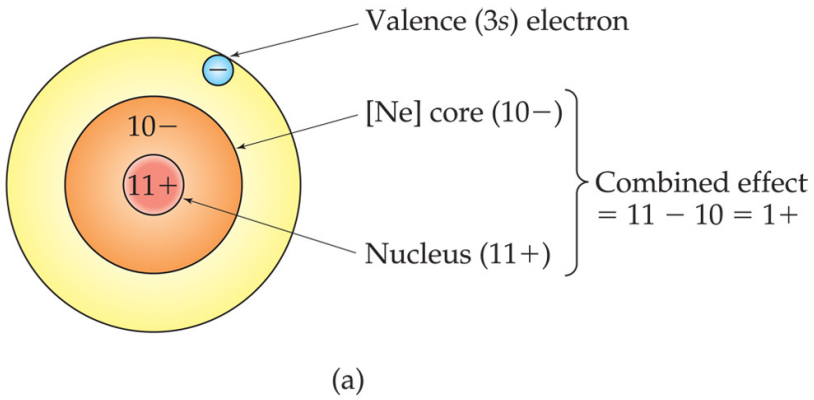
Periodic Trends

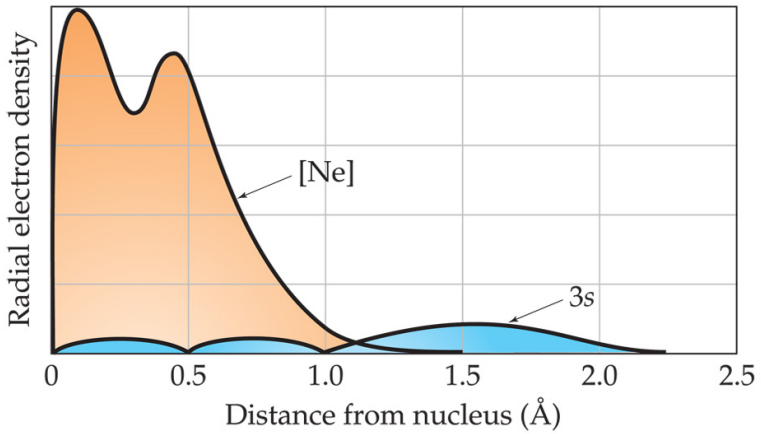
- In this chapter we'll explain why
- We'll then rationalize observed trends in
  - Sizes of atoms and ions.
  - Ionization energy.
  - Electron affinity.

Effective Nuclear Charge

Na atom looks like this:

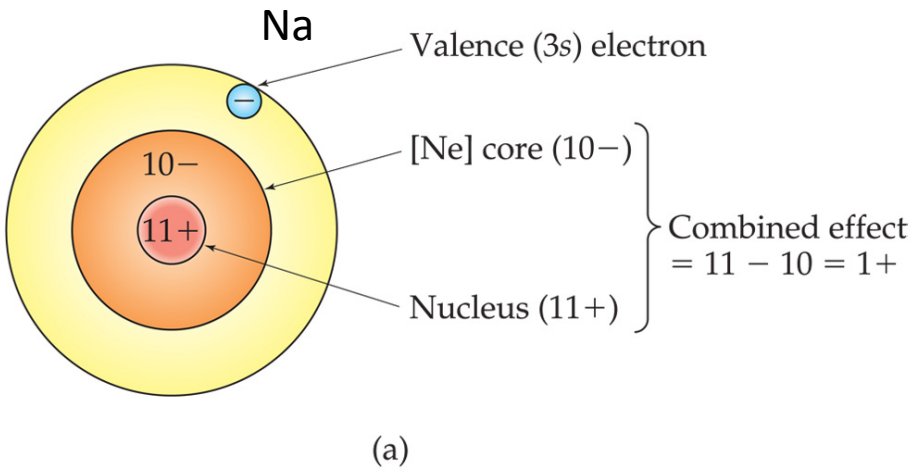


(a)

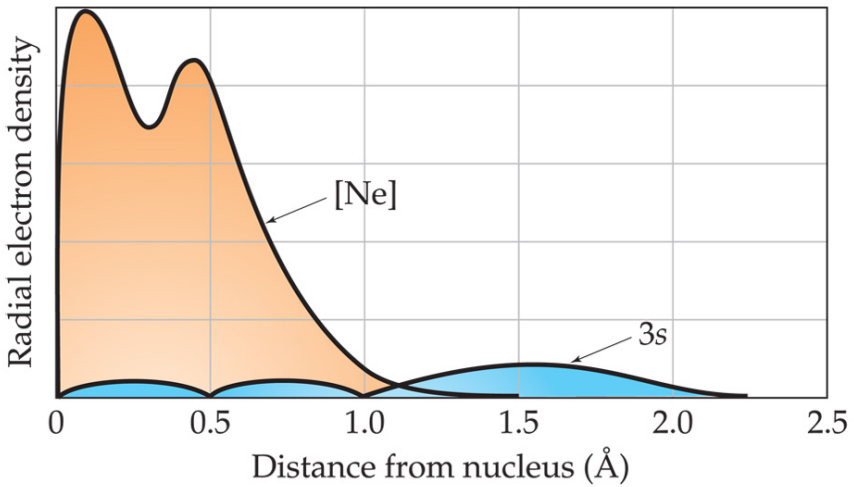


- In a many-electron atom, electrons are both attracted to the nucleus and repelled by other electrons.
- The nuclear charge that an electron "feels" depends on both factors.
- It's called Effective nuclear charge.
- electrons in lower energy levels "shield" outer electrons from positive charge of nucleus.

Effective Nuclear Charge



(a)



The effective nuclear charge, Z_{eff}, is:

$Z_{eff} = Z - S$

Where:

Z = atomic number

S = screening constant, usually close to the number of inner (n-1) electrons.

Effective Nuclear Charge

- Example: Which element's outer shell or "valence" electrons is predicted to have the largest Effective nuclear charge? Kr, Cl or O?

Valence electrons

Many chemical properties depend on the valence electrons.

Valence electrons: The outer electrons, that are involved in bonding and most other chemical changes of elements.

Rules for defining valence electrons.

1. In outer most energy level (or levels)
2. For main group (representative) elements (elements in s world or p world) electrons in filled d or f shells are not valence electrons
3. For transition metals, electrons in full f shells or full d shells are not valence electrons.

Examples: (valence electrons in blue)

P: [Ne]$3s^2 3p^3$

As: [Ar] $4s^2 3d^{10} 4p3$

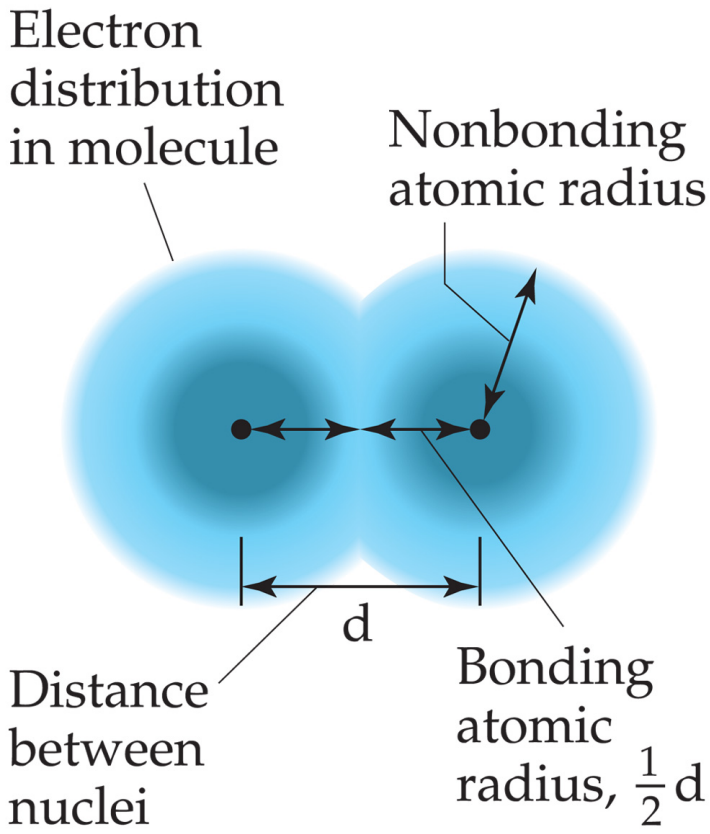
I: [Kr]$5s^2 4d^{10} 5p^5$

Ta: [Kr]$6s^2 4f^{14} 5d^3$

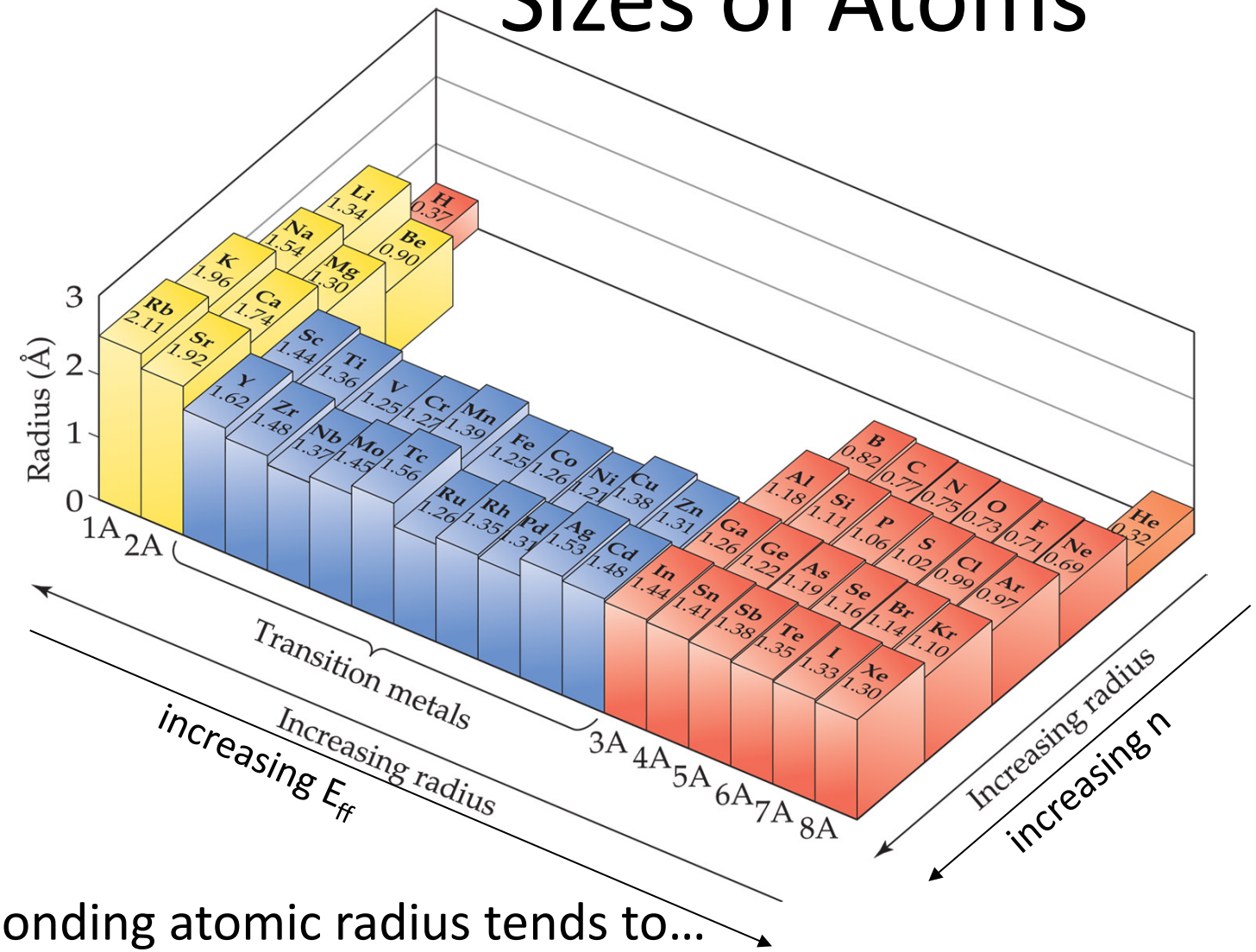
Zn: [Ar]$4s^2 3d^{10}$

Sizes of Atoms

The bonding atomic radius is defined as one-half of the distance between covalently bonded nuclei.



Sizes of Atoms

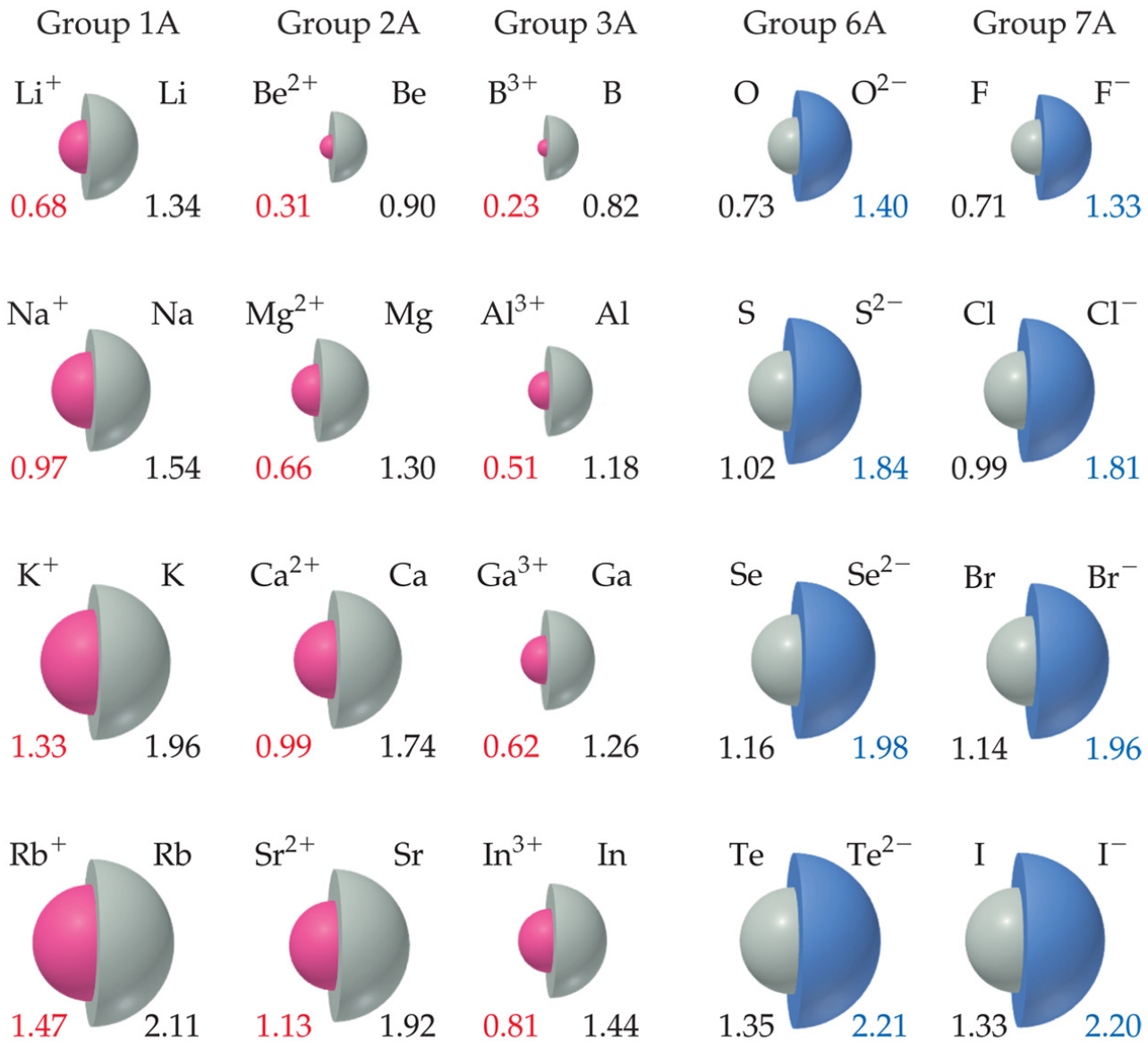


Bonding atomic radius tends to…

…decrease from left to right across a row due to increasing Z_{eff}.

…increase from top to bottom of a column due to increasing value of *n*

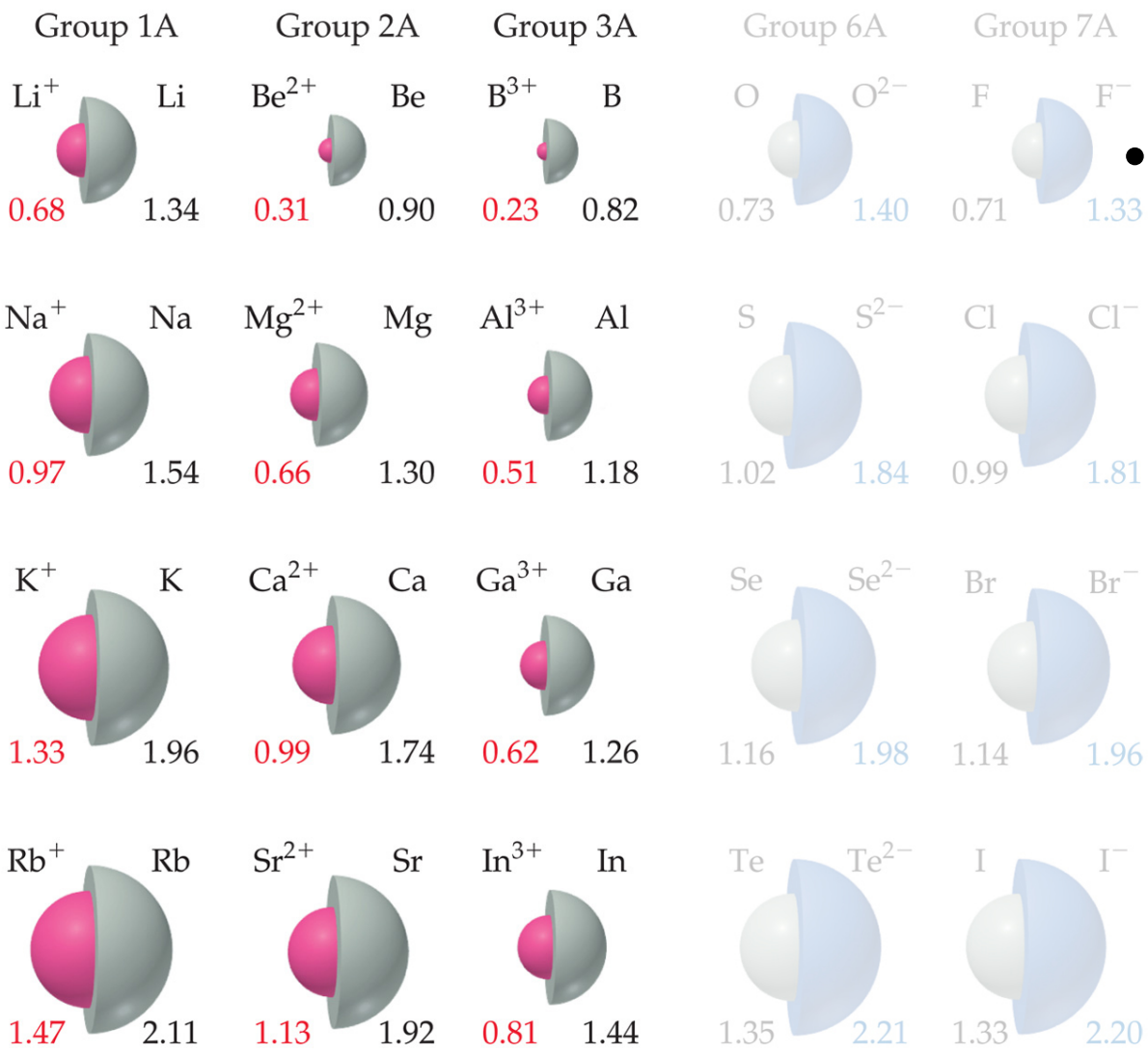
Sizes of Ions



Ionic size depends upon:

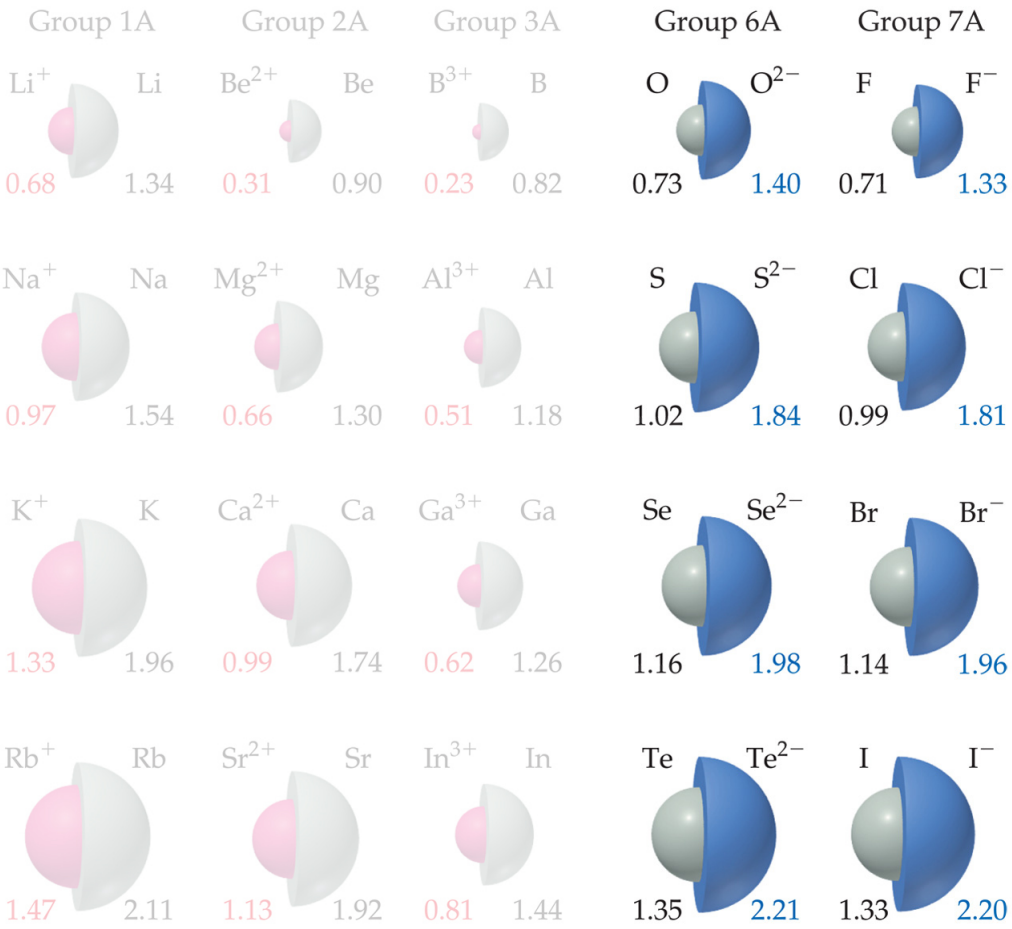
- Nuclear charge.
- Number of electrons.
- Orbitals in which electrons reside.

Sizes of Ions



- Cations are smaller than their parent atoms.
  - The outermost electron is removed and repulsions are reduced.

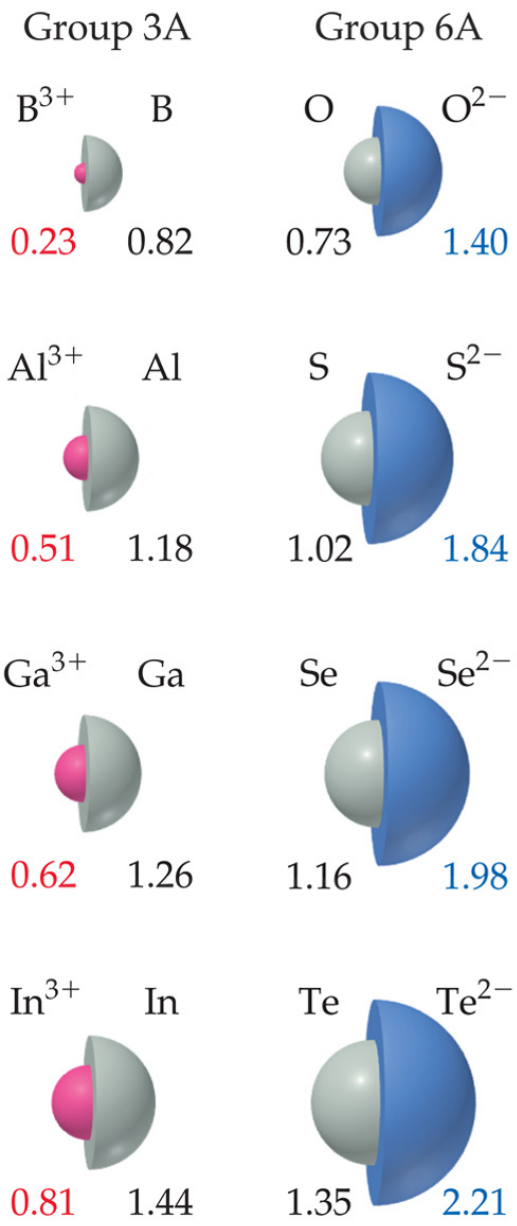
Sizes of Ions



- Anions are larger than their parent atoms.
  - Electrons are added and repulsions are increased.

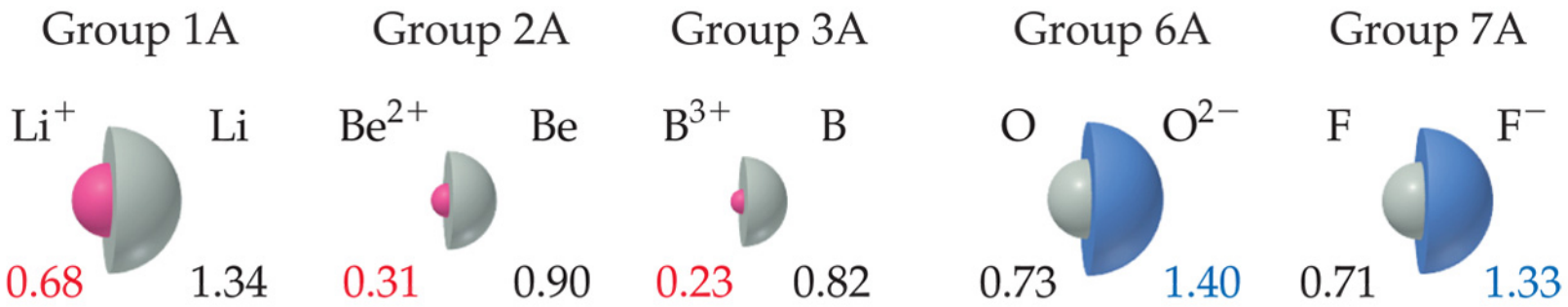
Sizes of Ions

- Ions increase in size as you go down a column.
  - Due to increasing value of *n*.



Sizes of Ions

- In an isoelectronic series, ions have the same number of electrons.
- Ionic size decreases with an increasing nuclear charge.



atom/ion size examples

- Put the following in order of size, smallest to largest:

- Na, Na^{+}, Mg, Mg^{2+}, Al, Al^{3+}, S, S^{2-}, Cl, Cl^{-}

Atom size examples

Al^{3+}, Mg^{2+}, Na^{+}, Cl, S, Al, Mg, Na, Cl^{-}, S^{2-}

Start with atoms with no n=3 electrons, order isoelectronic by nuclear charge.

Next, neutral atoms highest E_{ff} first

Last, anions, highest E_{ff} first

Ionization Energy

- Amount of energy required to remove an electron from the ground state of a gaseous atom or ion.
  - First ionization energy is that energy required to remove first electron.
  - Second ionization energy is that energy required to remove second electron, etc.

$El \text{ -------> } El^+ + e^-$

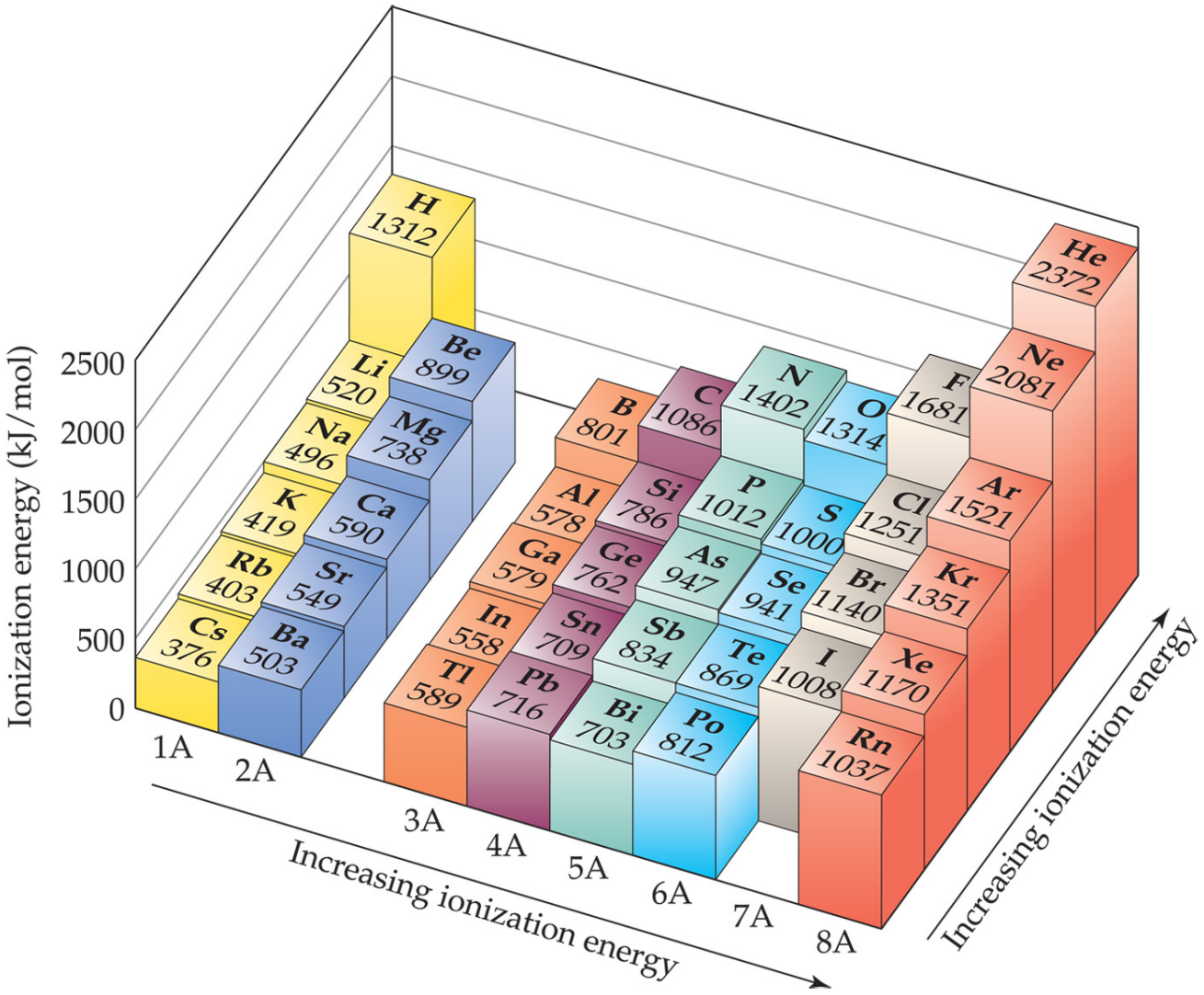
$Na \text{ -------> } Na^+ + e^-$

Ionization Energy

- It requires more energy to remove each successive electron.
- When all valence electrons have been removed, the ionization energy takes a quantum leap.

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4562			(inner-shell electrons)		
Mg	738	1451	7733				
Al	578	1817	2745	11,577			
Si	786	1577	3232	4356	16,091		
P	1012	1907	2914	4964	6274	21,267	
S	1000	2252	3357	4556	7004	8496	27,107
Cl	1251	2298	3822	5159	6542	9362	11,018
Ar	1521	2666	3931	5771	7238	8781	11,995

Trends in First Ionization Energies

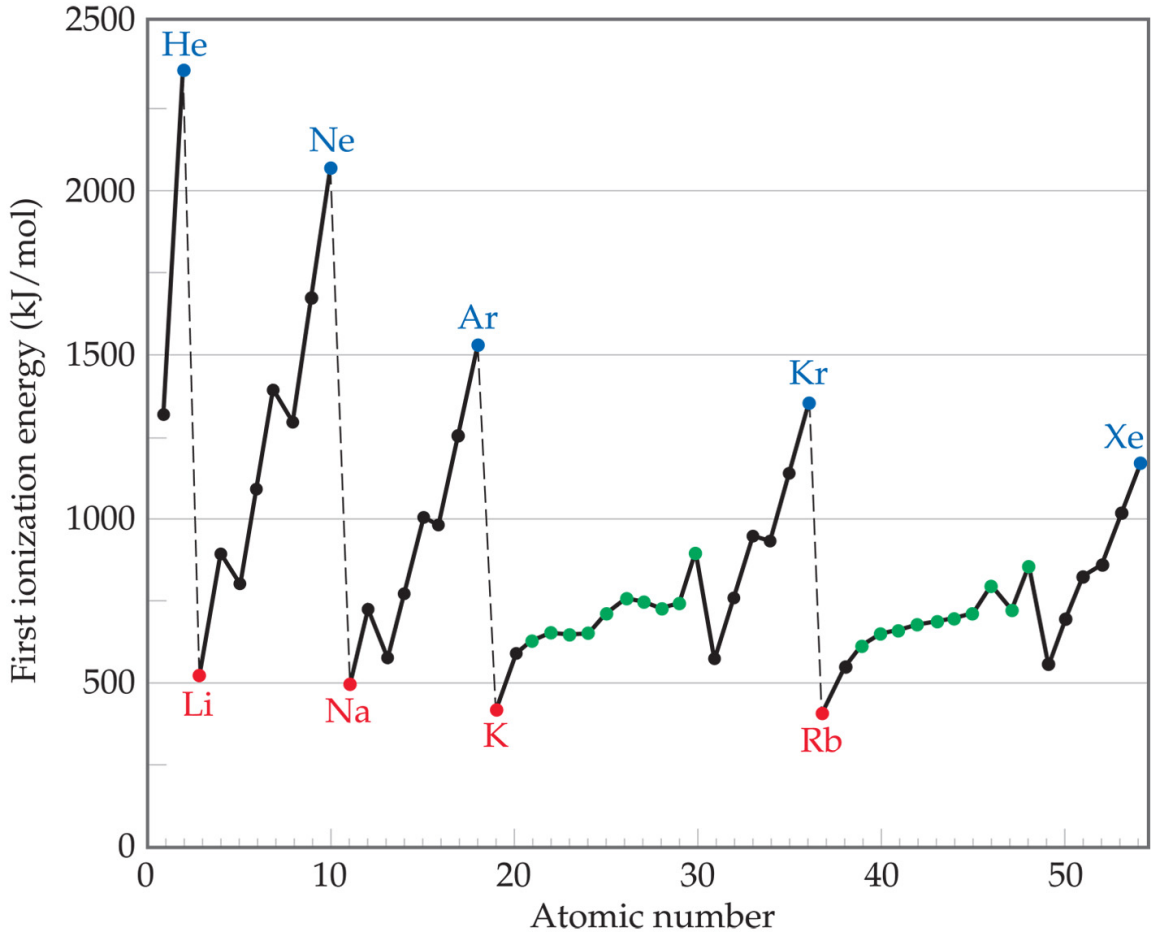


going down a column, less energy to remove the first electron.

- For atoms in the same group, Z_{eff} is essentially the same, but the valence electrons are farther from the nucleus.

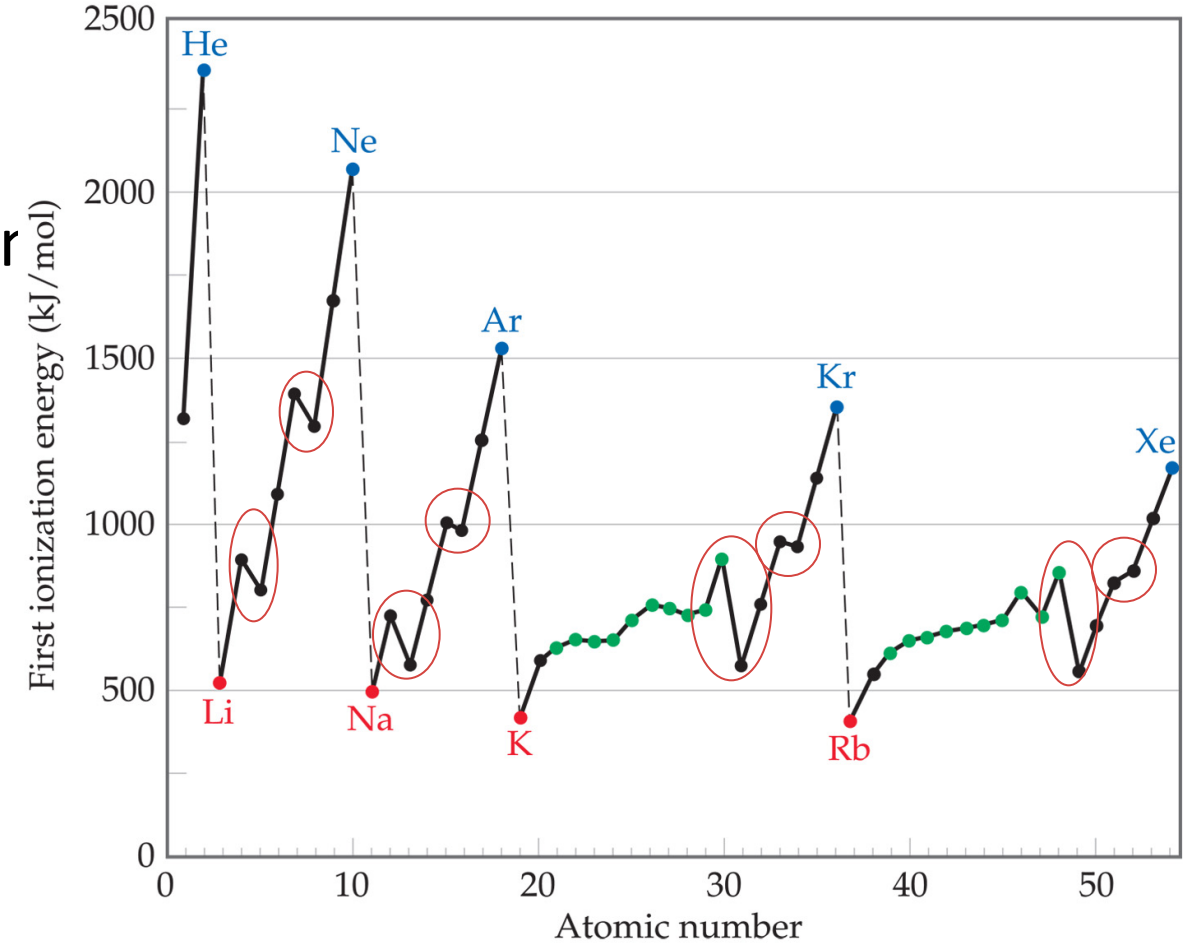
Trends in First Ionization Energies

- Generally, it gets harder to remove an electron going across.
  - As you go from left to to right, Z_{eff} increases.



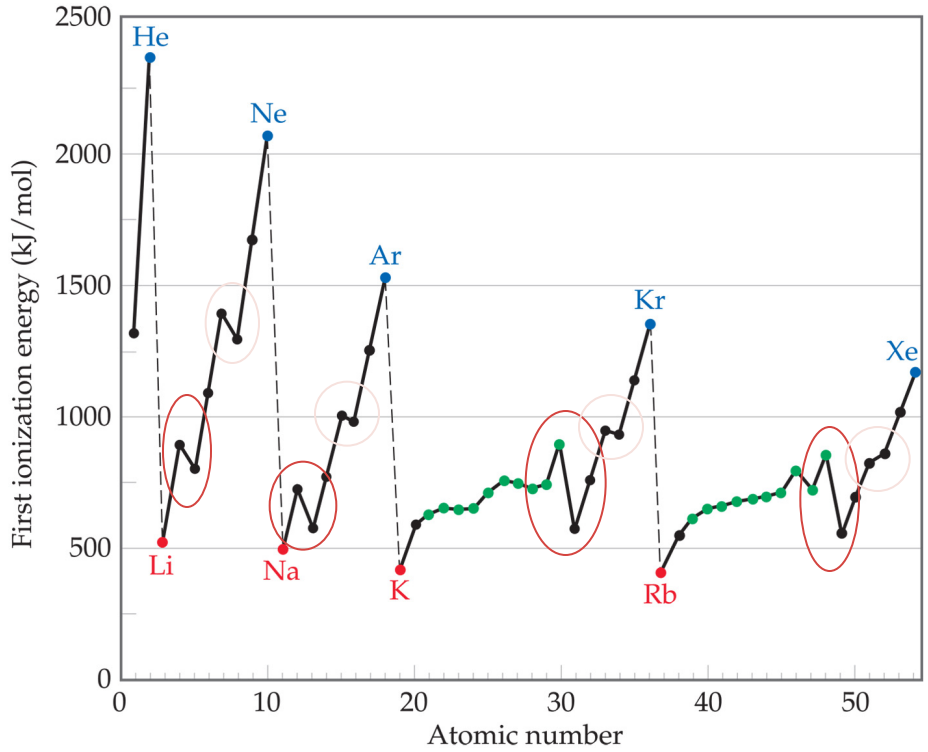
Trends in First Ionization Energies

On a smaller scale, there are two jags ir each line. Why?



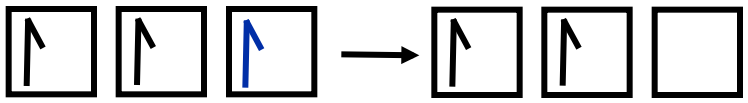
Trends in First Ionization Energies

- The first occurs between Groups IIA and IIIA.
- Electron removed from *p*-orbital rather than *s*-orbital
  - Electron farther from nucleus
  - Small amount of repulsion by *s* electrons.



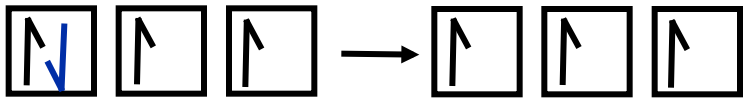
Trends in First Ionization Energies

- The second occurs between Groups VA and VIA.
  - Electron removed comes from doubly occupied orbital.
  - Repulsion from other electron in orbital helps in its removal.

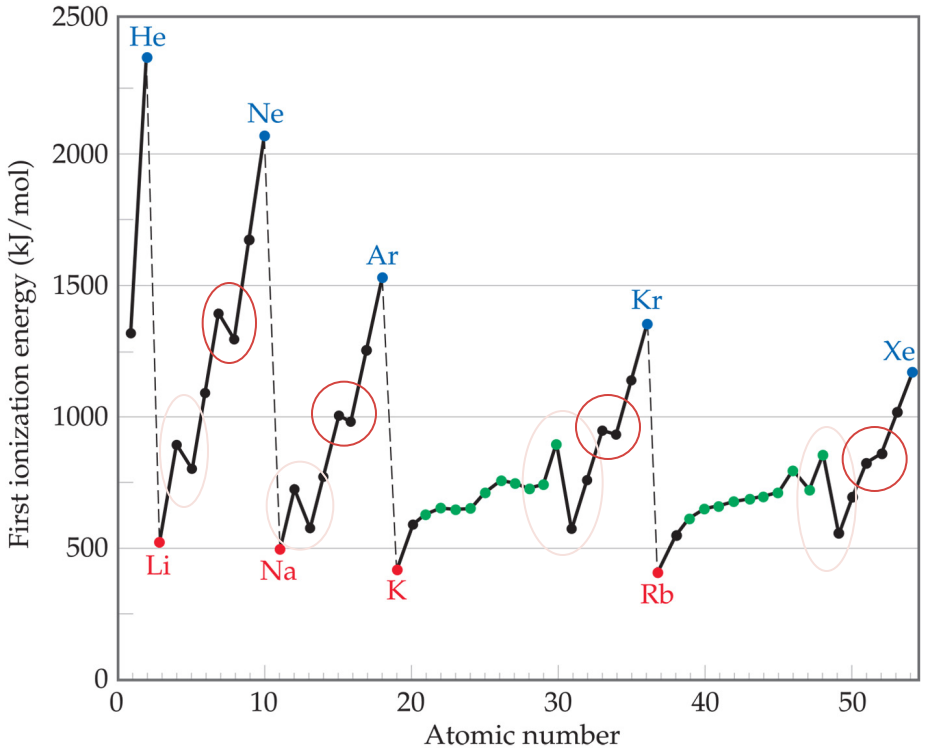


N

versus:

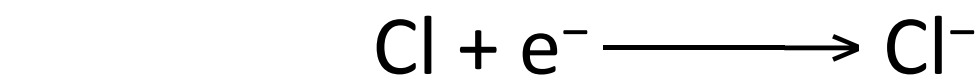


O



Electron Affinity

Energy change accompanying addition of electron to gaseous atom:

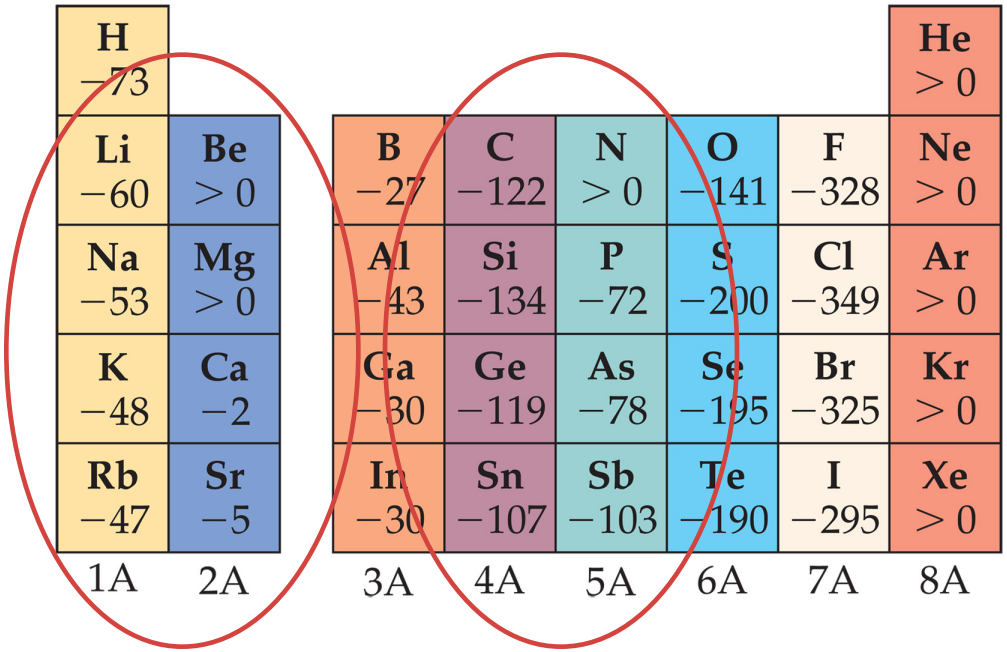


Trends in Electron Affinity

1A	2A	3A	4A	5A	6A	7A	8A
H −73							He > 0
Li −60	Be > 0	B −27	C −122	N > 0	O −141	F −328	Ne > 0
Na −53	Mg > 0	Al −43	Si −134	P −72	S −200	Cl −349	Ar > 0
K −48	Ca −2	Ga −30	Ge −119	As −78	Se −195	Br −325	Kr > 0
Rb −47	Sr −5	In −30	Sn −107	Sb −103	Te −190	I −295	Xe > 0

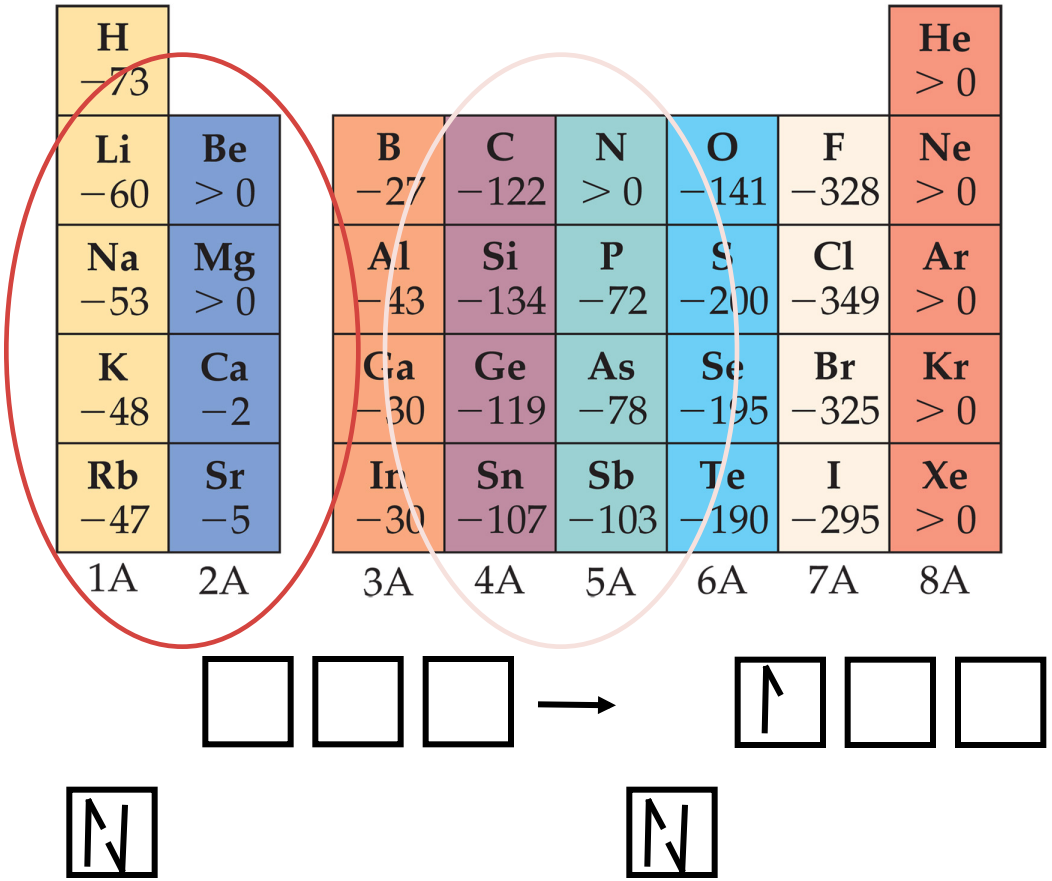
In general, electron affinity becomes more exothermic as you go from left to right across a row.

Trends in Electron Affinity



There are also two discontinuities in this trend.

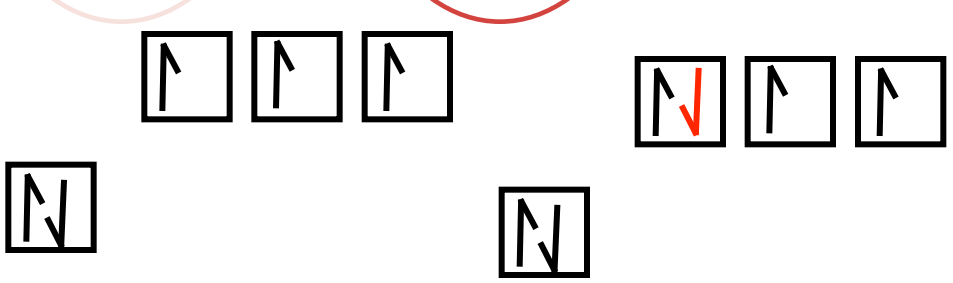
Trends in Electron Affinity



- The first occurs between Groups IA and IIA.
  - Added electron must go in *p*-orbital, not *s*-orbital.
  - Electron is farther from nucleus and feels repulsion from *s*-electrons.

Trends in Electron Affinity

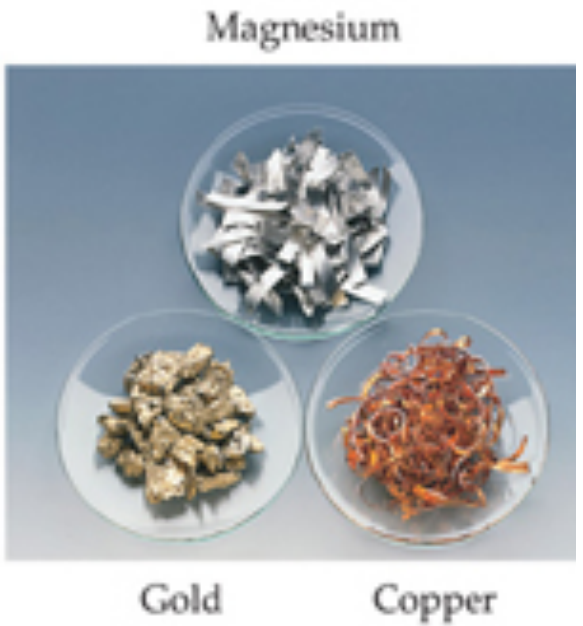
1A	2A	3A	4A	5A	6A	7A	8A
H −73							He > 0
Li −60	Be > 0	B −27	C −122	N > 0	O −141	F −328	Ne > 0
Na −53	Mg > 0	Al −43	Si −134	P −72	S −200	Cl −349	Ar > 0
K −48	Ca −2	Ga −30	Ge −119	As −78	Se −195	Br −325	Kr > 0
Rb −47	Sr −5	In −30	Sn −107	Sb −103	Te −190	I −295	Xe > 0



- The second occurs between Groups IVA and VA.
  - Group VA has no empty orbitals.
  - Extra electron must go into occupied orbital, creating repulsion.

Chemical Bonds

Three types:

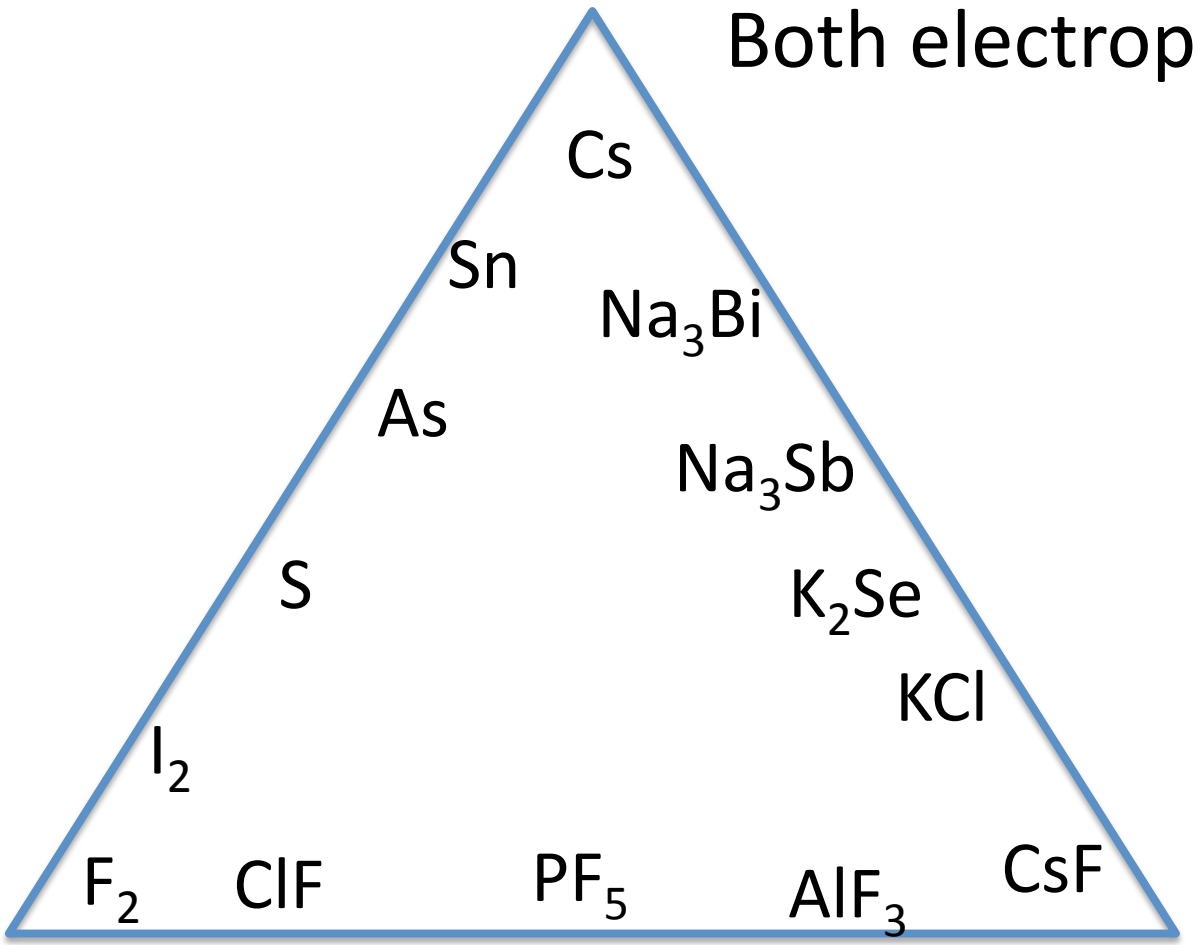


- Ionic
  Electrostatic attraction between ions

Covalent
Sharing of electrons

Metallic
Metal atoms bonded to several other atoms

Bonding a continuum



Both electronegative

One electropositive

One electronegative

Ionic Bonding

When a metal and a nonmetal get together

Energetics of Ionic Bonding

$2Na(s) + Cl_2(g) \text{ -------> } 2NaCl(s)$

TABLE 7.2 Successive

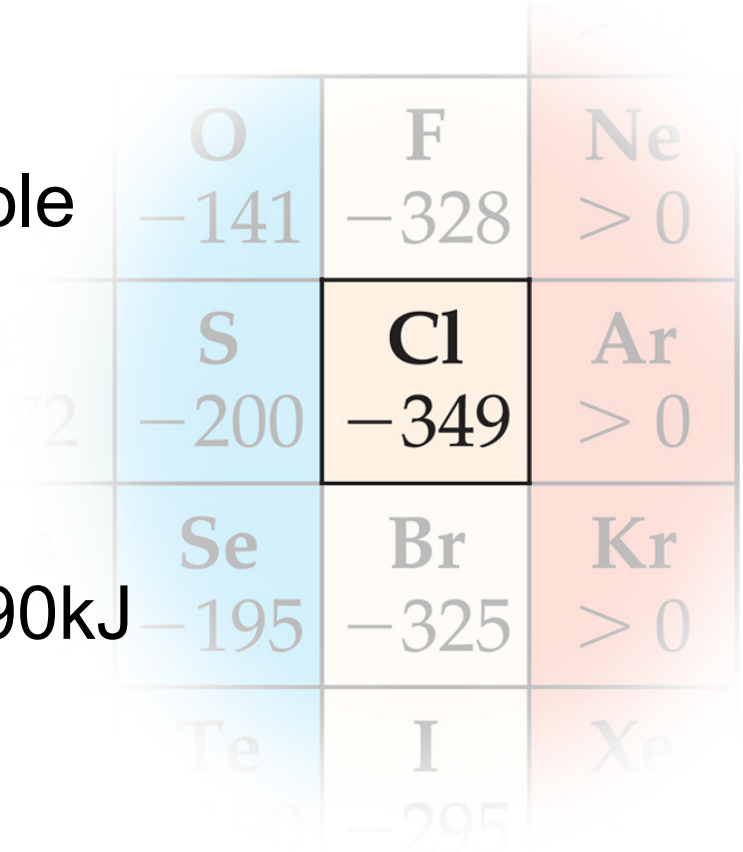
Element	I_1
Na	495
Mg	738

it takes 495 kJ/mol to remove 1 electron from sodium.

495x2 = 990 kJ/2 Na

Energetics of Ionic Bonding

We get **349 kJ/mol Cl** back by giving 1 electron to each 1 mole of Cl_2.

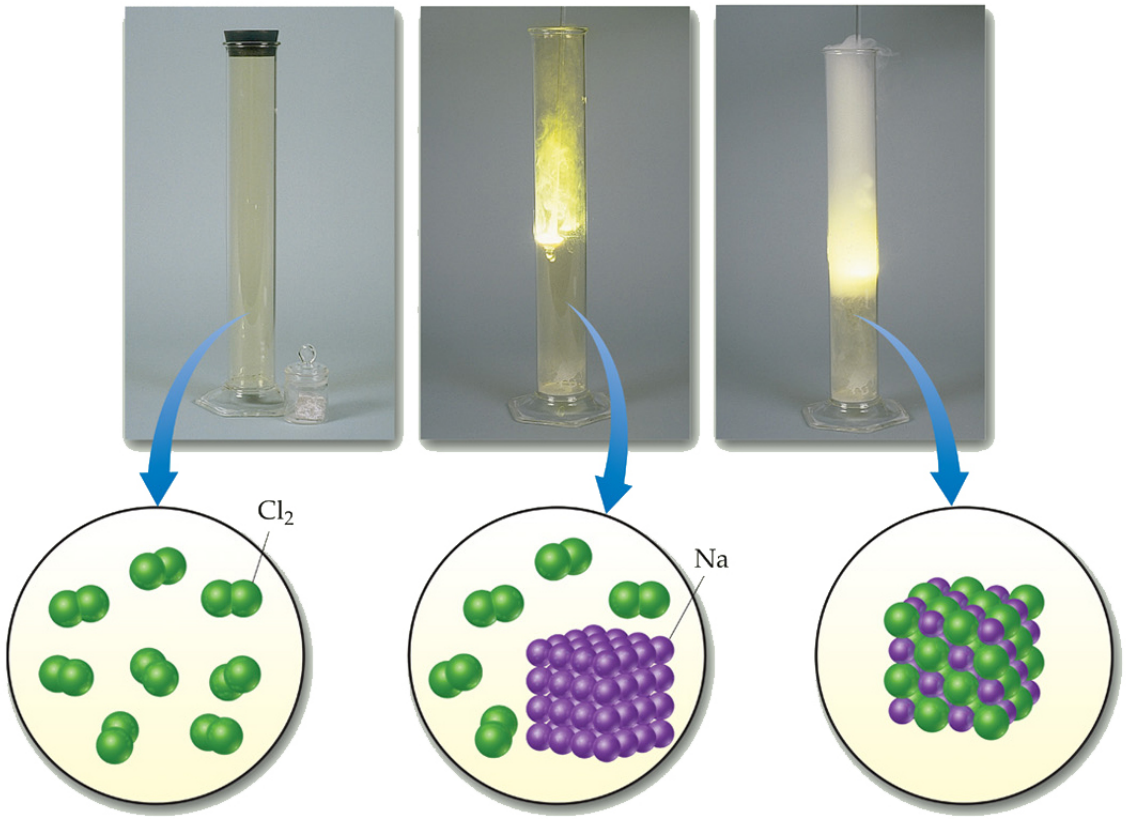


-349x2 = -700 kJ/mol Cl_2

990 kJ/2Na – 700 kJ/Mol Cl_2 = 290kJ

Energetics of Ionic Bonding

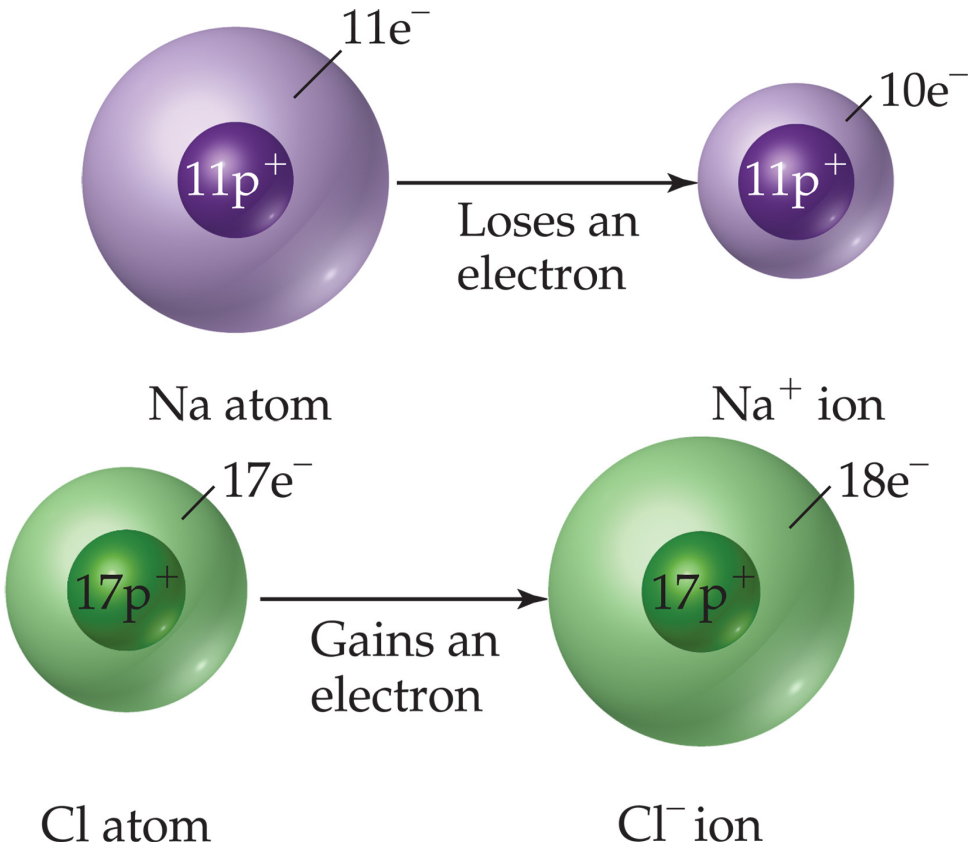
990 kJ/2Na – 700 kJ/Mol Cl_2 = 290kJ



But these numbers don't explain why the reaction of sodium metal and chlorine gas to form sodium chloride is so exothermic!

Energetics of Ionic Bonding

- There must be a third piece to the puzzle.
- What is as yet unaccounted for is the electrostatic attraction between the newly formed sodium cation and chloride anion.



Lattice Energy

- This third piece of the puzzle is the lattice energy:

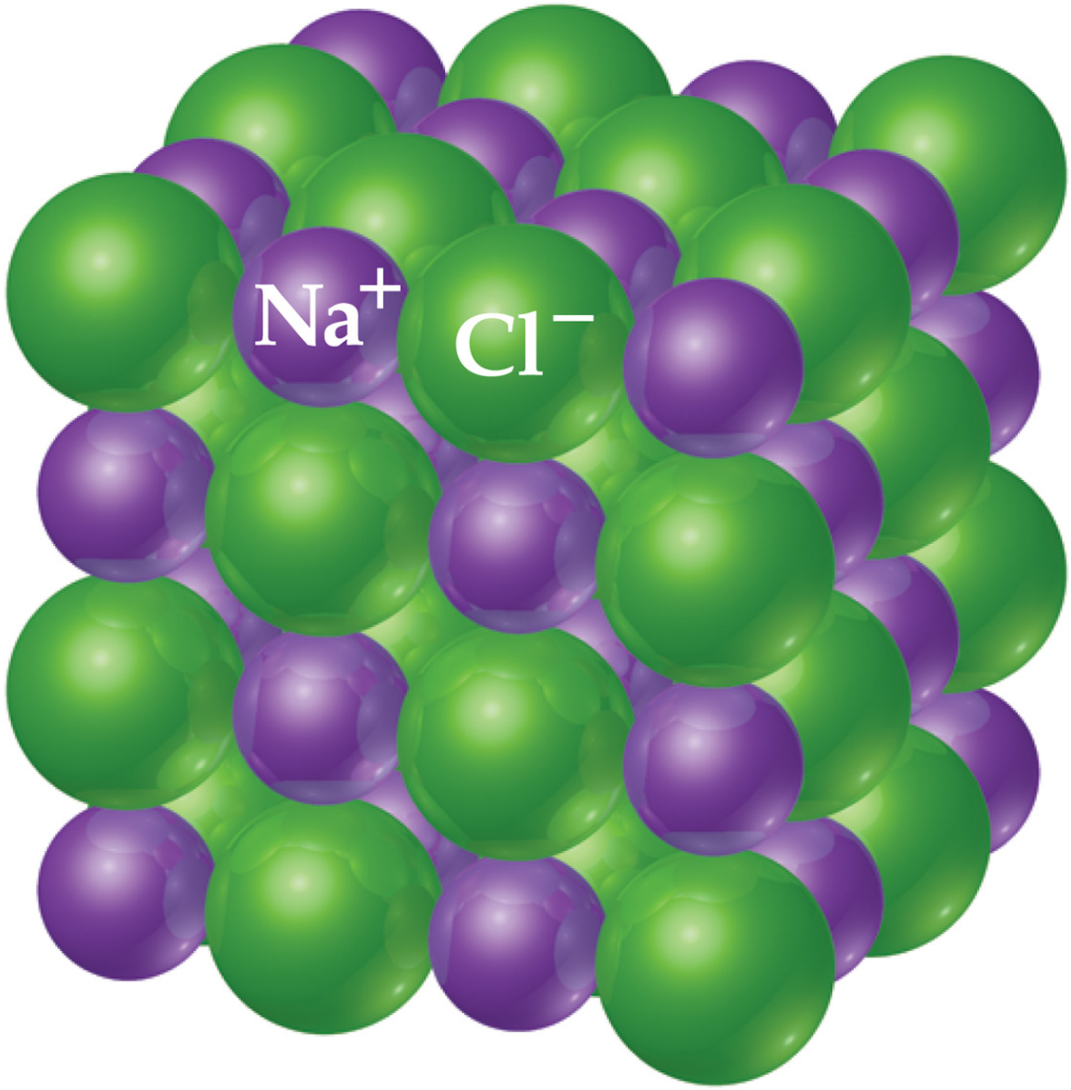
  The energy required to completely separate a mole of a solid ionic compound into its gaseous ions.

- The energy associated with electrostatic interactions is governed by Coulomb's law:

$$E_{el} = \kappa \frac{Q_1 Q_2}{d}$$

Lattice Energy

$$E_{el} = \kappa \frac{Q_1 Q_2}{d}$$



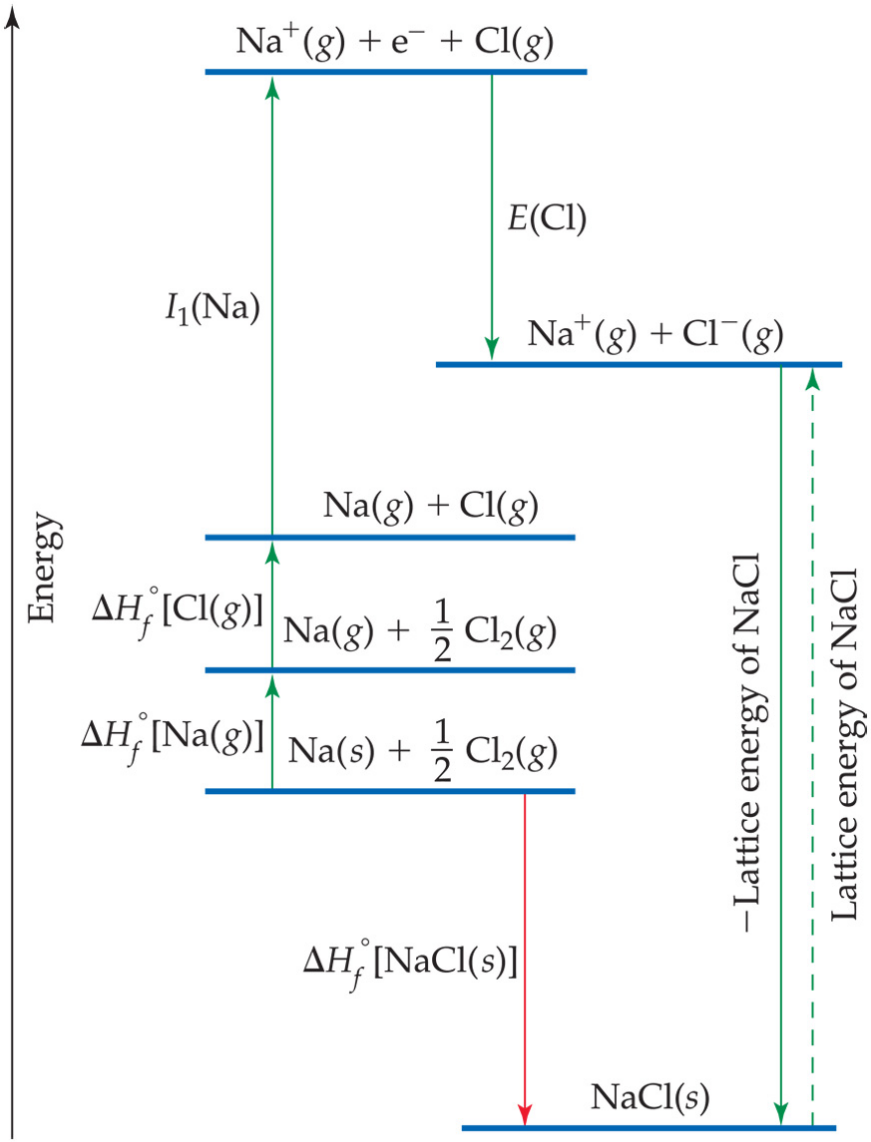
Lattice Energy

- Lattice energy, then, increases with the charge on the ions.
- It also increases with decreasing size of ions.

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (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		

Energetics of Ionic Bonding

$Na(s) + 1/2Cl_2(g)$ -----> $NaCl(s)$



By accounting for all three energies (ionization energy, electron affinity, and lattice energy), we can get a good idea of the energetics involved in such a process.

CEM 141 - Fall Semester 2012 – Exam 2 Rooms Monday, October 22nd
7:15pm-8:15pm

Section	Room	TA
1,2,3,4,5,6,7,8,9,10	N130 Business Complex	Koyeli, Mike, Robert
11,12,13,14,15,16,17,18,19,20	B115 Wells Hall	Yuan, Ben, Wenjing
21,22,23,24,25,26,27	138 Chemistry	Ruiqiong, Denise, Zhongqi
28,29,30,31	118 Psychology Bldg.	Ryan, Penghao
32,33,34,35	B117 Wells Hall	Xiaoxiao, Lihui
36,37,38,75,76	N100 Business Complex	Chenjia, Shuai, Scott, Mersedeh
39,40,41	128 Nat. Sci. Bldg.	Sujana, Shannon
42,43,44,45	1345 Engineering Bldg.	Jerome, Shuang
46,47,48,49,50,51,52,53	102 Conrad Hall	Preston, Nick, Krystin
54,55,56,57,58,59,60,61,62,63	1281 Anthony Hall	Ruipeng, Zhefei, Adeayo, Punsisi
64,65,66,67	402 Computer Center	Lindsey, Xiaoran
68,69,70	1279 Anthony Hall	Christopher, Shuxuan
71,72,73,74	N101 North Kedzie	Ali, Zahra
77,78,79,80	B119 Wells Hall	Chen, Zhiling
81,82,83,84	1410 BioMed & Phys. Sci	Monica, Brandon

Alternate Exam Monday, October 22nd 6:45am-7:45am room 138 Chemistry: Yan, Chengpeng

Energetics of Ionic Bonding

- These phenomena also help explain the "octet rule."

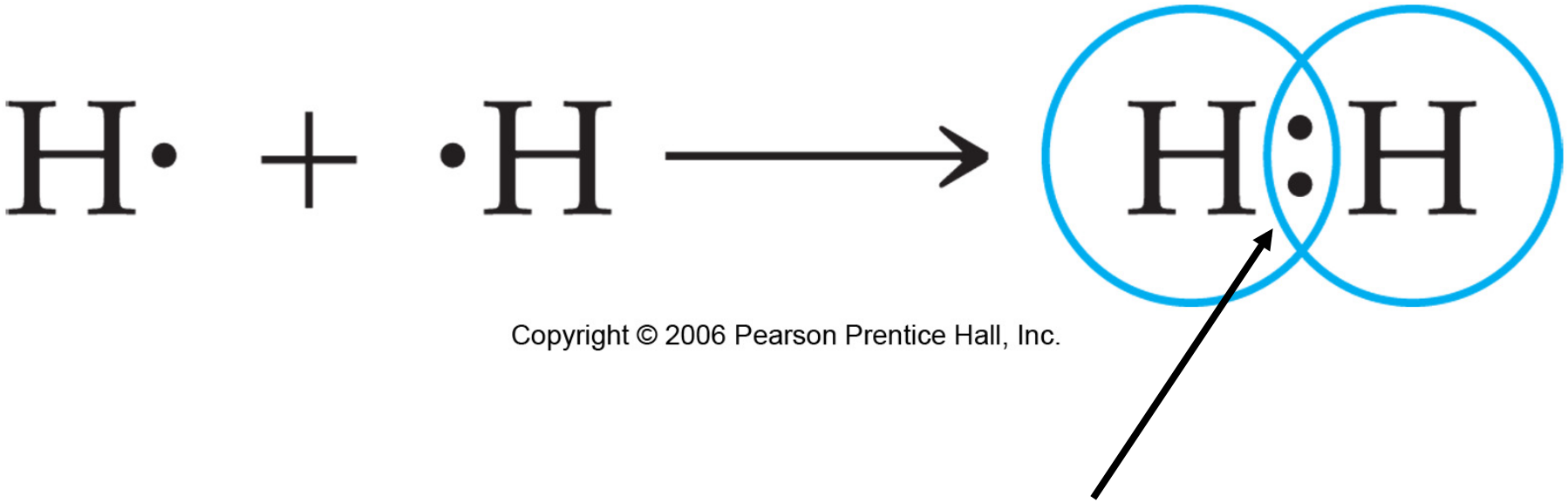
TABLE 7.2 Successive Values of Ionization E

Element	I_1	I_2	I_3
Na	495	4562	
Mg	738	1451	7733
Al	578	1817	2745
Si	786	1577	
P	1012	1907	

- Elements tend to lose or gain electrons once they attain a noble gas configuration because energy would be expended that cannot be overcome by lattice energies.

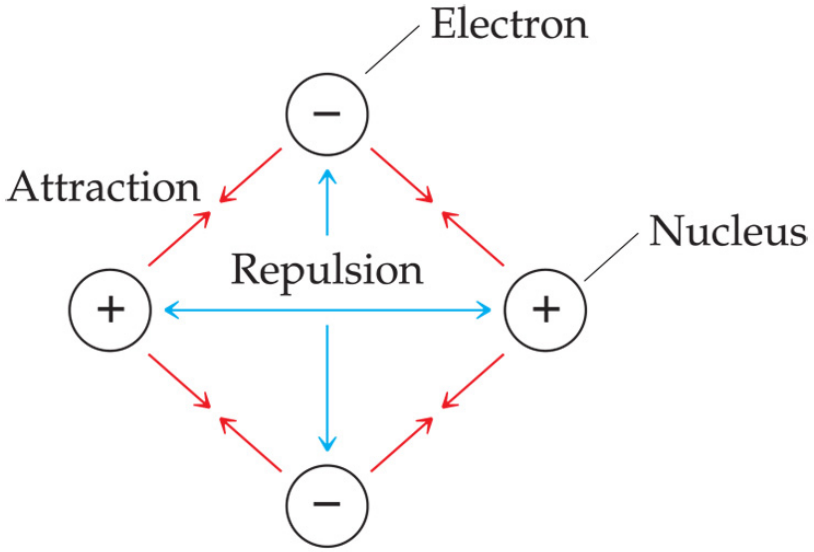
Covalent Bonding

What happens when nonmetals get together

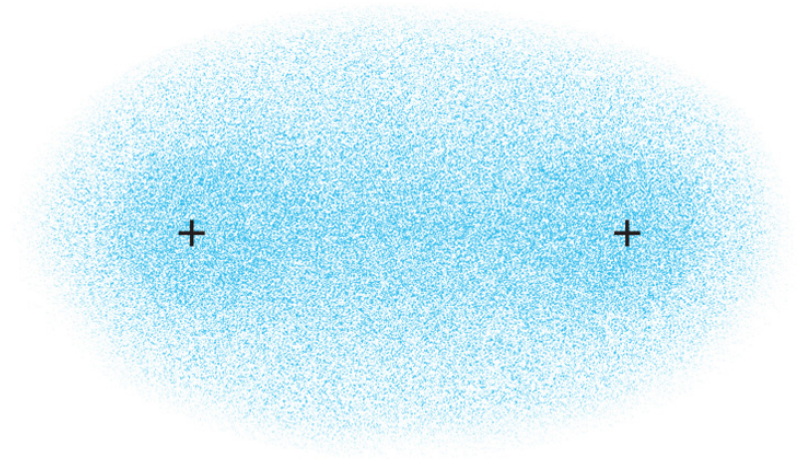


- **In these bonds atoms share electrons.**

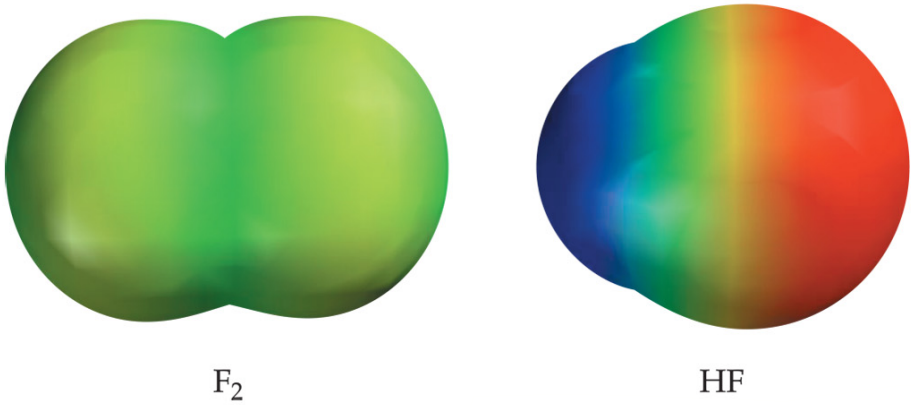
Covalent Bonding



- There are several electrostatic interactions in these bonds:
  - Attractions between electrons and nuclei
  - Repulsions between electrons
  - Repulsions between nuclei



Polar Covalent Bonds



F_2 HF

- Although atoms often form compounds by sharing electrons, the electrons are not always shared equally.

- Fluorine pulls harder on the shared electrons than hydrogen does.
- Therefore, the fluorine end has more electron density than the hydrogen end.
- But how do you know who pulls hardest?

Electronegativity:

Developed 1st by Linus Pauling like this:

H-F -→ H + F >> H-H -→ H + H or F-F → F + F

Why?

Because there is an ionic component to attraction in H-F F more – and H more + so the ionic component makes bond stronger.

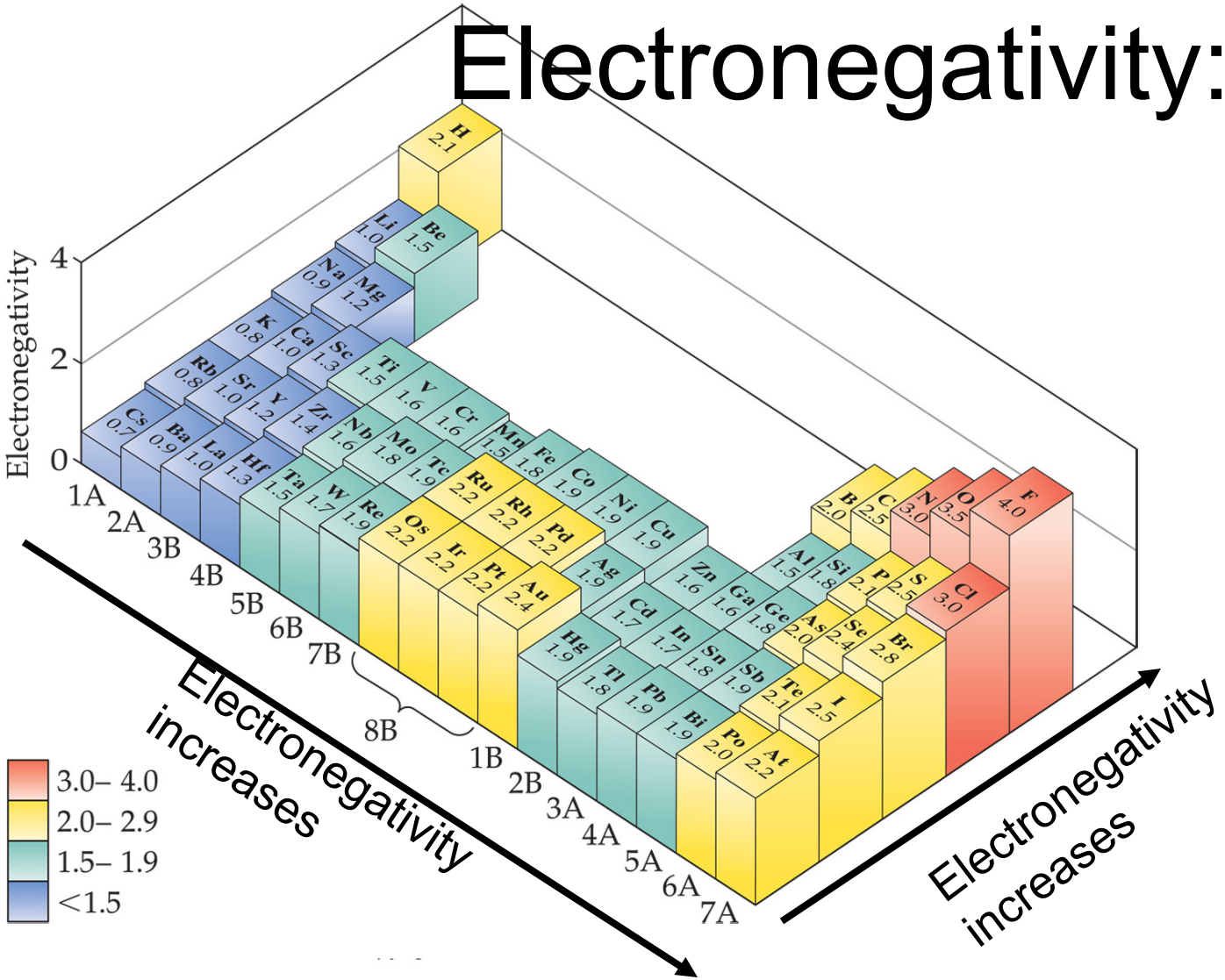
Electronegativity:

Developed 1st by Linus Pauling like this:

A measure of how much an atom attracts electrons *when it is in a molecule.*

- The ability of atoms in a molecule to attract electrons to itself.
- On the periodic table, electronegativity increases as you go…
  - …from left to right across a row.
  - …from the bottom to the top of a column.

Electronegativity:



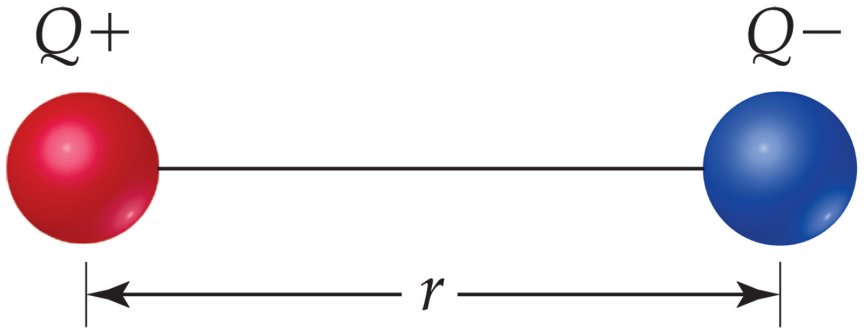
- On the periodic chart, electronegativity increases as you go…
  - …from left to right across a row.
  - …from the bottom to the top of a column.

Polar Covalent Bonds

- When two atoms share electrons unequally, a bond dipole results.
- The dipole moment, μ, produced by two equal but opposite charges separated by a distance, *r*, is calculated:

$$\mu = Qr$$

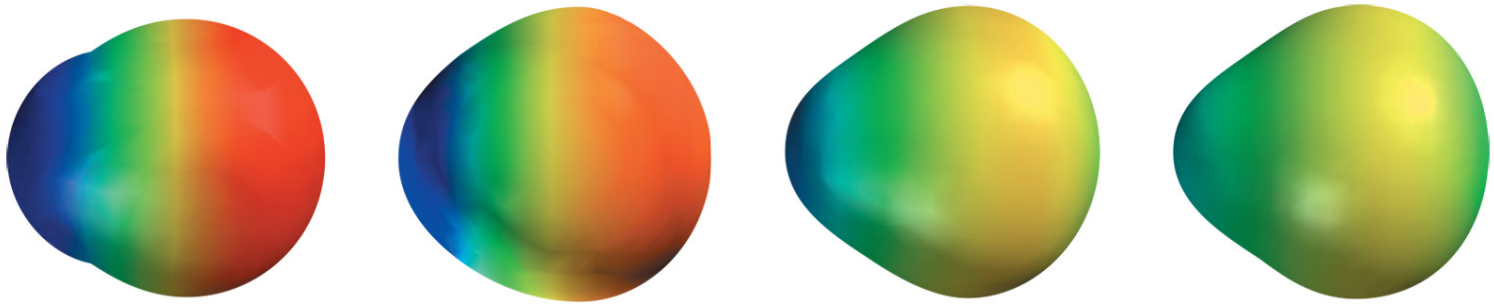
- It is measured in debyes (D).



Polar Covalent Bonds

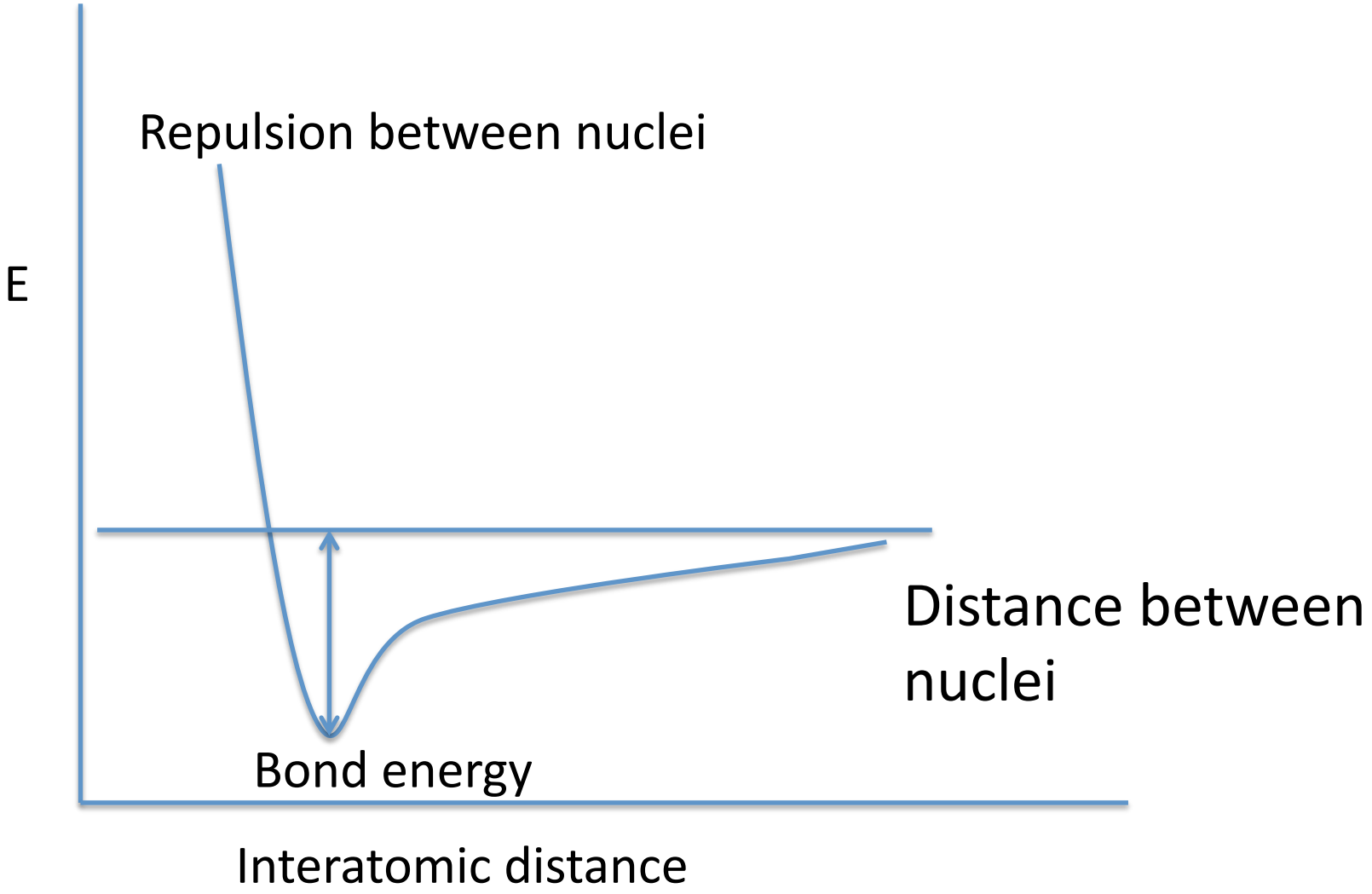
Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

The greater the difference in electronegativity, the more polar is the bond.



HF HCl HBr HI

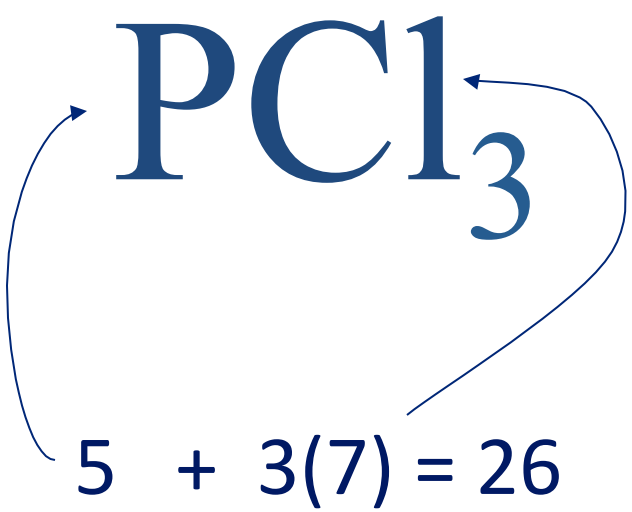
Covalent bonds



Lewis Structures

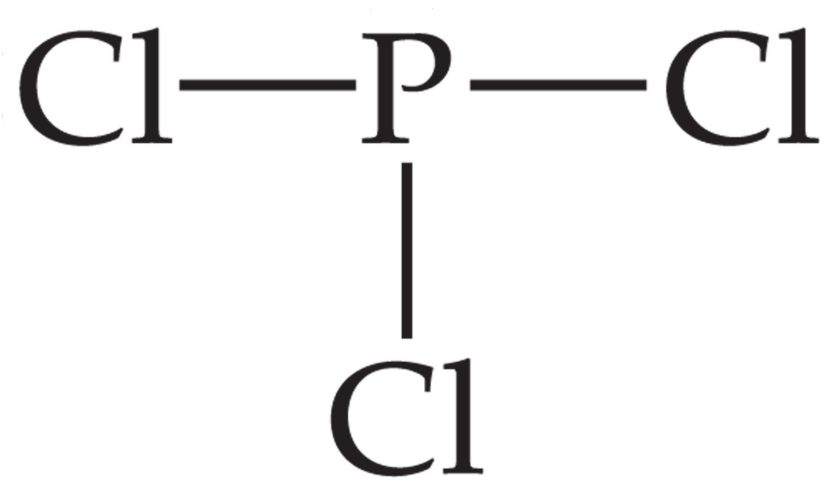
Lewis structures are representations of molecules showing all valence electrons, bonding and nonbonding.

Writing Lewis Structures



1. Find the sum of valence electrons of all atoms in the polyatomic ion or molecule.
   - If it is an anion, add one electron for each negative charge.
   - If it is a cation, subtract one electron for each positive charge.

Writing Lewis Structures

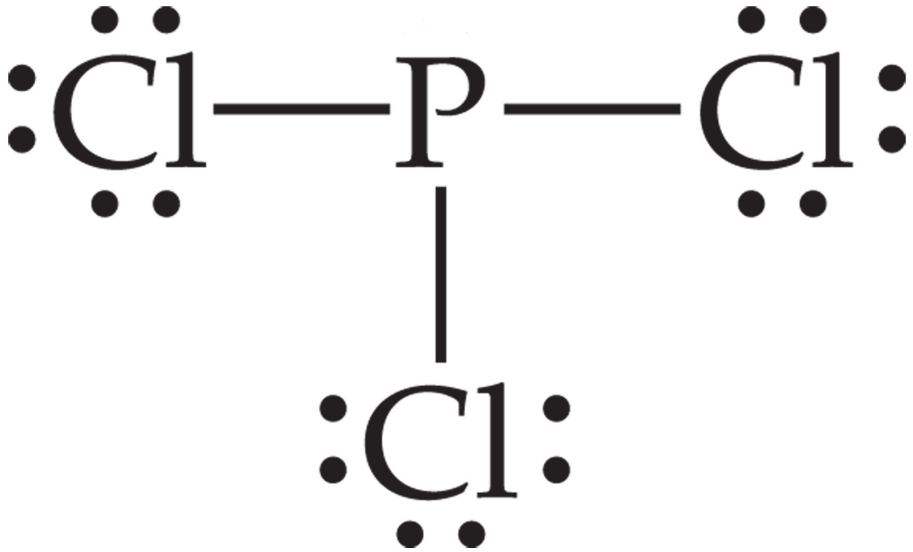


2. The central atom is the *least* electronegative element that isn't hydrogen (why?). Connect the outer atoms to it by single bonds.

Keep track of the electrons:

26 - 6 = 20

Writing Lewis Structures

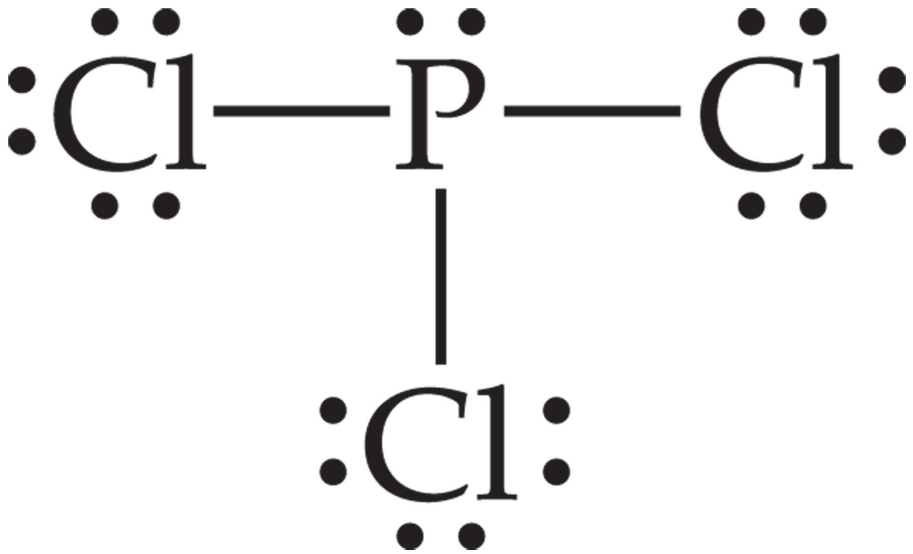


3. Fill the octets of the outer atoms.

Keep track of the electrons:

26 - 6 = 20 - 18 = 2

Writing Lewis Structures



4. Fill the octet of the central atom.

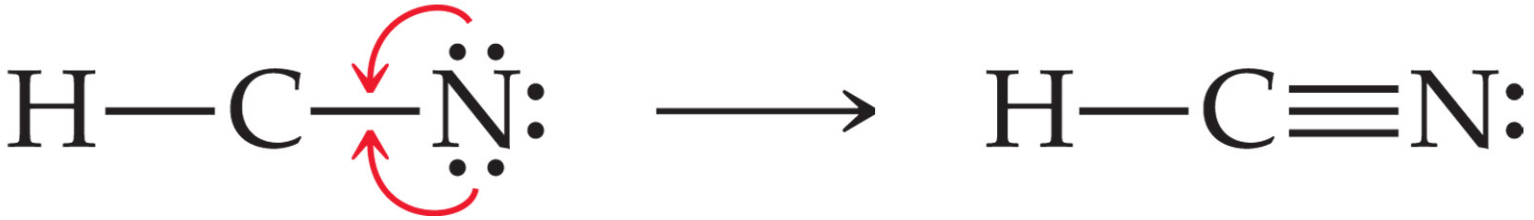
Keep track of the electrons:

26 - 6 = 20 - 18 = 2 - 2 = 0

Writing Lewis Structures

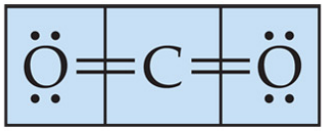
5. If you run out of electrons before the central atom has an octet…

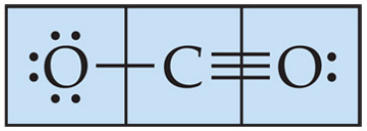
…form multiple bonds until it does.



Writing Lewis Structures

- Then assign formal charges.
  - For each atom, count the electrons in lone pairs and half the electrons it shares with other atoms.
  - Subtract that from the number of valence electrons for that atom: The difference is its formal charge.

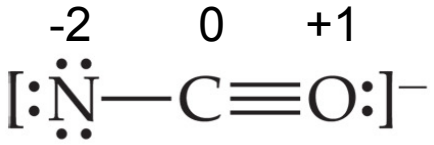


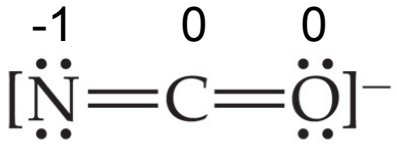


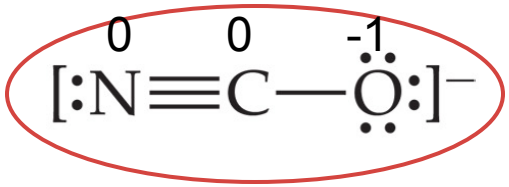
Valence electrons:	6	4	6	6	4	6
−(Electrons assigned to atom):	6	4	6	7	4	5
Formal charge:	0	0	0	−1	0	+1

Writing Lewis Structures

- The best Lewis structure…
  - …is the one with the fewest charges.
  - …puts a negative charge on the most electronegative atom.







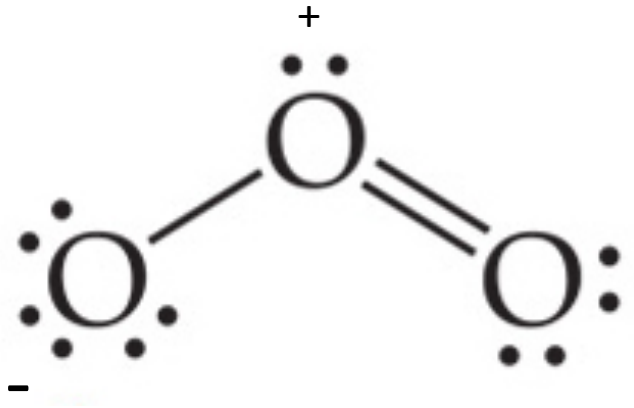
Resonance

Draw the Lewis structure for ozone, O_3.

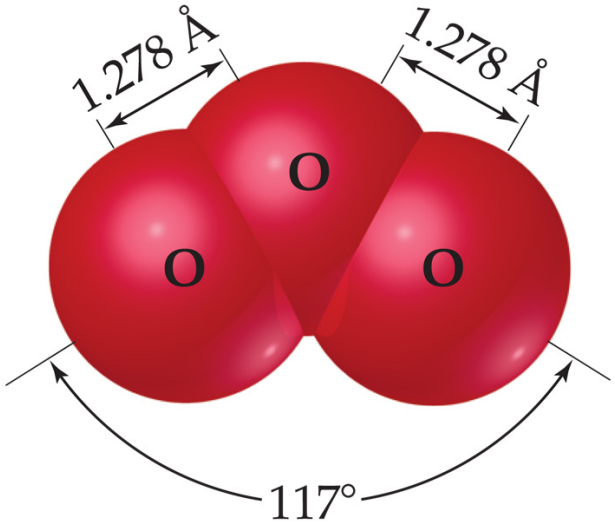
Resonance

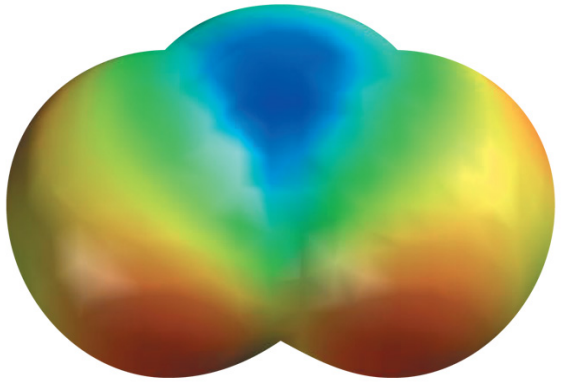
Draw the Lewis structure for ozone, O_3.

But why should one O be different from the other?



Resonance

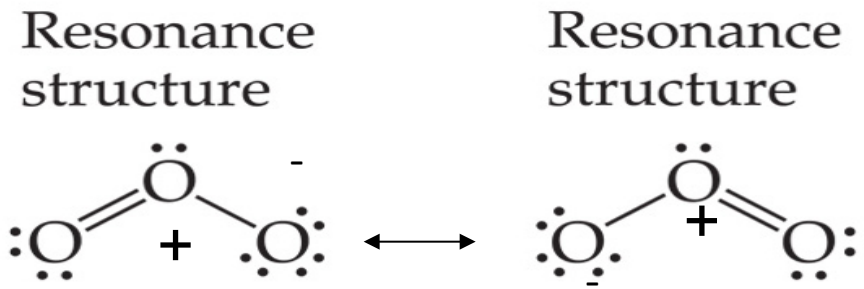




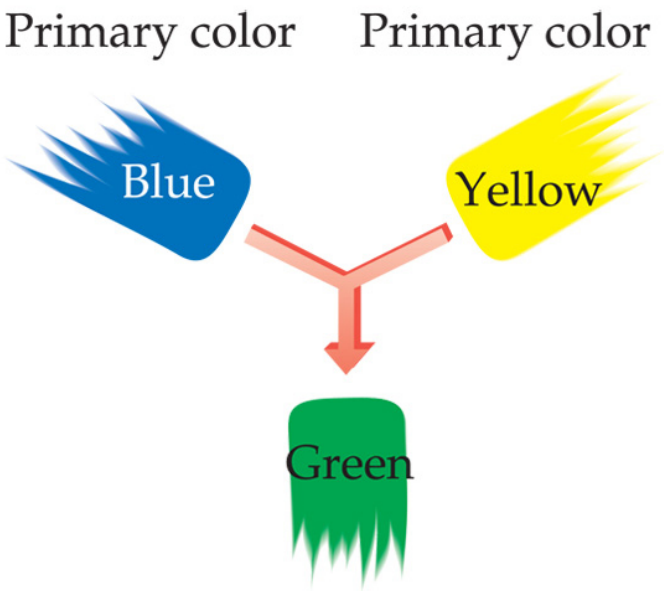
- It is at odds with the true, observed structure of ozone,
  - …both O—O bonds are the same length.
  - …both outer oxygens have a charge of -1/2.

Resonance

- One Lewis structure cannot accurately depict a molecule such as ozone.
- We use multiple structures, resonance structures, to describe the molecule.

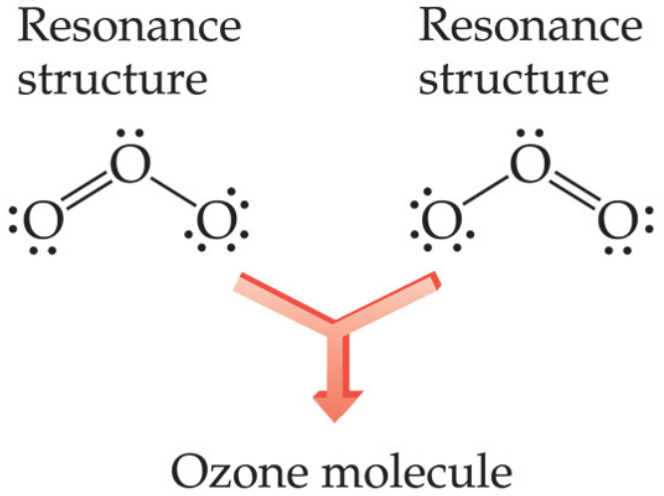


Resonance



Just as green is a synthesis of blue and yellow…

…ozone is a synthesis of these two resonance structures.



It is not jumping between the two.

Resonance

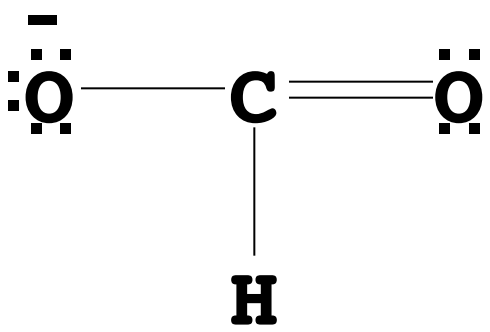
Draw resonance structure for:

HCO_2^-

Resonance

Draw Lewis structure for:

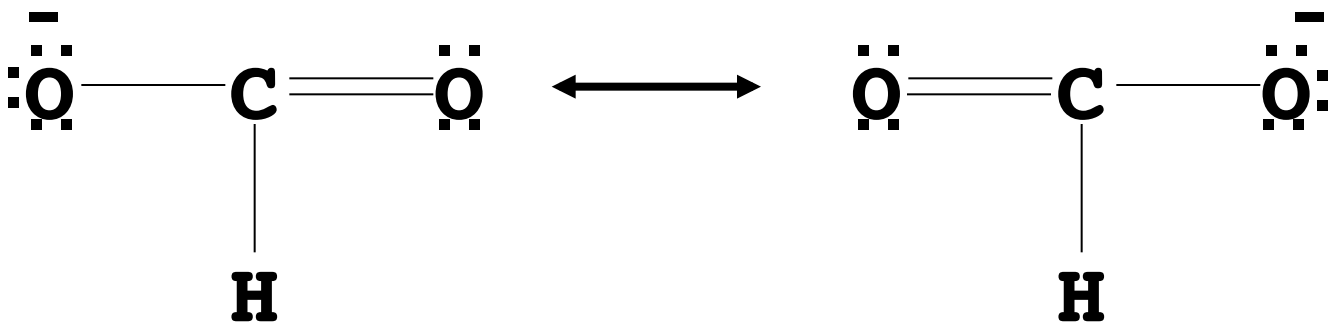
HCO_2^-



But why would the two oxygens be different?

Resonance

- In truth the electrons that make up the double bond are not localized, but rather are delocalized.

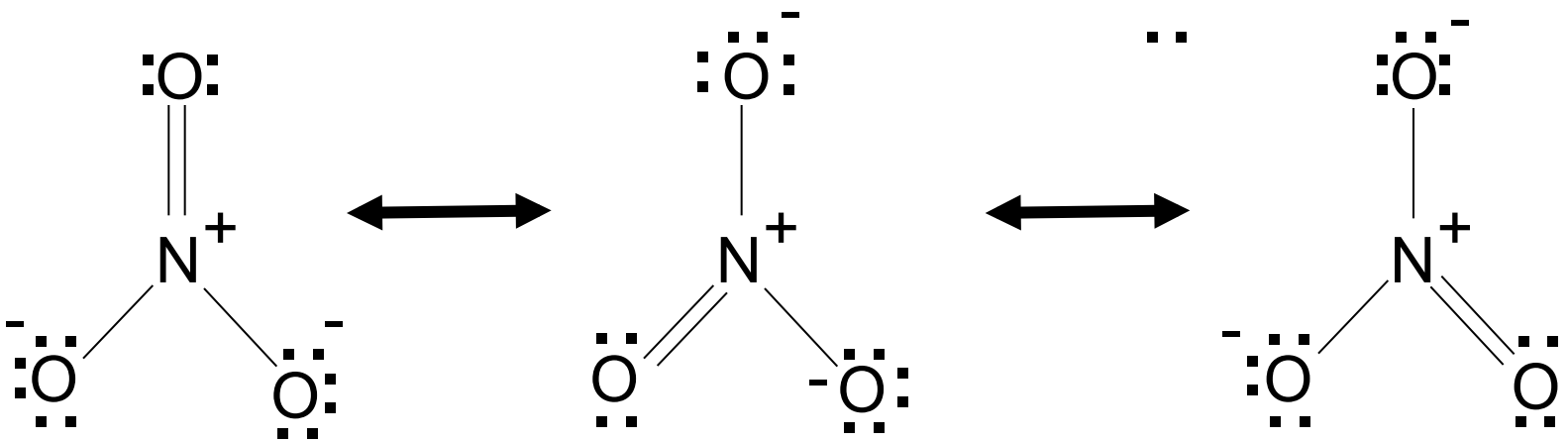


Resonance

- Draw the Lewis structure of NO_3^-

Resonance

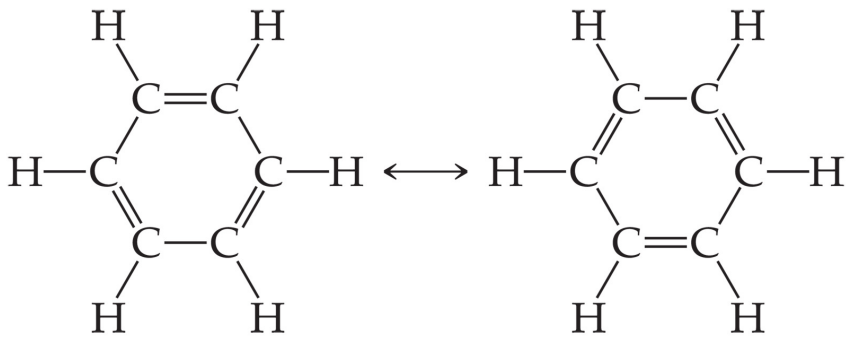
- Draw the Lewis structure of NO_3^-



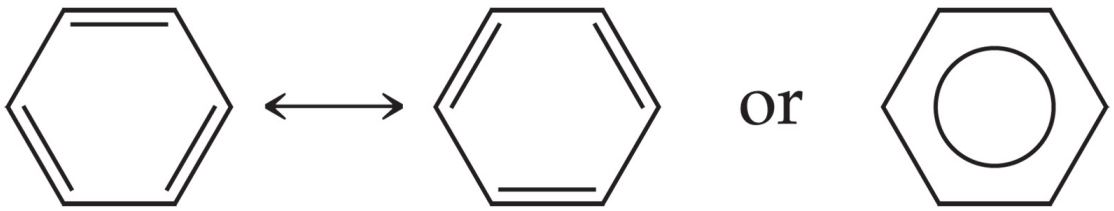
Resonance

- The organic compound benzene, C_6H_6 is a hexagon of carbon atoms with 6 H/s Draw the Lewis structure for benzene.

Resonance



- The organic compound benzene, C_6H_6, has two resonance structures.
- It is commonly depicted as a hexagon with a circle inside to signify the delocalized electrons in the ring.



Exceptions to the Octet Rule

- There are three types of ions or molecules that do not follow the octet rule:
  - Ions or molecules with an odd number of electrons.
  - Ions or molecules with less than an octet.
  - Ions or molecules with more than eight valence electrons (an expanded octet).

Odd Number of Electrons

Though relatively rare and usually quite unstable and reactive, there are ions and molecules with an odd number of electrons.

Odd Number of Electrons

- Example: NO

What's nitric oxide good for?

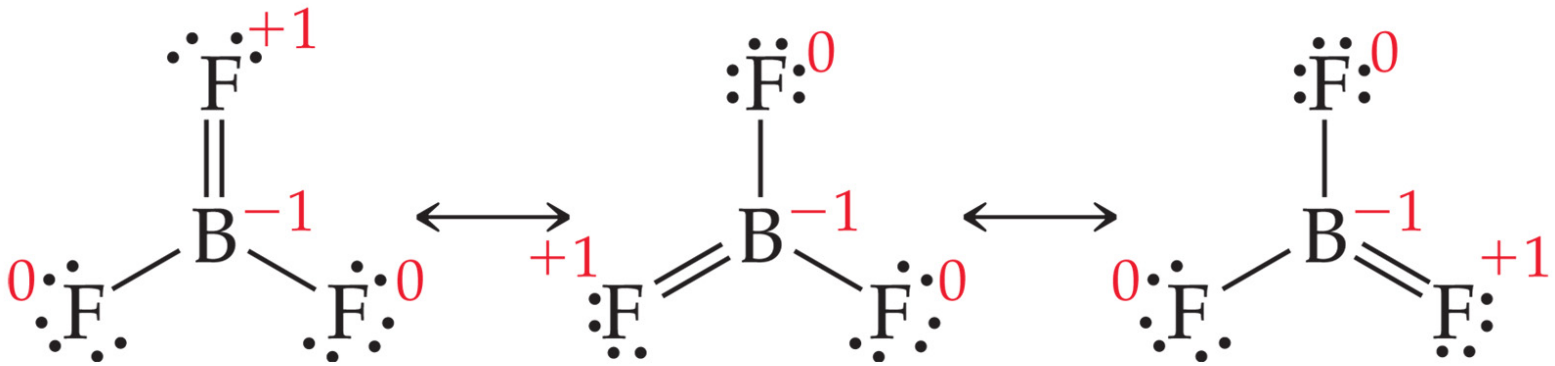
Fewer Than Eight Electrons

Draw the Lewis structure for BF_3:

Fewer Than Eight Electrons

Draw the Lewis structure for BF_3:

Fewer Than Eight Electrons

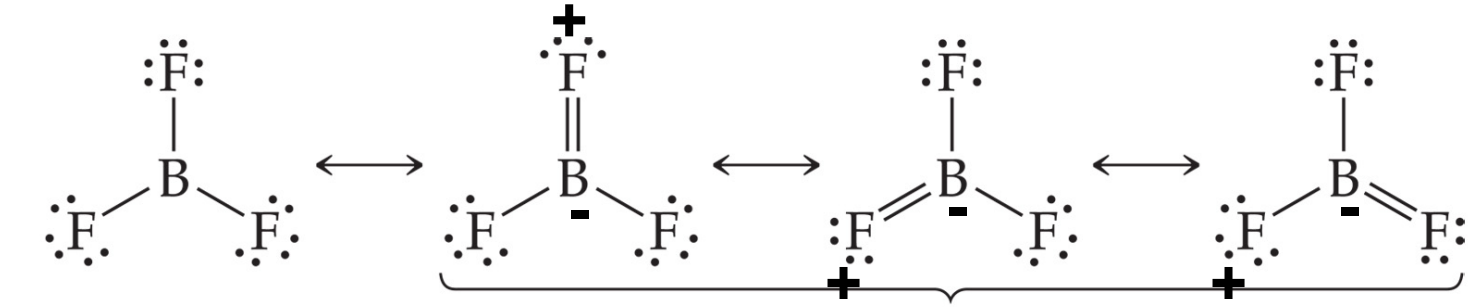


- Consider BF_3:
  - Giving boron a filled octet places a *negative* charge on the boron and a *positive* charge on fluorine.
  - This would not be an accurate picture of the distribution of electrons in BF_3.

Fewer Than Eight Electrons

Therefore, structures that put a double bond between boron and fluorine are much less important than the one that leaves boron with only 6 valence electrons.

Double bonds to halogens, especially F don't happen.

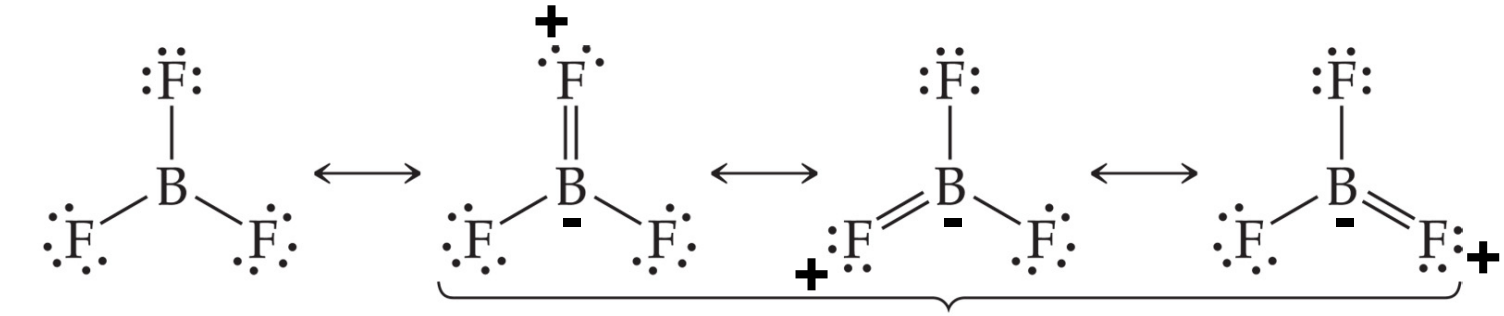


Most important

Less important

Fewer Than Eight Electrons

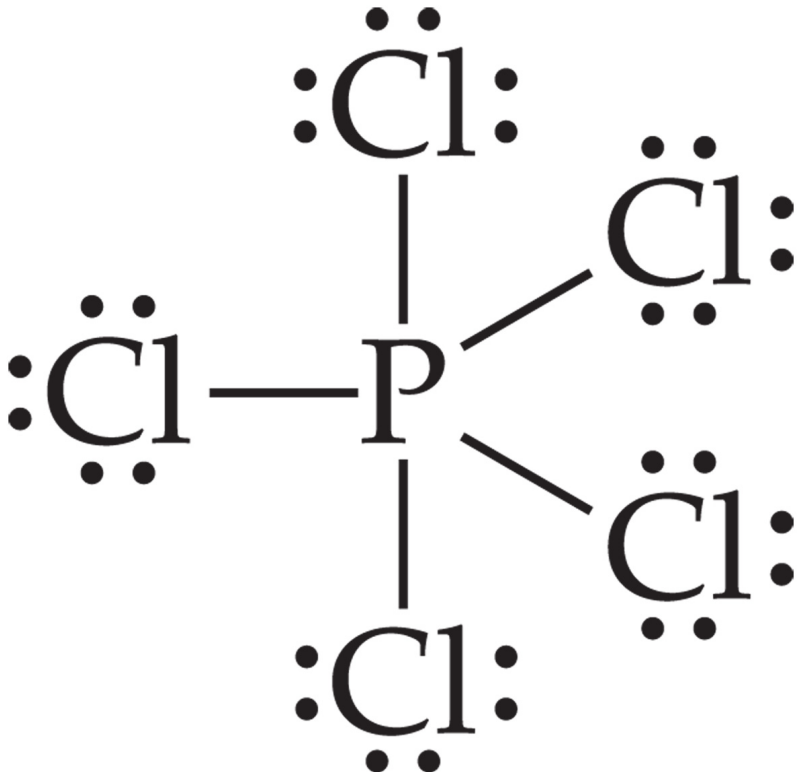
The lesson is: If filling the octet of the central atom results in a negative charge on the central atom and a positive charge on the more electronegative outer atom, don't fill the octet of the central atom.



More Than Eight Electrons

Draw the Lewis structure for PCl_5

More Than Eight Electrons



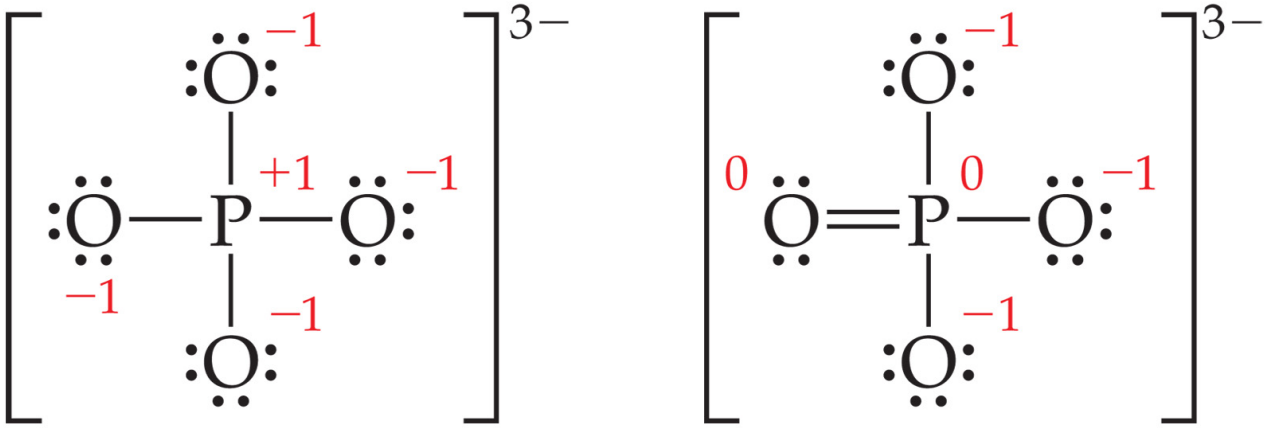
- The only way PCl_5 can exist is if phosphorus has 10 electrons around it.
- atoms on the 3rd row or below can go over an octet of electrons
  - Presumably *d* orbitals in these atoms participate in bonding.

More Than Eight Electrons

- Draw the Lewis structure for phosphate
- PO_4^{-3}

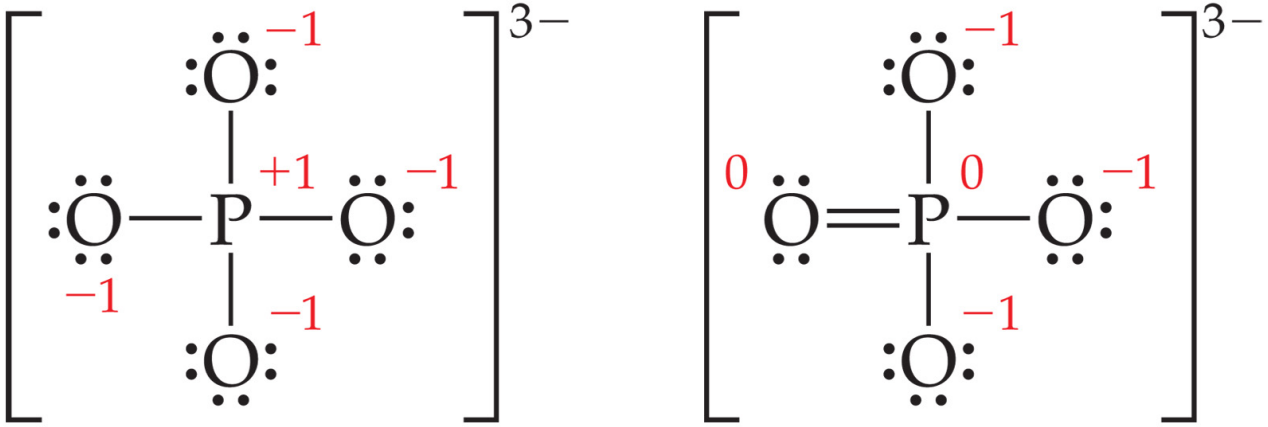
More Than Eight Electrons

Even though we can draw a Lewis structure for the phosphate ion that has only 8 electrons around the central phosphorus, a common Lewis structure puts a double bond between the phosphorus and one of the oxygens.



More Than Eight Electrons

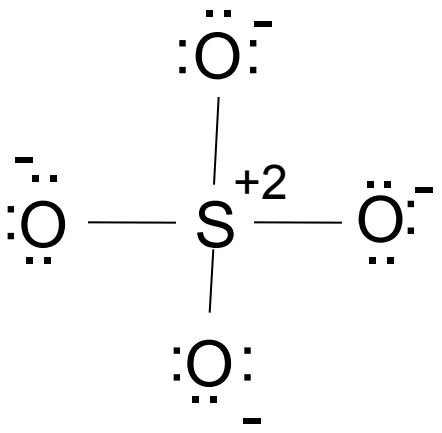
- This eliminates the charge on the phosphorus and the charge on one of the oxygens.
- The lesson is: When the central atom is on the 3rd row or below and expanding its octet eliminates some formal charges, you can do so.

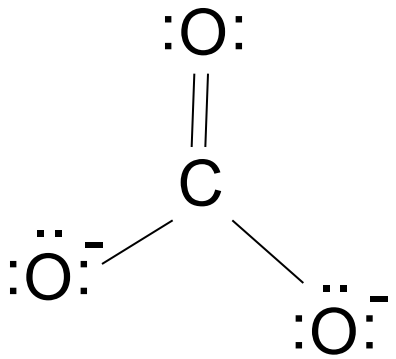


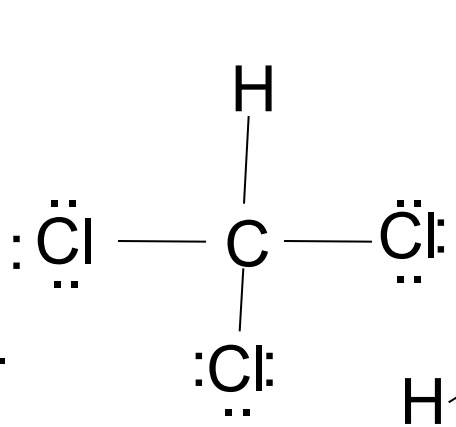
More Practice

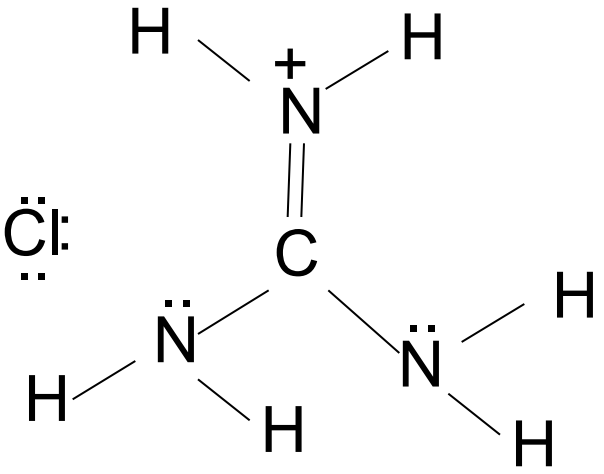
- Draw lewis structures for:
- SO_4^{-2}, CO_3^{-2}, $CHCl_3$, $CN_3H_6^{+}$ (H's are attached to the N's). SO_2, PO_3^{2-}, NO_2, BrO_3^{-},
- ClO_4^{-},

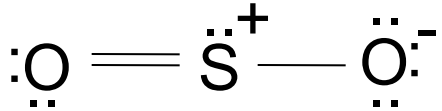
SO_4^{-2}, CO_3^{-2}, $CHCl_3$, $CN_3H_6^{+}$ (H's on N's). SO_2, PO_3^{1-}, NO, BrO_3^{-}, ClO_4^{-},

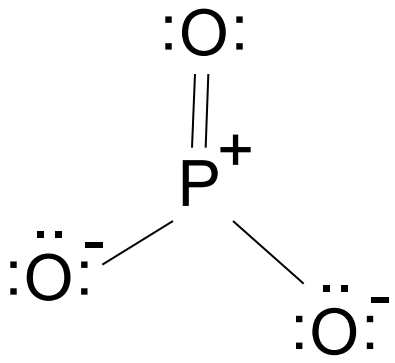


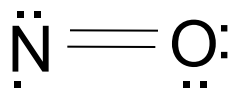


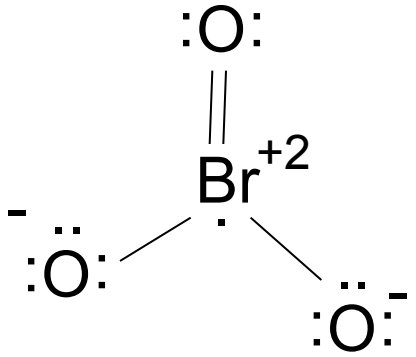


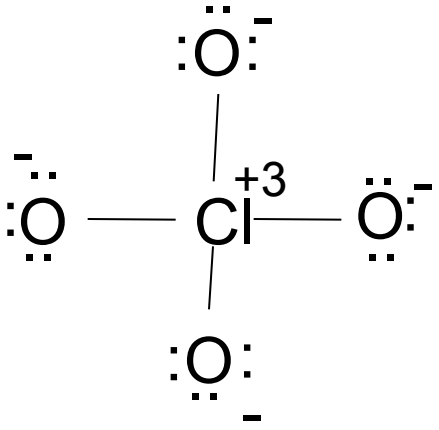




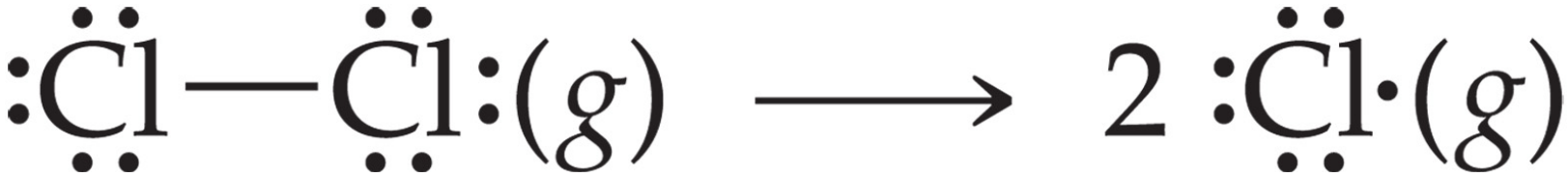








Covalent Bond Strength



$\Delta H = 242$ kJ/mol

- The strength of a bond is measured by determining how much energy is required to break the bond.
- This is the **bond enthalpy**.
- The bond enthalpy for a Cl—Cl bond, *D*(Cl—Cl), is 242 kJ/mol.

Average Bond Enthalpies

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Si—Cl	464						

Multiple Bonds

C=C	614	N=N	418	O_2	495
C≡C	839	N≡N	941		
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

- Average bond enthalpies are positive, because bond breaking is an endothermic process.

Average Bond Enthalpies

NOTE: These are *average* bond enthalpies, not absolute bond enthalpies; the C—H bonds in methane, CH_4, will be a bit different than the C—H bond in chloroform, $CHCl_3$.

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
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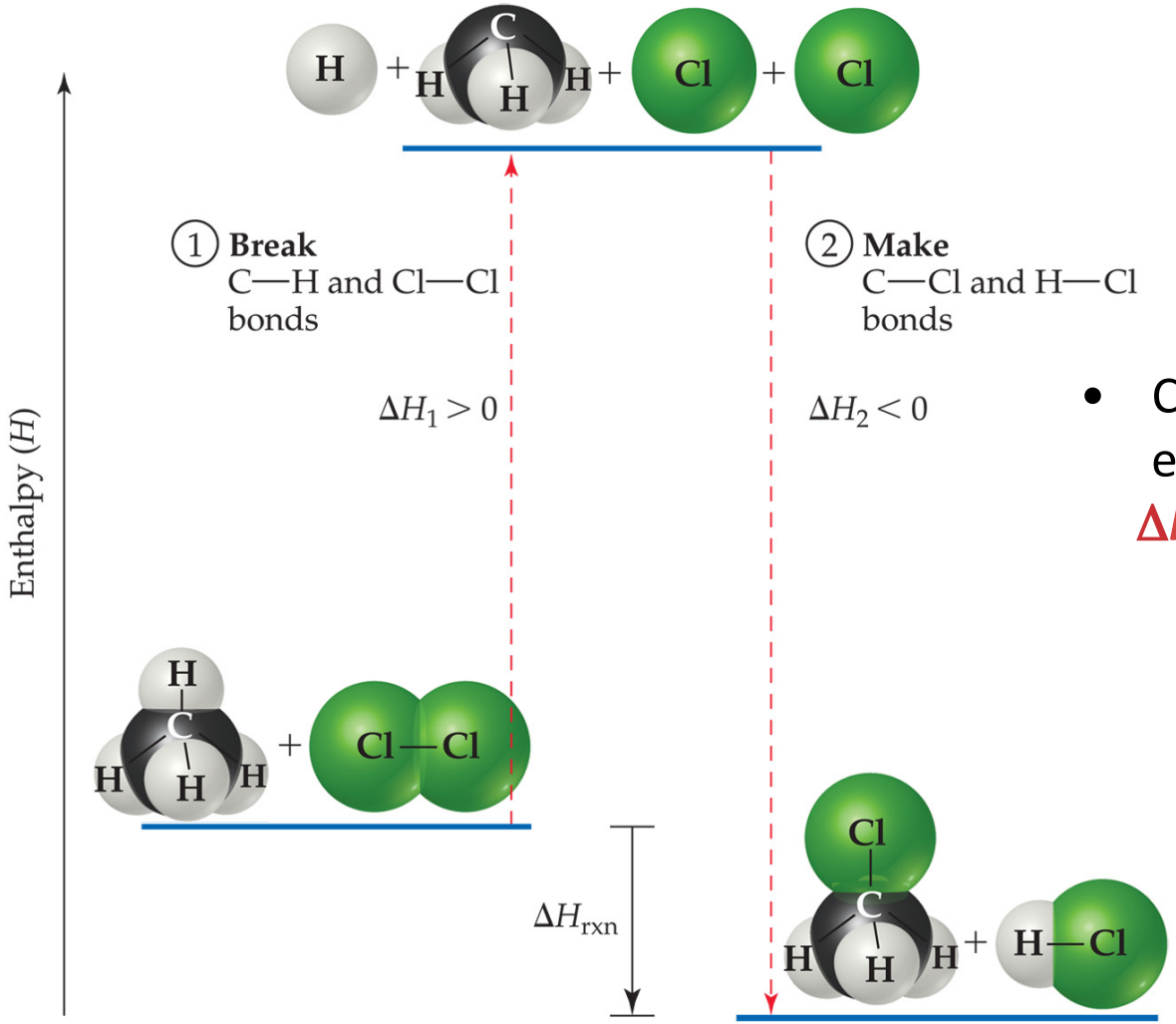
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

Enthalpies of Reaction



- Can use bond enthalpies to estimate ΔH for a reaction

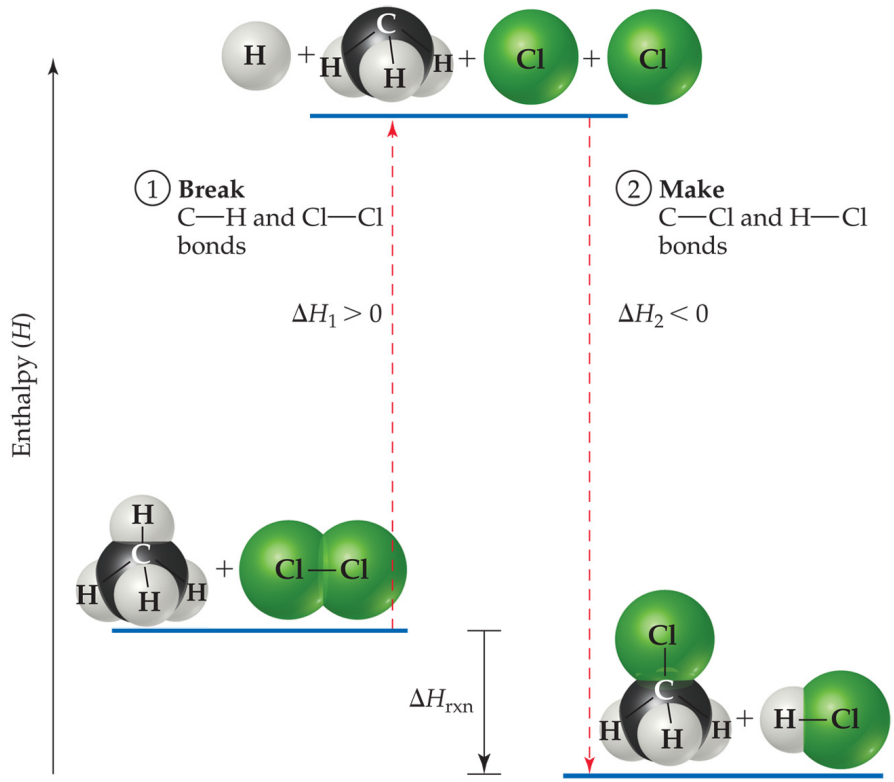
ΔH_{rxn} = Σ(bond enthalpies of bonds broken) - Σ(bond enthalpies of bonds formed)

This is a fundamental idea in chemical reactions. The heat of a reaction comes from breaking bonds and remaking bonds.

Enthalpies of Reaction

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

In this example, one C—H bond and one Cl—Cl bond are broken; one C—Cl and one H—Cl bond are formed.



Enthalpies of Reaction

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

So,

ΔH_{rxn} = [D(C—H) + D(Cl—Cl) - [D(C—Cl) + D(H—Cl)

= [(413 kJ) + (242 kJ)] - [(328 kJ) + (431 kJ)]

= (655 kJ) - (759 kJ)

= -104 kJ

Bond Enthalpy and Bond Length

Bond	Bond Length (Å)	Bond	Bond Length (Å)
C—C	1.54	N—N	1.47
C=C	1.34	N=N	1.24
C≡C	1.20	N≡N	1.10
C—N	1.43	N—O	1.36
C=N	1.38	N=O	1.22
C≡N	1.16		
		O—O	1.48
C—O	1.43	O=O	1.21
C=O	1.23		
C≡O	1.13		

- We can also measure an average bond length for different bond types.
- As the number of bonds between two atoms increases, the bond length decreases.

Enthalpy problem:

- Calculate the enthalpy for:
- $CH_4 + O_2 \text{ ---> } CO_2 + H_2O$

- $HC{\equiv}CH + O_2 \text{ ------> } CO_2 + H_2O$

Enthalpy problem:

- Calculate the enthalpy for:
- $CH_4 + 3/2O_2$ ---> $CO_2 + 2H_2O$
- 4(C--H) + 3/2(O==O) - 2(C==O) - 4(OH)
- 4(413) + 3/2(495) - 2(800) - 4(463) = -563 kJ

- HC CH + $5/2O_2$ ------> $2CO_2 + H_2O$

- 1(CC) + 2CH + 5/2(O=O) - 4(C==O) - 2(OH)
- 1(834) + 2(413) +5/2(495) - 4(800) - 2(463) = -1229 kJ