Chemistry 1B
Fall 2016 Topic 9

Chemistry 1B

Fall 2016

experience ~~Lecture~~ 9

(chapter 13; pp 596-614)

1

bonding in molecules

- **Chapter 13 (pp 596-614)– Overview of bonding and ionic bonding (lect 9)**
- **Chapter 13 (pp 621-650)- (pp 602-606) "Classical" picture of bonding and molecular geometry (lect 10-12)**
- **Chapter 19 (pp 940-944;- 952-954; 963-970) Bonding in transition metal complexes (lect 13-14)**
- **Chapter 14- Quantum mechanical description of bonding**

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types of bonding

- **Ionic**
- **Covalent**
- **Metallic**

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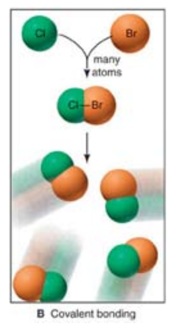
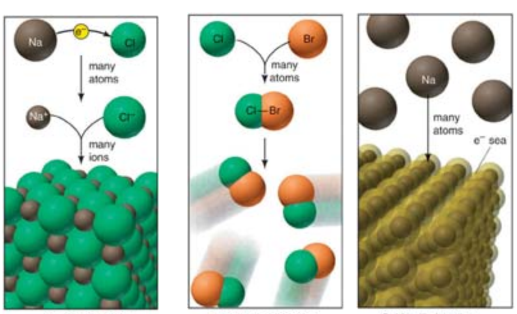
general properties of the 3-types of bonding (Silberberg fig.9.2)



B Covalent bonding

4

general properties of the 3-types of bonding (Silberberg fig.9.2)



A Ionic bonding B Covalent bonding C Metallic bonding

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hello Lewis electron-dot diagrams

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Fall 2016 Topic 9

G. N. Lewis- UC Berkeley

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G.N. Lewis 1916

The Atom and the Molecule
by Gilbert N. Lewis
Journal of the American Chemical Society
Volume 38, 1916, pages 762-786
Received January 26, 1916

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G.N. Lewis 1916

The Cubical Atom.
A number of years ago, to account for the striking fact which has become known as Abegg's law of valence and countervalence, and according to which the total difference between the maximum negative and positive valences or polar numbers of an element is frequently **eight** and is in no case more than eight, I designed what may be called the theory of the cubical atom. This theory, while it has become familiar to a number of my colleagues, has never been published, partly because it was in many respects incomplete. Although many of these elements of incompleteness remain, and although the theory lacks to-day much of the novelty which it originally possessed, it seems to me more probable intrinsically than some of the other theories of atomic structure which have been proposed, and I cannot discuss more fully the nature of the differences between polar and nonpolar compounds without a brief discussion of this theory.

The pictures of atomic structure which are reproduced in Fig. 2,1 and in which the circles represent the electrons in the outer shell of the

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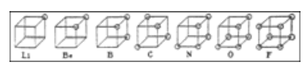
G.N. Lewis 1916

The Cubical Atom.

……..

The pictures of atomic structure which are reproduced in Fig. 2,1 and in which the circles represent the electrons in the outer shell of the



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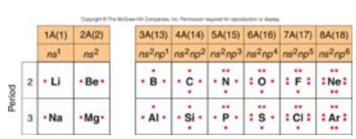
Lewis electron-dot symbols for atom
(kernels or Lewis Valence Electron Diagrams LVEDs)



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Lewis hypothesis (first look)

To form compounds, atoms will gain, lose, or share electrons to attain "complete outer shells".

For hydrogen, a "complete shell" corresponds to 2 electrons ($1s^2$).

For atoms in period 'n', a "complete shell" often corresponds to 8 electrons ($ns^2\,np^6$) *octet structure*.

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order of material:

- ionic bonding (pp. 606-614)
- covalent bonding (pp. 615-650; 602-606)
- metallic bonding
  (extra fun, but no extra tuition charge $$$'s)

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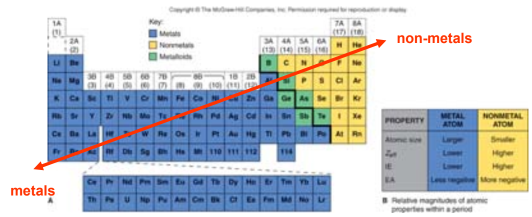
remember metals vs nonmetals and the periodic table



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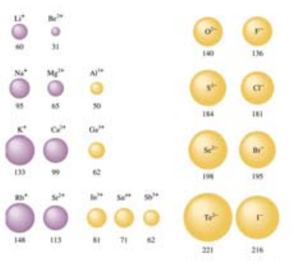
size of ions (Zumdahl, figure 13.8)



$r \approx 52.9 \text{ pm} \dfrac{n^2}{Z_{eff}}$

n and Z_{eff} of outermost electron

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Electronegativity (more: pp. 600-606; later)

- **Electronegativity-** ***the tendency of an atom to attract electrons and to 'hold on to' its own electrons***
- **Mulliken: $(EN)_{MUL}$ = (IE – EA)/2 (arbitrary units)**
  (see ch13 prob 13.18)
- **e.g. for Na $(EN)_{MUL}$ = [(496) - (-52.9)]/2=274 (kJ/mol)**
  for Cl $(EN)_{MUL}$ = [(1256) - (-349)]/2=802 (kJ/mol)
- **High electronegativity-** ***wants to accept electrons***
  Low electronegativity- ***will donate electrons***
  atoms with high electronegativity are *electronegative*
  atoms with low electronegativity are *electropositive*
- **non-metals are electronegative**
  metals are electropositive

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ionic bonding

- **metallic atoms *lose* electrons to attain an 'octet' structure**
- **nonmetallic atoms *gain* electrons to attain an 'octet' structure**

$$\underset{[Ne]3s}{Na} + \underset{[Ne]3s^2 3p^5}{Cl} \longrightarrow \underset{[Ne]}{Na^+} + \underset{[Ne]3s^2 3p^6}{Cl^-}$$

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HW#4 Prob. 30 (Zumdahl 13.26)

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video 05 – LATTICE ENERGY summary and bottom line

- In ionic compounds cations(+) are formed by metal atoms (lowish IE's) donating electrons to non-metals (largish EA's) to form anions(-)
- In many instances *[e.g. Na(g) + Cl(g) → Na⁺(g) + Cl⁻ (g)]* the process is energetically unfavorable (endothermic, needs to absorb energy)
- However ionic compounds do exist as crystalline solids due to the favorable (exothermic) **LATTICE ENERGY** associated with the process of gas phase ions going to solids [e.g. $Na^+(g) + Cl^-(g) \rightarrow Na^+Cl^-(s)$]

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what you need to master about *LATTICE ENERGY*

- Coulombic forces stabilize ionic bonds in crystalline solids:

$$E = k\frac{Q_A Q_B}{R_{AB}}$$ (opposite charges, large negative energies **STABILIZE**)

- The magnitude of the lattice energy depends on charges and sizes of ions:
  - the magnitude of the ionic charges **(Q_AQ_B);** the **larger** the greater stabilization [e.g. *for $Ca^{2+}(SO_4)^{2-}$ $(Q_AQ_B) = -4$ and for $Na^+Cl^-(s)$ $(Q_AQ_B) = -1$; thus lattice energy greater for $Ca(SO_4)$*]
  - the interionic distance $\mathbf{R_{AB}}$ (sum of ionic radii); the **smaller** the greater stabilization
    [e.g. R_{AB} for $Na^+Cl^-(s)$ smaller than R_{AB} $K^+Cl^-(s)$; thus lattice energy greater for NaCl]

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Ionic Bonding

and Lattice Energy

(Pp 609-613)

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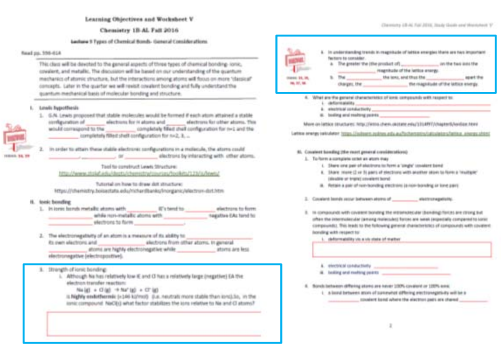
Learning Objectives V- section II.3



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previous lecture

Introduction to types of bonding

- ionic, covalent, metallic
- covalent- octets and much more soon
- metallic- added value topic soon
- ionic between
  metals (low IE, gives up e⁻ relatively easily)
  + non-metal (large negative EA, wants to accept e⁻ relatively strongly)

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ionic bonding

- **metallic atoms *lose* electrons to attain an 'octet' structure**
- **nonmetallic atoms *gain* electrons to attain an 'octet' structure**

Na + Cl → Na⁺ + Cl⁻
[Ne]3s [Ne]$3s^23p^5$ → [Ne] [Ne]$3s^23p^6$

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factoids relating to the heat of a reaction (ch 9):

- ΔH, the change in enthalpy for a reaction, is the HEAT given off or absorbed by the reaction (for our purposes $\Delta H \approx$ energy change)
- if heat is **given off** by the reaction [surroundings heat up], the reaction is **EXOTHERMIC and $\Delta H < 0$** *[products MORE STABLE than reactants]*

- if heat is **absorbed** by the reaction [surroundings cool], the reaction is **ENDOTHERMIC and $\Delta H > 0$** *[reactants MORE STABLE than products; ionization is endothermic, IE > 0]*

- ΔH for a complex process can be calculated by summing ΔH's for the individual steps of the process

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Why should (does) Na^+ Cl^- exist?

Table 12.7
IE=+495 kJ/mol
energy in

146 kJ/mol + Na(g) + Cl(g) → Na^+ (g) + Cl^- (g)

energy out
EA=-349 kJ/mol
Table 12.8

NET ENERGY CHANGE = + 146 kJ/mol (+495kJ-349kJ)

ENDOTHERMIC
*gas phase ions **unstable** relative to atoms*

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does Li^+ F^- exist?

Table 12.7
IE=520 kJ/mol

192 kJ/mol + Li(g) + F(g) → Li^+ (g) + F^- (g)

energy out
EA=-328 kJ/mol
Table 12.8

NET ENERGY CHANGE = + 192 kJ/mol (520 – 328)

ENDOTHERMIC
*gas phase ions **unstable** relative to atoms*

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an enigma ???

so if Li^++F^- is unstable relative to Li + F
why
does one get stable
crystals of lithium fluoride??

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but Li^+F^- is a salt (solid) figure 13.10

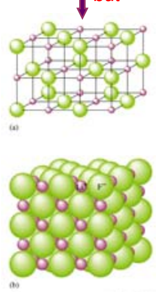
192kJ +Li(g) + F(g) → Li^+ (g) + F^- (g) $\xrightarrow{\text{but}}$ Li^+F^-(s) + energy

endothermic

[lattice energy]

but

exothermic
favorable



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lattice energy (LE): ions in gas ⟶ ions in solid (crystal lattice)

Li^+ (g) + F^- (g) ⟶ Li^+F^- (s) + 1047 kJ/mole

lattice energy of LiF(s)= -1047 kJ/mole
exothermic
stabilizes ionic solids

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neutral atoms ⟶ ionic solid   stabilization by lattice energy

- 855 kJ/mol

Li(g) + F(g) ⟶ Li^+F^- (s) + 855 kJ/mole heat

+ 192 kJ/mol (IE+EA) endothermic

-1047 kJ/mol lattice energy exothermic

Li^+ (g) + F^- (g)

ΔH= +192 kJ/mol – 1047 kJ/mol=-855 kJ/mole

exothermic

Li^+F^-(s) STABLE relative to Li(g) + F(g)

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Born cycle: measuring lattice energies (fig. 13.9)
*(**are not responsible** for this concept)*

heat given off by

Li^+ (g) + F^- (g) ⟶ Li^+F^- (s)

difficult to measure directly

Born cycle: find an alternative set of reactions where heat of reaction CAN be measured for each step and the combinations of these reactions leads to
Li^+ (g) + F^- (g) ⟶ Li^+F^- (s)

Use this cycle to compute Lattice Energy (LE)

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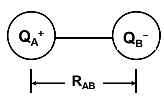
Coulombs Law, electrostatic energy (p 597, 612)



$$E = \frac{Q_A Q_B}{4\pi\varepsilon_0 R_{AB}}$$
$$= 2.31\times10^{-19}\ J\ nm\ \frac{Q_A Q_B}{R_{AB}}$$
$$= k\frac{Q_A Q_B}{R_{AB}}$$

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two important factors in estimating LATTICE ENERGIES

$$E = k\frac{Q_A Q_B}{R_{AB}}$$

- interionic distance (ionic radii): larger R_{AB} gives smaller lattice energy (less exothermic)
- charges on ions: greater charges on ions $Q_A Q_B$ gives larger lattice energy (more exothermic)
- additionally the "Madelung constant" is needed to account for the 3D ionic interactions in an actual crystal

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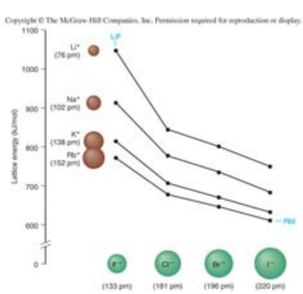
Silberberg figure 9.7



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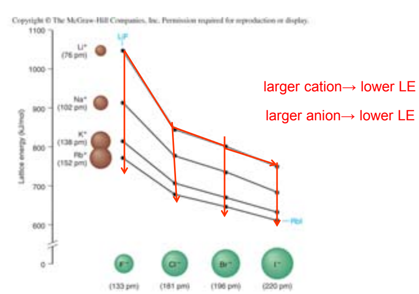
Silberberg figure 9.7



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*trends in lattice energy (you **ARE** responsible for this)*
(HW#4 prob 35 Z#13.32)

LiF MgO NaF

$$\text{Lattice Energy} = k\frac{Q_A Q_B}{R_{AB}}$$

• ionic charge $Q_A Q_B$ (p. 612) (usually more important)

Mg^{2+}·Li^{+},Na^{+},O^{2-},F^{-}

• ionic size (R_{AB})

Li^{+} smaller than Na^{+}

lowest LE *(least negative, least exothermic)* < < greatest LE *(most negative most exothermic)*

-923 kJ -1047 kJ -3916 kJ

lattice energy (molar)

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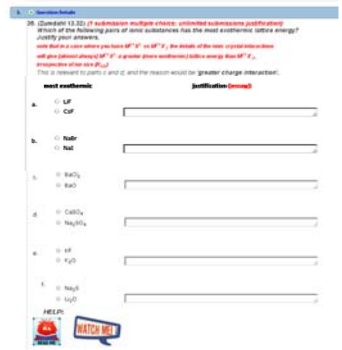
WebAssign HW#4 prob 31 (Zumdahl 13.32)



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*a riddle: **how are different bonding types like different styles of parenting ?***

parenting and the three major types of bonding !!!

1. Which type of child rearing scenario is most analogous to ionic bonding ?

   ***a.** hippie commune ; **b.** (very) old fashion parenting; **c.** modern (politically correct) parenting*

2. Which type of child rearing scenario is most analogous to covalent bonding ?

   ***a.** hippie commune ; **b.** (very) old fashion parenting; **c.** modern (politically correct) parenting*

3. Which type of child rearing scenario is most analogous to metallic bonding ?

   ***a.** hippie commune ; **b.** (very) old fashion parenting; **c.** modern (politically correct) parenting*

(explain your answers)

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skip for later (pp 618-619)

• Bond energies, bond lengths, bond order
(after Lewis structures chapter 13.10-13.12)

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factoids about ionic compounds

• 'strong' metals and 'strong' nonmetals are likely to form ionic compounds

• lattice energy stabilizes solids

• hydration of ions in aqueous solvents can contribute to solubility (Olmstead figure 2.2)

• ionic compounds 'crack' (fig Silb 9.8)

• ionic compounds have high boiling and melting points (table Silb 9.1) (fig. Silb 9.10)

• ionic compounds conduct electricity in molten (liquid) phase or in solution (Silb fig. 9.9)

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covalent bonding (sharing of electrons): MUCH MORE LATER

- sharing of electrons leads to lower energy than two isolated atoms (figure 13.01) ➡
- lone or non-bonding pairs
- more than one-pair of electrons may be shared to form stable 'octet' (single, double, triple bonds with bond orders 1, 2, 3 respectively)
- covalent bonding **CANNOT** be satisfactorily explained by classical electrostatics, but we need quantum mechanics chapter 14

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factoids about covalent bonding in molecules

- usually bonding between atoms of similar electronegativity (metallic bonding will be special case)
- many covalently bound molecules have strong intramolecular forces (the covalent bonds) but weak intermolecular forces; thus relatively low melting and boiling points (figure 9.14) ➡
- poor conductors
- some atoms form extended networks of covalent bonds with high melting/ boiling points and hardness (figure 9.15) ➡ graphene ➡

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fully ionic vs fully covalent the TRUTH lies in between (sec 13.6)

- electron transfer in ionic compounds may be incomplete
- two atoms may not equally share electrons in a covalent bond
- the greater the ΔEN the more ionic (figure S9.22) ➡
- polar covalent bonds and covalency in ionic bonds (figure 13.11) (figure S9.21), (figure 13.12), ➡
- continuum across period (more covalent as ΔEN decreases) (figure S9.25), (figure S9.24) ➡

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more about electronegativity

- the degree of 'attraction' of a given atom for electrons (its own and from other atoms)
- Mulliken scale: $(EN)_{MUL}$ = (IE – EA)/2 (arbitrary units)
- Pauling electronegativities (section 13.2) trends (figure Zumdahl 13.3, figure Silb 9.19) HW#4 ➡ ➡
- oxidation number and electronegativity (common valences) (table 13.5, figure Silb 9.3) HW#4 ➡ ➡

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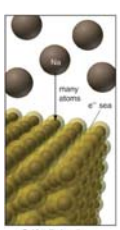
bonding in metals

electron sea model



© Metallic bonding

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properties of metals related to electron sea model

- electrical and thermal conductivity
- moderate melting point; high boiling point (table S9.7) (figure S9.26) ➡
- malleability (figure S9.27) ➡

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big picture: structure and properties

- **Ionic**
- **Covalent**
- **Metallic**

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a riddle: **how are different bonding types like different styles of parenting ?**

parenting and the three major types of bonding !!!

sharing electrons ⇔ sharing child rearing responsibilities

1. Which type of child rearing scenario is most analogous to ionic bonding ?

   a. *hippie commune ;* ***b.*** *(very) old fashion parenting;* ***c.*** *modern (politically correct) parenting*

2. Which type of child rearing scenario is most analogous to covalent bonding ?

   a. *hippie commune ;* ***b.*** *(very) old fashion parenting;* ***c.*** *modern (politically correct) parenting*

3. Which type of child rearing scenario is most analogous to metallic bonding ?

   a. *hippie commune ;* ***b.*** *(very) old fashion parenting;* ***c.*** *modern (politically correct) parenting*

(explain your answers)

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END OF LECTURE
9

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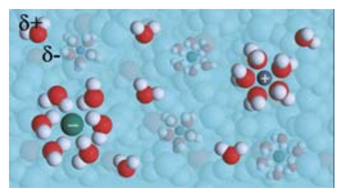
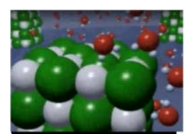
Olmstead figure 2.2: hydration of ions





https://www.youtube.com/watch?v=EBfGcTAJF4o

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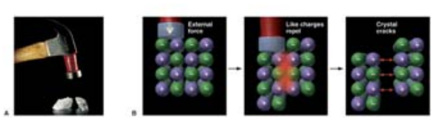
Silberberg figure 9.8



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Silberberg table 9.1

Table 9.1 Melting and Boiling Points of Some Ionic Compounds

Compound	mp (°C)	bp (°C)
CsBr	636	1300
NaI	661	1304
$MgCl_2$	714	1412
KBr	734	1435
$CaCl_2$	782	>1600
NaCl	801	1413
LiF	845	1676
KF	858	1505
MgO	2852	3600

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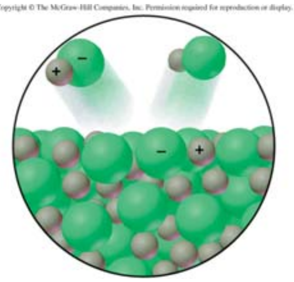
Silberberg figure 9.10



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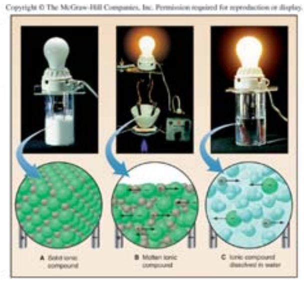
Silberberg figure 9.9



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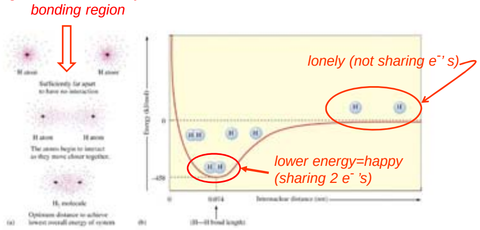
Zumdahl figure 13.1



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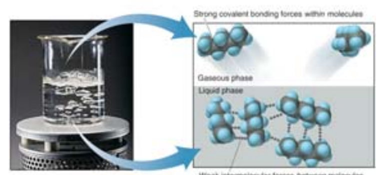
Silberberg figure 9.14



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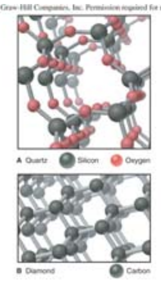
Silberberg figure 9.15



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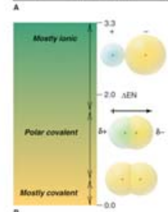
Zumdahl, Table 13.1; Silberberg figure 9.22

ΔEN	IONIC CHARACTER
>1.7	Mostly ionic
0.4-1.7	Polar covalent
<0.4	Mostly covalent
0	Nonpolar covalent

A

TABLE 13.1 The Relationship Between Electronegativity and Bond Type

Electronegativity Difference in the Bonding Atoms	Bond Type
Zero	Covalent
Intermediate	Polar covalent
Large	Ionic



B

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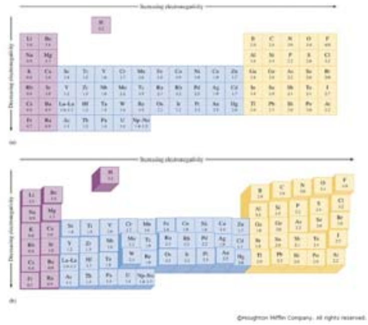
Pauling electronegativity (figure 13.3)



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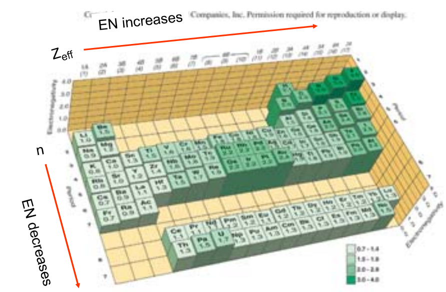
Silberberg figure 9.19



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HW #4 prob 29

29. (Zumdahl 13.15) *(3 submissions)* Without using figures from the text, predict the order of **increasing** electronegativity
in each of the following groups of elements.
(Use the appropriate = or < symbol to separate substances in the list.)

(a) C, N, O (b) S, Se, Cl

(c) Si, Ge, Sn (d) Tl, S, Ge

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Zumdahl Table 2.5 and 13.5, Silberberg figure 9.3

TABLE 13.5 Common Ions with Noble Gas Electron Configurations in Ionic Compounds

Group 1A	Group 2A	Group 3A	Group 6A	Group 7A	Electron Configuration
H^-, Li^+	Be^{2+}				[He]
Na^+	Mg^{2+}	Al^{3+}	O^{2-}	F^-	[Ne]
K^+	Ca^{2+}		S^{2-}	Cl^-	[Ar]
Rb^+	Sr^{2+}		Se^{2-}	Br^-	[Kr]
Cs^+	Ba^{2+}		Te^{2-}	I^-	[Xe]

TABLE 2.5 Common Polyatomic Ions

Ion	Name	Ion	Name
NH_4^+	ammonium	CO_3^{2-}	carbonate
NO_2^-	nitrite	HCO_3^-	hydrogen carbonate (bicarbonate is a widely used common name)
NO_3^-	nitrate		
SO_3^{2-}	sulfite	ClO^-	hypochlorite
SO_4^{2-}	sulfate	ClO_2^-	chlorite
HSO_4^-	hydrogen sulfate (bisulfate is a widely used common name)	ClO_3^-	chlorate
		ClO_4^-	perchlorate
OH^-	hydroxide	$C_2H_3O_2^-$	acetate
CN^-	cyanide	MnO_4^-	permanganate
PO_4^{3-}	phosphate	$Cr_2O_7^{2-}$	dichromate
HPO_4^{2-}	hydrogen phosphate	CrO_4^{2-}	chromate
$H_2PO_4^-$	dihydrogen phosphate	O_2^{2-}	peroxide

KNOW:
NH_4^+, NO_3^-, SO_4^{2-}, HSO_4^-, CN^-, OH^-, PO_4^{3-}, CO_3^{2-}, HCO_3^-, $C_2H_3O_2^-$, MnO_4^-

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HW#4 prob 32

32 Zumdahl 12.33. *(6 submissions)*
Predict the empirical formulas for the ionic compounds formed from the following pairs of elements. Name each compound.
In the chemPad either use _ (underscore; now working) or subscript pad button the to indicate subscripts and be sure not to have any spaces in the formula;
for example to enter Na_2SO_4 use Na_2SO_4

	elements	empirical formula	name
a.	Al and S		
b.	K and N		

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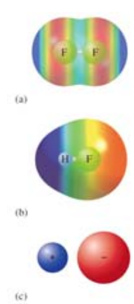
Bond polarity (figure 13.12 Zumdahl)



pure covalent

polar covalent

pure ionic

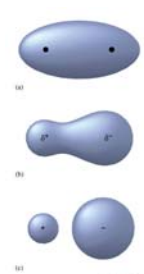


fig 13.11, 5th edition

red= highest electron density
blue= lowest electron density

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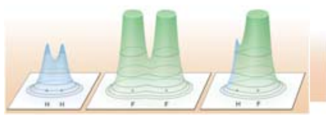
Silberberg figure 9.21 (covalent electron density)



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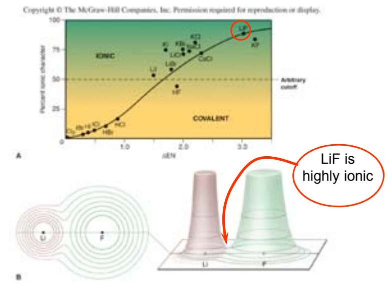
percent ionic character (Zumdahl figure 13.12; Silberberg figure 9.23)



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Silberberg figure 9.25

more covalent as one goes across row

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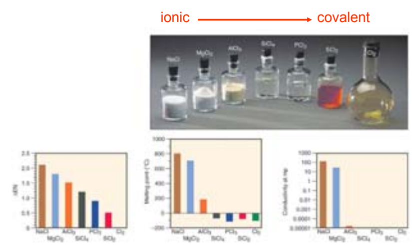
Silberberg figure 9.24 (X-Cl) X: NaCl $\Rightarrow$ Cl_2



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Silberberg figure table 9.7

Table 9.7 Melting and Boiling Points of Some Metals

Element	mp (°C)	bp (°C)
Lithium (Li)	180	1347
Tin (Sn)	232	2623
Aluminum (Al)	660	2467
Barium (Ba)	727	1850
Silver (Ag)	961	2155
Copper (Cu)	1083	2570
Uranium (U)	1130	3930

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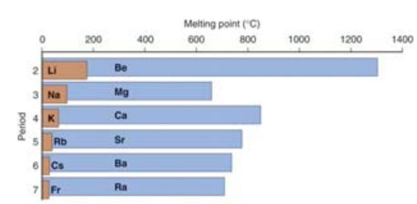
Silberberg figure 9.26

2nd period metals harder to melt



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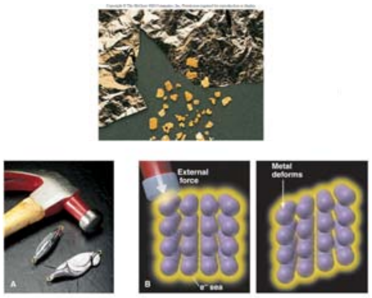
Silberberg figure 9.27



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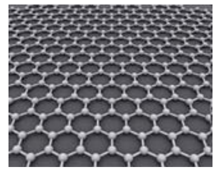
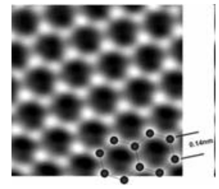
graphene

Graphene is a one-atom-thick planar sheet of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice.





Potential applications
Graphene transistors
Integrated circuits
Anti-bacterial
Single molecule gas detection

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2010 Nobel Prize in physics

Nobel Prize in physics won by Russian duo working in Manchester

"for groundbreaking experiments regarding the two-dimensional material **graphene**",

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