화학 General Chemistry
034.020-005

2018 Spring Semester

Tue/Thr 9:30~10:45
Building 028-302

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Lecture 2. Chemical Bond

Q1. Why do we need to know **Chemical Bond**?

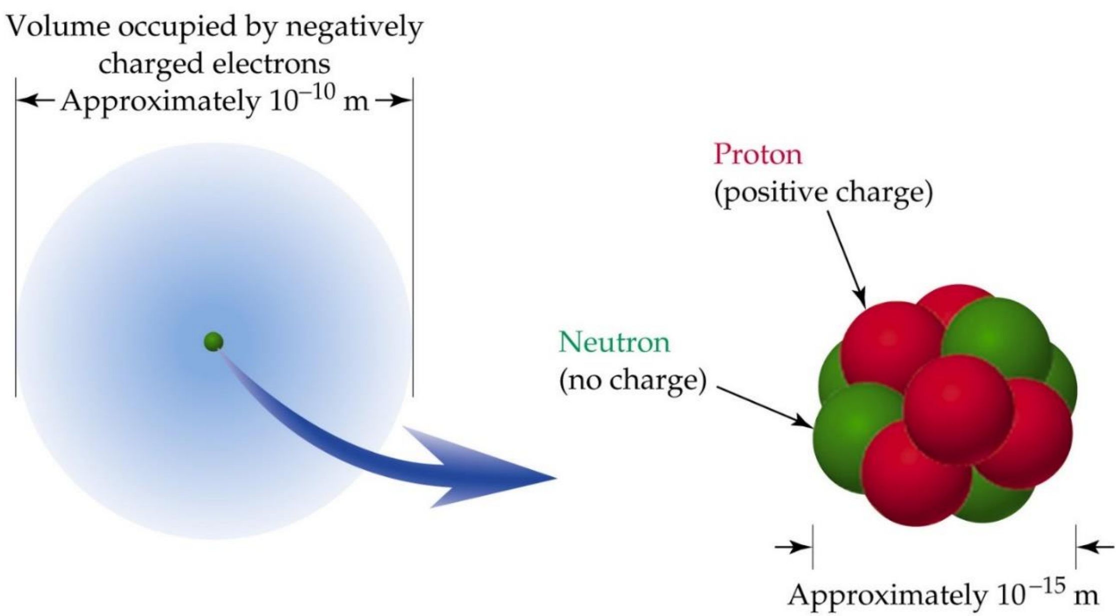
Chemistry is the science to study "matters and the transformation of matters". Therefore, we need to know **how the matters are formed and are changed** so that we can even design new materials by the formation of new chemical bond.

Q2. **Chemical Bonds**

a. Bondings between

b. Chemical bond formation when energetically more

c. Determined by the electron configuration of each atom:



Q2. **Chemical Bonds**

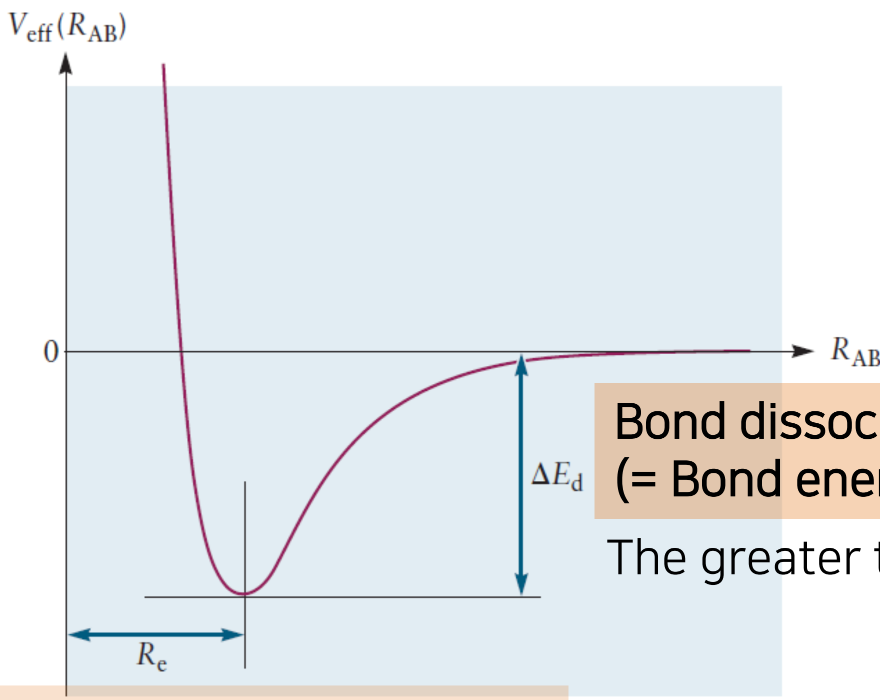
a. Bonding between **atoms**

b. Chemical bond formation **when energetically more stable.**

c. Determined by the electron configuration of each atom: **valence electron**

Principles of Chemical Bonds

For a diatomic molecule AB



Bond dissociation energy
(= Bond energy for a diatomic molecule)

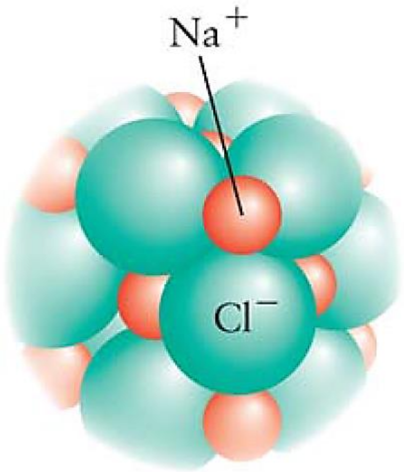
The greater the ΔE_d, the more stable the molecule.

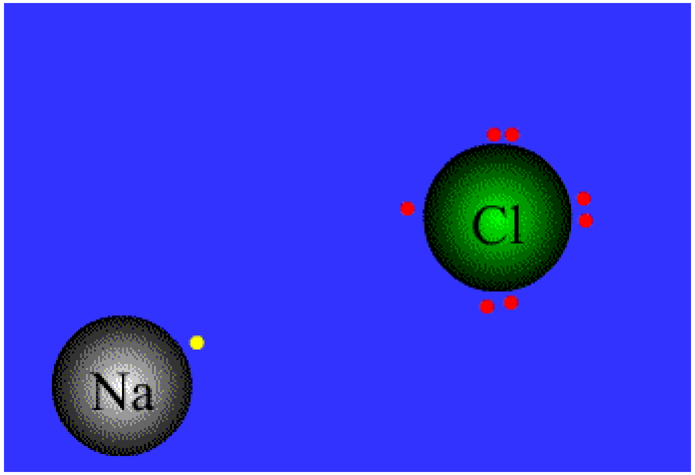
Equilibrium bond length

Ionic Bonds

2.1. The Ions that Elements Form

Induced by **electrostatic attraction** between **cation and anion**





Electron configurations

Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$ ($[Ne]3s^1$) Na^+: $1s^2\ 2s^2\ 2p^6$ ($[Ne]$)

Cl: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ ($[Ne]\ 3s^2\ 3p^5$) Cl^-: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ ($[Ar]$)

Q2. **Chemical Bonds**

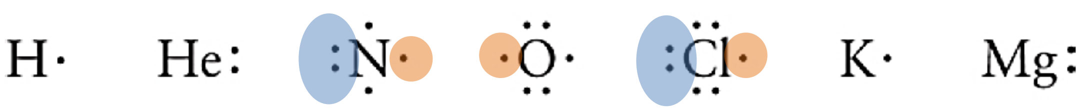
a. Bonding between **atoms**

b. Chemical bond formation **when energetically more stable.**

c. Determined by the electron configuration of each atom: valence electron

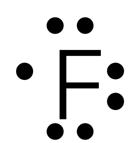
2.2. Lewis Symbols

Depict **valence electrons as dots**



Paired electrons, unpaired electron

H· 1-valence electron of H-atom



7-valence electrons:
[He] $(2s)^2(2p)^5$
2 + 5 = 7 electrons

$CaCl_2$

2.3. The Energetics of Ionic Bond Formation

$Na(g) \rightarrow Na^+(g) + e^-(g)$	$494\ kJ \cdot mol^{-1}$
$Cl(g) + e^-(g) \rightarrow Cl^-(g)$	$-349\ kJ \cdot mol^{-1}$
$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$	$-787\ kJ \cdot mol^{-1}$
$Na(g) + Cl(g) \rightarrow NaCl(s)$	$-642\ kJ \cdot mol^{-1}$

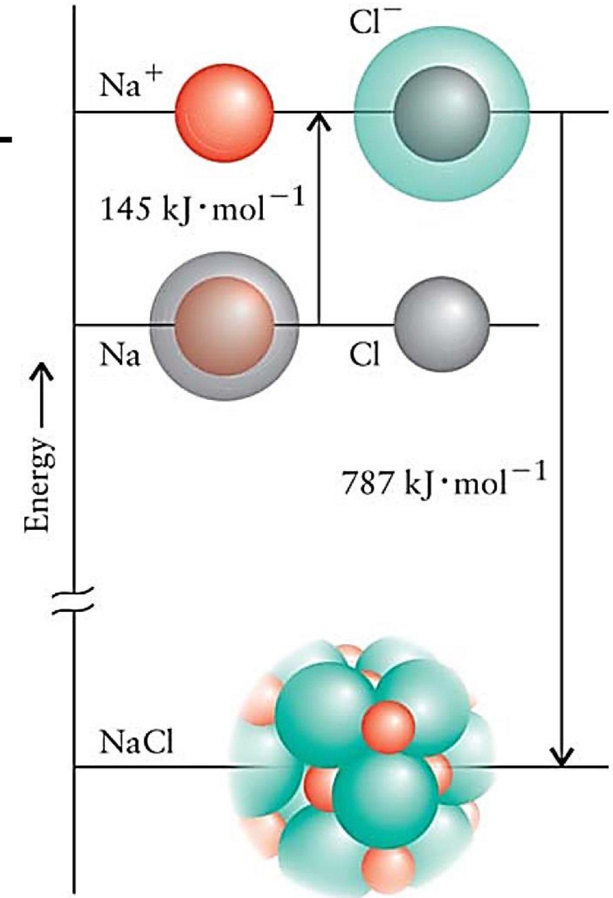
Endothermic & Exothermic Reaction ??

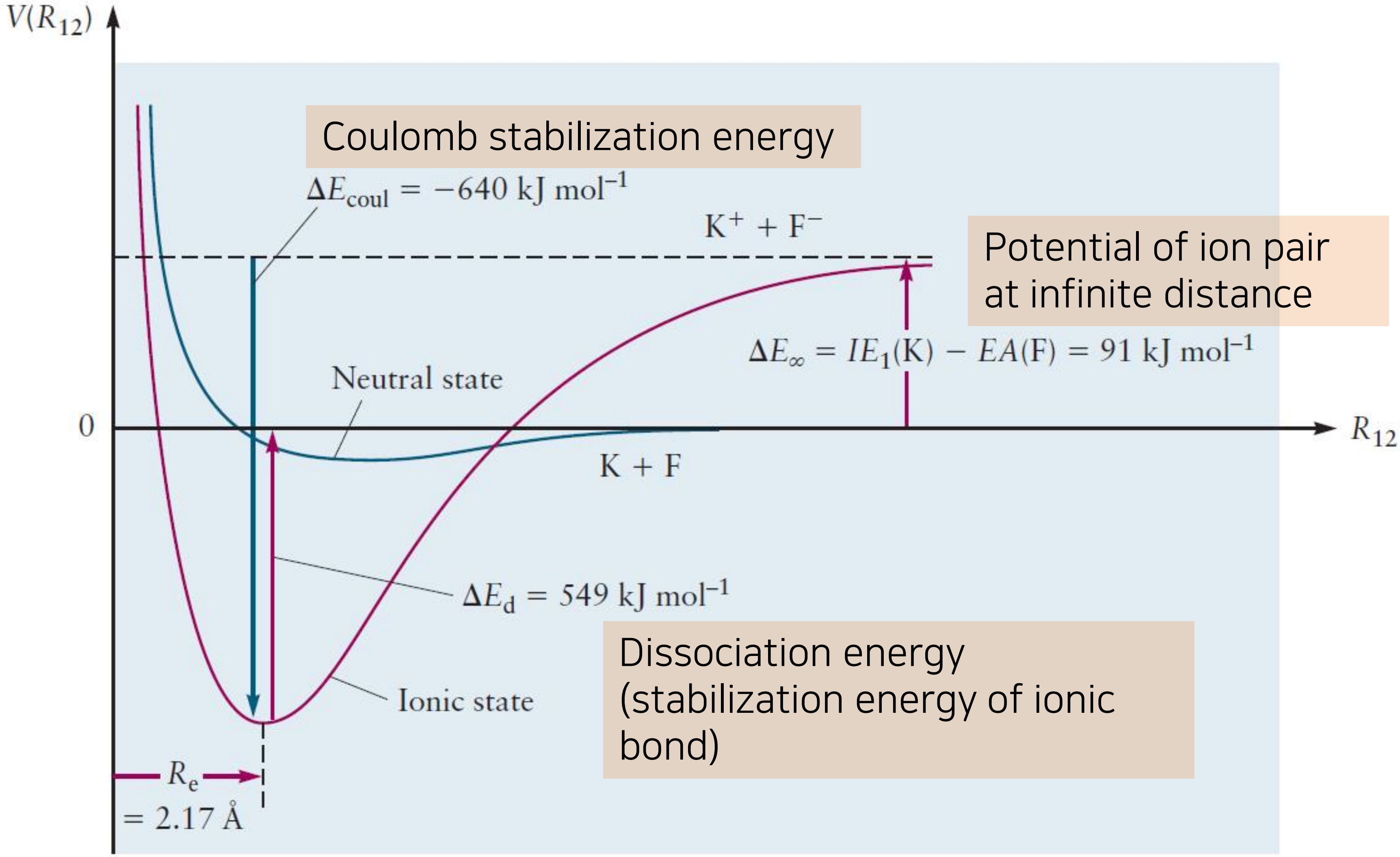
$$K \longrightarrow K^+ + e^- \qquad \Delta E = IE_1 = +419\ \text{kJ mol}^{-1}$$

$$F + e^- \longrightarrow F^- \qquad \Delta E = -EA = -328\ \text{kJ mol}^{-1}$$

$$\Delta E_\infty = IE_1(K) - EA(F) = +91\ \text{kJ mol}^{-1}$$

ΔE_∞ is always positive.





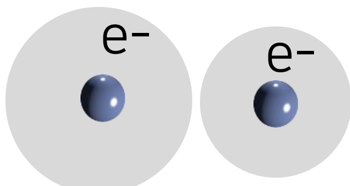
$V(R_{12})$
Coulomb stabilization energy
$\Delta E_{coul} = -640$ kJ mol^{-1}
$K^+ + F^-$
Potential of ion pair
at infinite distance
$\Delta E_\infty = IE_1(K) - EA(F) = 91$ kJ mol^{-1}
Neutral state
0
R_{12}
K + F
$\Delta E_d = 549$ kJ mol^{-1}
Dissociation energy
(stabilization energy of ionic
bond)
Ionic state
R_e
= 2.17 Å

Ionic bonding: Coulomb stabilization energy

Bonding between cation (+) and anion (-):
$(A^+)(B^-)$, follows coulomb's law

$$V(R) = \frac{(Q_+ e)(Q_- e)}{4\pi\varepsilon_0 R} = 2.31\times10^{-19}\, J\cdot nm\left(\frac{Q_+ Q_-}{R}\right)$$

ex) $Na^+ + Cl^- \rightarrow NaCl$



Electron clouds of Na^+ and Cl^- are not shared.

Melting temperatures of NaCl vs NaF:

$T_{melting}(NaF)$ $T_{melting}(NaCl)$

** R(Na-F) < R(Na-Cl)

Coulomb potential between two individual ions

$$E_{P,12} = \frac{(z_1 e) \times (z_2 e)}{4\pi\varepsilon_0 r_{12}} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_{12}}$$

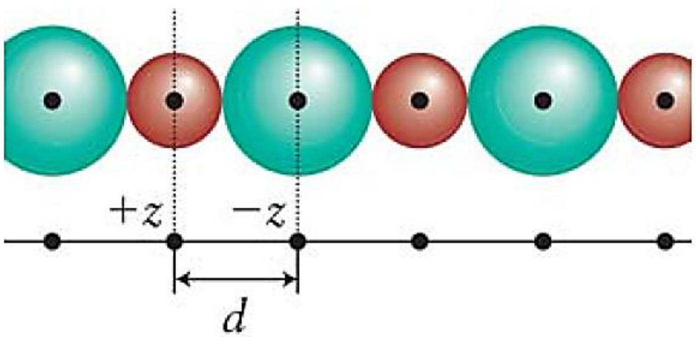
표 4.2 여러 가지 이온화합물의 격자에너지

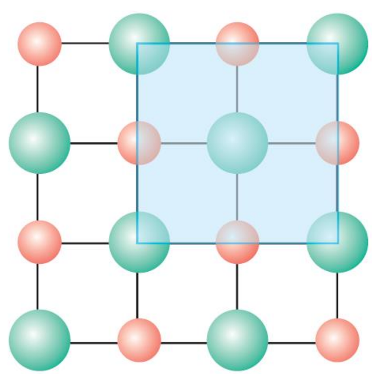
화합물	격자에너지(kJ/mol)	화합물	격자에너지(kJ/mol)
LiF	1030	$MgCl_2$	2326
LiCl	834	$SrCl_2$	2127
LiI	730		
NaF	910	MgO	3795
NaCl	788	CaO	3414
NaBr	732	SrO	3217
NaI	682		
KF	808	ScN	7547
KCl	701		
KBr	671		
CsCl	657		
CsI	600		

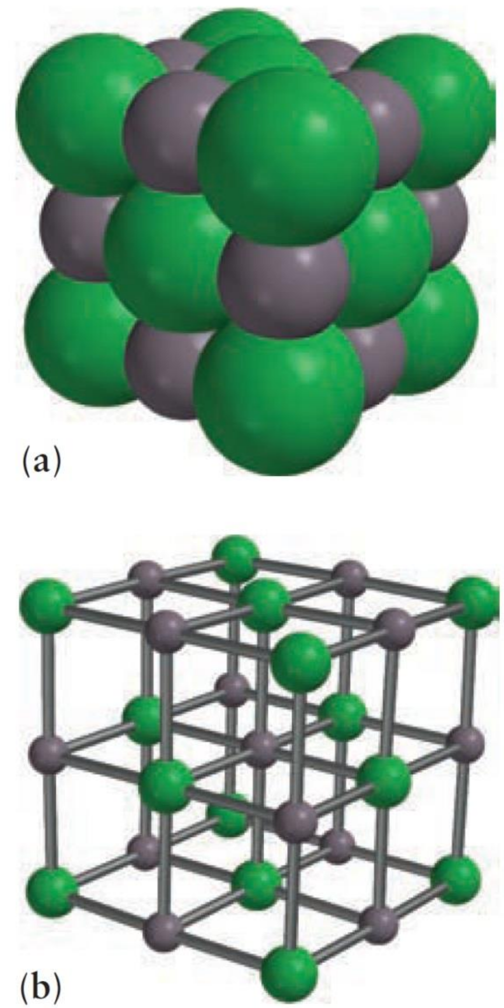
2.4. Interactions between Ions

Lattice energy

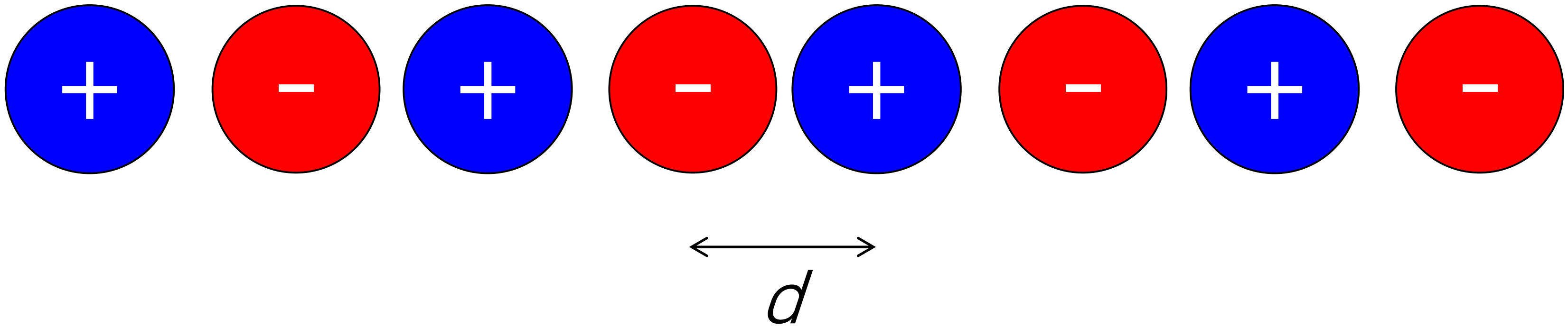
In an ionic solid, each cation is attracted to all the anions. → complexity







Madelung's constant (k) in Lattice Energy



Energy of one atom in 1-dimension crystal:

$$E = 2\times\frac{(+e)(-e)}{4\pi\varepsilon_0(d)} + 2\times\frac{(-e)(-e)}{4\pi\varepsilon_0(2d)} + 2\times\frac{(-e)(+e)}{4\pi\varepsilon_0(3d)} + \ldots$$

$$= \frac{e^2}{4\pi\varepsilon_0 d}\times 2\times\left(-1+\frac{1}{2}-\frac{1}{3}+\frac{1}{4}-\frac{1}{5}+\ldots\right)$$

$$= \frac{e^2}{4\pi\varepsilon_0 d}\times k$$

k = Madelung's constant: dependents on crystal structure.

Lattice energy is negative (exothermic).

Calculation of enthalpy change of crystal formation:

$$Li(s) + \frac{1}{2}F_2(g) \longrightarrow LiF(s)$$

$Li(s) \rightarrow Li(g)$: ΔH(sublimination) = 161 kJ/mol

$Li(g) \rightarrow Li^+ + e^-$: ΔH(ionization energy) = 520 kJ/mol

$1/2F_2(g) \rightarrow F(g)$: ΔH(dissociation energy) = 77 kJ/mol

$F(g) + e^- \rightarrow F^-(g)$: ΔH(electron affinity) = -328 kJ/mol

$Li^+(g) + F^-(g) \rightarrow LiF(s)$: ΔH(lattice energy) = -1047 kJ/mol

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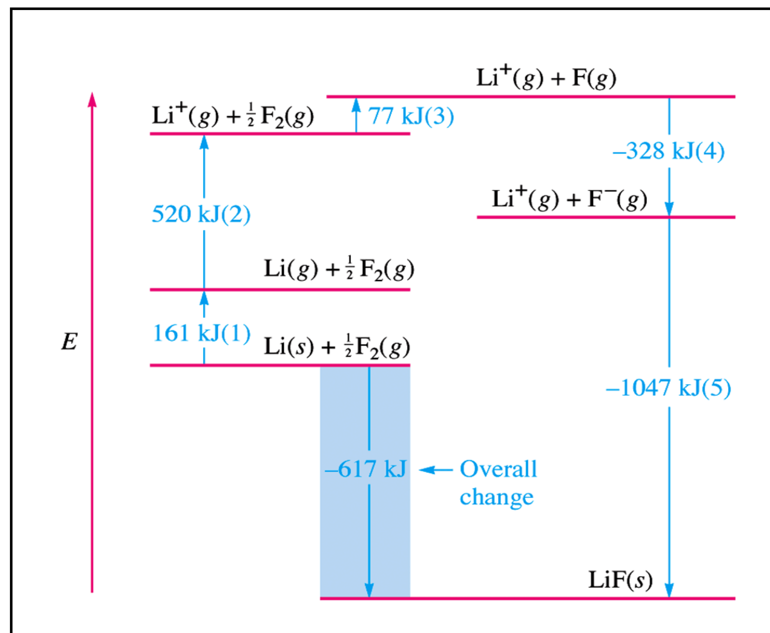
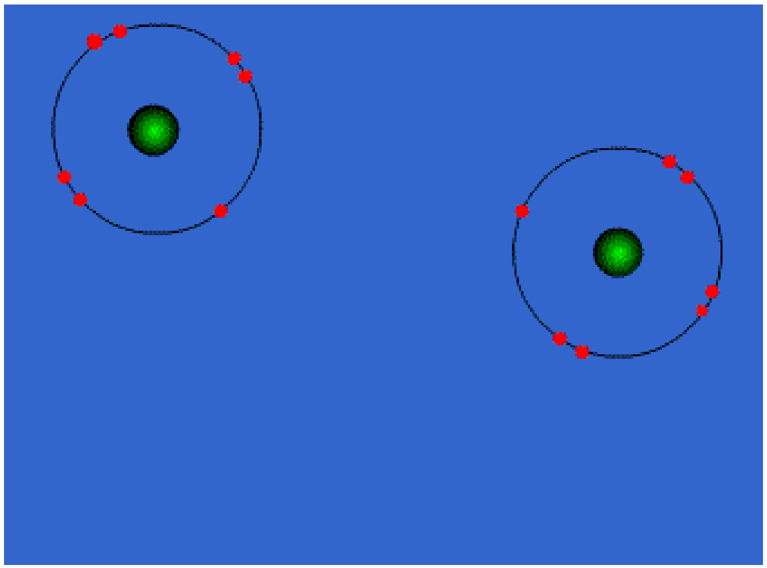
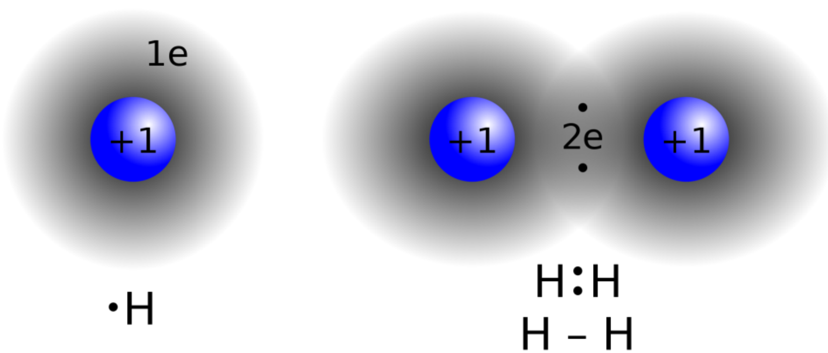
$Li(s) + 1/2F_2(g) \rightarrow LiF(s)$ ΔH (overall) = -617 kJ/mol

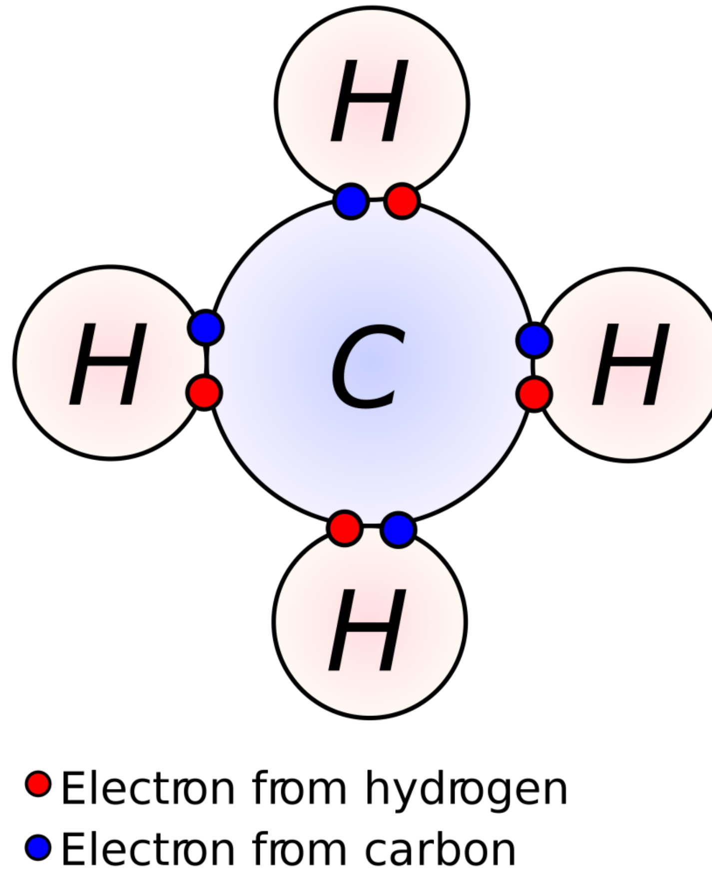


Covalent Bonds

Electrons shared between two atoms → octet rule





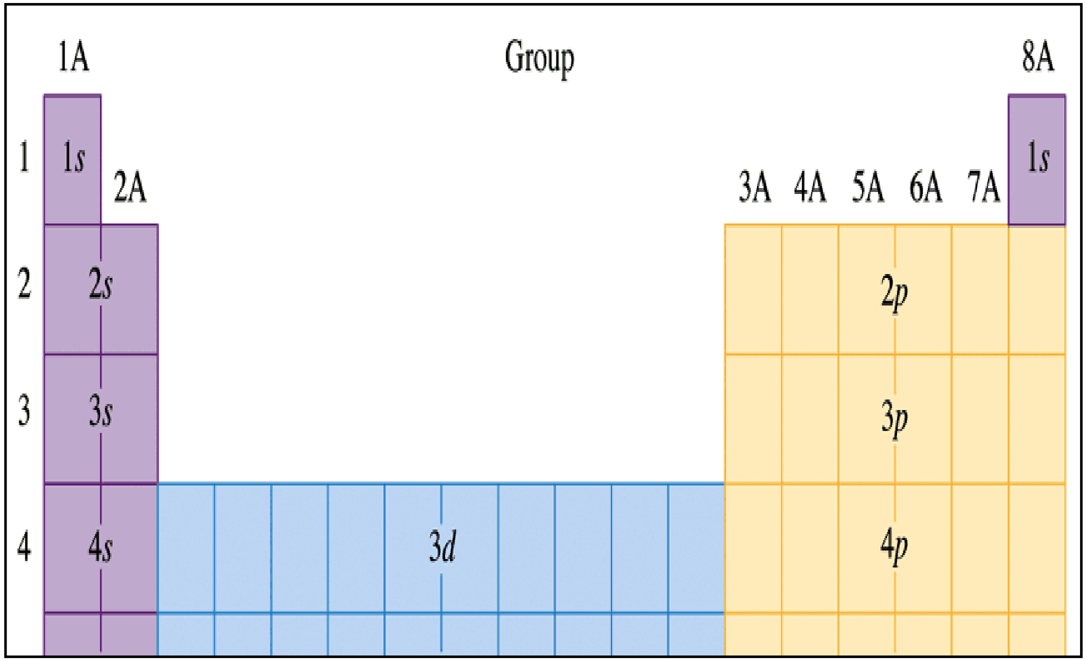


Octet rule for covalent bond:

Atoms want to have closed shell electron configuration

H-atom → wants to have **two electrons ($1s^2$)**

From Boron (B) to Chlorine (Cl) → want to have **8 electrons (octet, $2s^2 2s^6$)**



Stable with 2e

Stable with 8e

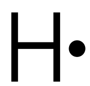
Stable with 8e

Octet rule

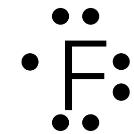
Stable with 8e or 18e

Lewis structure and octet rules:

* Specify the number of valence electrons as dots:

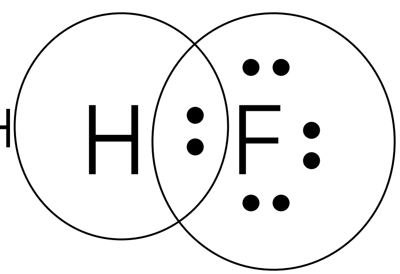


1-valence electron
of H-atom



7-valence electrons:
[He] $(2s)^2(2p)^5$
2 + 5 = 7 electrons

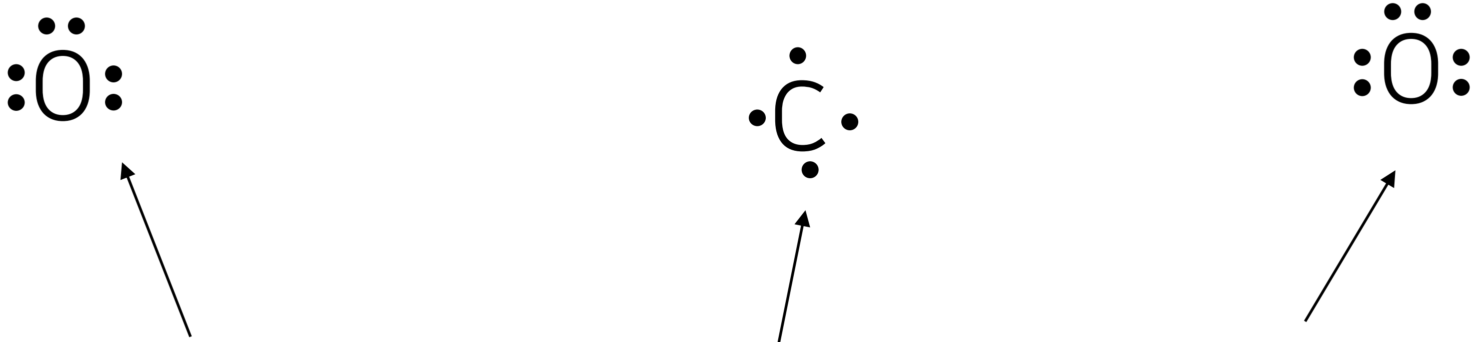
2 electros for H



8 electrons for F

Two electrons are shared:

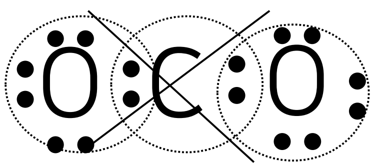
H—F



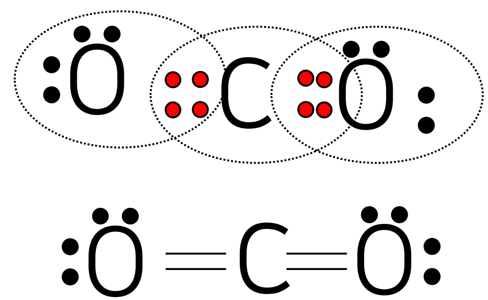
6 electrons 4 electrons 6 electrons

Total number of valence electrons = 6 (O) + 4 (C)+ 6 (O) = 16

8 4 8



8 8 8



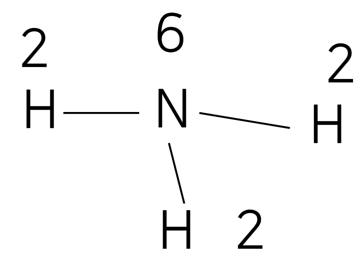
Tips on drawing Lewis structure

NH_3

- Count total number of valence electrons.

5(N)+3(H)= 8 electrons

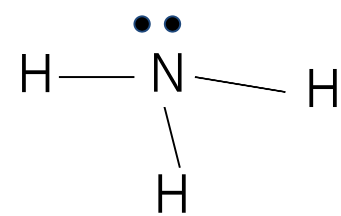
- Draw single bonds



- Use the remaining electrons to achieve noble gas configuration for each atom

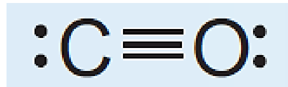
2 electrons remaining

8 – 6 (3 bonds) = 2

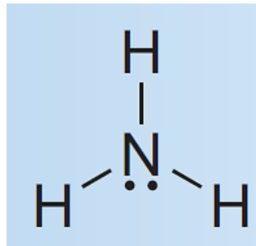


Exercises

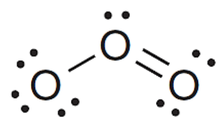
CO_2, CO



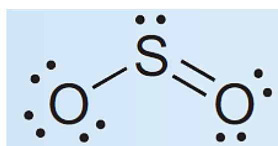
NH_3



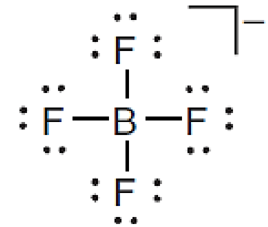
O_3



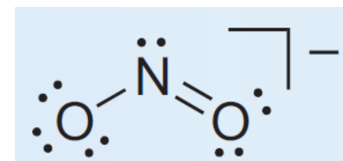
SO_2



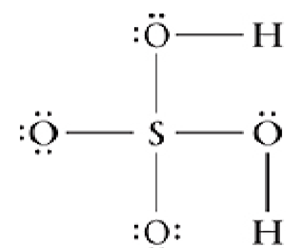
BF_4^-



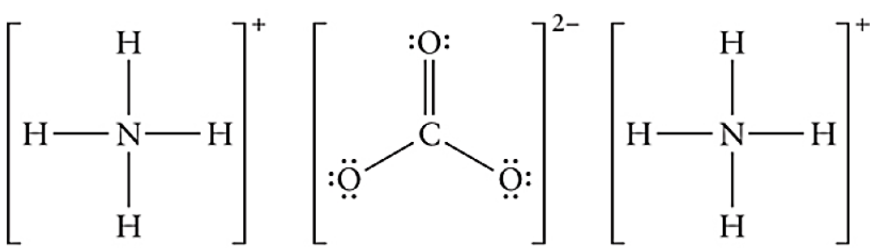
NO_2^-

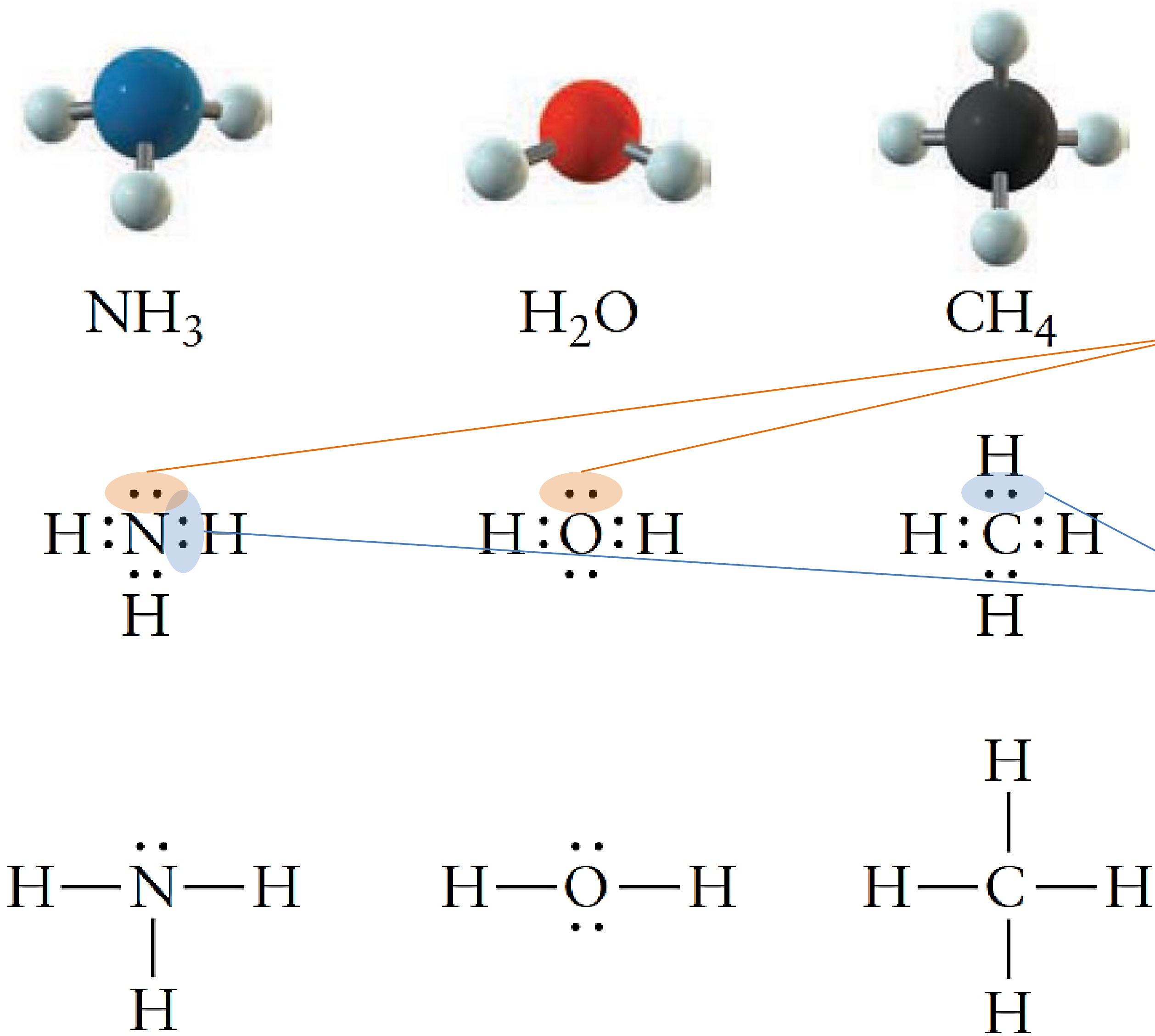


SO_4^{2-}, H_2SO_4



$(NH_4)_2CO_3$

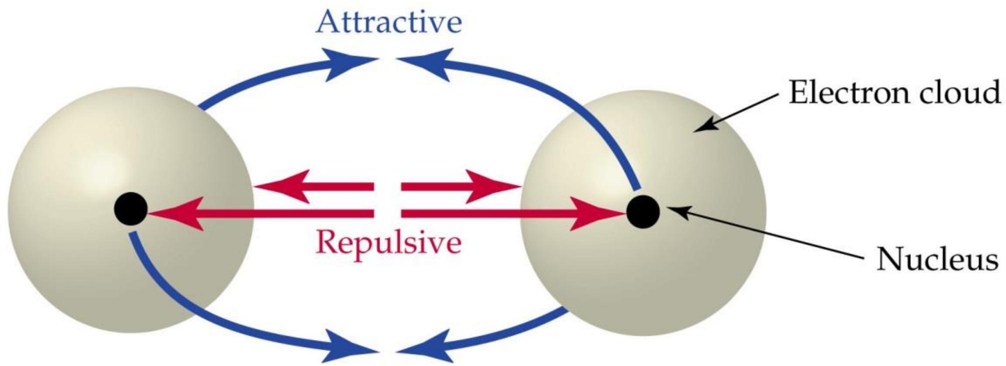


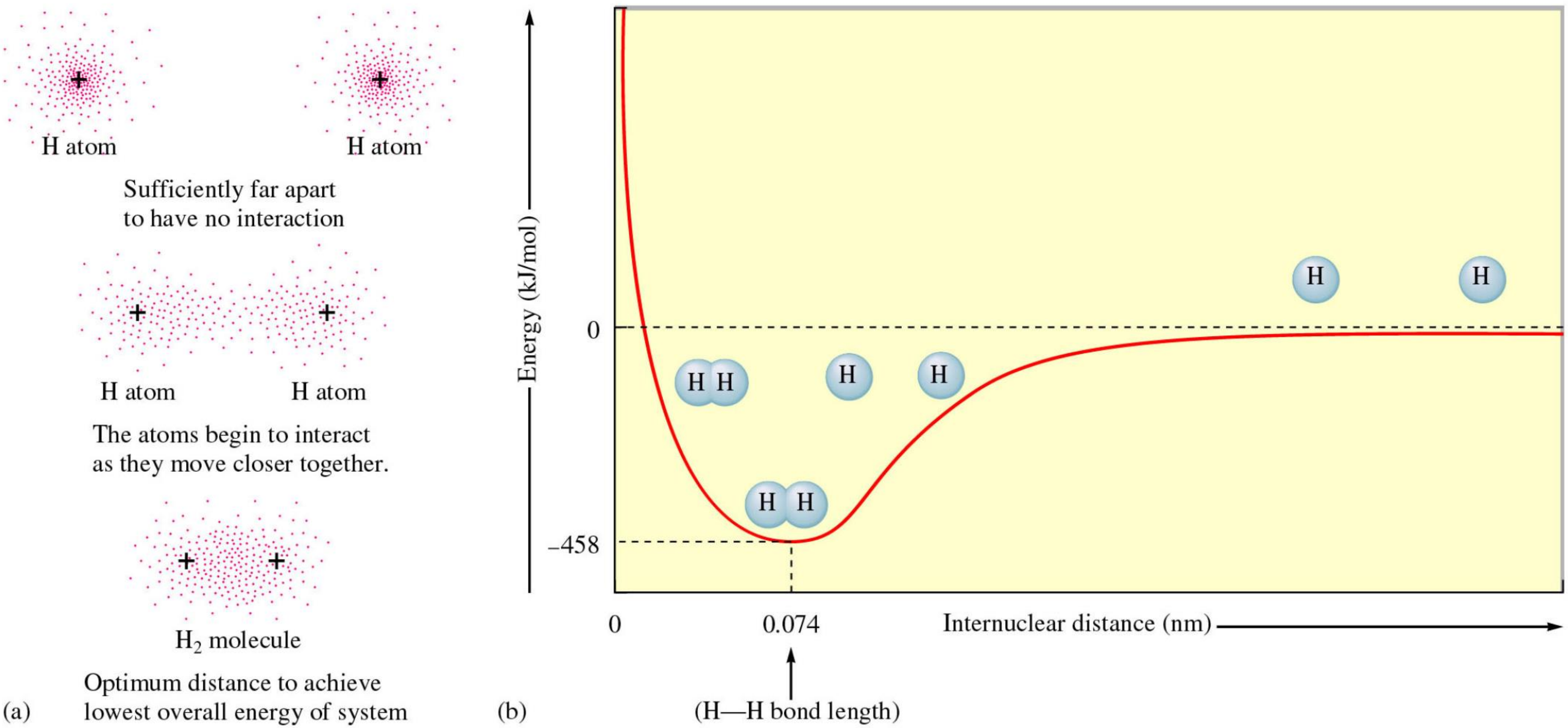


Lone pair e-

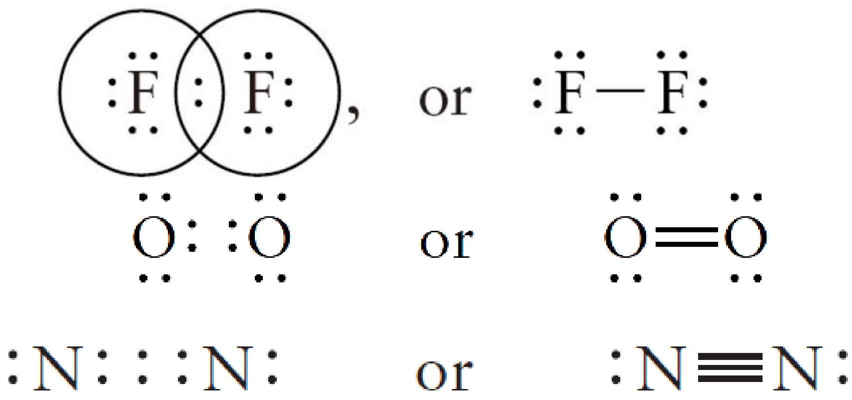
Shared pair e-
Bonding pair

No information
about the shape
of the molecules!
: Chapter3


Attractive
Electron cloud
Repulsive
Nucleus


H atom
H atom
Sufficiently far apart
to have no interaction
H atom
H atom
The atoms begin to interact
as they move closer together.
H_2 molecule
Optimum distance to achieve
lowest overall energy of system
(a)
Energy (kJ/mol)
0
–458
H H
H
H
H H
H
H
0
0.074
Internuclear distance (nm)
(H—H bond length)
(b)

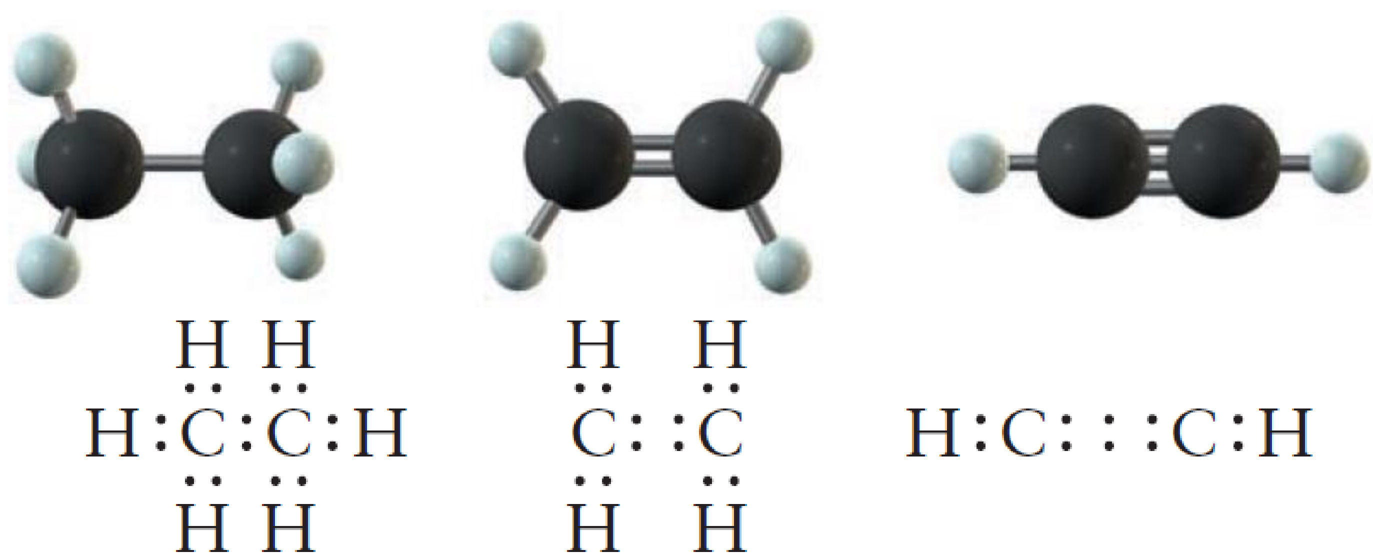
Bond order = # of shared electrons between a specific pair of atoms / 2



1.42 Å, 155 kJ/mol

1.21 Å, 495 kJ/mol

1.10 Å, 942 kJ/mol



1.54 Å, 345 kJ/mol 1.34 Å, 612 kJ/mol 1.20 Å, 809 kJ/mol

2.8. Formal Charge

Formal Charge is defined with the following assumptions

1) The bonding is perfectly covalent

2) Each atom has exactly a half-share in the bonding electrons

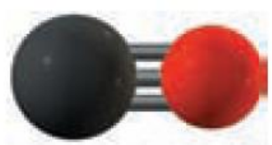
$$\boldsymbol{Formal\ Charge = V - (L + \frac{1}{2}B)}$$

V = # of valence (e-)s in the free atom

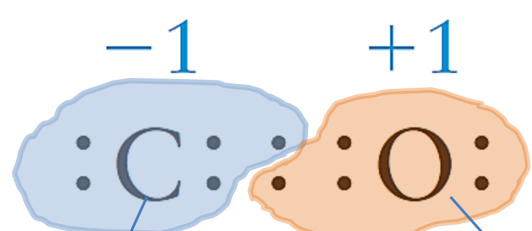
L = # of lone pair (e-)s

B = # of shared pair (e-)s

Example



:C: : :O:



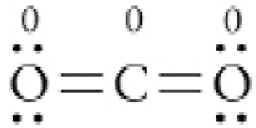
C: $1s^2 2s^2 2p^2$
O: $1s^2 2s^2 2p^4$

6-(2+(1/2)*6)
=6-(2+3)=+1

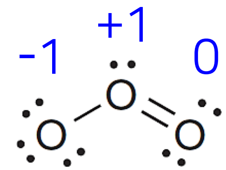
4-(2+(1/2)*6)=4-(2+3)=-1

Exercises

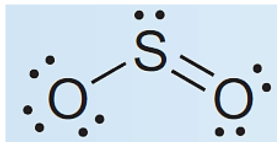
CO_2



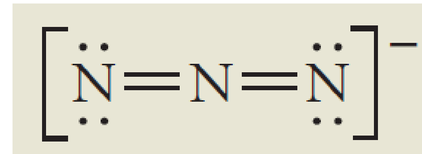
O_3



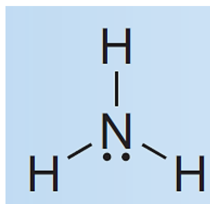
SO_2



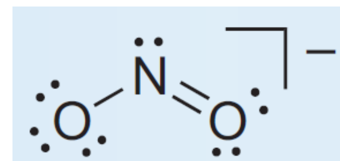
N_3^-



NH_3

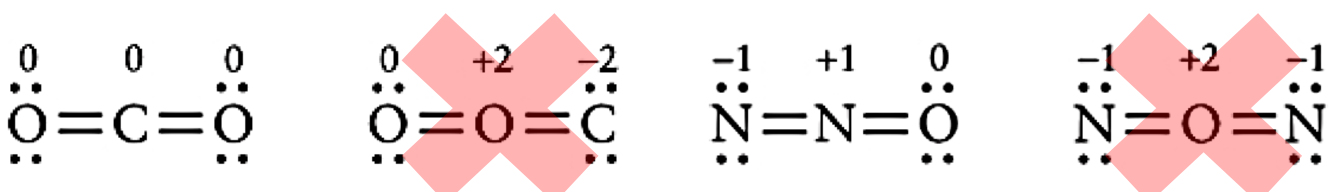


NO_2^-



◈ The formal charges of the individual atoms are closest to zero

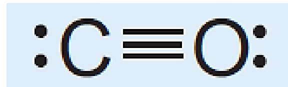
→ the **lowest energy** arrangement of the atoms and electrons



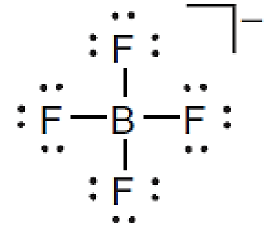
Exercise

Please practice!!!

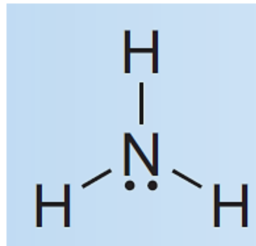
CO_2, CO



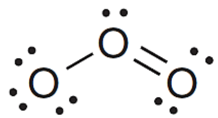
BF_4^-



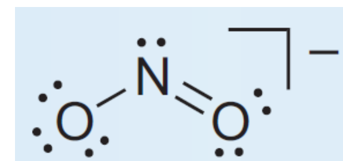
NH_3



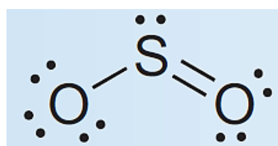
O_3



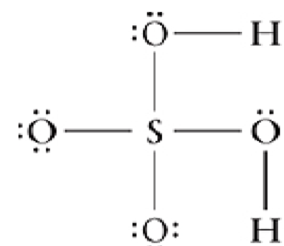
NO_2^-



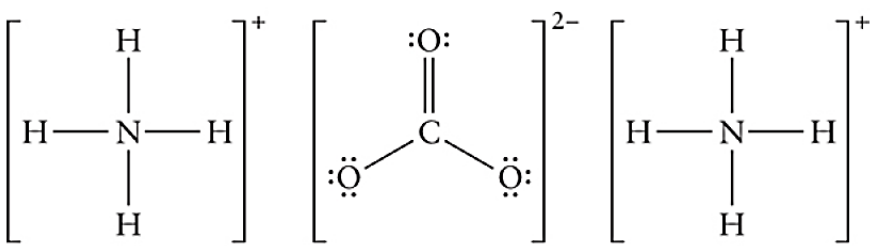
SO_2



SO_4^{2-}, H_2SO_4

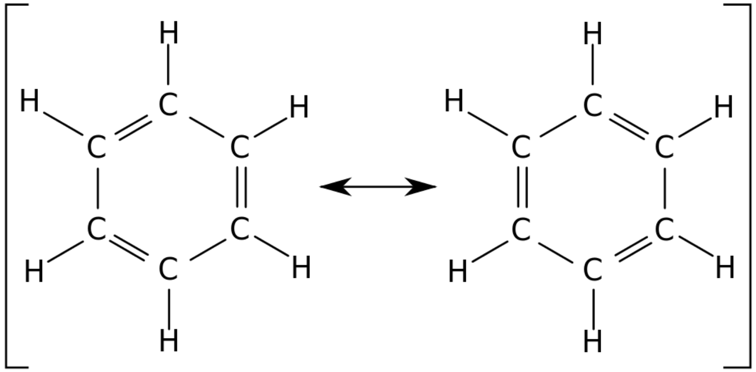


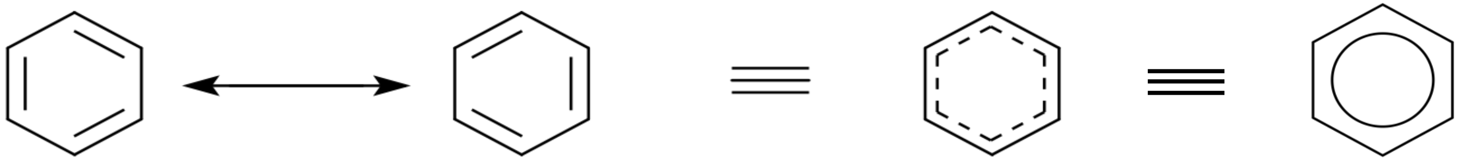
$(NH_4)_2CO_3$



2.7. Resonance

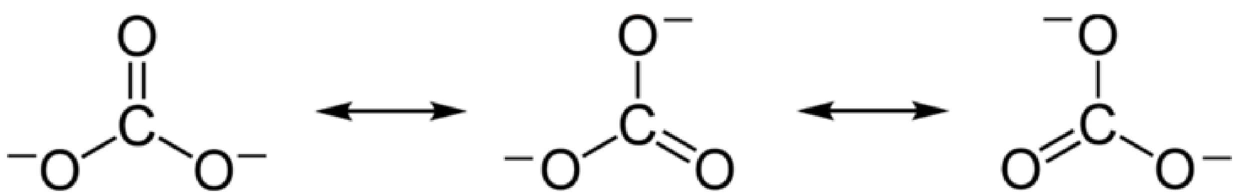
Some molecules can be represented by **different Lewis structure** in which the locations of the electrons (not the nuclei) vary. → resonance structure



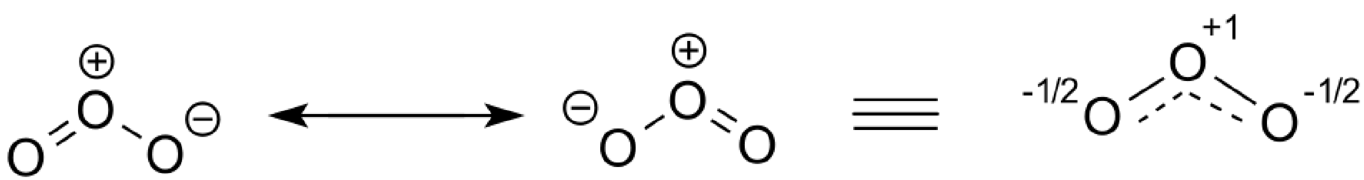


◈ Delocalization

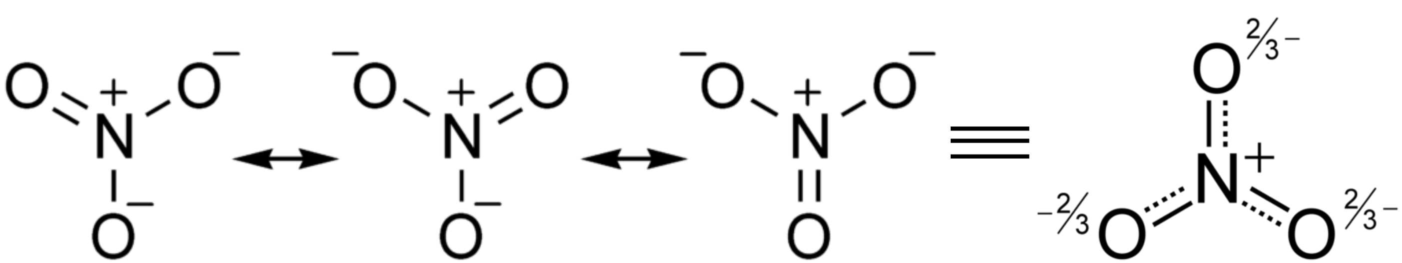
: Shared electrons are distributed over several pairs of atoms and cannot be identified with just one pair of atoms



carbonate



ozone; trioxygen



nitrate

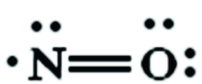
Exception to the Octet Rule

2.9. Radicals and Biradicals

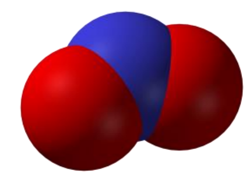
Radical

An atom, molecule, or ion that has unpaired valence electrons

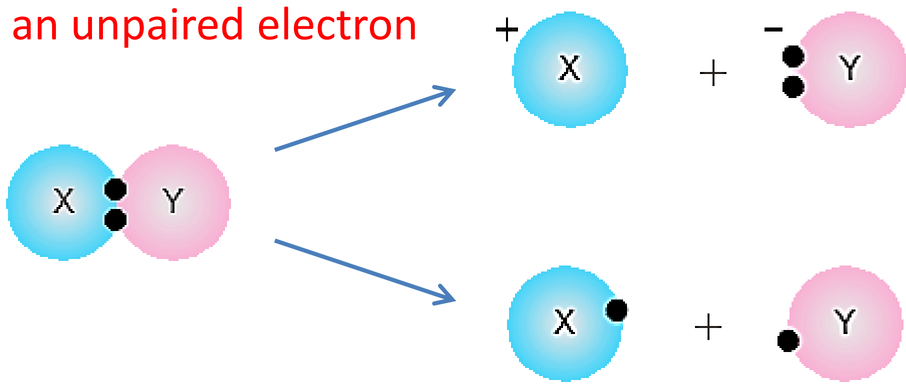
$NO, NO_2, \cdot CH_3, \cdot OH, \cdot O_2^-$

24(3X8) – 17(5+6+6)=7
7/2=3.5 bonds??
3 bonds+ an unpaired electron



16(2X8) – 11(5+6)=5
5/2=2.5 bonds??
2 bonds+ an unpaired electron



H^+ Cl^-

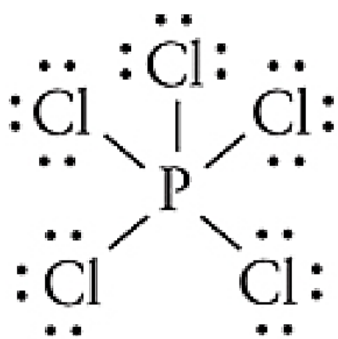
$H_3C\cdot$ $\cdot OH$

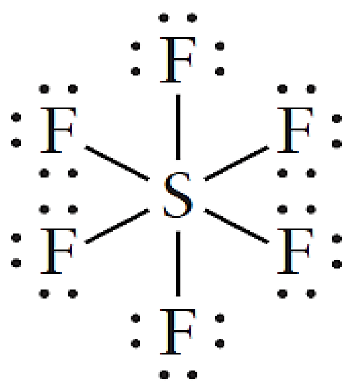
2.10. Expanded Valence Shells

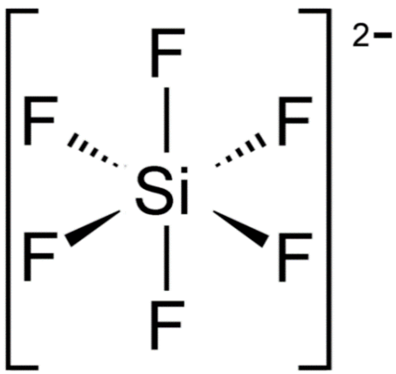
Hypervalent compound

more than 8 valence electrons

$$PCl_3\ (l) + Cl_2\ (g) \rightarrow PCl_5\ (g)$$



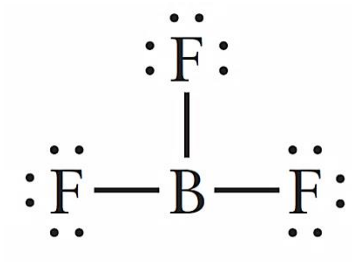


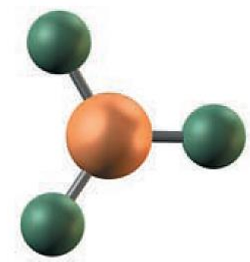


When the central atom in a molecule has empty d-orbitals close in energy to the valence orbitals…such as P, S, Si, Cl…

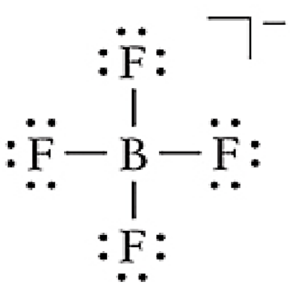
2.11. The Unusual Structures of Some Group 13/III Compounds

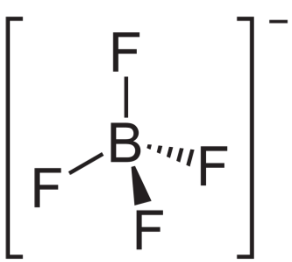
Incomplete octet: Fewer than 8 valence electrons

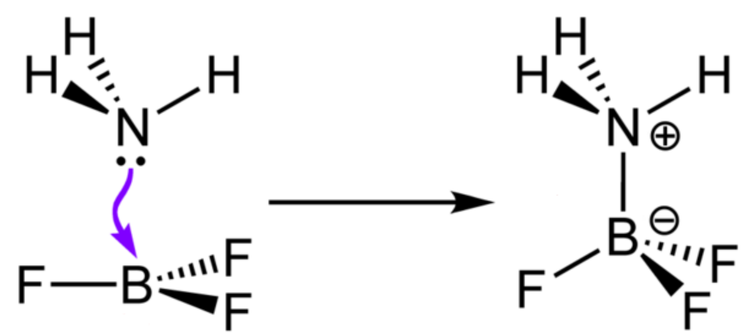




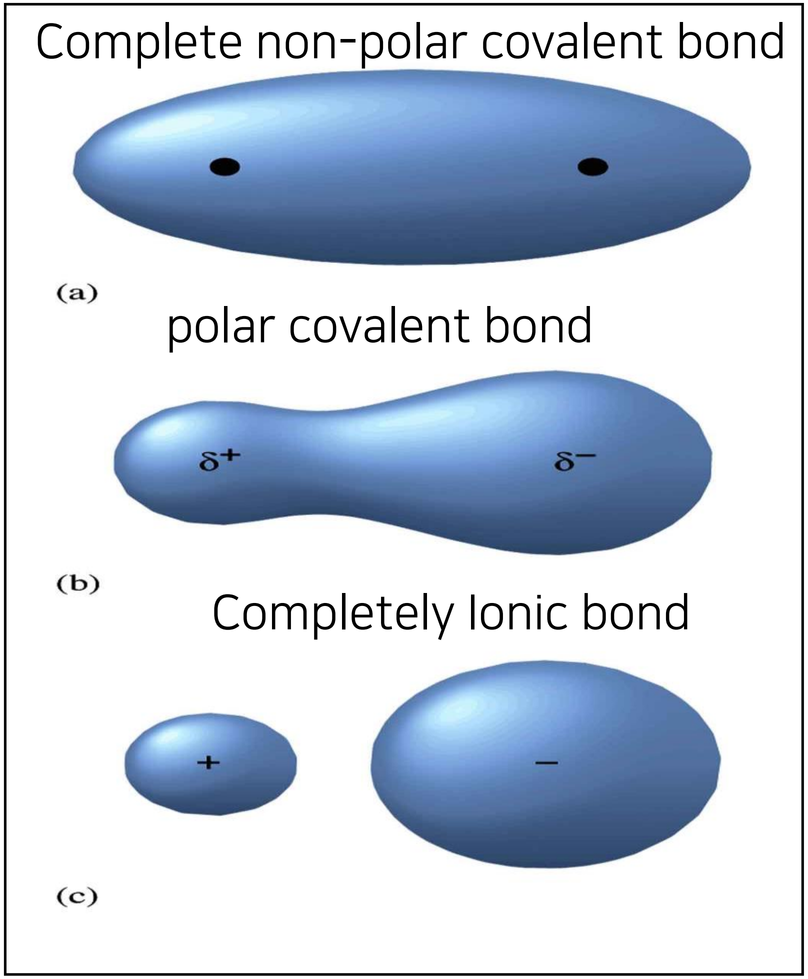
Coordinate covalent bond







In real AB-type chemical bonds, there is no 100% ionic or 100% covalent bond !



Homo-diatomic (AA) molecules (F_2, H_2)
→ 100% Covalent

NaI: less ionic, more covalent

NaCl: more ionic, less covalent

How do we quantify the ionic character?

Polar covalent bonds

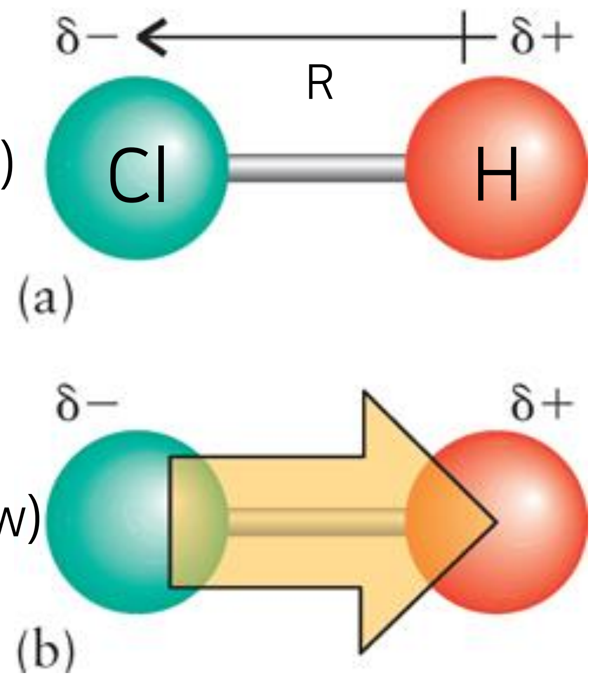
Some atoms like to have electrons

Some atoms do not like electrons

Partial charges

dipole direction (old)

dipole direction (new)



Typo here!

$$\mu = \delta R$$

SI-unit of dipole moment, μ = C. m
Common unit of dipole moment = Debye (D)
1 D = 3.336×10^{-30} C.m

For HCl, experimentally measure μ= 1.1 Debye and R = 100 pm = 10^{-10} m
$\delta = 1.1 \times 3.336 \times 10^{-30}$ C. m / 10^{-10} m = $1.1 \times 3.336 \times 10^{-20}$ C = 3.7×10^{-20} C = 0.23e

2.12. Correcting the Covalent Model: Electronegativity

Electronegativity (χ)

Electron-pulling power of an atom

when it is a part of a molecule

Not the same as “electron affinity” because electron affinity is determined in the gas phase with a discrete atom.
vs
Electronegativity: when it is a part of a molecule.

1) Mulliken scale

$$\chi = \frac{1}{2}(I + E_{ea})$$

2) Table: Electronegativity in Linus Pauling scale

	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
				H 2.2				He
2	Li 1.0	Be 1.6	B 2.0	C 2.6	N 3.0	O 3.4	F 4.0	Ne
3	Na 0.93	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2	Ar
4	K 0.82	Ca 1.3	Ga 1.6	Ge 2.0	As 2.2	Se 2.6	Br 3.0	Kr
5	Rb 0.82	Sr 0.95	In 1.8	Sn 2.0	Sb 2.1	Te 2.1	I 2.7	Xe
6	Cs 0.79	Ba 0.89	Tl 2.0	Pb 2.3	Bi 2.0	Po 2.0	At	Rn

H 2.20																	He
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

Roughly,

$$(\chi_A - \chi_B) \geq 2 \qquad \text{ionic}$$
$$0.5 \leq (\chi_A - \chi_B) \leq 1.5 \qquad \text{polar covalent}$$
$$(\chi_A - \chi_B) \leq 0.5 \qquad \text{covalent}$$

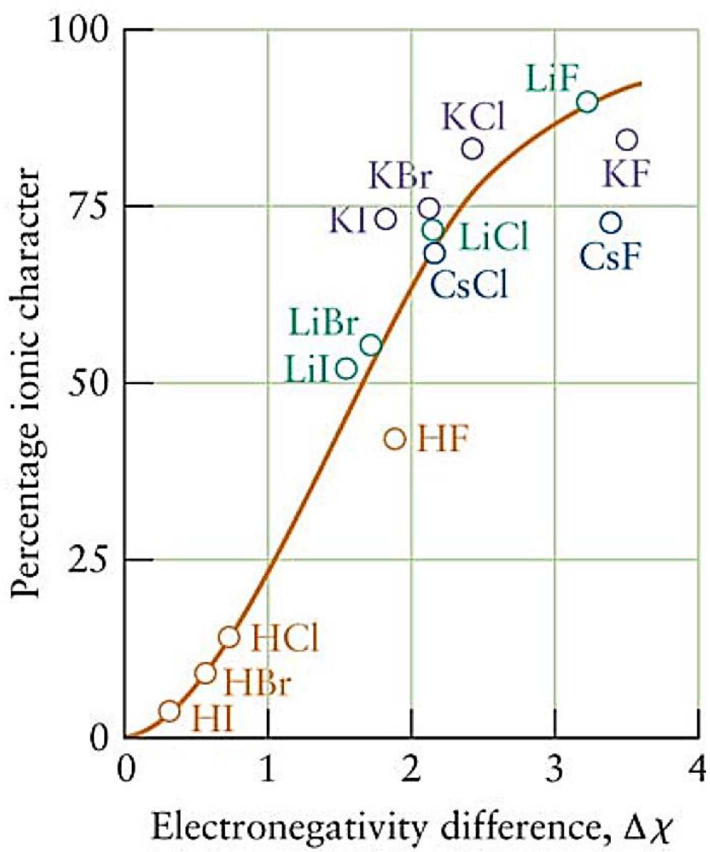


TABLE 3.7

Dipole Moments of Diatomic Molecules

Molecule	Bond Length (Å)	Dipole Moment (D)	% Ionic Character (100 δ)
H_2	0.751	0	0
CO	1.131	0.112	2
NO	1.154	0.159	3
HI	1.620	0.448	6
ClF	1.632	0.888	11
HBr	1.424	0.828	12
HCl	1.284	1.109	18
HF	0.926	1.827	41
CsF	2.347	7.884	70
LiCl	2.027	7.129	73
LiH	1.604	5.882	76
KBr	2.824	10.628	78
NaCl	2.365	9.001	79
KCl	2.671	10.269	82
KF	2.176	8.593	82
LiF	1.570	6.327	84
NaF	1.931	8.156	88

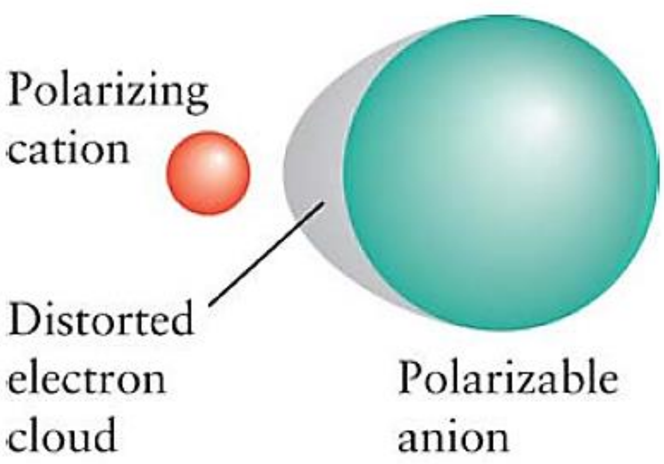
2.13. Correcting the Ionic Model: Polarizability

Polarizing power

- Property of ions (or atoms) that cause distortions of electron clouds

Highly **Polarizable** ions (or atoms)

- Readily undergo a large distortion of their electron cloud



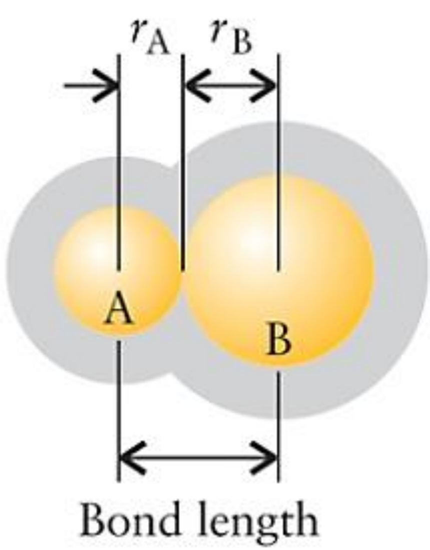
All ionic bonds have some covalent character.

The Strengths & Lengths of Covalent Bonds

2.14. Bond Strength

2.15. Variation in Bond Strength

2.16. Bond Length



Covalent radii of hydrogen atom and the p-block elements (in picometer)

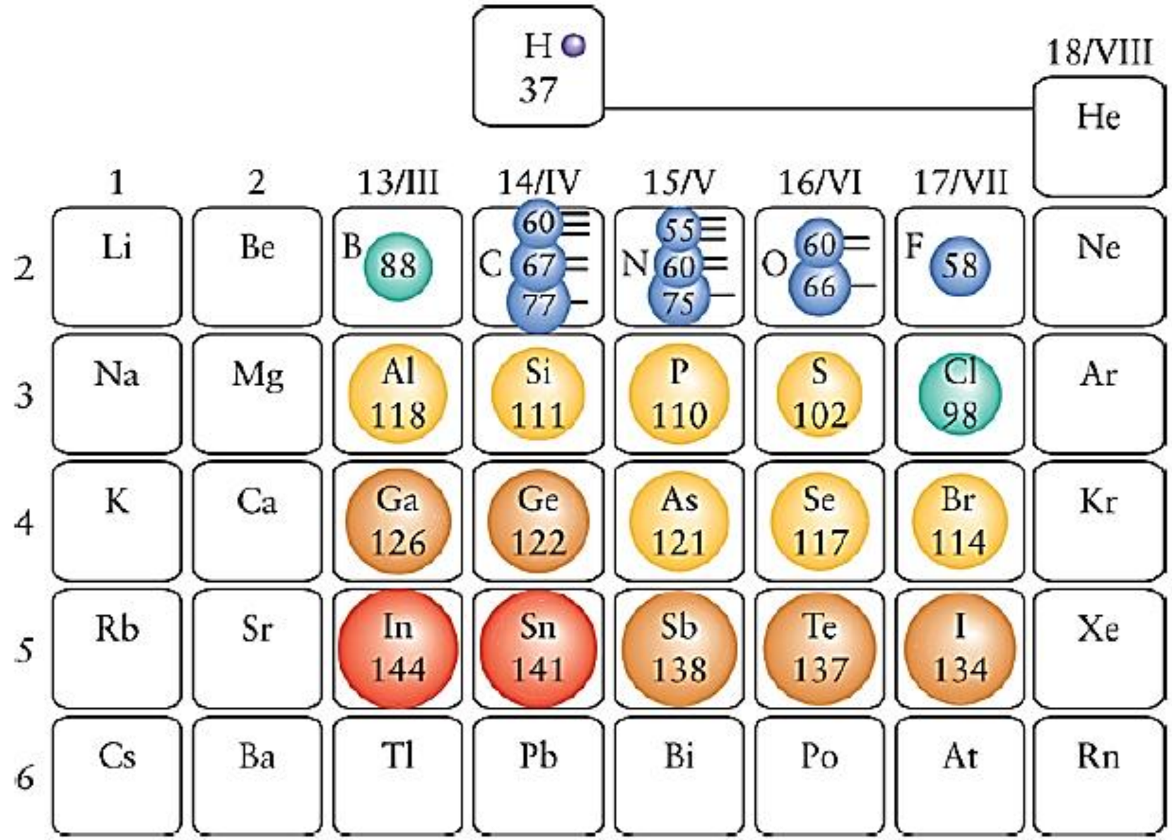


TABLE 3.3

Properties of Diatomic Molecules

Molecule	Bond Length (Å)	Bond Energy (kJ mol^{-1})
H_2	0.751	433
N_2	1.100	942
O_2	1.211	495
F_2	1.417	155
Cl_2	1.991	240
Br_2	2.286	190
I_2	2.669	148
HF	0.926	565
HCl	1.284	429
HBr	1.424	363
HI	1.620	295
ClF	1.632	252
BrF	1.759	282
BrCl	2.139	216
ICl	2.324	208
NO	1.154	629
CO	1.131	1073

TABLE 3.5

Three Types of Carbon–Carbon Bonds

Bond	Molecule	Bond Length (Å)	Bond Energy (kJ mol^{-1})
C—C	C_2H_6 (or H_3CCH_3)	1.536	345
C=C	C_2H_4 (or H_2CCH_2)	1.337	612
C≡C	C_2H_2 (or HCCH)	1.204	809

TABLE 3.6

Average Bond Lengths (in Å)

C—C	1.54	N—N	1.45	C—H	1.10
C=C	1.34	N=N	1.25	N—H	1.01
C=C	1.20	N≡N	1.10	O—H	0.96
C—O	1.43	N—O	1.43	C—N	1.47
C=O	1.20	N=O	1.18	C≡N	1.16