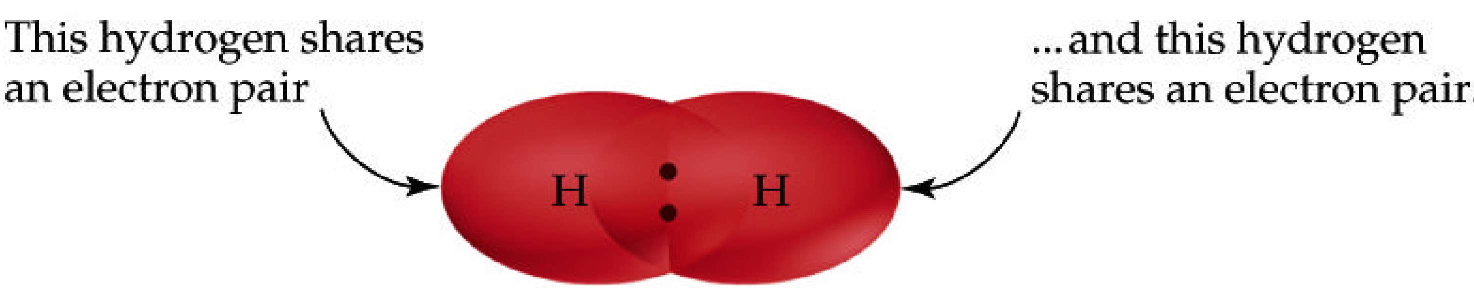
Covalent Bonds (Diatomic Molecules)

- Covalent chemical bonds involve the sharing of a pair of valence electrons by two atoms, in contrast to the transfer of electrons in ionic bonds.
- Covalent bonds lead to stable molecules if they share electrons in such a way as to create a noble gas configuration (***octet: ns^2np^6***) for each atom.

Hydrogen gas (H_2) forms the simplest covalent bond in the diatomic hydrogen molecule.

$$H + H \rightarrow H{-}H$$

Bonding Pair of electrons (bp) "***single bond***"

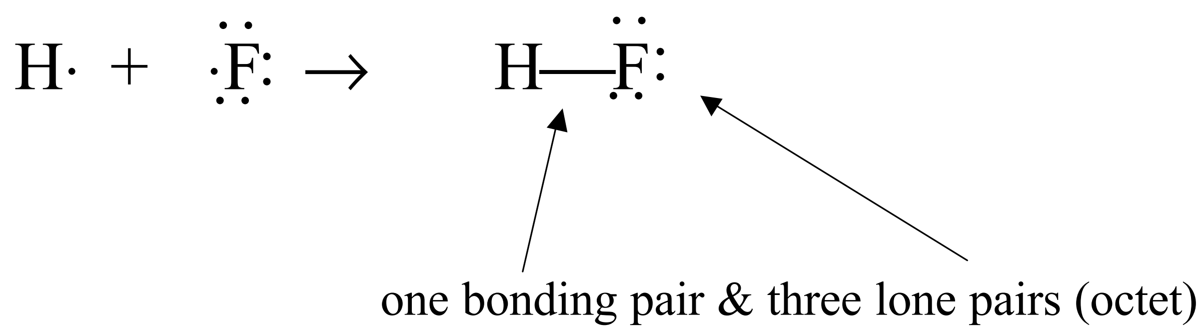


Lone Pairs:

- Since hydrogen has only one electron in its valence, it satisfies the ***octet rule*** with a ***duet***.

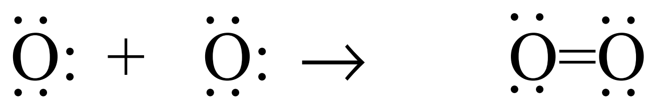
- When other covalent species form, there are additional electron pairs that do not participate in bonding.

These are called "***lone pairs***" (lp)

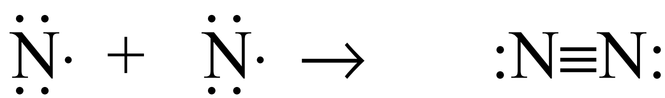


Multiple bonds:

The oxygen and nitrogen that makes up the bulk of the atmosphere also exhibits covalent bonding in forming diatomic molecules.



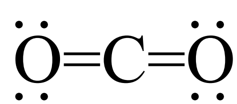
"***double bond***"



"***triple bond***"

Polyatomic Molecules (More than two atoms)

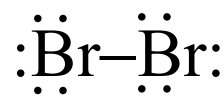
Carbon dioxide: CO_2



Electronegativity and Bond Polarity

In a purely covalent bond, the electrons in the bond are shared evenly between the bonding atoms.

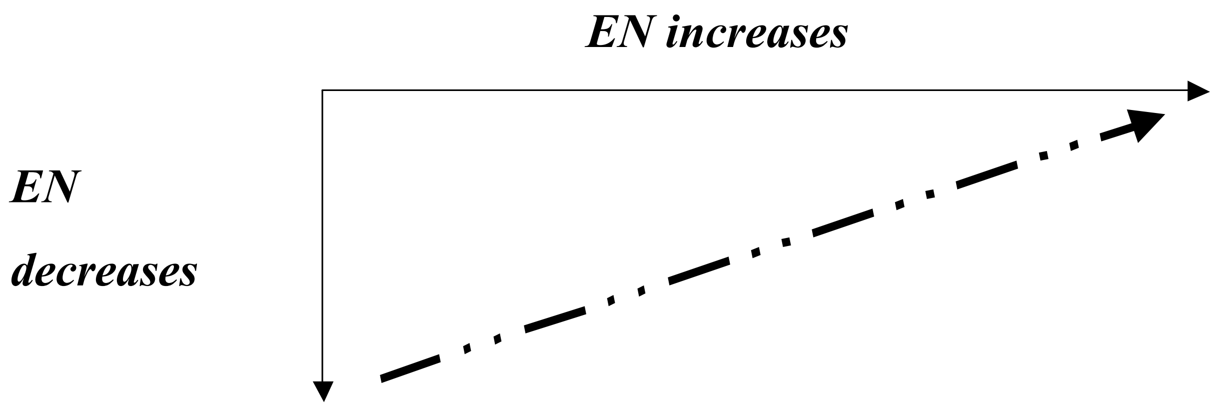
An example would be a homo-nuclear diatomic molecule such as Br_2.



However, each element has different tendency to attract electrons in a covalent bond and the measure of this tendency is given by a quantity known as the ***Electronegativity*** (EN) of an atom.

Linus Pauling developed the electronegativity scale. It is related to the ***ionization energy*** and the ***electron affinity*** of an atom.

The trend on the periodic table follows Z_{eff}:



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

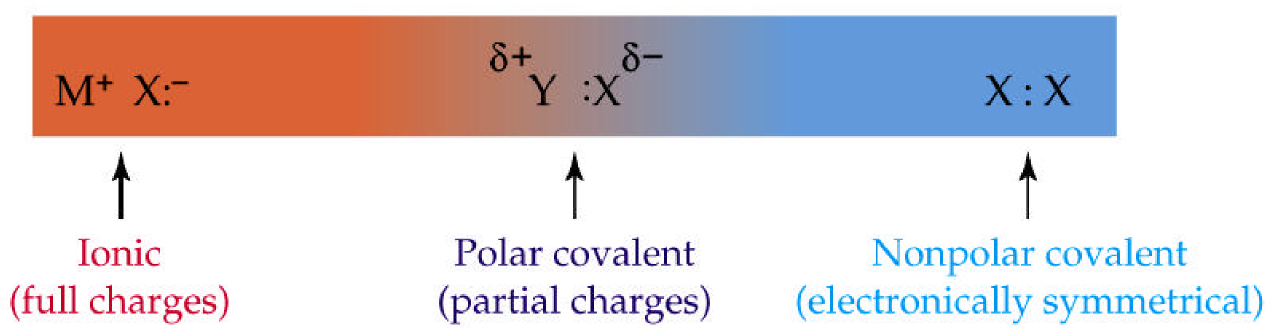
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
H 2.1																
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 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														

*Lanthanides: 1.1–1.3
†Actinides: 1.3–1.5

When there exists a difference in the EN between the two bonding atoms, (ΔEN) the bond is said to be ***polar***.

Example:

	DEN	***Bond***
Br_2	0	non-polar
HCl	0.9	polar-covalent
NaF	3.1	ionic

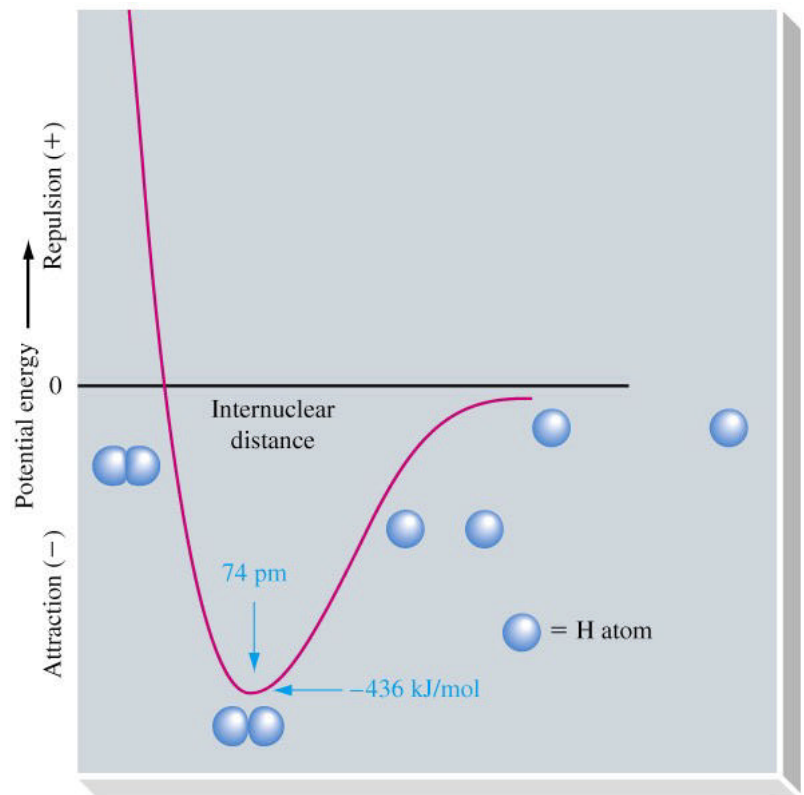


Bond Strength in Covalent Molecules:

A covalent bond is governed by a potential energy diagram that is a combination of two forces:

(1) the ***attractive forces*** driven by the stability attained by bond formation and

(2) the ***repulsive forces*** that exist between the like charges of each nucleus.



The two define a "***well***" that's depth is the covalent bond energy.

- As long as the molecule is in the well, it is bound.
- When the molecule is in the bottom of the well (the lowest point) the internuclear distance is the covalent bond length.
- Separation of the nuclei results in bond breaking.

Bond Strength and Bond Properties:

Covalent bond strength increases with increasing ΔEN

example: HCl bond is stronger than the HBr bond

Covalent bond strength increases with increasing bond order

example: O=O bond in stronger than O-O bond

triple > double > single

Bond length decreases with increasing bond order (Strength)

example: O=O bond is shorter than O-O bond

TABLE 11.2 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—Cl	127.4	C—O	143	O=O	121
H—Br	141.4	C=O	120	F—F	143
H—I	160.9	C—Cl	178	Cl—Cl	199
				Br—Br	228
				I—I	266

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

TABLE 11.3 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—Cl	431	C—O	360	O=O	498
H—Br	364	C=O	736[b]	F—F	159
H—I	297	C—Cl	339	Cl—Cl	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 that average bond energies.
[b]The value for the C=O bonds in CO_2 is 799 kJ/mol.

Predicting Lewis Structures: The NAS Rule

The Lewis structure of a molecule that obeys the octet rule can be predicted using a set of rules that takes into account the number of electrons needed to satisfy the octet rule (N) and the number of electrons available (A) to predict the number of electron that are to be shared. This and the relative electronegativities of each atom in the molecule can lead to the Lewis structure.

The NAS Rule:

(1) Let "N" equal the # of electrons needed by each atom to satisfy the octet.

N = 2 for hydrogen and 8 for all others

(2) Let "A" equal the # of electrons available from each based on its Lewis dot configuration.

H and Group 1 have one, Group 2 has two, Group 3 has three…… Group 8 has eight

(3) Let S = N – A

where the # of bonding pairs equals the number of shared electrons divided by 2 and the number of lone pairs is the number available divided by 2 minus the number of bonding pairs.

(4) The central atom is most often the atom in the molecule with the lowest electronegativity.

Example: H_4O (water)

N = 8 (for O) + 2×2 (for each H) = 8 + 4 = 12

A = 6 (for O) + 2×1 (for each H) = 6 + 2 = 8

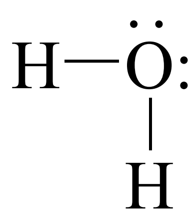
S = N – A

S = 12 (needed) – 8 (available) = 4

number of bonding pairs = S /2 = 4 / 2 = 2 (bp)

number of lone pairs = A /2 – bp = 8 / 2 – 2 = 2 (lp)

Since hydrogen (H) can only form one bond, oxygen (O) must be in the center



$N = 8 \text{ (for C)} + 4 \times 2 \text{ (for each H)} = 8 + 8 = 16$

$A = 4 \text{ (for C)} + 4 \times 1 \text{ (for each H)} = 4 + 4 = 8$

$S = N - A$

$S = 16 \text{ (needed)} - 8 \text{ (available)} = 8$

number of bonding pairs = $S/2$ = $8/2$ = 4 (bp)

number of lone pairs = $A/2 - bp$ = $8/2 - 4$ = 0 (lp)

Since hydrogen (H) can only form one bond, carbon (C) must be in the center