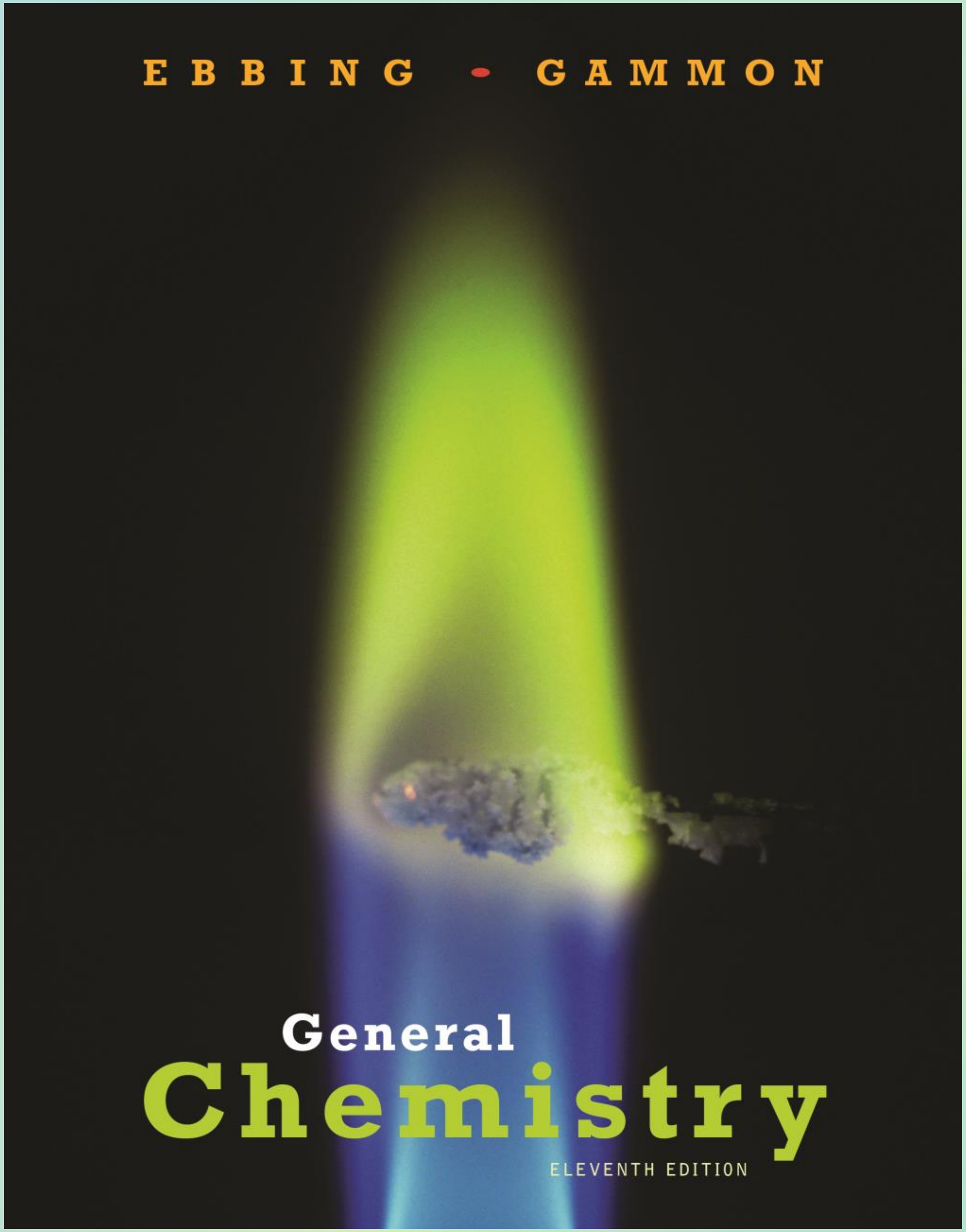
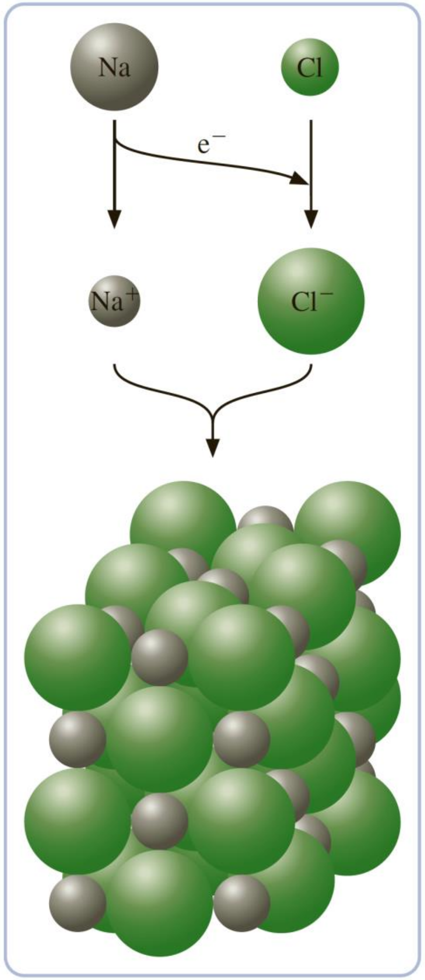


Ionic and Covalent Bonding

➢ **Ionic Bonds** **9.1** Describing Ionic Bonds



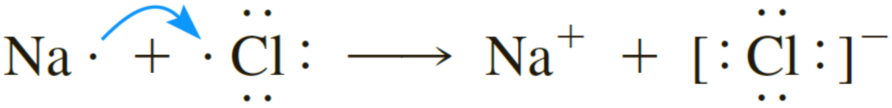
- ✓ An **ionic bond** is *a chemical bond formed by the electrostatic attraction between positive and negative ions.*
- ✓ The bond forms between two atoms when one or more electrons are transferred from the valence shell of one atom to the valence shell of the other.
- ✓ The atom that loses electrons becomes a *cation* (positive ion), and the atom that gains electrons becomes an *anion* (negative ion).
- ✓ As a result of the electron transfer, ions are formed, each of which has a noble-gas configuration.

$$\mathrm{Na([Ne]3}s^{1}) + \mathrm{Cl([Ne]3}s^{2}3p^{5}) \longrightarrow \mathrm{Na^{+}([Ne])} + \mathrm{Cl^{-}([Ne]3}s^{2}3p^{6})$$

Low ionization E High electron affinity

➢ Lewis Electron-Dot Symbols

✓ is *a symbol in which the electrons in the valence shell of an atom or ion are represented by dots placed around the letter symbol of the element*



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

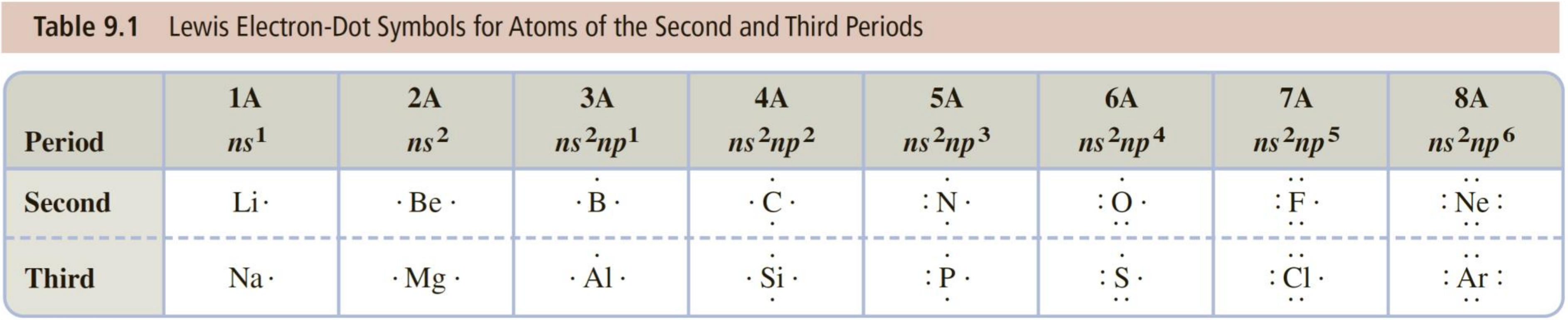
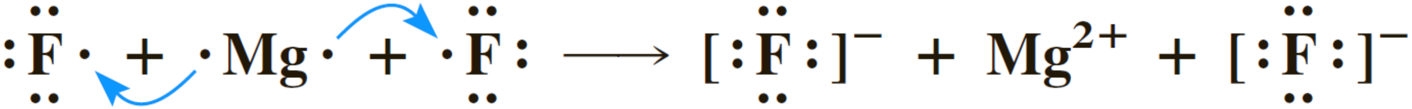


Table 9.1 Lewis Electron-Dot Symbols for Atoms of the Second and Third Periods

Period	1A ns^1	2A ns^2	3A ns^2np^1	4A ns^2np^2	5A ns^2np^3	6A ns^2np^4	7A ns^2np^5	8A ns^2np^6
Second	$\mathrm{Li}\cdot$	$\cdot\mathrm{Be}\cdot$	$\cdot\overset{\cdot}{\mathrm{B}}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{C}}}\cdot$	$:\overset{\cdot}{\underset{\cdot}{\mathrm{N}}}\cdot$	$:\overset{\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}\cdot$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}\cdot$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Ne}}}:$
Third	$\mathrm{Na}\cdot$	$\cdot\mathrm{Mg}\cdot$	$\cdot\overset{\cdot}{\mathrm{Al}}\cdot$	$\cdot\overset{\cdot}{\underset{\cdot}{\mathrm{Si}}}\cdot$	$:\overset{\cdot}{\underset{\cdot}{\mathrm{P}}}\cdot$	$:\overset{\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}\cdot$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot$	$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Ar}}}:$

(Q) Use Lewis electron-dot symbols to represent the transfer of electrons from magnesium to fluorine atoms to form ions with noble-gas configurations



$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}\cdot + \cdot\mathrm{Mg}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}: \longrightarrow [:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:]^{-} + \mathrm{Mg}^{2+} + [:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{F}}}:]^{-}$$

➢ Energy Involved in Ionic Bonding

✓ Formation of an ionic bond between a sodium atom and a chlorine atom:

(1) $Na_{(g)} \rightarrow Na^{+}_{(g)} + e^{-}$ ΔH i.e = 496 kJ/mol

(2) $Cl_{(g)} + e^{-} \rightarrow Cl^{-}_{(g)}$ ΔH E.A = −349 kJ/mol

✓ The overall energy is (496 − 349) = 147 kJ/mol

→the process requires more energy to remove an electron from the sodium atom than is gained when the electron is added to the chlorine atom.

→ formation of ions from the atoms is not in itself energetically favorable.

BUT When positive and negative ions bond →energy is released to make the overall process favorable.

Coulomb's law

$$E = \frac{kQ_1Q_2}{r}$$

Coulomb's law states that *the potential energy obtained in bringing two charges* Q1 *and* Q2, *initially far apart, up to a distance* r *apart is directly proportional to the product of the charges and inversely proportional to the distance between them.*

$$E = \frac{kQ_1Q_2}{r}$$

k = 8.99 x10^9 J.m/C^2

The charge on Na^+ is +*e* and that on Cl^- is −*e*.

e= 1.602 x10^{-19} C

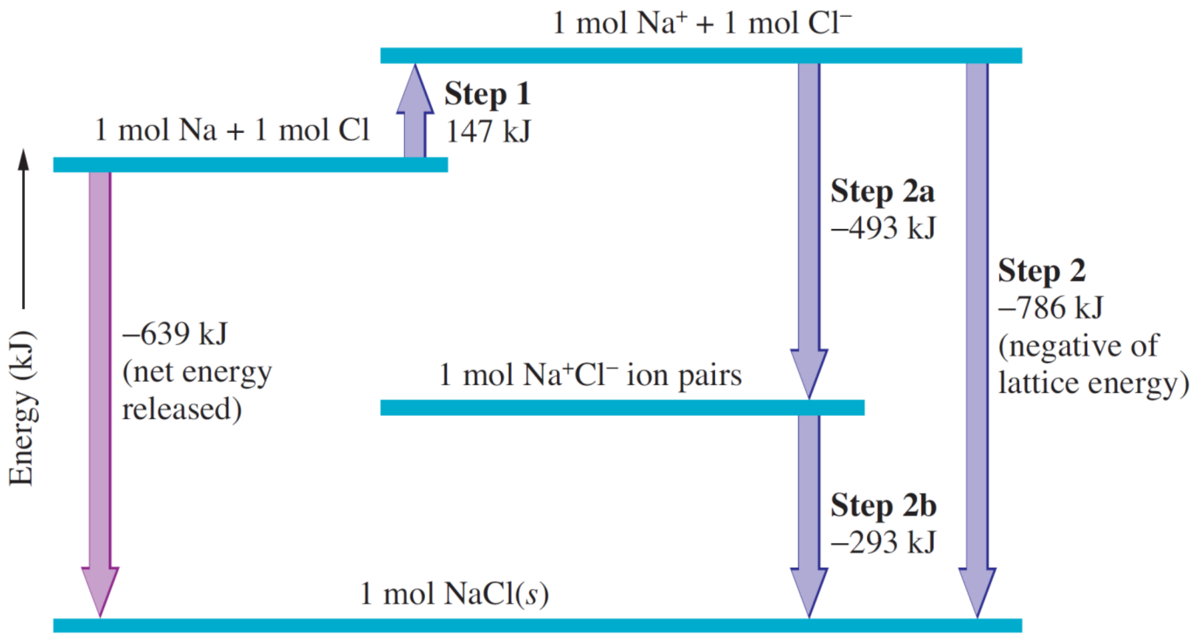
r = distance between Na^+ and Cl^- = 282 pm, or 2.82 x 10^{-10} m.

$$E = \frac{-(8.99 \times 10^9\ \mathrm{J \cdot m/C^2}) \times (1.602 \times 10^{-19}\ \mathrm{C})^2}{2.82 \times 10^{-10}\ \mathrm{m}} = -8.18 \times 10^{-19}\ \mathrm{J}$$

- ✓ The minus sign means energy is released
- ✓ This energy is for the formation of one ion pair
- ✓ Multiplying by Avogadro's number, 6.02 x 10^{23} → −493 kJ/mol

- ✓ The **lattice energy** is *the change in energy that occurs when an ionic solid is separated into isolated ions in the gas phase.* For sodium chloride, the process is

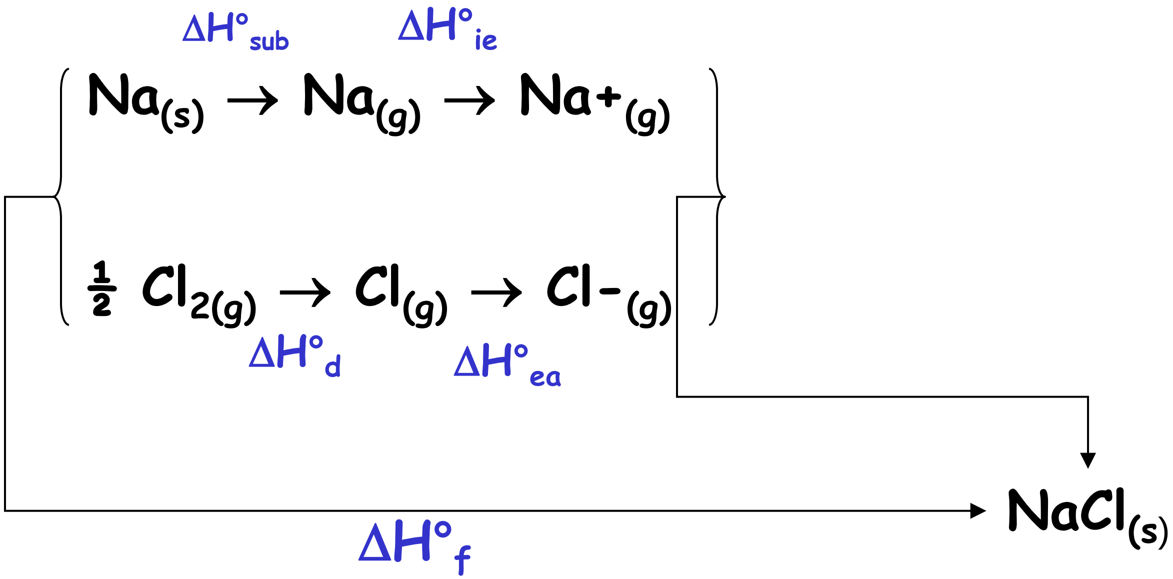
$$\mathrm{NaCl}(s) \longrightarrow \mathrm{Na}^{+}(g) + \mathrm{Cl}^{-}(g)$$



- ✓ The negative sign shows that there has been a net decrease in energy, which you expect when stable bonding has occurred.

- ✓ Ionic bond forms between elements if the ionization energy of one is sufficiently small and the electron affinity of the other is sufficiently large

The Born-Haber Cycle for NaCl (Energy diagram)



$\Delta H°_{sub}$ $\Delta H°_{ie}$

$Na_{(s)} \rightarrow Na_{(g)} \rightarrow Na^{+}_{(g)}$

$\frac{1}{2}\, Cl_{2(g)} \rightarrow Cl_{(g)} \rightarrow Cl^{-}_{(g)}$

$\Delta H°_{d}$ $\Delta H°_{ea}$

$NaCl_{(s)}$

$\Delta H°_{f}$

$$\Delta H°_{f} = \Delta H°_{sub} + \Delta H°_{ie} + 1/2\ \Delta H°_{d} + \Delta H°_{ea} + U_o$$

U_o = Lattice Energy

$$-411 = 109 + 496 + 1/2\ (242) + (-349) + U_o$$

$$U_o = -788 \text{ kJ/mol}$$

You must use the correct stoichiometry and signs to obtain the correct lattice energy.

➢ Properties of Ionic Substances

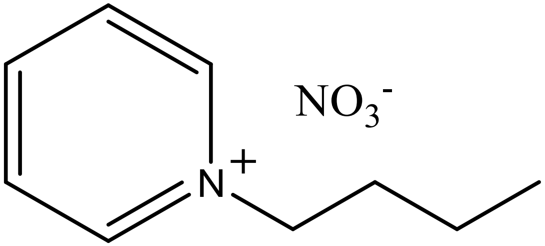
- ✓ Strong ionic bonds (strong electrostatic interaction) → high-melting points of ionic solids.

m.p of MgO (2800 °C) > m.p NaCl (801 °C)

$$E = \frac{kQ_1Q_2}{r}$$

charges (Mg^{2+} and O^{2-}), charges (Na^{+} and Cl^{-}),

- ✓ The liquid melt from an ionic solid consists of ions, and so the liquid melts conducts an electric current.
- ✓ Ionic liquids have low m.p (RT) because of the cations are large and non-spherical.



9.2 Electron Configurations of Ions

➢ Ions of the Main-Group Elements

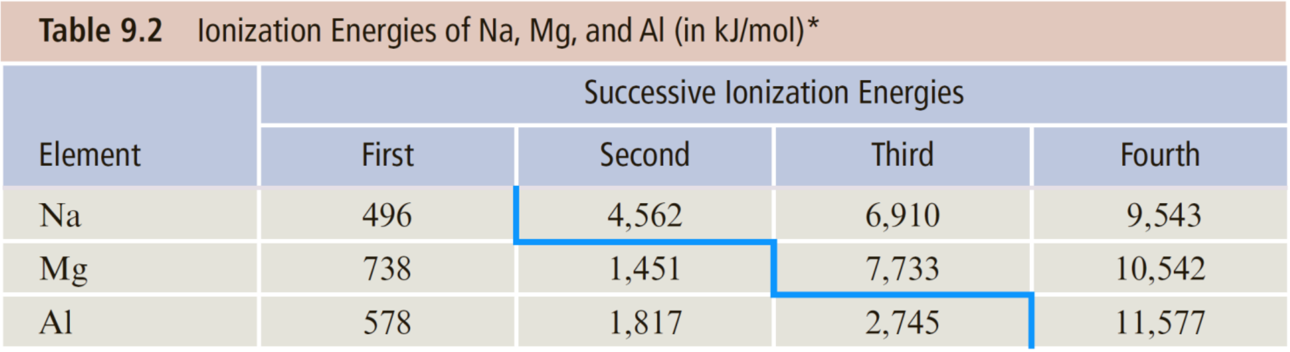


Table 9.2 Ionization Energies of Na, Mg, and Al (in kJ/mol)*

Element	Successive Ionization Energies			
	First	Second	Third	Fourth
Na	496	4,562	6,910	9,543
Mg	738	1,451	7,733	10,542
Al	578	1,817	2,745	11,577

- ✓ Valence electrons are easily removed
- ✓ Much higher energy is needed to remove further electrons.
- → No compounds are found with ions having charges greater than the group number.
- ✓ Boron (Group 3A) doesn't form ionic compounds with B^{3+} ions, the bonding is normally covalent.
- ✓ The remaining elements of Group 3A do form compounds containing 3^+ ions because of decreasing ionization energy.
- ✓ Thallium in 3A, Period 6, has compounds with 1^+ ions and compounds with 3^+ ions

$$\mathrm{Tl}([\mathrm{Xe}]4f^{14}5d^{10}6s^{2}6p^{1}) \longrightarrow \mathrm{Tl}^{+}([\mathrm{Xe}]4f^{14}5d^{10}6s^{2}) + e^{-}$$

✓ The first three elements of Group 4A (C, Si, and Ge) are metalloids and usually form covalent rather than ionic bonds.

✓ Tin (Sn) and lead (Pb) (group 4A) commonly form ionic compounds with 2^+ ions.

✓ Tin forms tin(II) chloride, $SnCl_2$, which is an ionic compound and tin(IV) chloride $SnCl_4$ which is a covalent compound.

✓ Bi (group 5A) forms ionic Bi^{3+} cpds and covalent Bi^{5+} cpds.

✓ Anions of Groups 5A to 7A gain electrons (large EA) to form noble-gas or pseudo-noble-gas configurations.

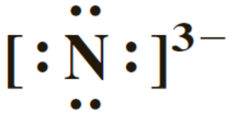
✓ Hydrogen forms compounds of the 1^- ion, H^- (hydride ion).

✓ Although the electron affinity of nitrogen ($2s^22p^3$) = 0

✓ N^{3-} ion ($2s^22p^6$) is stable in the presence of Li^+ (Li_3N)and other alkaline earth elements ions (Mg_3N_2).

(Q)Write the electron configuration and the Lewis symbol for N^{3-}.

N: [He]$2s^22p^3$ N^{3-}: [He]$2s^22p^6$



Sn: [Kr]$4d^{10}5s^25p^2$

Sn^{2+} : [Kr]$4d^{10}5s^2$

Sn^{4+} : [Kr]$4d^{10}$

➢ Transition-Metal Ions

✓ *M* $^{2+}$ is a common oxidation state as two electrons are removed from the outer ***ns*** shell.

Fe: [Ar] $4s^2\,3d^6$

Fe^{2+} : [Ar] $3d^6$ loses 4*s* electrons first

Fe^{3+} : [Ar] $3d^5$ then loses 3*d* electrons

(Q) What are the correct electron configurations for Cu & Cu^{2+} ?

A. [Ar] $3d^9 4s^2$, [Ar] $3d^9$

B. [Ar] $3d^{10} 4s^1$, [Ar] $3d^8 4s^1$

C. [Ar] $3d^{10} 4s^1$, [Ar] $3d^9$

D. [Ar] $3d^9 4s^2$, [Ar] $3d^{10} 4s^1$

E. [K] $3d^9 4s^2$, [Ar] $3d^9$

(Q) What are the correct electron configurations for zirconium(II) and zirconium(IV) ions?

A. [Kr] $5d^2$ [Kr] $4d^1$

B. [Ar] $4d^2 5s^2$ [Ar] $5s^2$

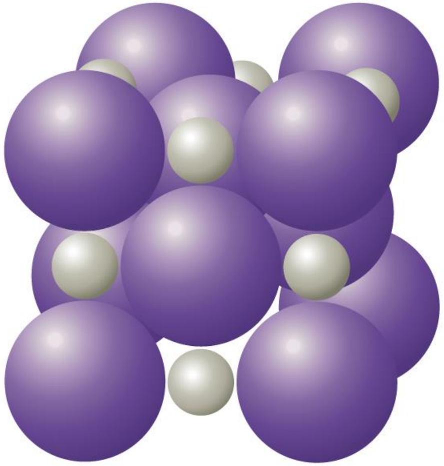
C. [Kr] $4d^2$ [Kr]

D. [Kr] $4d^6 5s^2$ [Kr] $4d^6$

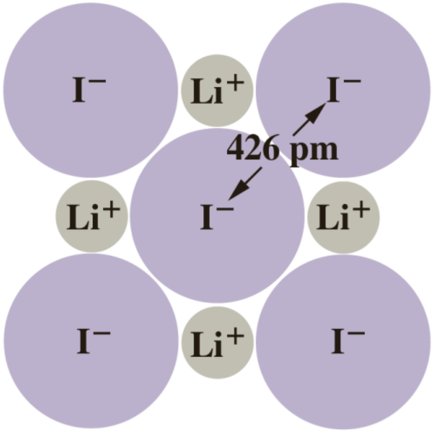
E. [Rb] $4d^2$ [Rb]

➢ 9.3 Ionic Radii

Determining the iodide ion radius in the lithium iodide (LiI) crystal



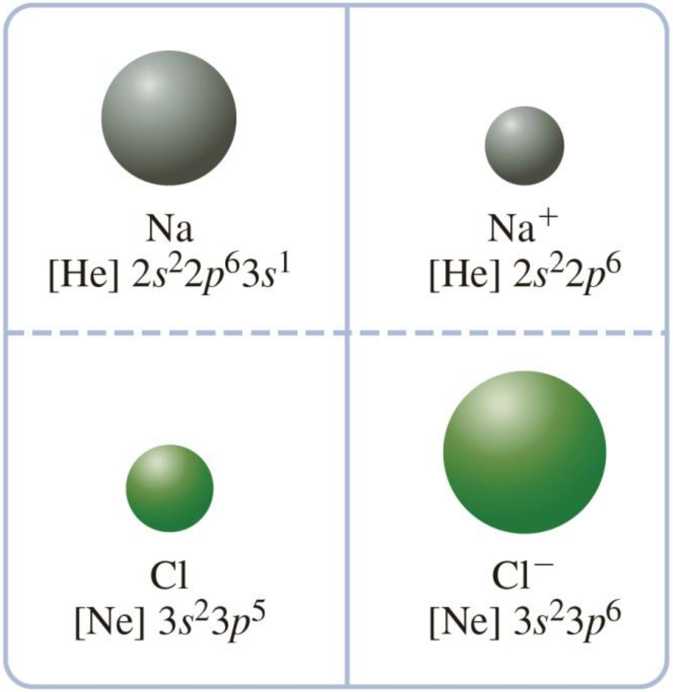
a A three-dimensional view of the crystal.



Ionic radius of I^-
= 426 / 2 = 213 pm

Exercise 9.6
arrange the following ions in order of increasing ionic radius: Sr^{2+}, Mg^{2+}, Ca^{2+}.

$Mg^{2+} < Ca^{2+} < Sr^{2+}$



✓ Ionic radii increase down any column because of the addition of electron shells.

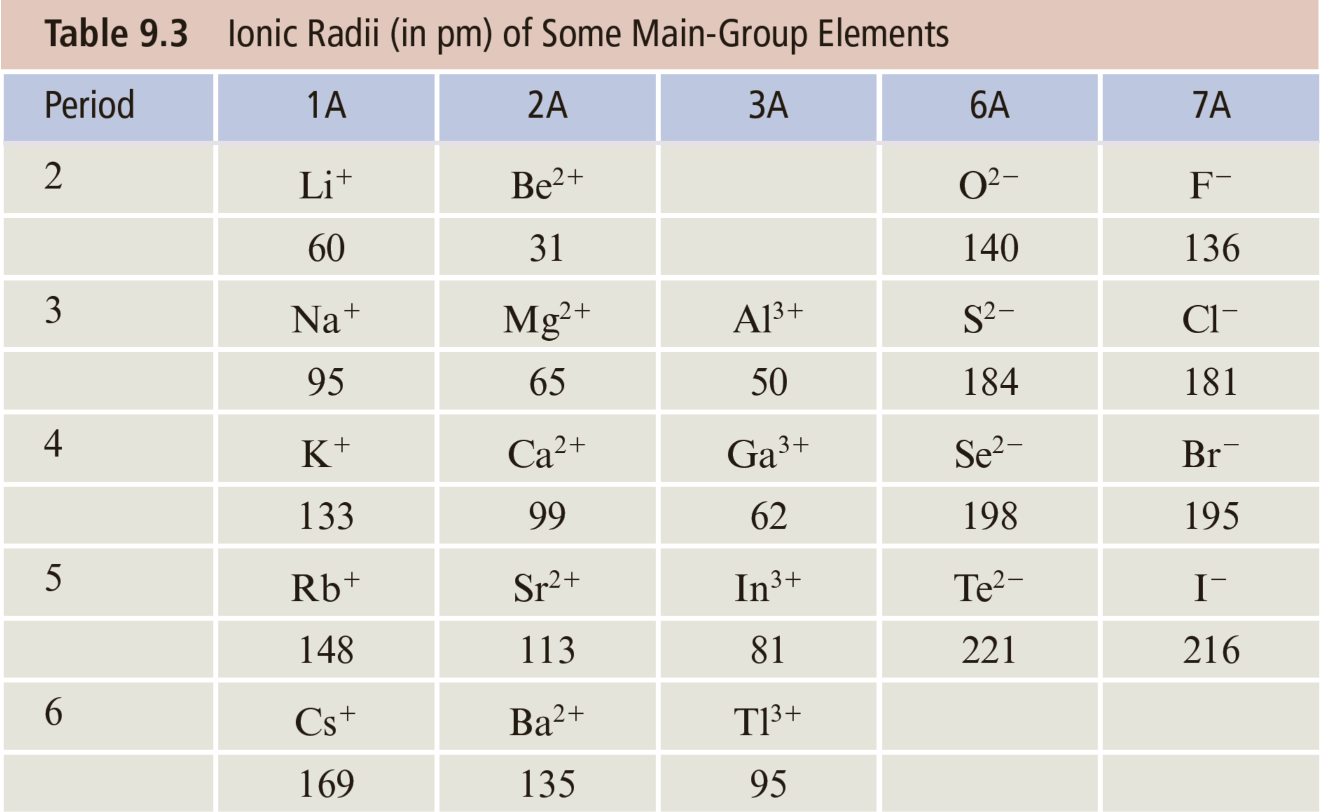


Table 9.3 Ionic Radii (in pm) of Some Main-Group Elements

Period	1A	2A	3A	6A	7A
2	Li^{+}	Be^{2+}		O^{2-}	F^{-}
	60	31		140	136
3	Na^{+}	Mg^{2+}	Al^{3+}	S^{2-}	Cl^{-}
	95	65	50	184	181
4	K^{+}	Ca^{2+}	Ga^{3+}	Se^{2-}	Br^{-}
	133	99	62	198	195
5	Rb^{+}	Sr^{2+}	In^{3+}	Te^{2-}	I^{-}
	148	113	81	221	216
6	Cs^{+}	Ba^{2+}	Tl^{3+}		
	169	135	95		

- ➢ Pattern across a period

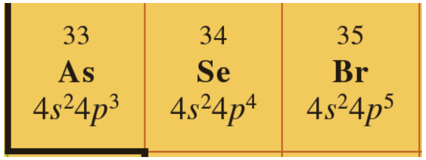
Cation	Na^+	Mg^{2+}	Al^{3+}
Radius (pm)	95	65	50

Anion	S^{2-}	Cl^-
Radius (pm)	184	181

- ✓ All of these cations have Ne configuration $1s^22s^22p^6$ but different nuclear charges (they are isoelectronic).
- ✓ **Isoelectronic** *refers to different species having the same number and configuration of electrons*

9.47 Arrange the following in order of increasing ionic radius:

As^{3-}, Se^{2-}, Br^-



33	34	35
As	**Se**	**Br**
$4s^24p^3$	$4s^24p^4$	$4s^24p^5$

$Br^- < Se^{2-} < As^{3-}$

- ✓ Within an isoelectronic series, the radius increases as the atomic number decreases

(Q) arrange the following ions in order of decreasing ionic radius:
F^-, Mg^{2+}, O^{2-}

isoelectronic series→ Mg^{2+} (Z=12) **<** F^- (Z=9) **<** O^{2-} (Z=8)

9.49 Arrange the following in order of increasing ionic radius: F^-, Na^+, and N^{3-}.

isoelectronic series→ Na^+ (Z=11) **<** F^- (Z=9) **<** N^{3-} (Z=7)

9.48 Which has the larger radius, N^{3-} or P^{3-}? **P^{3-}**

- **Covalent Bonds**
  - ✓ *a chemical bond formed by the sharing of a pair of electrons between atoms*.

9.4 Describing Covalent Bonds

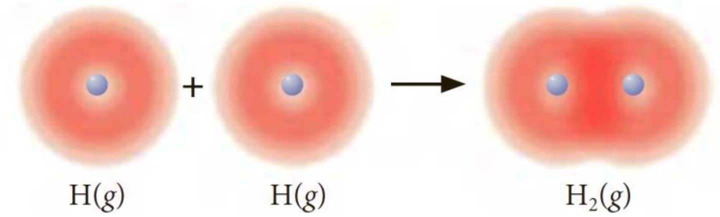


Figure 9.10 ▲

The electron probability distribution for the H_2 molecule The electron density (shown in red) occupies the space around both atoms.

- ✓ The distance between nuclei at minimum energy is called the *bond length* of H_2.

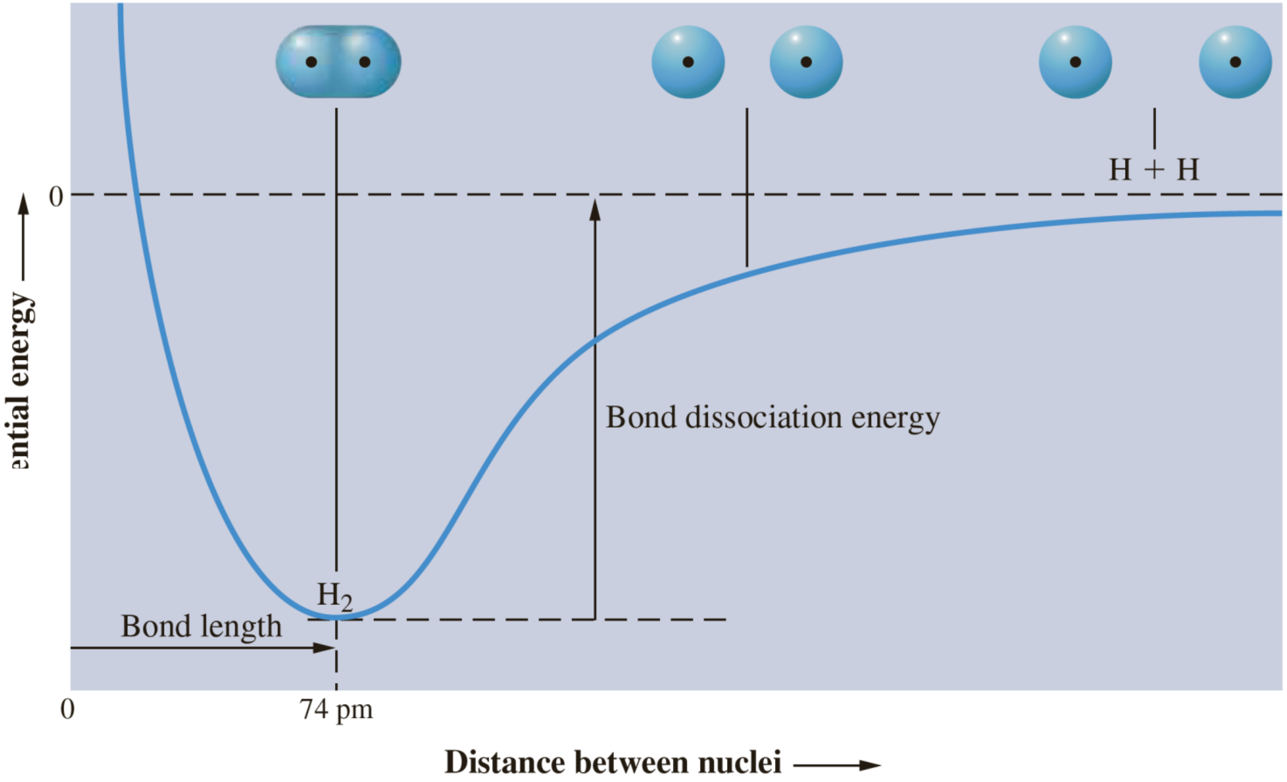
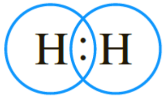


Figure 9.11 ◄

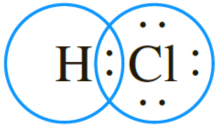
Potential-energy curve for H_2 The stable molecule occurs at the bond distance corresponding to the minimum in the potential-energy curve.

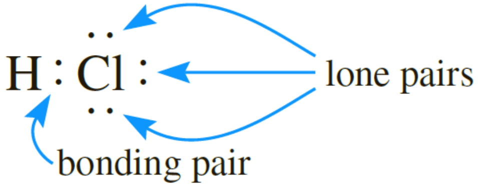
Lewis Formulas

$H\cdot + \cdot H \longrightarrow H:H$

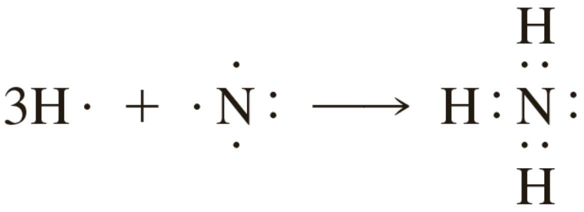


$H\cdot + \cdot\overset{..}{\underset{..}{Cl}}: \longrightarrow$





$$H:\overset{..}{\underset{..}{Cl}}:$$



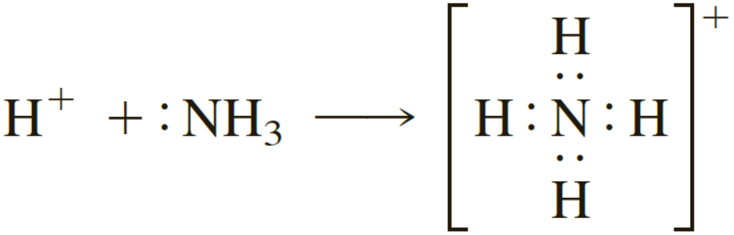
$$3H\cdot + \cdot\overset{\cdot}{\underset{\cdot}{N}}: \longrightarrow H:\overset{\overset{H}{..}}{\underset{\underset{H}{..}}{N}}:$$

Coordinate Covalent Bonds

✓ is *a bond formed when both electrons of the bond are donated by one atom*

$A\cdot + \cdot B \longrightarrow A:B$

$A + :B \longrightarrow A:B$

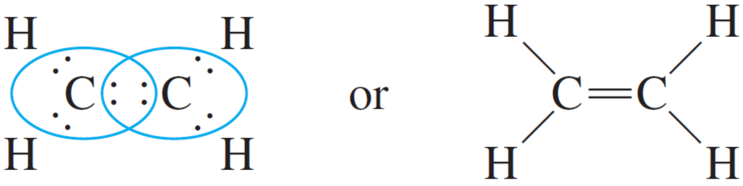


$$H^{+} + :NH_3 \longrightarrow \left[H:\overset{\overset{H}{..}}{\underset{\underset{H}{..}}{N}}:H \right]^{+}$$

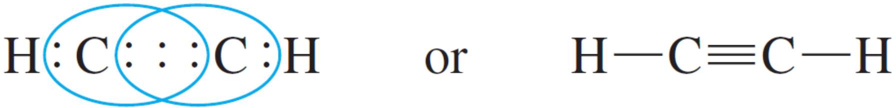
- **Octet Rule**

✓ *The tendency of atoms in molecules to have eight electrons in their valence shells (two for hydrogen atoms)*

- **Multiple Bonds**



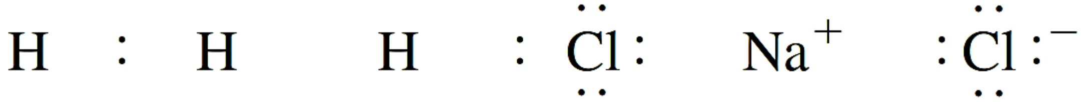
Ethylene



Acetylene

9.5 Polar Covalent Bonds (Polar Bonds)

✓ is *a covalent bond in which the bonding electrons spend more time near one atom than the other.*



Nonpolar covalent   Polar covalent   Ionic

➢ **Electronegativity** is *a measure of the ability of an atom in a molecule to draw bonding electrons to itself.*

✓ Mulliken electronegativity (χ): $X = \frac{I.E. + E.A.}{2}$

✓ F has large *E.A.* and large *I.E.* → large electronegativity

✓ Li has small *E.A.* and small *I.E.* → small electronegativity

✓ Pauling's electronegativity (χ): depends on bond enthalpies

✓ *Electronegativity increases from left to right and decreases from top to bottom in the periodic table.*

✓ Metals are the least electronegative elements (they are *electropositive*) and nonmetals the most electronegative.

✓ The absolute value of the difference in electronegativity of two bonded atoms gives a rough measure of the polarity of a bond

H—H, H—Cl, and Na—Cl

$\Delta\chi$: 0.0 0.9 2.1

$$\overset{\delta+}{\mathrm{H}}\text{—}\overset{\delta-}{\mathrm{Cl}}$$

Polar molecule

➢ Writing Lewis Electron-Dot Formulas

These will be done in class:

H_2O, NH_3, CCl_2F_2, CO_2, SCl_2, $POCl_3$, $COCl_2$, HSO_3Cl, CO_3^{2-}, NH_4^+, BF_4^-, H_3O^+, ClO_2^-.

CONCEPT CHECK 9.2

Each of the following may seem, at first glance, to be plausible electron-dot formulas for the molecule N_2F_2. Most, however, are incorrect for some reason. What concepts or rules apply to each, either to cast it aside or to keep it as the correct formula?

a

b

c

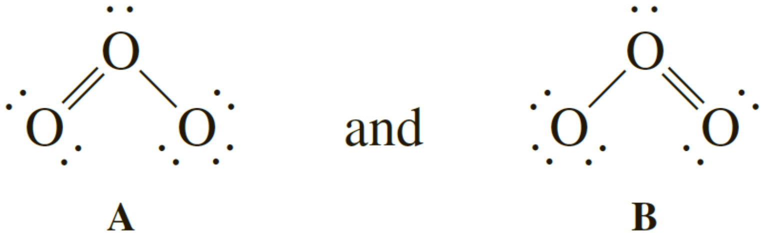
d

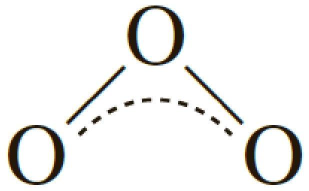
e

f

9.7 Delocalized Bonding: Resonance

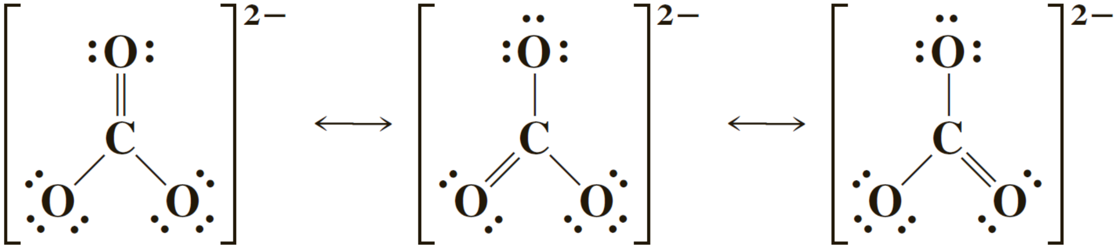
Ozone (O_3)





- ✓ The lengths of the two oxygen–oxygen bonds (that is, the distances between the atomic nuclei) are both 128 pm.
- ✓ **delocalized bonding**

CO_3^{2-}



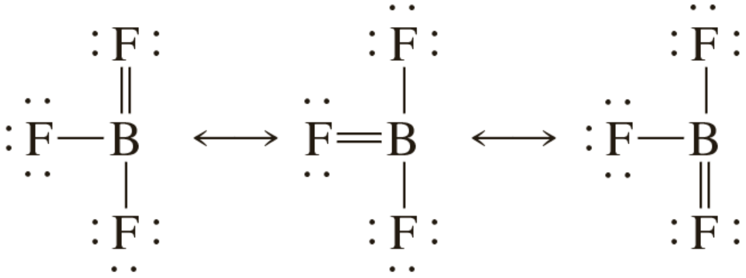
NO_3^-

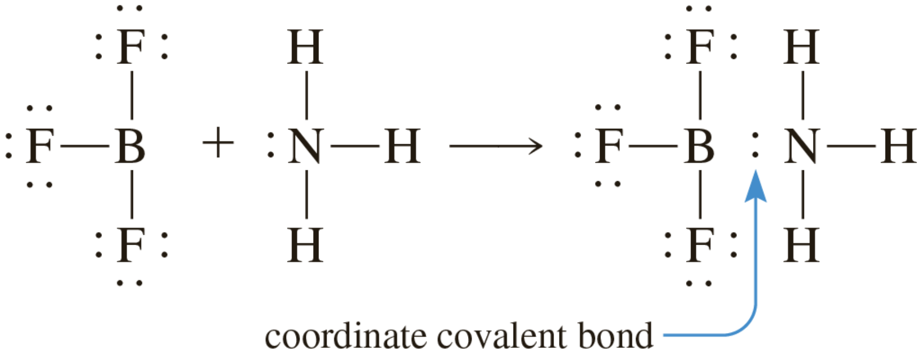
9.8 Exceptions to the Octet Rule

These will be done in class:

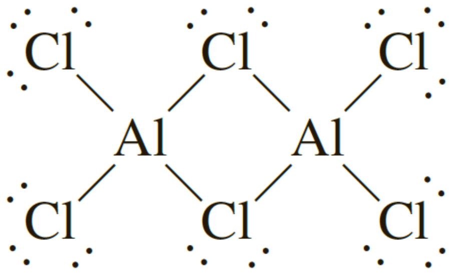
PF_5, SF_6, XeF_4, SF_4

BF_3, $BeCl_2$,





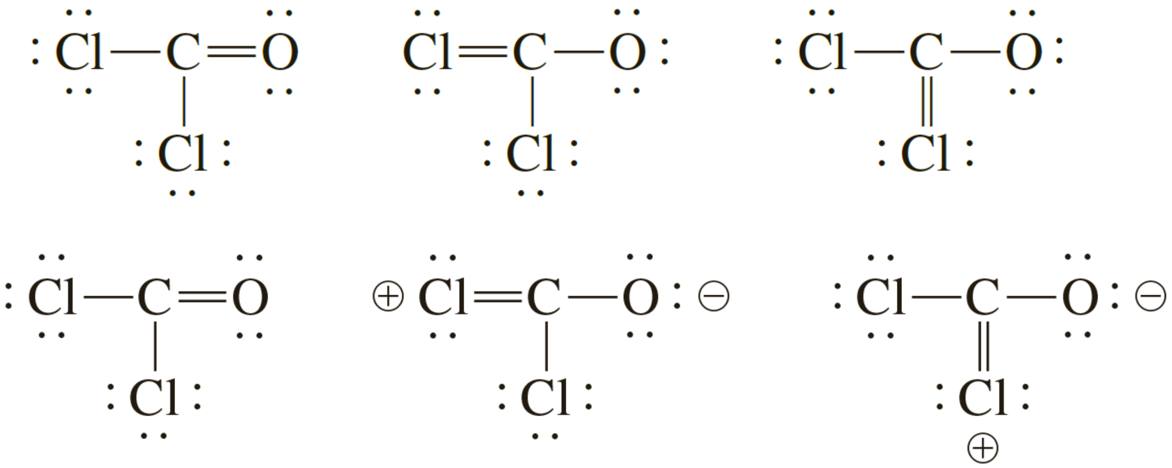
$AlCl_3$ @ RT & at melting point (very low 192°C**)**



two of the Cl atoms are in ***bridge* positions**

9.9 Formal Charge and Lewis Formulas

$COCl_2$



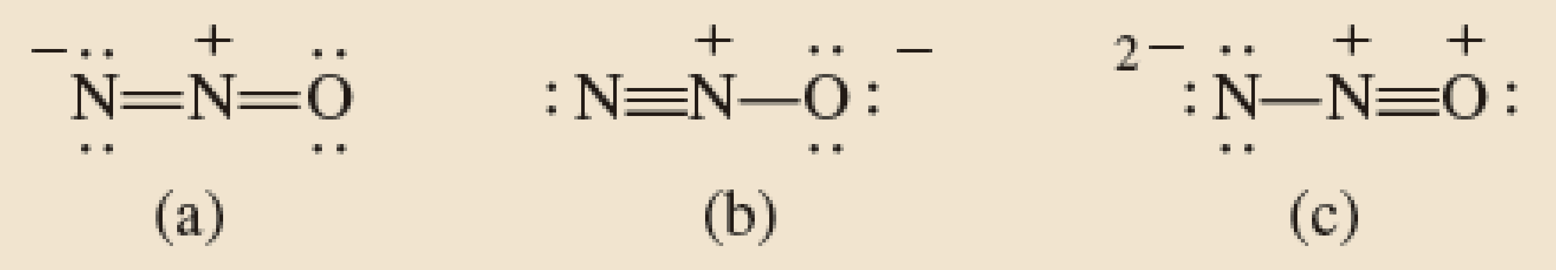
RULE A Whenever you can write several Lewis formulas for a molecule, choose the one having the lowest magnitudes of formal charges.

RULE B When two proposed Lewis formulas for a molecule have the same magnitudes of formal charges, choose the one having the negative formal charge on the more electronegative atom.

RULE C When possible, choose Lewis formulas that do not have like charges on adjacent atoms.

(Q) Write the Lewis formula that best describes the charge distribution in the sulfuric acid molecule, H_2SO_4, according to the rules of formal charge. (HNO_3, H_3PO_4, HCN)

(Q) Draw three resonance structures for the molecule nitrous oxide, N_2O (the atomic arrangement is NNO)

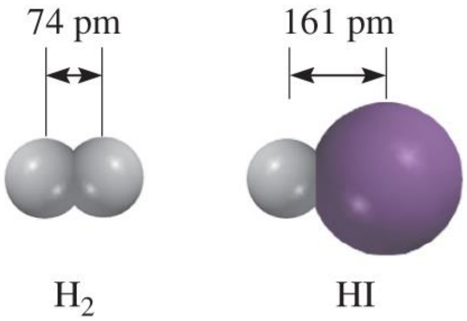


(a) (b) (c)

Structure (b) is the most important one because the negative charge is on the more electronegative oxygen atom.

Structure (c) is the least important one because it has a larger separation of formal charges. Also, the positive charge is on the more electronegative oxygen atom.

➢ 9.10 Bond Length and Bond Order



covalent radius:

Covalent radius of an atom X = half of the covalent bond length of a homonuclear X-X single bond.

If covalent radius of (C = 76 pm) & (Cl = 102 pm) → covalent radius of C-Cl = (76 + 102) = 178 pm

chloromethane, CH_3Cl, 178.4 pm;

tetrachloromethane, CCl_4, 176.6 pm;

Bond lengths:

Triple bond < Double Bond < Single Bond

3 2 1

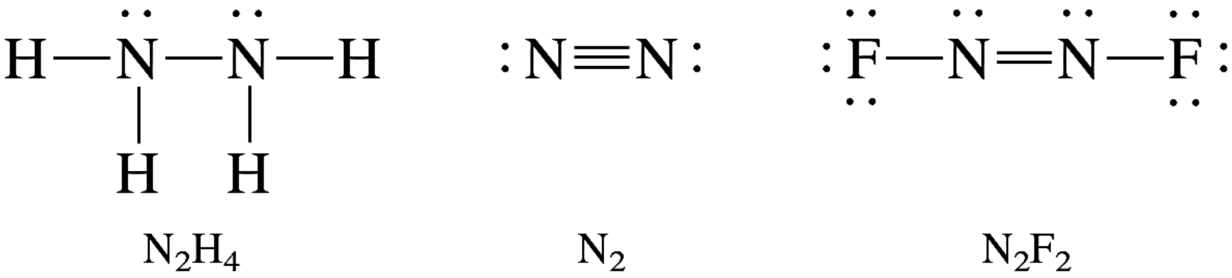
Average Bond Lengths of Some Common Single, Double, and Triple Bonds

Bond Type	Bond Length (pm)
C—H	107
C—O	143
C═O	121
C—C	154
C═C	133
C≡C	120
C—N	143
C═N	138
C≡N	116
N—O	136
N═O	122
O—H	96

➢ Trends for atomic radii

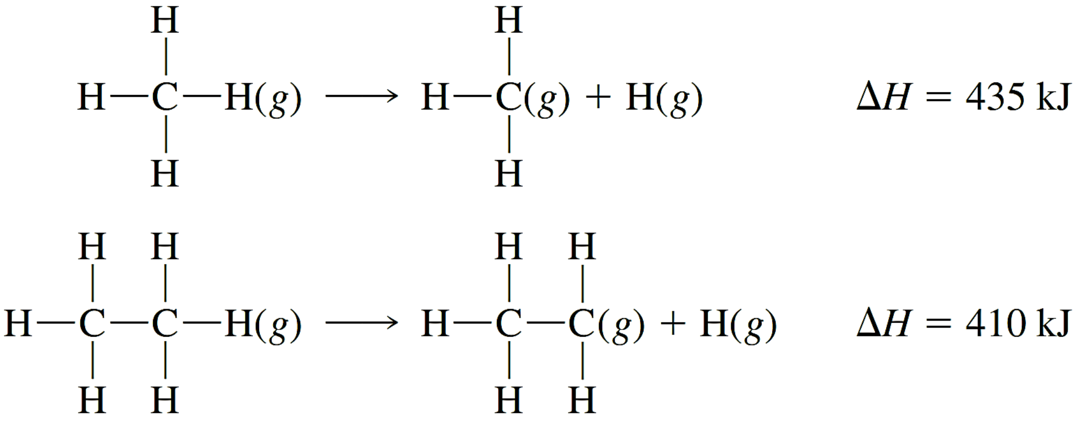
1. Within a period, the covalent radius tends to decrease with increasing atomic number.
2. Within a group, the covalent radius tends to increase with period number.

(Q) Consider the molecules N_2H_4, N_2, and N_2F_2.
Which molecule has the shortest nitrogen–nitrogen bond?
Which has the longest nitrogen–nitrogen bond?



9.11 Bond Enthalpy (BE)

“bond enthalpy” and “bond energy” are often used interchangeably



$$\mathrm{CH_4}(g) \longrightarrow \mathrm{CH_3}(g) + \mathrm{H}(g) \qquad \Delta H = 435\ \mathrm{kJ}$$

$$\mathrm{C_2H_6}(g) \longrightarrow \mathrm{C_2H_5}(g) + \mathrm{H}(g) \qquad \Delta H = 410\ \mathrm{kJ}$$

$$\mathrm{CH_4}(g) \longrightarrow \mathrm{C}(g) + 4\mathrm{H}(g);\ \Delta H = 1662\ \mathrm{kJ}$$

$$\rightarrow \quad BE(\mathrm{C{-}H}) = \tfrac{1}{4} \times 1662\ \mathrm{kJ} = 416\ \mathrm{kJ}$$

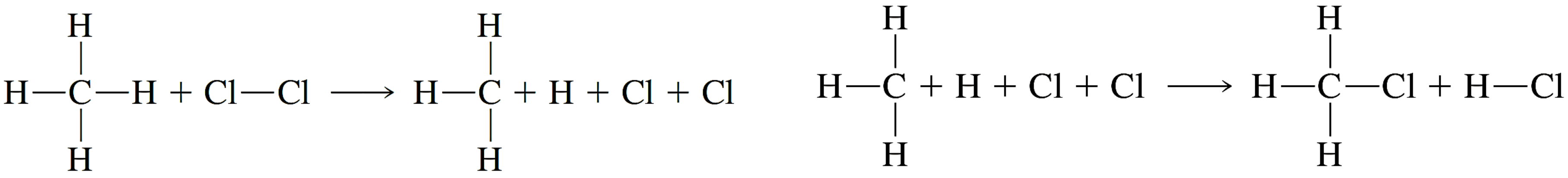
- ✓ Because it takes energy to break a bond, bond enthalpies are always positive numbers.
- ✓ Bond enthalpy is a measure of the strength of a bond: the larger the bond enthalpy, the stronger the chemical bond

(Q) Use bond enthalpies to estimate the enthalpy change for the following reaction:

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

Given that bond enthalpies (kJ/mol) for:

(C-H) = 413, (Cl-Cl) = 242, (C-Cl) = 328, (H-Cl) = 431,



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}H + Cl{-}Cl \longrightarrow H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}} + H + Cl + Cl} \qquad \mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}} + H + Cl + Cl \longrightarrow H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}Cl + H{-}Cl}$$

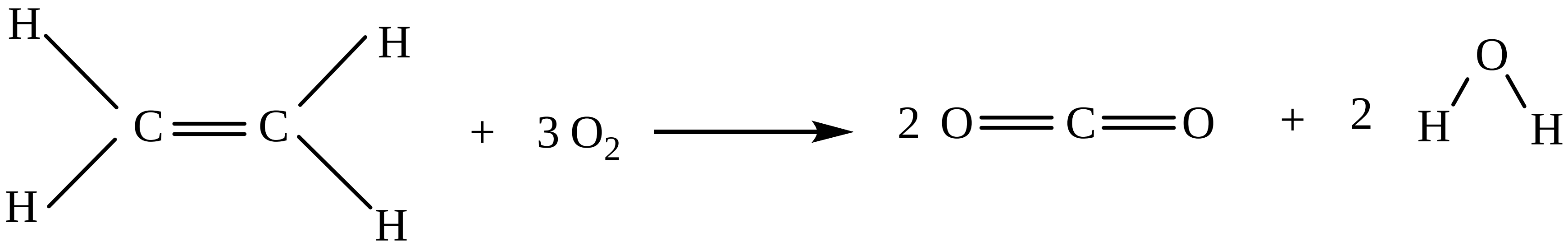
$$\begin{aligned}\Delta H &\simeq BE(\mathrm{C{-}H}) + BE(\mathrm{Cl{-}Cl}) - BE(\mathrm{C{-}Cl}) - BE(\mathrm{H{-}Cl}) \\ &= (413 + 242 - 328 - 431)\ \mathrm{kJ} \\ &= -104\ \mathrm{kJ}\end{aligned}$$

In general, the enthalpy of reaction is (approximately) equal to the sum of the bond enthalpies for bonds broken minus the sum of the bond enthalpies for bonds formed.

Exercise 9.18 Use bond enthalpies to estimate the enthalpy change for the combustion of ethylene, C_2H_4, according to the equation

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g)$$

Given that bond enthalpies (kJ/mol) for:
(C=C) = 614, (C-H) = 413, (O=O) =498, (C=O) = 804, (O-H) = 463



ΔH = {[614 + (4 × 413) + (3 × 498)] − [(4 × 804) + (4 × 463)]} kJ
= −1308 kJ