Electron Configuration - Periodic Table

- Noble gas core: An inner Electron shell configuration resembling one of the noble gases (He, Ne, Ar, Kr, Xn)

$1s^2$ (He) $1s^22s^22p^6$ (Ne) $1s^22s^22p^63s^23p^6$ (Ar)

- Pseudo-noble gas core: For n >= 4 (Kr, Ze, Rn) the n-1 d subshell is filled, i.e., $(n-1)d^{10}$

Kr $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$ or [Ar] $3d^{10}4s^24p^6$

Ze [Kr] $4d^{10}5s^25p^6$

Rn [Ze] $5d^{10}6s^26p^6$

- Valence Electrons – ns & np electrons that reside in the outermost shell of an atom or those electrons that reside outside the Noble gas core- or the Pseudo-Noble gas core

Electron Configuration - Periodic Table

- Valence Electrons
  - Primarily involved in chemical reactions
  - Elements within a given group (down a column in the Periodic Table) have the same valence shell configuration – $1s^1$ $2s^1$ $3s^1$ $4s^1$ $5s^1$
  - This accounts for the similarity of the chemical properties among groups of elements
  - The main-group elements (1A – 8A) all have the same valence-shell configurations

    ns^anp^b (n is Period No. or Quantum No.)
  - The electrons that are filling in the d-subshell of the transition (d-block) elements are also considered valence electrons

Fe $[Ar]3d^64s^2$

Describing Ionic Bonds

- An **ionic bond** is a chemical bond formed by the electrostatic attraction between positive and negative ions
  - This type of bond involves the ***transfer*** of electrons from one atom (usually a metal from Group IA or IIA) to another (usually a nonmetal from Group 7A or the top of Group 6A)
  - Metal with low Ionization Energy (IE) absorbs energy and loses one or two electrons (IE is positive)
  - Nonmetal with high Electron Affinity (EA) loses energy gaining one or two electrons (EA is negative)
  - The number of electrons lost or gained by an atom is determined by its need to be "**isoelectronic**" with its nearest noble gas, i.e., same electron configuration

Describing Ionic Bonds

- Such noble gas configurations and the corresponding ions are particularly stable
  - The atom that loses the electron becomes a positively charged ion, i.e., a **cation** (positive)

$$\mathbf{Na\ ([Ne]3s^1) \rightarrow Na^+\ ([Ne]) + e^-}$$

Sodium ion has the same electron configuration as Ne ($1s^2 2s^2 2p^6$)

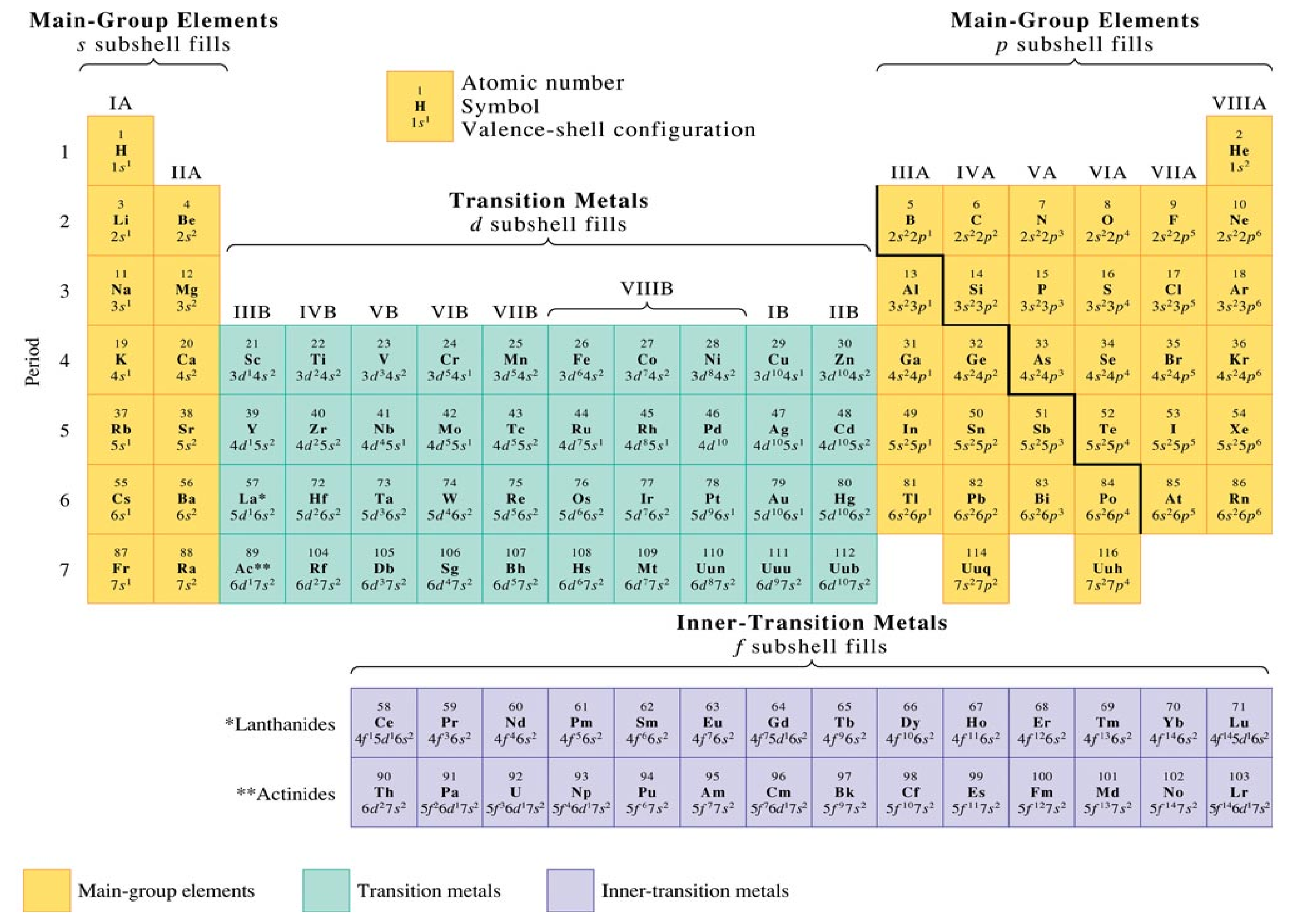
  - The atom that gains the electron becomes a negatively charged ion, i.e.,

an **Anion**

$$\mathbf{Cl\ ([Ne]3s^2 3p^5) + e^- \rightarrow Cl^-\ ([Ne]3s^2 3p^6)}$$

$$\mathbf{or\ \ Cl^-\ ([Ar])}$$

The Periodic Table



Main-Group Elements
s subshell fills

Transition Metals
d subshell fills

Main-Group Elements
p subshell fills

1 **H** $1s^1$	
	Atomic number Symbol Valence-shell configuration

Period	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1 **H** $1s^1$																	2 **He** $1s^2$
2	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
3	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
4	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^14s^2$	22 **Ti** $3d^24s^2$	23 **V** $3d^34s^2$	24 **Cr** $3d^54s^1$	25 **Mn** $3d^54s^2$	26 **Fe** $3d^64s^2$	27 **Co** $3d^74s^2$	28 **Ni** $3d^84s^2$	29 **Cu** $3d^{10}4s^1$	30 **Zn** $3d^{10}4s^2$	31 **Ga** $4s^24p^1$	32 **Ge** $4s^24p^2$	33 **As** $4s^24p^3$	34 **Se** $4s^24p^4$	35 **Br** $4s^24p^5$	36 **Kr** $4s^24p^6$
5	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^15s^2$	40 **Zr** $4d^25s^2$	41 **Nb** $4d^45s^1$	42 **Mo** $4d^55s^1$	43 **Tc** $4d^55s^2$	44 **Ru** $4d^75s^1$	45 **Rh** $4d^85s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10}5s^1$	48 **Cd** $4d^{10}5s^2$	49 **In** $5s^25p^1$	50 **Sn** $5s^25p^2$	51 **Sb** $5s^25p^3$	52 **Te** $5s^25p^4$	53 **I** $5s^25p^5$	54 **Xe** $5s^25p^6$
6	55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La*** $5d^16s^2$	72 **Hf** $5d^26s^2$	73 **Ta** $5d^36s^2$	74 **W** $5d^46s^2$	75 **Re** $5d^56s^2$	76 **Os** $5d^66s^2$	77 **Ir** $5d^76s^2$	78 **Pt** $5d^96s^1$	79 **Au** $5d^{10}6s^1$	80 **Hg** $5d^{10}6s^2$	81 **Tl** $6s^26p^1$	82 **Pb** $6s^26p^2$	83 **Bi** $6s^26p^3$	84 **Po** $6s^26p^4$	85 **At** $6s^26p^5$	86 **Rn** $6s^26p^6$
7	87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac**** $6d^17s^2$	104 **Rf** $6d^27s^2$	105 **Db** $6d^37s^2$	106 **Sg** $6d^47s^2$	107 **Bh** $6d^57s^2$	108 **Hs** $6d^67s^2$	109 **Mt** $6d^77s^2$	110 **Uun** $6d^87s^2$	111 **Uuu** $6d^97s^2$	112 **Uub** $6d^{10}7s^2$		114 **Uuq** $7s^27p^2$		116 **Uuh** $7s^27p^4$		

Inner-Transition Metals
f subshell fills

*Lanthanides	58 **Ce** $4f^15d^16s^2$	59 **Pr** $4f^36s^2$	60 **Nd** $4f^46s^2$	61 **Pm** $4f^56s^2$	62 **Sm** $4f^66s^2$	63 **Eu** $4f^76s^2$	64 **Gd** $4f^75d^16s^2$	65 **Tb** $4f^96s^2$	66 **Dy** $4f^{10}6s^2$	67 **Ho** $4f^{11}6s^2$	68 **Er** $4f^{12}6s^2$	69 **Tm** $4f^{13}6s^2$	70 **Yb** $4f^{14}6s^2$	71 **Lu** $4f^{14}5d^16s^2$
**Actinides	90 **Th** $6d^27s^2$	91 **Pa** $5f^26d^17s^2$	92 **U** $5f^36d^17s^2$	93 **Np** $5f^46d^17s^2$	94 **Pu** $5f^67s^2$	95 **Am** $5f^77s^2$	96 **Cm** $5f^76d^17s^2$	97 **Bk** $5f^97s^2$	98 **Cf** $5f^{10}7s^2$	99 **Es** $5f^{11}7s^2$	100 **Fm** $5f^{12}7s^2$	101 **Md** $5f^{13}7s^2$	102 **No** $5f^{14}7s^2$	103 **Lr** $5f^{14}6d^17s^2$

🟨 Main-group elements
🟩 Transition metals
🟪 Inner-transition metals

Atoms vs Ions

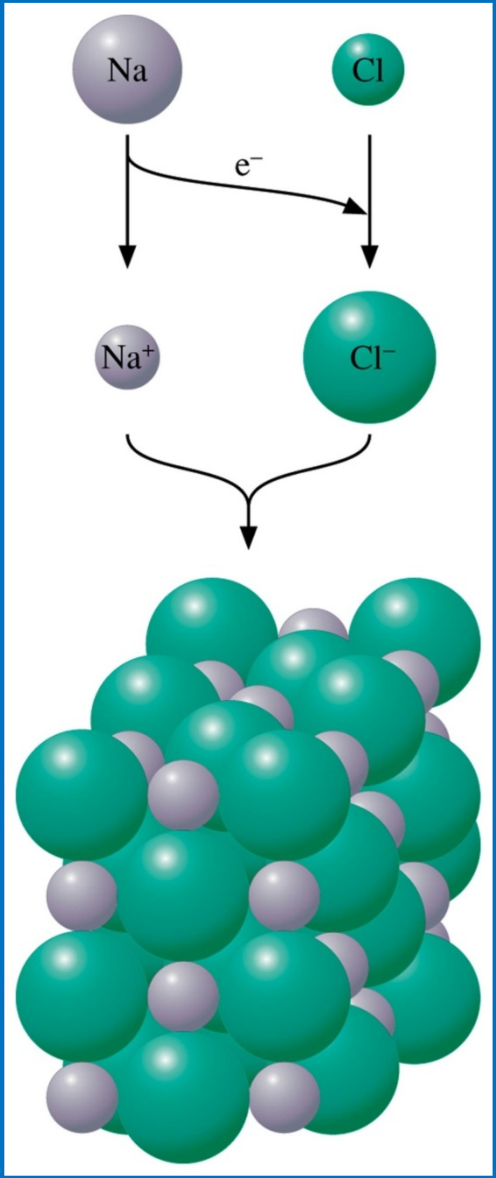
Grey and Green Ions

$Na(g) \rightarrow Na^+(g) + e^-$

$Cl(g) + e^- \rightarrow Cl^-(g)$

$\underline{Na^+(g) + Cl^-(g) \rightarrow NaCl(s)}$

$Na + Cl \rightarrow NaCl(s)$



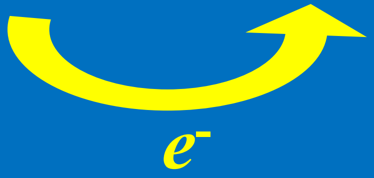
Note change in size of ion relative to atom

Ionic Lattice 1:1

Describing Ionic Bonds

- Consider the transfer of valence electrons from a Sodium atom to a Chlorine atom

$$\mathrm{Na} + \mathrm{Cl} \rightarrow \mathrm{Na}^{+} + \mathrm{Cl}^{-}$$



e^{-}

  - The resulting ions are electrostatically attracted to one another
  - The attraction of these oppositely charged ions for one another is the **ionic bond**

Electron Configurations of Ions

- As metals lose electrons to form **cations** and establish a "noble gas" configuration, the electrons are lost from the valence shell first
  - For example, Magnesium generally loses two electrons from its 3s subshell to look like the "Neon" core

$$\mathbf{Mg} \rightarrow \mathbf{Mg^{2+}} \quad \mathbf{(+2\,e^-)}$$

$1s^2 2s^2 2p^6 3s^2$ $1s^2 2s^2 2p^6$

$\mathbf{[Ne]3s^2}$ $\mathbf{[Ne]}$

Electron Configurations of Ions

- Transition metals also lose electrons from the valence shell first, which may not be the last subshell to fill (Recall the "Aufbau sequence")
  - For example, zinc generally loses two electrons from its 4s subshell to adopt a:

"pseudo" noble gas configuration

$$\mathbf{Zn} \rightarrow \mathbf{Zn^{2+}} \quad \mathbf{(+2\ e^{-})}$$

$$\mathbf{[Ar]4s^{2}3d^{10}} \qquad \mathbf{[Ar]3d^{10}}$$

In general, the 3d subshell is filled after the 4s subshell is filled, with two exceptions – Cr & Cu

Electrostatic Effect on Ionic Radii

- The **ionic radius** is a measure of the size of the spherical region around the nucleus of an ion within which the electrons are most likely to be found
  - Cations are **smaller** than their parent atoms
  - Anions are **larger** than their parent atoms
  - Ionic radii increase down any column because of the addition of electron shells (electron repulsion dominates nuclear charge increase)
  - In general, cations across any horizontal period decrease in radius (nuclear charge more dominant than electron repulsion)
  - When you reach the anions, there is an abrupt increase in radius, and then the radius again decreases

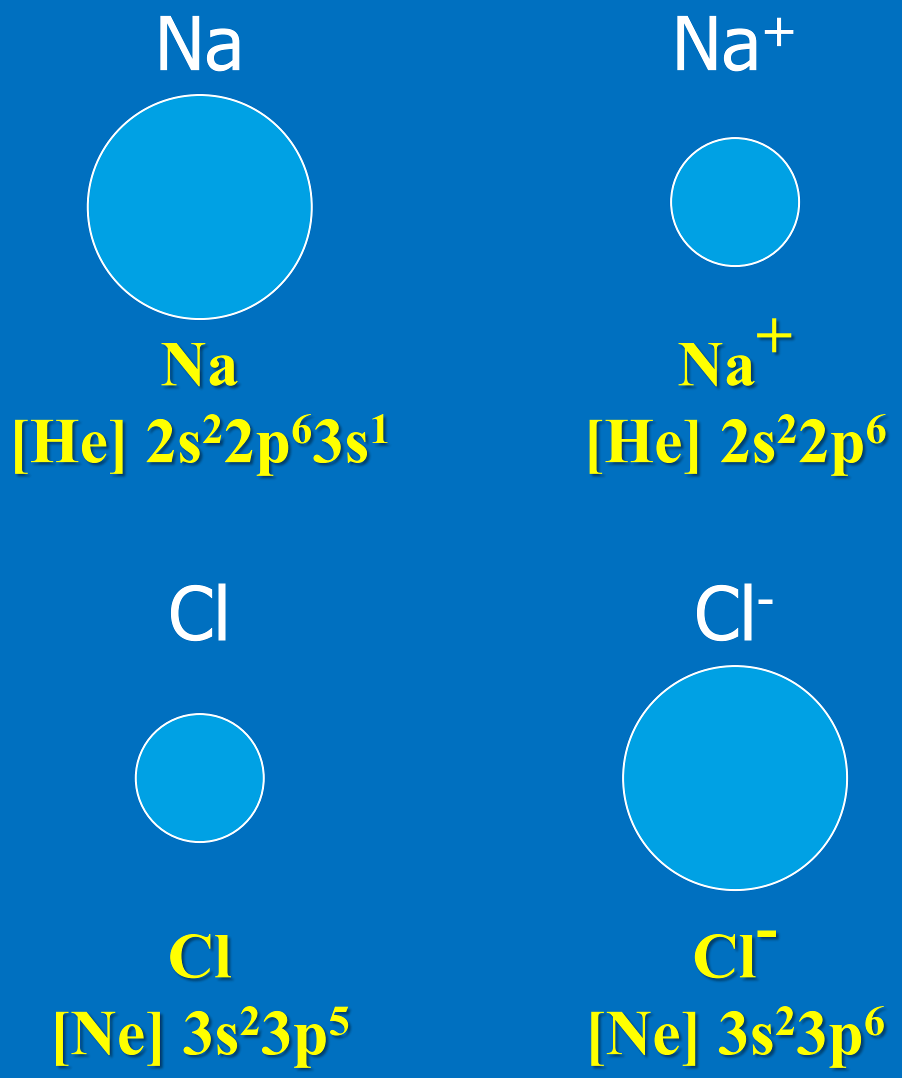
Ionic Radii

When a Cation forms, electrons are removed from outer shell

The resulting decrease in electron repulsion allows nuclear charge to pull remaining electrons closer

When an Anion forms, electrons are added to the outer level

The increase in electron repulsion causes the electron cloud to occupy more space



Na

Na^+

Na
[He] $2s^22p^63s^1$

Na^+
[He] $2s^22p^6$

Cl

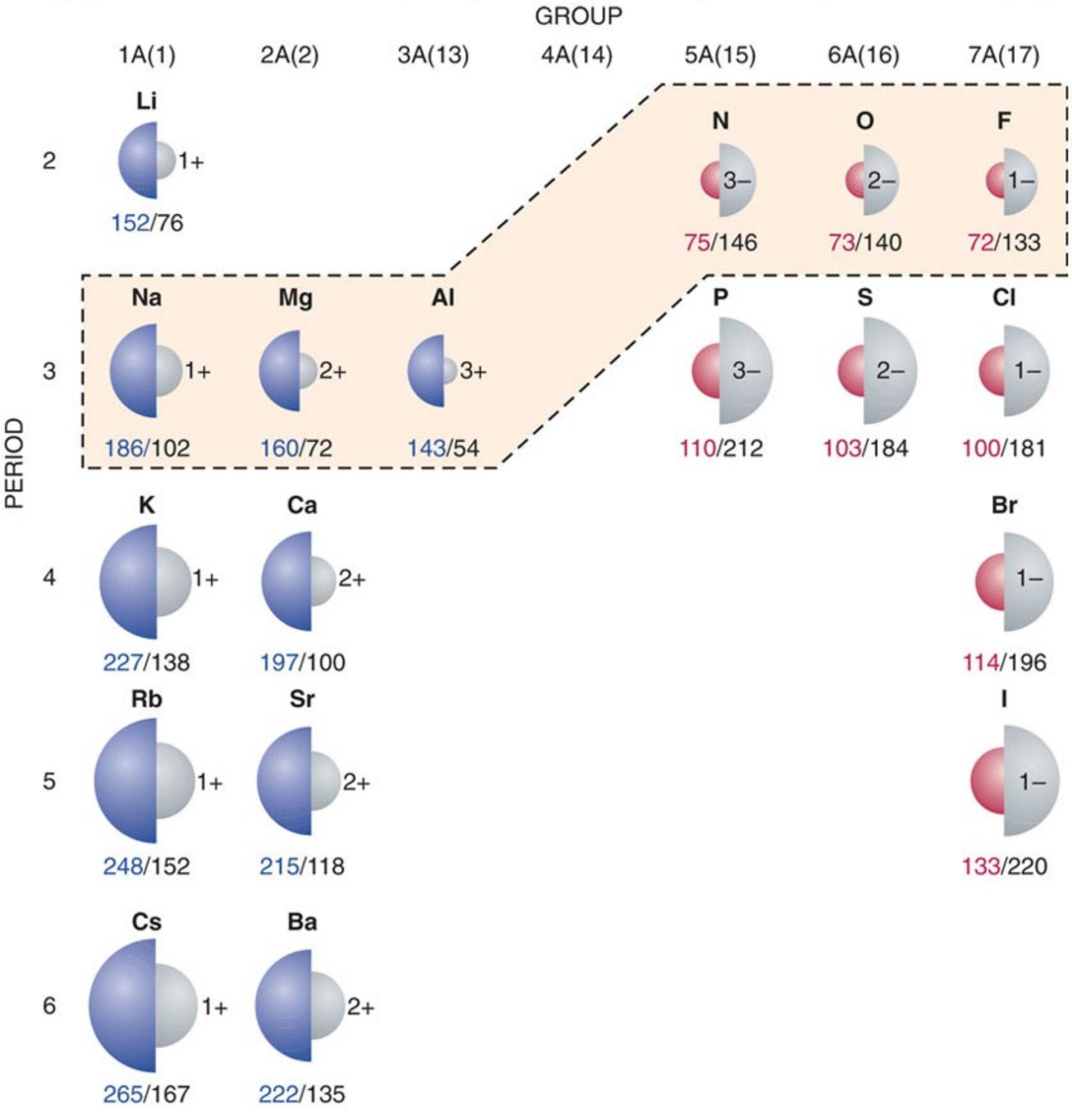
Cl^-

Cl
[Ne] $3s^23p^5$

Cl^-
[Ne] $3s^23p^6$

Ionic Radii

- Ionic Size increase down a group
  - Number of energy levels increases
- Ionic Size becomes more complicated across a period
  - Decreases among Cations
  - Increase dramatically with first Anion
  - Subsequent Decrease within Anions



Ionic Radii

- Within an **isoelectronic group** of ions, the one with the greatest nuclear charge will be the smallest

For example, look at the ions listed below

$_{20}Ca^{2+}$ $_{19}K^{+}$ $_{18}Ar$ $_{17}Cl^{-}$ $_{16}S^{2-}$

All have the same Noble Gas configuration

$1s^2 2s^2 2p^6 3s^2 3p^6$ - $[Ne]3s^2 3p^6$ (18 e^-)

They all have the same number of electrons (18), but different numbers of protons

Con't on Next Slide

Ionic Radii

- In this group, Calcium has the greatest nuclear charge (2^+) thus, the smallest radius

$$_{20}Ca^{2+} < {}_{19}K^{+} < {}_{18}Ar < {}_{17}Cl^{-} < {}_{16}S^{2-}$$

  - All have 18 electrons
  - Decreasing # protons going from left to right
  - Sulfur has only 16 protons to attract its 18 electrons, thus, the electrons have less attraction to the nucleus and electron repulsion results in electron cloud expanding outward increasing the radius

Electrostatic Effect - Lattice Energy

- Lattice energy is the result of electrostatic interactions among ions
- Lattice energy ($\Delta H^o_{lattice}$) is the Enthalpy change that occurs when:

1 mol of ionic solid separates into gaseous ions

$$LiF(s) \rightarrow Li^+(g) + F^-(g)$$

$\Delta H_{lattice}$ is always Positive (Endothermic)

- The magnitude of Lattice Energy is dependent on:
  - Ionic Size
  - Ionic Charge
  - Ionic Arrangement

Electrostatic Effect - Lattice Energy

- Coulombs Law states that electrostatic energy between two charges (Q1 & Q2) is directly proportional to the produce of their magnitudes and inversely proportional to the square of the distance between them

$$E = kQ_1Q_2/r^2$$

- The Electrostatic relationship between charges can be extended to Lattice Energy – it is directly proportional
- In an Ionic solid, the distance between Cations and Anions is effectively the sum of their individual radii
- Restating Coulombs law for lattice energy:

$$\text{Electrostatic Energy} \propto \frac{\text{cation charge} \times \text{anion charge}}{\text{cation radius} + \text{anion radius}} \propto \Delta H^0_{\text{lattice}}$$

Electrostatic Effect - Lattice Energy

- Compare Lithium Fluoride & Magnesium Oxide

	LiF	MgO
Cation Radii	Li^+ – 76 pm	Mg^{2+} – 72 pm
Anion Radii	F^- – 133 pm	O^{2-} – 140 pm

Since Radii are similar, the difference is the singly charged Li^+ & F^- ions versus the doubly charged Mg^{+2} & O^{2-} ions

The difference in lattice energy is significant

$\Delta H^o_{lattice}$ LiF = 1050 kJ/mol

$\Delta H^o_{lattice}$ MgO = 3923kJ/mol

Electrostatic Effect - Lattice Energy

- The transfer of an electron from a metal to a nonmetal is not, in itself, energetically favorable; it requires an input of energy (ΔH positive)

- However, when these oppositely charged ions come together, energy is released (ΔH negative)

- Additional energy is released when the ion pairs get close enough to actually solidify into the ionic solid

- This net release of energy (-ΔH) for the formation of an ionic solid from the separate gaseous ions is the negative of the **lattice energy** ($\Delta H_{lattice}$), which is always positive

Electrostatic Effect - Lattice Energy

- Lattice energy can not be measured directly
- It is determined from Hess's Law, which states:

The total Enthalpy change (ΔH^o_f) is the sum

of the Enthalpy changes of all individual reactions

$$\Delta H^o_f = \Delta H^o_1 + \Delta H^o_2 + \Delta H^o_3 + \ldots\ldots + (-\Delta H^o_{lattice})$$

- The law follows from the fact that ΔH for a process depends only on the difference between the final and initial states
  - An overall reaction occurs through a series of individual reactions steps
  - Each step has its own Enthalpy change - ΔH
  - Adding the steps gives the overall process

Born-Haber Process

- Use the Born-Haber cycle to compute lattice energy (unknown) from known Enthalpies
- The **Born–Haber cycle** is an approach to analyzing reaction energies
- The cycle is concerned with the formation of an ionic compound from the reaction of a metal (often a Group I or Group II element) with a non-metal
- Born–Haber cycles are used primarily as a means of calculating Lattice Energies (or more precisely Enthalpies) which cannot otherwise be measured directly

Born-Haber Process

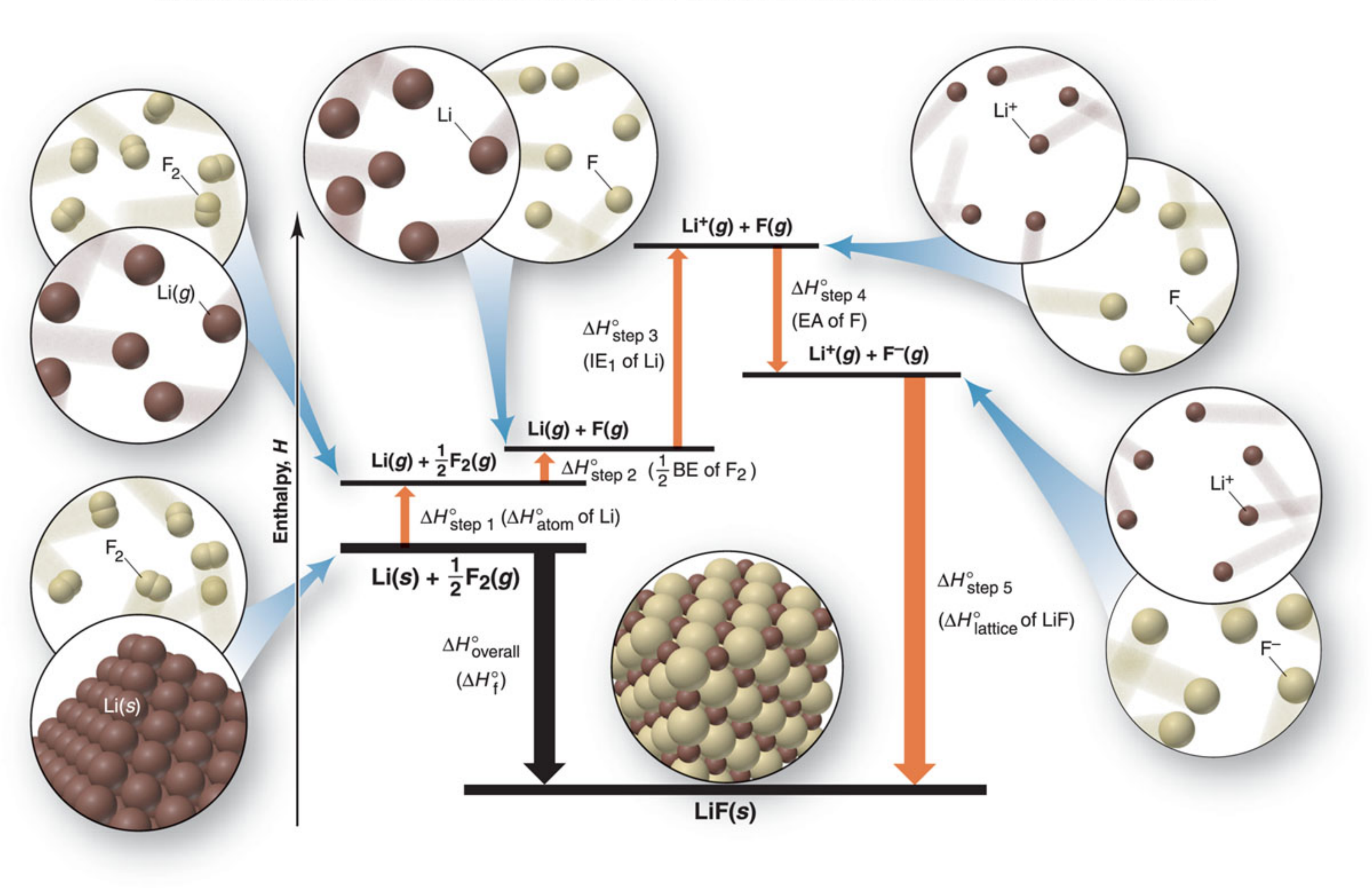
- Recall the Lattice energy is the Enthalpy change involved in the formation of an ionic compound from gaseous ions

- Some chemists define it as the energy to break the ionic compound into gaseous ions

- The former definition is invariably Exothermic and the latter is Endothermic

- A Born–Haber cycle applies Hess’s Law to calculate the Lattice Enthalpy by comparing the standard Enthalpy change of formation of the ionic compound (from the elements) to the Enthalpy required to make gaseous ions from the elements

Born-Haber Cycle for Lithium Fluoride



Practice Problem

Calculate Lattice Energy of LiF

- The individual reactions that take part in the formation of an ionic solid, such as LiF, starting with the elements include:
- Gasification of the elements

$Li_{(s)} \rightarrow Li_{(g)}$ $\qquad$ $\frac{1}{2} F_{2(g)} \rightarrow F_{(g)}$

- Ionization of the gaseous elements (IE & EA)

$Li_{(g)} \rightarrow Li^{+}_{(g)} + e^{-}$ $\qquad$ $F_{(g)} + e^{-} \rightarrow F^{-}_{(g)}$

- Formation of the crystalline ionic solid from the gaseous ions

$Li^{+}_{(g)} + F^{-}_{(g)} \rightarrow LiF_{(s)}$

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Practice Problem

- Lattice Energies are calculated by means of the Born-Haber Cycle, a series of chosen steps from elements to ionic solid
- Example Problem - Calculate Lattice Energy in the formation of Lithium Fluoride (LiF)

ΔH^o_f of $LiF_{(s)}$ = sum of ΔH^o values for multistep path

Step 1 – Convert 1 mole solid Li to gaseous atoms

$$Li_{(s)} \rightarrow Li_{(g)} \qquad \Delta H^o_{step\ 1} = 161\ kJ$$

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Practice Problem

Step 2 – Convert ½ mole F_2 molecule to gaseous F atoms

$\frac{1}{2} F_{2(g)} \rightarrow F_{(g)} \quad \Delta H^{o}_{step\ 2} = \frac{1}{2}$ BE of F_2 (159 kJ) = 79.5 kJ

Note: BE = Bond Energy

Step 3 – Add Ionization Energy (IE) to remove 2s electron from Li

$Li_{(g)} \rightarrow Li^{+}_{(g)} + e^{-} \qquad \Delta H^{o}_{step\ 3} = IE = 520$ kJ

Step 4 – Lose Electron Affinity (EA) energy to add electron to atom of Fluoride

$F_{(g)} + e^{-} \rightarrow F^{-}_{(g)} \qquad \Delta H^{o}_{step\ 4} = EA = -328$ kJ

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Practice Problem

Step 5 – Form crystalline ionic solid from gaseous ions

This Enthalpy change (negative of Lattice Energy) is the unknown to be determined

$Li^{+}_{(g)} + F^{-}_{(g)} \rightarrow LiF_{(s)} \quad \Delta H^{o}_{step\ 5} = -\Delta H^{o}_{lattice}$ of LiF = ?

Known: Enthalpy change of formation (ΔH^{o}_{f}) for reaction

$Li_{(s)} + 1/2F_{2(g)} \rightarrow LiF_{(s)} \quad \Delta H^{o}_{overall} = \Delta H^{o}_{f} = -617\ kJ$

Practice Problem

Step 6 – Set up the 5 reactions and add them together

$Li_{(s)} \rightarrow \cancel{Li}_{(g)} \qquad \Delta H^o_{\text{step 1}} = 161 \text{ kJ}$

$\frac{1}{2} F_{2(g)} \rightarrow \cancel{F}_{(g)} \qquad \Delta H^o_{\text{step 2}} = \frac{1}{2} \text{ BE of } F_2 \text{ (159 kJ)} = 79.5 \text{ kJ}$

$\cancel{Li}_{(g)} \rightarrow \cancel{Li}^+_{(g)} + \cancel{e^-} \qquad \Delta H^o_{\text{step 3}} = \text{IE} = 520 \text{ kJ}$

$\cancel{F}_{(g)} + \cancel{e^-} \rightarrow \cancel{F}^-_{(g)} \qquad \Delta H^o_{\text{step 4}} = \text{EA} = -328 \text{ kJ}$

$\cancel{Li}^+_{(g)} + \cancel{F}^-_{(g)} \rightarrow LiF_{(s)} \qquad \Delta H^o_{\text{step 5}} = -\Delta H^o_{\text{lattice}} \text{ of LiF} = ?$

$Li_{(s)} + 1/2F_{2(g)} \rightarrow LiF_{(s)} \qquad \Delta H^o_{\text{overall}} = \Delta H^o_f = -617 \text{ kJ}$

Con't on next side

Practice Problem

Step 7 – Using Hess's Law, set known ΔH^o_f equal to the sum of the ΔH^o values for the 5 steps

$$\Delta H^o_f = \Delta H^o_1 + \Delta H^o_2 + \Delta H^o_3 + \Delta H^o_4 + (-\Delta H^o_{lattice})$$

Solve for $(-\Delta H^o_{lattice})$

$$-\Delta H^o_{lattice} = \Delta H^o_f - (\Delta H^o_1 + \Delta H^o_2 + \Delta H^o_3 + \Delta H^o_4)$$

$$= -617 \text{ kJ} - [161 \text{ kJ} + 79.5 \text{ kJ} + 520 \text{ kJ} + (-328 \text{ kJ})]$$

$$= -1050 \text{ kJ}$$

$\Delta H^o_{lattice} = 1050$ kJ (solid LIF(s) $\rightarrow Li^+ + F^-$) [Lattice Energy]

Note: lattice energy is always positive

Lattice energy dominates energy involved in the multistep process

Practice Problem

The Lattice Energy of an ionic solid such as NaCl is the Enthalpy change ΔH^o for the process in which the solid changes to ions. For example,

$NaCl(s) \rightarrow Na^+(g) + Cl^-(g$ $(\Delta H_{lattice} = 786 \text{ kJ/mol})$

Assume:

IE for $Na(g) \rightarrow Na^+(g)$ $(\Delta H = 496 \text{ kJ/mol})$

EA for $Cl(g) + 1\ e- \rightarrow Cl^-(g)$ $(\Delta H = -349 \text{ kJ/mol})$

What is ΔH for the following process:

$$Na(g) + Cl(g) \rightarrow NaCl(s)$$

$$\begin{array}{llll}
\cancel{Na^+}(g) + \cancel{Cl^-}(g) & \rightarrow & NaCl(s) & \Delta H = -786 \text{ kJ/mol} \\
Na(g) & \rightarrow & \cancel{Na^+(g)} + \cancel{1e^-} & \Delta H = 496 \text{ kJ/mol} \\
Cl(g) + \cancel{1e^-} & \rightarrow & \cancel{Cl^-(g)} & \Delta H = -349 \text{ kJ/mol} \\
\hline
Na(g) + Cl(g) & \rightarrow & NaCl(s) & \Delta H = -639 \text{ kJ/mol}
\end{array}$$

Properties of Ionic Compounds

- Ionic Solids
  - Hard – Do not dent
  - Rigid – Do not bend
  - Brittle – Crack without deforming
- Properties due to powerful attractive forces holding ions together
- Moving ions out of position requires significant energy to overcome these forces

Covalent Bonds

- When two nonmetals bond, they often share electrons since they have similar attractions for them. This sharing of valence electrons is called the **covalent bond**
  - These atoms will share sufficient numbers of electrons in order to achieve a noble gas electron configuration (that is, eight valence electrons – ns^2np^6)

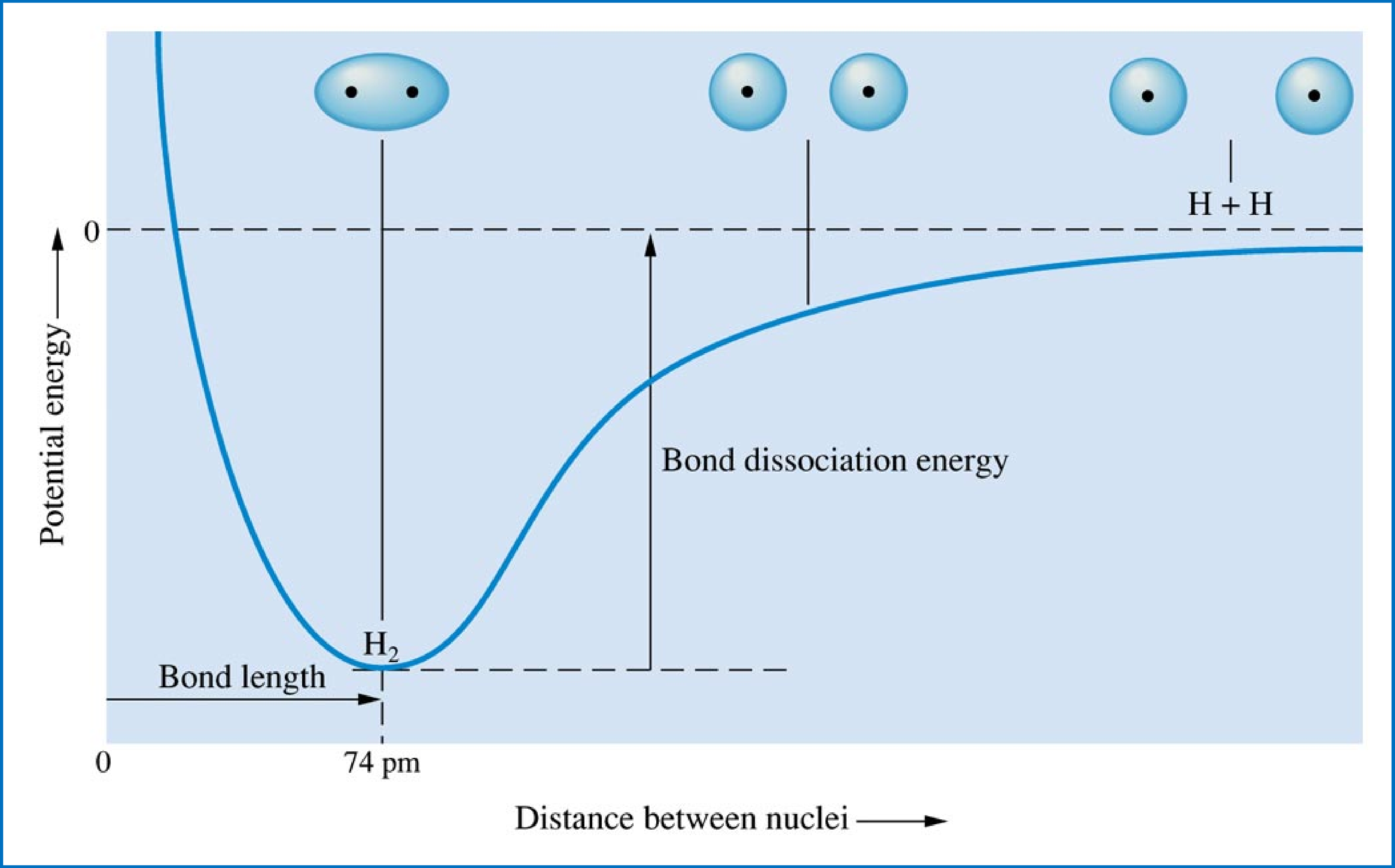
Covalent Bonding

- A Covalent Bond is formed through the **sharing** of two electrons
- Covalent Bonding is an idealized bonding between two atoms, generally two nonmetals, with little difference in their tendencies to lose or gain electrons
- Each nonmetal holds onto its own electrons tightly (high IE) and tends to attract other electrons (EA)
- Shared electron pair is said to be ***localized***, spending most of their time between two atoms
- Covalent Bonding usually results in the formation of Molecules as opposed to individual ions in a bonded solid

Formation of a Covalent Bond

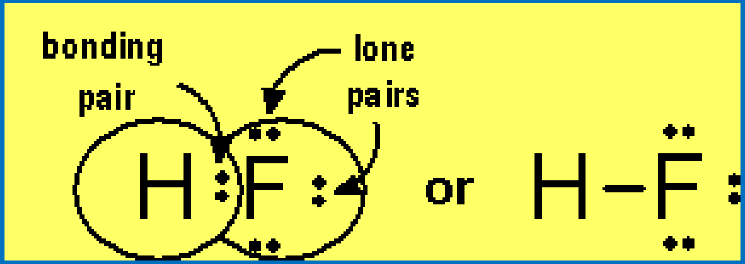
- As the distance between two nuclei decreases, each starts to attract each other's electron(s)
- This lowers potential energy
- As atoms draw closer, the system becomes progressively lower in energy
- As attractions increase so do repulsions between the nuclei and between electrons
- At some internuclear distance, maximum attraction is achieved, i.e., the system is at the minimum energy point (bottom of energy well)
- A Covalent bond is a balance between:
    - Nucleus-Electron attractions and
    - Electron-Electron and nucleus-nucleus repulsions

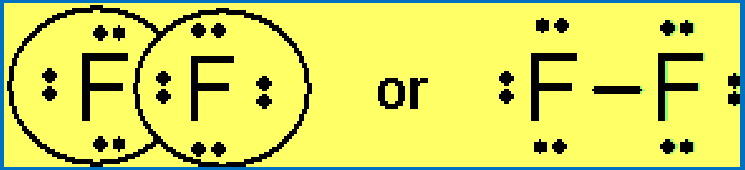
Potential Energy Curve for H_2



Bonding Pairs & Lone Pairs

- Achieving a full outer shell of valence electrons in a covalent compound differs from that of ionic compounds
- Each atom in a covalent bond "counts" the shared electrons as belonging entirely to itself
- The two electrons in the shared electron pair simultaneously fill the outer level of both atoms
- An outer-level electron pair that is not involved in bonding is called a "lone pair"





Properties of Covalent Compounds

- The Covalent Bond model proposes that electron sharing between pairs of atoms leads to strong, localized bonds, usually within individual molecules
- Covalent substances are poor conductors of electricity because the electrons are localized as either shared or unshared pairs, i.e. they do not move like ions do in ionic compounds or metal/metal compounds)
- This model appears inconsistent with observed physical properties of covalent substances
  - Most covalent substances are gases, liquids, or low-melting solids
  - If covalent bonds are so strong, why do these substances melt and boil at such low temperatures?

Properties of Covalent Compounds

- There are two sets of forces at play with covalent compounds
  - Strong covalent bonding forces hold the atoms together within the molecule
  - Weak intermolecular forces hold separate molecules near each other in the macroscopic sample
  - It is the <u>weak</u> forces <u>between</u> the molecules, <u>not</u> the <u>strong</u> covalent bonds <u>within</u> each molecule, that are responsible for the observed physical properties
- There are some covalent substances called "network covalent solids" that do not consist of separate molecules, but are held together by covalent bonds that extend in three-dimensions throughout the sample, such as in diamonds and quartz

Metal with Metal Bonding

- Metals are generally large and have few outer electrons which are well shielded by filled inner electron levels
- The have low Ionization Energies (IE) – lose electrons easily, but do not gain them readily (slightly negative or positive Electron Affinity (EA)
- Valence electrons are pooled and evenly distributed around metal-ion cores (nucleus plus inner electrons).
- Such electrons are ***delocalized*** moving freely throughout the metal

Practice Problem

Which member of each pair is more metallic?

a. Na or Cs   b. Mg or Rb   c. As or N

Ans: Metallic behavior increases to the **left** and **down** on the periodic table

a) Cs is more metallic since it is further down the alkali metal group than Na

b) Rb is more metallic since it is both to the left and down from Mg

c) As is more metallic since it is further down Group 5A than N

Practice Problem

Which member of each pair is less metallic?

a. I or O   b. Be or Ba   c. Se or Ge

Ans: Metallic behavior increases to the left and down on the periodic table

a. Oxygen (O) - slightly left, but much higher group–wise than Iodine (I)

b. Beryllium (Be) - higher in the Group 2A column than Barium (Ba)

c. Selenium (Se) - further to the right than Germanium (Ge) on the Period 4 row

Coordinate Covalent Bonds

- When bonds form between atoms that both donate an electron, you have:

$$A\cdot + \cdot B \rightarrow A:B$$

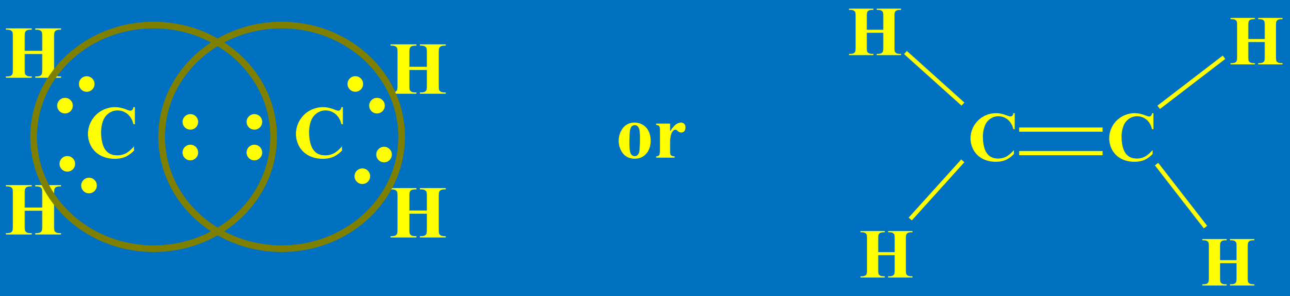
  - It is, however, possible that both electrons are donated by one of the atoms. This is called a **Coordinate Covalent Bond**

$$A + :B \rightarrow A:B$$

Multiple Bonds

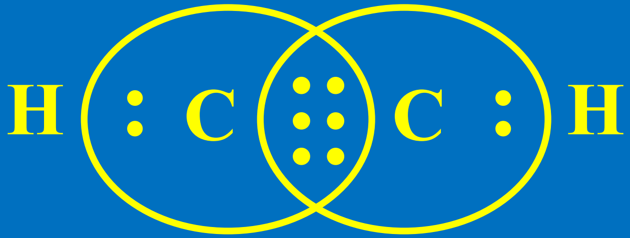
- In the molecules described so far, each of the bonds has been a **single bond**, that is, a covalent bond in which a single pair of electrons is shared
  - It is possible to share more than one pair.

A **double bond** involves the sharing of two pairs between atoms



Multiple Bonds

- **Triple bonds** are covalent bonds in which three pairs of electrons are shared between atoms



or

$H-C\equiv C-H$

Polar Covalent Bonds

- A **polar covalent bond** is one in which the bonding electrons spend more time near one of the two atoms involved
  - When the atoms are alike, as in the H-H bond of H_2, the bonding electrons are shared equally forming a:

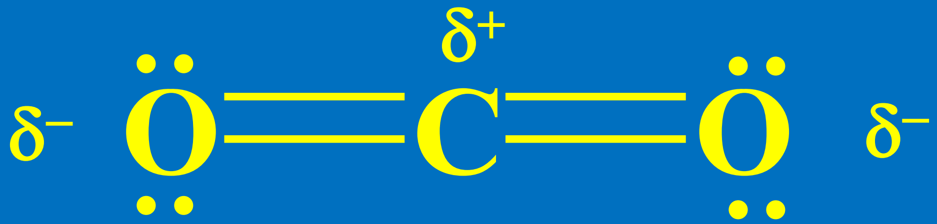
    "nonpolar" covalent bond

  - When the two atoms are of different elements, thus, different electronegativities, the bonding electrons are not shared equally, resulting in a:

    "polar" covalent bond

Polar Covalent Bonds

- For example, the bond between carbon and oxygen in CO_2 is considered polar because the shared electrons spend more time orbiting the oxygen atoms
    - The result is a partial negative charge on the oxygens (denoted δ**-**) and a partial positive charge on the carbon (denoted δ**+**)



$$\delta^{-}\ \ddot{\underset{\cdot\cdot}{O}}=\overset{\delta^{+}}{C}=\ddot{\underset{\cdot\cdot}{O}}\ \delta^{-}$$

Polar Covalent Bonds

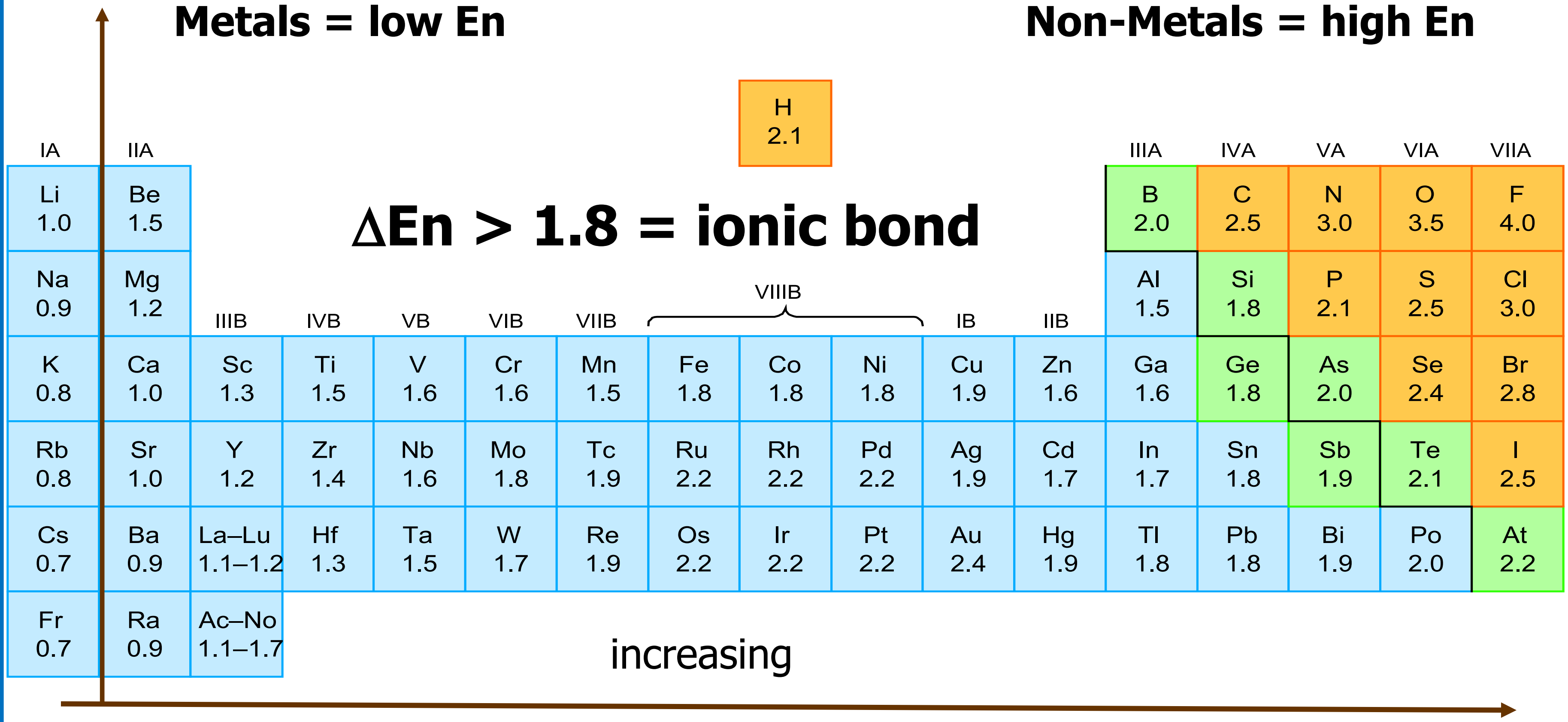
- **Electronegativity** is a measure of the ability of an atom in a molecule to draw bonding electrons to itself
  - In general, electronegativity increases from the lower-left corner to the upper-right corner of the periodic table
- The current electronegativity scale, developed by Linus Pauling, assigns a value of

4.0 to Fluorine

and a value of

0.7 to Cesium

Electronegativities



Metals = low En

Non-Metals = high En

ΔEn > 1.8 = ionic bond

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA
								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 0.7	Ba 0.9	La–Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 1.7	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–No 1.1–1.7														

increasing

Electronegativity = measure of the ability of an atom in a molecule to <u>attract</u> bonding electrons to itself

Ionic vs Covalent

- How to predict “Ionic” vs “Covalent”
- The absolute value of the difference in electronegativity of two bonded atoms gives a rough measure of the **polarity** of the bond
  - When this difference is small (less than 0.5), the bond is **nonpolar**
  - When this difference is large (greater than or equal to 0.5), the bond is considered **polar**
  - If the difference exceeds approximately 1.8, sharing of electrons is no longer possible and the bond becomes **ionic**

Ionic vs Covalent

Are the bonds in each of the following substances ionic, nonpolar covalent, or polar covalent?

KCl	Ionic – K is a metal and Cl is a nonmetal
P_4	Nonpolar Covalent – Phosphorus is a nonmetal
SO_2	Polar Covalent – Both S & O are nonmetals, but each differs in electronegativity
Br_2	Nonpolar covalent – Br is a nonmetal
NO_2	Polar Covalent – Both N & O are nonmetals, each differs in electronegativity
BF_3	Polar Covalent (Ionic?) – B (Metalloid) & F (nonmetal, △En (4.0 – 2.0 = 2.0) – (ionic?)

Ionic vs Covalent

Which is the more polar bond in each of the following pairs:

a. Br - CL or b. F - Cl

b is more polar :

ΔEn for F - CL is 4.0 - 3.0 = 1.0

ΔEn for Br - CL is 3.0 - 2.8 = 0.2

c. H - O or d. Se - H

c is more polar :

ΔEn for H - O is 3.5 - 2.1 = 1.4

ΔEn for Se - H is 2.4 - 2.1 = 0.3

Ionic vs Covalent

Rank the members of each set of compounds in order of decreasing ionic character of their bonds

a. PCl_3, PBr_3, PF_3

$\Delta EN\ PCl_3 = 3.0 - 2.1 = 0.9$

$\Delta EN\ PBr_3 = 2.8 - 2.1 = 0.7$

$\Delta EN\ PF_3 = 4.0 - 2.1 = 1.9$

$\therefore$ $P–F_3$ (1.9) > $P–Cl_3$ (0.9) > $P–Br_3$ (0.7)

b. BF_3, NF_3, CF_4

$\Delta EN\ BF_3 = 4.0 – 2.0 = 2.0$

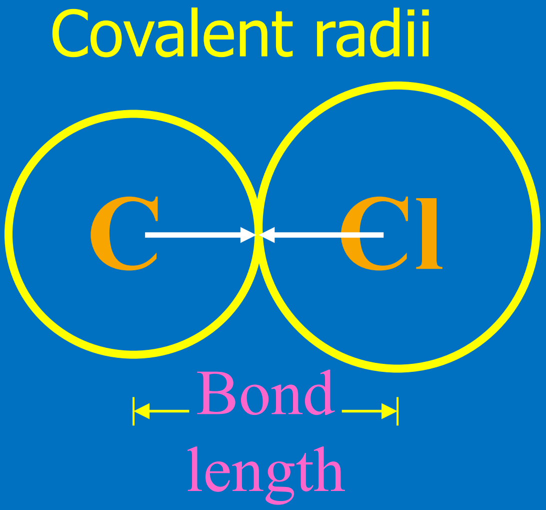
$\Delta EN\ NF_3 = 4.0 – 3.0 = 1.0$

$\Delta EN\ CF_4 = 4.0 – 2.5 = 1.5$

$\therefore$ $B–F_3$ (2.0) > $C–F_4$ (1.5) > $N–F_3$ (1.0)

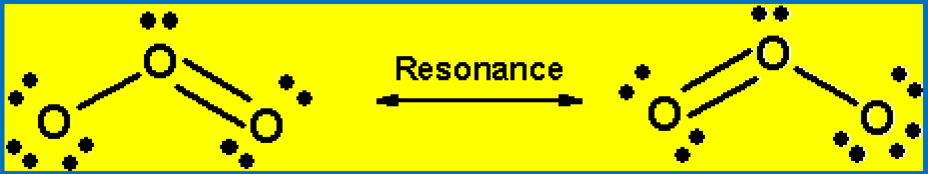
Bond Length and Bond Order

- **Bond length** (or **bond distance**) is the distance between the nuclei in a bond
- Knowing the bond length in a molecule can sometimes give clues as to the type of bonding present
- **Covalent radii** are values assigned to atoms such that the sum of the radii of atoms "A" and "B" approximate the A-B bond length



Bond Length and Bond Order

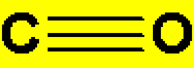
- **Bond order**, determined by the Lewis structure, is a measure of the number of bonding electron pairs between atoms (bond structures)
  - Single bonds have a bond order of 1
  - Double bonds have a bond order of 2
  - Triple bonds (the maximum number) have a bond order of 3
  - A fractional bond order is possible in molecules and ions that have resonance structures
    - In the example of ozone, the bond order would be the average of a double bond and a single bond or 1.5 (3 pairs divided by 2 bond structures)



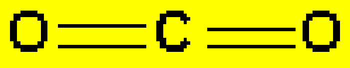
Practice Problem

- What is the bond order of the bonds in the Carbon Monoxide (CO), Carbon Dioxide (CO_2) molecules, and the Carbonate (CO_3^{2-}) ion

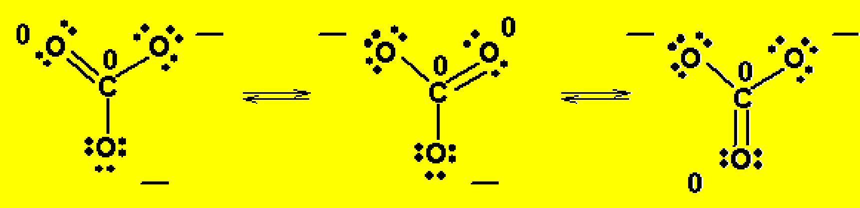
Bond Order



3



2

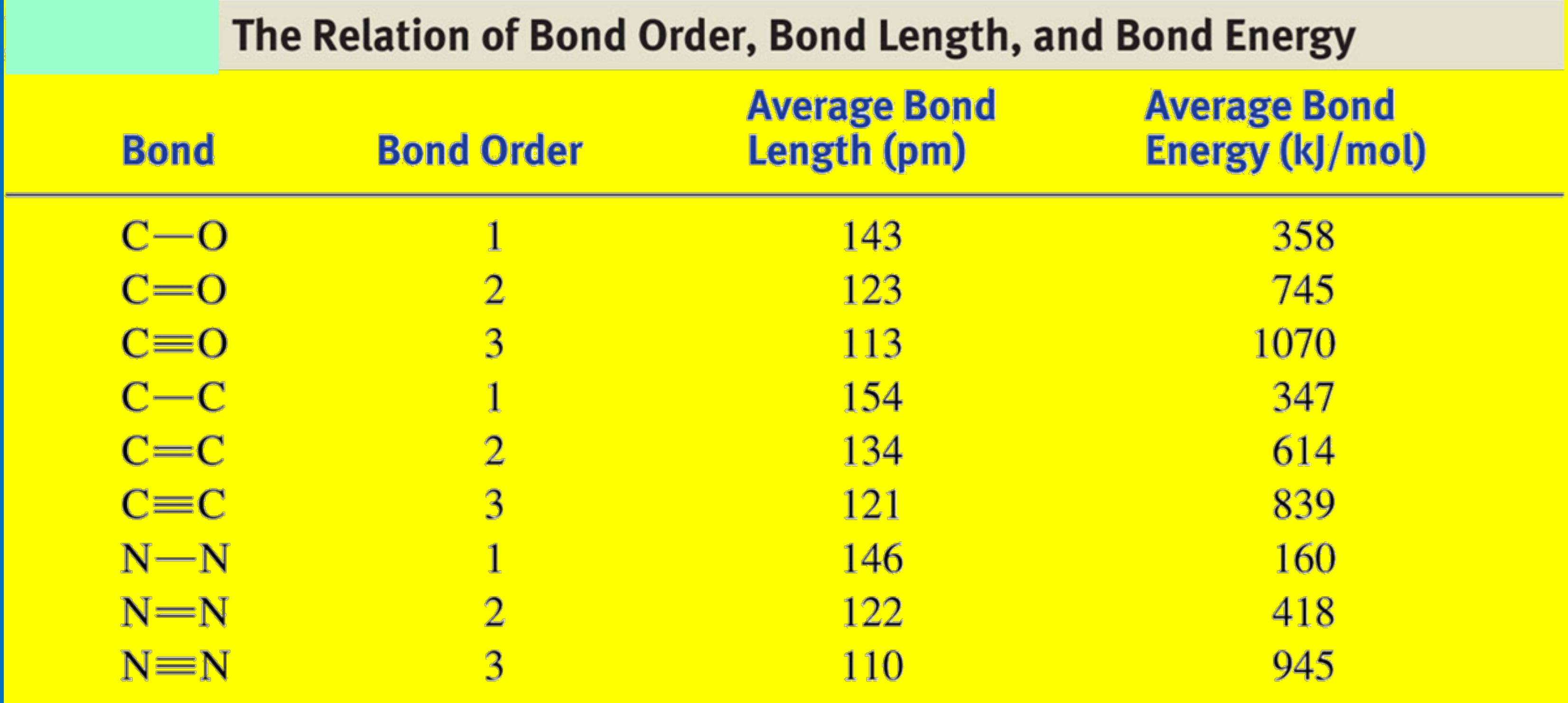


4/3 = 1.3

4 bonded pairs;
3 bond structures

Bond Length and Bond Order

- Bond Length
  - Bond length depends on bond order
  - As the bond order increases, the bond gets shorter and stronger



The Relation of Bond Order, Bond Length, and Bond Energy

Bond	Bond Order	Average Bond Length (pm)	Average Bond Energy (kJ/mol)
C—O	1	143	358
C═O	2	123	745
C≡O	3	113	1070
C—C	1	154	347
C═C	2	134	614
C≡C	3	121	839
N—N	1	146	160
N═N	2	122	418
N≡N	3	110	945

Bond Energy

- **Bond Energy** (denoted BE) is defined as the average Enthalpy change (ΔH) for the breaking of an A-B bond in a molecule in its gas phase

- In any reaction, the quantity of heat absorbed to break reactant bonds would be:

$(\Delta H^{o}_{\text{reactants}}$ positive value)

- The quantity of heat released when the atoms rearrange to form product bonds would be:

$(\Delta H^{o}_{\text{products}}$ negative value)

Bond Energy

- In an Exothermic reaction, the total ΔH^o for the product bonds formed is greater than for the reactant bonds and the ΔH^o_{rxn} is negative
- In an Endothermic reaction, the total ΔH^o for the product bonds being formed is smaller than that for the reactant bonds being broken and the ΔH^o_{rxn} is positive
- The sum of the Enthalpy changes is another form of the heat of reaction ΔH^o_{rxn}

In terms of Enthalpy

$$\Delta H^o_{\mathrm{rxn}} = \sum \Delta H^o_{\mathrm{bonds\ broken}} + \sum \Delta H^o_{\mathrm{bonds\ formed}}$$

In terms of Bond Energy

$$\Delta H^o_{\mathrm{rxn}} = \sum \mathrm{BE}_{\mathrm{bonds\ broken}} \ominus \sum \mathrm{BE}_{\mathrm{bonds\ formed}}$$

The minus sign here is needed because all bond energies are positive

Bond Energy

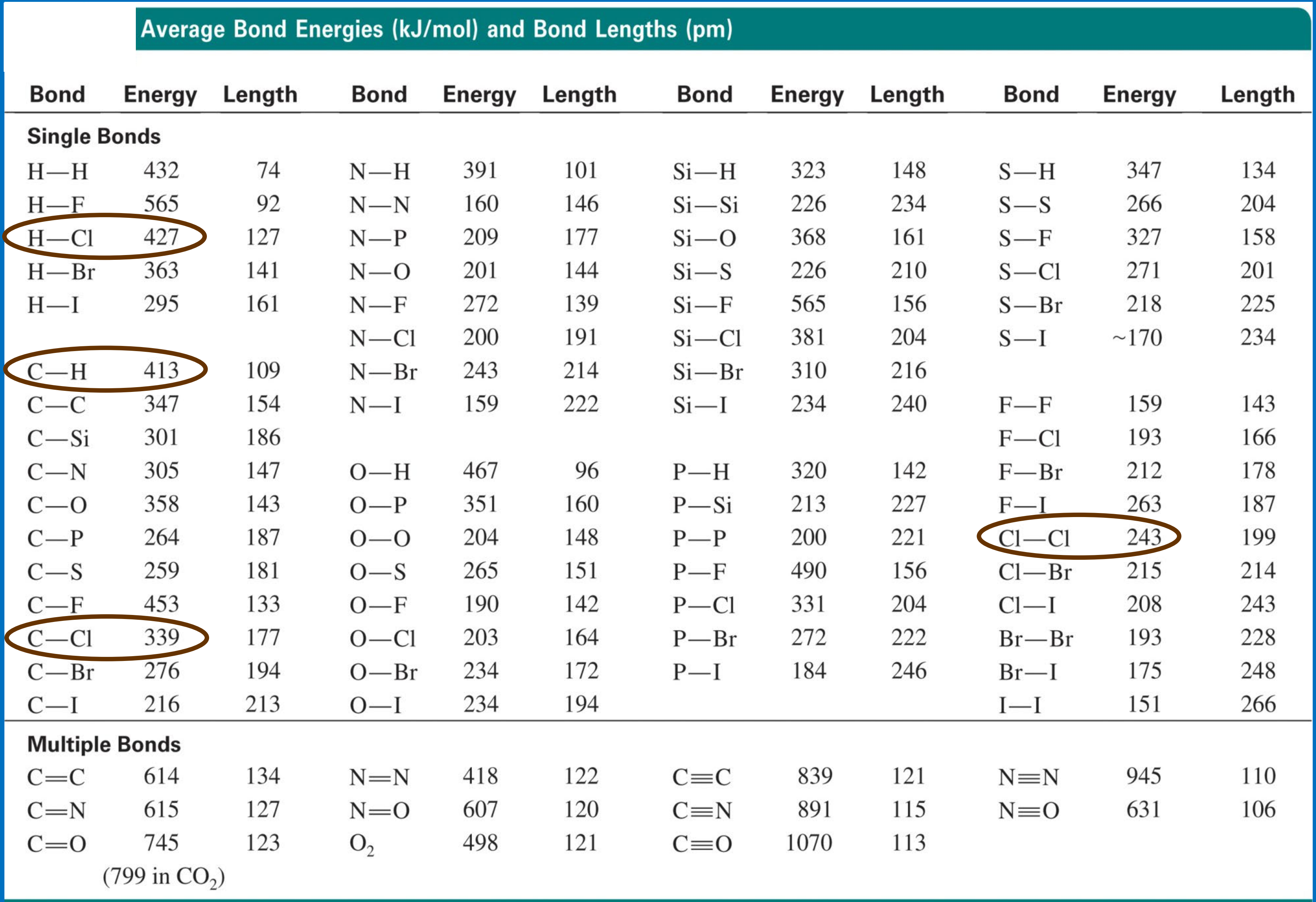
- To illustrate, let’s estimate the ΔH for the following reaction.

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

  - In this reaction, one C-H bond and one Cl-Cl bond must be broken
  - In turn, one C-Cl bond and one H-Cl bond are formed

Con’t on next slide

Bond Energy



Average Bond Energies (kJ/mol) and Bond Lengths (pm)

Bond	Energy	Length	Bond	Energy	Length	Bond	Energy	Length	Bond	Energy	Length
Single Bonds											
H—H	432	74	N—H	391	101	Si—H	323	148	S—H	347	134
H—F	565	92	N—N	160	146	Si—Si	226	234	S—S	266	204
H—Cl	427	127	N—P	209	177	Si—O	368	161	S—F	327	158
H—Br	363	141	N—O	201	144	Si—S	226	210	S—Cl	271	201
H—I	295	161	N—F	272	139	Si—F	565	156	S—Br	218	225
			N—Cl	200	191	Si—Cl	381	204	S—I	~170	234
C—H	413	109	N—Br	243	214	Si—Br	310	216			
C—C	347	154	N—I	159	222	Si—I	234	240	F—F	159	143
C—Si	301	186							F—Cl	193	166
C—N	305	147	O—H	467	96	P—H	320	142	F—Br	212	178
C—O	358	143	O—P	351	160	P—Si	213	227	F—I	263	187
C—P	264	187	O—O	204	148	P—P	200	221	Cl—Cl	243	199
C—S	259	181	O—S	265	151	P—F	490	156	Cl—Br	215	214
C—F	453	133	O—F	190	142	P—Cl	331	204	Cl—I	208	243
C—Cl	339	177	O—Cl	203	164	P—Br	272	222	Br—Br	193	228
C—Br	276	194	O—Br	234	172	P—I	184	246	Br—I	175	248
C—I	216	213	O—I	234	194				I—I	151	266
Multiple Bonds											
C═C	614	134	N═N	418	122	C≡C	839	121	N≡N	945	110
C═N	615	127	N═O	607	120	C≡N	891	115	N≡O	631	106
C═O	745 (799 in CO_2)	123	O_2	498	121	C≡O	1070	113			

Bond Energy

- Referring to Table on the previous slide (Table 9.2 in Silberberg text) for the Bond Energies, a little simple arithmetic yields ΔH

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

$$\Delta H^o_{rxn} = \sum BE_{bonds\ broken} - BE_{bonds\ formed}$$

$$\Delta H^o_{rxn} = [BE(C-H) + BE(Cl-Cl)] - [BE(C-Cl) + BE(H-Cl)]$$

$$\Delta H^o_{rxn} = (413 + 243)_{broken}\ kJ - (339 + 427)_{formed}\ kJ$$

$$\Delta H^o_{rxn} = -110\ kJ$$ Exothermic (energy released)

Summary Equations

Coulombs Law $\mathbf{E = kQ_1Q_2/r}$

$$\textbf{Electrostatic Energy} \infty \frac{\textbf{cation charge} \times \textbf{anion charge}}{\textbf{cation radius} + \textbf{anion radius}} \infty \Delta H^{o}_{\text{lattice}}$$

In terms of Enthalpy

$$\Delta H^{o}_{\text{rxn}} = \sum \Delta H^{o}_{\text{reactant bonds broken}} + \sum \Delta H^{o}_{\text{product bonds formed}}$$

In terms of Bond Energy (BE)

$$\Delta H^{o}_{\text{rxn}} = \sum \text{Be}_{\text{reactant bonds broken}} - \sum \text{Be}_{\text{product bonds formed}}$$

The minus sign here is needed because all bond energies are positive

Hess's Law: $\Delta H^{o}_{f} = \Delta H^{o}_{1} + \Delta H^{o}_{2} + \Delta H^{o}_{3} + \Delta H^{o}_{4} + (-\Delta H^{o}_{\text{lattice}})$