

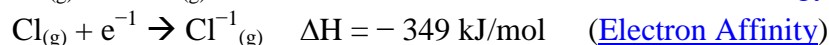
Chapter 9 Ionic and Covalent Bonding  
(Sections [7.1](#), [7.2](#), [7.3](#), [7.4](#), [7.5](#), [8.1](#), [8.2](#), and [8.3](#) in OpenStax)

### Ionic Bonds

- An ionic bond is formed by electrostatic attraction between cations (positive) and anions (negative).
- Some elements, primarily metals like Na (with [Ne]3s<sup>1</sup>), lose e<sup>-1</sup>'s easily to obtain a noble gas e<sup>-1</sup> configuration. Na becomes Na<sup>+1</sup>, which has [Ne] or 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>.
- Other elements, primarily nonmetals like Cl (with [Ne]3s<sup>2</sup>3p<sup>5</sup>), gain e<sup>-1</sup>'s easily to obtain a noble gas e<sup>-1</sup> configuration. Cl becomes Cl<sup>-1</sup>, which has [Ar] or [Ne]3s<sup>2</sup>3p<sup>6</sup>.
- Alternating positive and negative ions are held together to form the ionic solid (crystal).
- Bonding implies an overall decrease in net energy (stability increases).

Ionic bonding can be considered as two steps:

- First, there is an e<sup>-1</sup> transfer to form ions.



$$\Delta H_{\text{total}} = + 496 - 349 = + 147 \text{ kJ/mol}$$

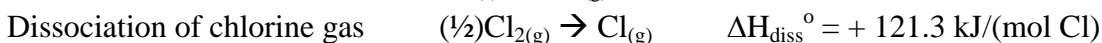
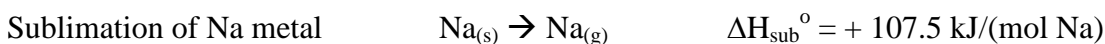
- Then, the gas phase ions attract each other to form a crystal.  $\text{Na}^{+1}_{(g)} + \text{Cl}^{-1}_{(g)} \rightarrow \text{NaCl}_{(s)}$   
This follows Coulomb's law, where Q's are the charges for the ions, and Q<sub>1</sub> = - Q<sub>2</sub>.

$$\text{Lattice Energy} = \text{sum of all } (kQ_1Q_2/r)\text{'s} = \Sigma(-kQ_1^2/r) = - 787 \text{ kJ/mol}$$

### Determining Lattice Energy (LE) with the Born-Haber cycle

- The lattice energy is released by converting the monatomic gaseous ions into a solid crystal. So, energy input would be needed to convert the ionic solid into isolated gas phase ions.
- Actual direct measurement of LE is difficult. But, it can be determined indirectly through the Born-Haber cycle, which forms NaCl<sub>(s)</sub> stepwise. First, the elements are converted into monatomic gases. Then, the gases are ionized. Finally, the ionized gases are crystallized to form the ionic solid. The last step releases LE.

- Converting Na and Cl<sub>2</sub> into monatomic gases involves:



- Ionization of Na<sub>(g)</sub> and Cl<sub>(g)</sub> into Na<sup>+1</sup><sub>(g)</sub> and Cl<sup>-1</sup><sub>(g)</sub> is as shown earlier (+ 496 and - 349 kJ). So, the total except for lattice energy is found by: (107.5 + 121.3) + (496 - 349) = + 375.8 kJ
- The heat of formation for Na<sub>(s)</sub> + (1/2)Cl<sub>2(g)</sub> → NaCl<sub>(s)</sub> is - 411.2 kJ (from [Appendix G](#)).

$$\text{This gives us:} \quad \Delta H_f^{\circ} \text{ of NaCl}_{(s)} = - 411.2 \text{ kJ} = + 375.8 + \text{LE}$$

$$\text{So, the lattice energy is:} \quad \text{LE} = (- 411.2) - (375.8) = - 787 \text{ kJ/mol}$$

### Ionic Solids

- Ionic solids typically have high melting points due to strong electrostatic attractions.

$$T_M (\text{NaCl}) = 801^{\circ}\text{C} \quad T_M (\text{MgO}) = 2800^{\circ}\text{C}$$

- MgO has a much higher T<sub>M</sub> than NaCl because the ionic charges are + 2 and - 2, and Coulombs law is a function of the charges (Q<sub>1</sub> and Q<sub>2</sub>).

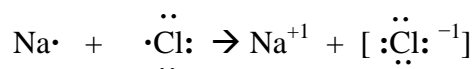
- Ionic Solids typically do *not* conduct electricity when solid because both ions have stable  $e^{-1}$  configurations, and do not easily gain or lose  $e^{-1}$ 's.
- Ionic liquids *do* conduct electricity because the ions can move, and thus carry current.
- Ionic solutions also conduct electricity for the same reason – ions can move.

### Electronic Configuration

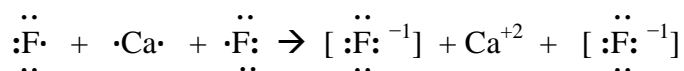
- Metal elements in columns IA, IIA, and IIIA have same number of valence  $e^{-1}$ 's as their column number, and they lose those valence  $e^{-1}$ 's to get a noble gas  $e^{-1}$  configuration. Examples include  $\text{Na}^+$ ,  $\text{Mg}^{+2}$ , and  $\text{Al}^{+3}$ .  
B is the exception. It is nonmetallic and forms covalent bonds instead.
- Nonmetals in rows 2, 3, and 4 of columns IIIA, IVA, and VA do not form cations easily. They prefer to bond covalently and form molecules instead. Examples include B, C, and N.
- Higher periods (rows 5 and 6) of IIIA, IVA, and VA are metallic, and are often stable with  $s^2$ . That is, they keep both  $e^{-1}$ 's in their s subshell, along with their filled d subshells. They gain a charge equal to column number minus two by losing their  $e^{-1}$ 's from p only. Examples include  $\text{Tl}^+$ ,  $\text{Sn}^{+2}$ ,  $\text{Pb}^{+2}$  and  $\text{Bi}^{+3}$ .
- A charge of + 4 is less common, and the compounds involved are often covalent, like  $\text{SnCl}_4$ .
- Columns VIA and VIIA, except for Po, are nonmetals and gain  $e^{-1}$ 's to obtain a noble gas  $e^{-1}$  configuration. Their charge is column number minus eight. Examples include  $\text{S}^{-2}$  and  $\text{Cl}^{-1}$ .
- Transition metals (B columns) do not usually obtain a noble gas configuration. They lose  $e^{-1}$ 's from their s subshell first, then maybe one or two  $e^{-1}$ 's from their d subshell.

### Lewis $e^{-1}$ Dot Symbols

- Valence  $e^{-1}$ 's (outermost s and p) of atoms are shown as [dots](#) around the element's symbol.
- The dots allow us to account for the  $e^{-1}$ 's as they are transferred to create the ions.



#### Ex 9.01 Dot Symbol Reaction to form $\text{CaF}_2$



#### Ex 9.02 Electron Configuration for the Oxide Ion ( $\text{O}^{-2}$ )

- O has eight  $e^{-1}$ 's total, and six of these  $e^{-1}$ 's are dots in the valence shell (2s and 2p).
- This means O is  $[\text{He}]2s^22p^4$ , and two more  $e^{-1}$ 's would fill the 2p subshell.
- So  $\text{O}^{-2}$  is  $[\text{He}]2s^22p^6$ , or  $[\text{Ne}]$ , and its Lewis symbol has eight dots.

#### Ex 9.03 Electron Configurations for the Iron(II) and Iron(III) Ions ( $\text{Fe}^{+2}$ and $\text{Fe}^{+3}$ )

- In Example 8.04, we saw that Fe is  $[\text{Ar}]4s^23d^6$ .
- Transition metals often lose the two  $e^{-1}$ 's in the outermost s subshell first.
- So,  $\text{Fe}^{+2}$  is  $[\text{Ar}]3d^6$ . Next, an  $e^{-1}$  from 3d can be removed, so  $\text{Fe}^{+3}$  is  $[\text{Ar}]3d^5$ .

## Ionic Radius

- Ionic Radius is the size of the sphere around an ion's nucleus, where the  $e^{-1}$ 's are located.
- Cations are smaller than their uncharged atoms because they lost  $e^{-1}$ 's.  
Loss of  $e^{-1}$ 's decreases the electron-electron repulsion, so that the remaining  $e^{-1}$ 's can get closer to the nucleus. Also, losing all of the outer shell  $e^{-1}$ 's leaves only the inner shells.
- Anions are larger than their uncharged atoms because they gained  $e^{-1}$ 's.  
Adding  $e^{-1}$ 's increases the electron-electron repulsion, pushing them farther apart.
- Sizes of ions follow same periodic table trends as uncharged atoms:  
Size decreases across row, as protons are added ( $Z$  increases).  $\text{Na}^{+1} > \text{Mg}^{+2}$  and  $\text{O}^{-2} > \text{F}^{-1}$   
Size increases down a column, as shells are added ( $n$  increases).  $\text{Ca}^{+2} > \text{Mg}^{+2}$  and  $\text{Cl}^{-1} > \text{F}^{-1}$
- Ions which have the same total number and configuration of  $e^{-1}$ 's are called isoelectronic.  
For example, each of these ions has a total of ten  $e^{-1}$ 's :  $\text{O}^{-2}$ ,  $\text{F}^{-1}$ ,  $\text{Na}^{+1}$ , and  $\text{Mg}^{+2}$ .
- The size trend for an **isoelectronic series** is determined by the **number of protons only**, because the **number of electrons** is the **same** for all of the ions.  
Protons pull the  $e^{-1}$ 's inward, so size **decreases** as the number of protons **increases**.

### Ex 9.04 Size Trend for Isoelectronic Ions ( $\text{O}^{-2}$ , $\text{F}^{-1}$ , $\text{Na}^{+1}$ , and $\text{Mg}^{+2}$ )

- These ions are all isoelectronic with [Ne], and each has ten  $e^{-1}$ 's total.
- Increasing the protons will decrease the size if the number of electrons is constant.  
 $\text{O}^{-2}$  (8 protons)  $>$   $\text{F}^{-1}$  (9 protons)  $>$   $\text{Na}^{+1}$  (11 protons)  $>$   $\text{Mg}^{+2}$  (12 protons)

## Covalent Bonds

- Covalent Bonds are formed by sharing  $e^{-1}$ 's, and the orbitals of the two atoms overlap, so that the  $e^{-1}$  pair is attracted to and bonded with both nuclei.
- A normal covalent bond uses one  $e^{-1}$  from each of two atoms to create a shared pair of  $e^{-1}$ 's.
- Lewis dot formulas put the  $e^{-1}$  pair (2 dots) directly between the two symbols (H:H).
- The potential energy ( $E_{\text{Pot}}$ ) [diagram](#) shows the minimum energy at a bond length of 74 pm.  
This is the most stable distance between the nuclei of two covalently-bonded H atoms.

## Coordinate Covalent Bonds

- Both shared  $e^{-1}$ 's came from the same atom.
- For example, in the acid-base reaction for ammonia, the N atom donates a (nonbonding) pair of  $e^{-1}$ 's to the  $\text{H}^{+1}$  (has no  $e^{-1}$ 's).  
 $\text{H}^{+1} + \text{:NH}_3 \rightarrow \text{H:NH}_3^{+1}$  (same as ammonium or  $\text{NH}_4^{+1}$ )

## Octet Rule

- Atoms in covalent molecules tend to have eight valence  $e^{-1}$ 's total, including those that are shared, such as in  $\text{F}_2$  and  $\text{CCl}_4$ .
- This is because these atoms are stable with their valence s and p subshells filled.
- There are exceptions, and some atoms can have fewer or more valence  $e^{-1}$ 's.  
For example, in the compound  $\text{BF}_3$ , the B has only six valence  $e^{-1}$ 's.  
Also, the P atom in  $\text{PF}_5$  has ten valence  $e^{-1}$ 's.

## Multiple Bonds

- More than one pair of  $e^{-1}$ 's can be shared between two atoms.
- Show 2 pairs of dots for double bonds.  $H_2C::CH_2$
- C, N, O, and S can form double bonds.  $::O::C::O::$
- Show 3 pairs of dots for triple bonds.  $H:C:::C:H$
- Only C and N can form triple bonds.  $H:C:::N:$

## Polar Covalent Bonds and Electronegativity (e/n)

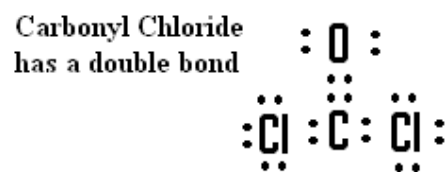
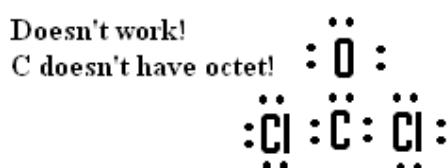
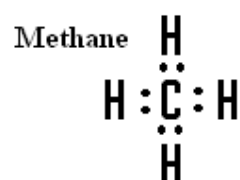
- Polar covalent bonds occur where bonding  $e^{-1}$ 's spend more time nearer to one atom, rather than the other. The  $e^{-1}$ 's stay closer to the atom which has a higher attraction for  $e^{-1}$ 's.
- The e/n is a measure of an atom's ability to draw  $e^{-1}$ 's to itself.
- Linus Pauling's scale uses bond energies to assign numbers from 0 to 4 to atoms. Values increase across a row, and decrease down a column.
- Here is a periodic table diagram with [e/n values](#).  
F (lighter and nonmetallic) in the *top right* of the table has the *highest* value (4.0).  
Fr (heavier and metallic) in the *lower left* of the table has the *lowest* value (0.7).
- The difference between e/n values for two bonded atoms roughly measures the bond polarity. Generally, if the result is  $< 0.5$ , the bond is nonpolar. Polar covalent bonds range from 0.5 to 1.5, and a value  $> 1.5$  is primarily an ionic bond (not covalent).
- For HCl, the Cl has the higher e/n (3.0 vs. 2.1), so it attracts  $e^{-1}$ 's more so than H.  
 $3.0 - 2.1 = 0.9$  The value is between 0.5 and 1.5, so H-Cl is a polar covalent bond.  
The Cl has a partial negative charge ( $\delta^-$ ), and the H has a partial positive charge ( $\delta^+$ ).

## Ex 9.05 C-C, C-N, and O-H Bond Polarities

- For C-C, the e/n difference is  $2.5 - 2.5 = 0.0$ , which is completely nonpolar.
- For C-N, the e/n difference is  $3.0 - 2.5 = 0.5$ , which is slightly polar. N is  $\delta^-$  and C is  $\delta^+$ .
- For O-H, the e/n difference is  $3.5 - 2.1 = 1.4$ , which is very polar. O is  $\delta^-$  and H is  $\delta^+$ .

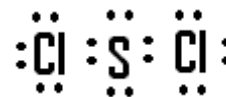
## Rules for Drawing Lewis Dot Formulas for Covalent Molecules and Ions

1. First, find the total number of valence  $e^{-1}$ 's for the entire molecule.  
Add one  $e^{-1}$  for each negative charge, and subtract one  $e^{-1}$  for each positive charge.
2. Write the skeleton structure with the atomic symbols, showing which atoms are bonded together. Bond the atoms together by placing a pair of dots between them.
3. Then, put dots around the outside atoms to satisfy the octet rule.
4. Put the remaining dots around the central atom.  
If there are less than 8  $e^{-1}$ 's on the central atom, there may be a multiple bond present.



Ex 9.06 Dot Structure for Sulfur Dichloride (SCl<sub>2</sub>)

- Cl-S-Cl has 6 + 7(2) = 20 e<sup>-1</sup>'s, and 16 are needed to give the Cl's octets.
- Out of that 16 e<sup>-1</sup>'s, there are 4 e<sup>-1</sup>'s in two bonds shared w/ S.
- This leaves 4 e<sup>-1</sup>'s, which will complete S's octet.

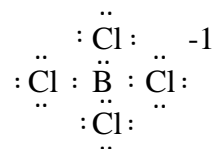


Ex 9.07 Dot Structure (diagrams on previous page) for Carbonyl Chloride (COCl<sub>2</sub>)

- COCl<sub>2</sub> has 4 + 6 + 2(7) = 24 e<sup>-1</sup>'s, and all 24 e<sup>-1</sup>'s are needed for the O and Cl's octets.
- But drawing single bonds only will give six e<sup>-1</sup>'s only to C in the three bonds with C.
- So, a double bond between C and O is needed to give 2 more e<sup>-1</sup>'s to C.

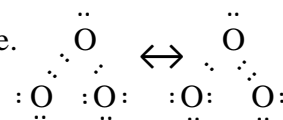
Ex 9.08 Dot Structure for the Tetrachloroborate Anion (BCl<sub>4</sub><sup>-1</sup>)

- BCl<sub>4</sub><sup>-1</sup> is an anion with one extra e<sup>-1</sup>. It has 3 + 4(7) + 1 = 32 e<sup>-1</sup>'s.
- All 32 e<sup>-1</sup>'s are needed for the four F's octets.
- The four single bonds give B an octet as well.



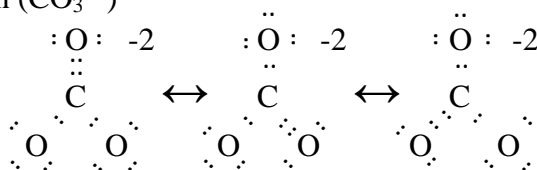
Resonance (Delocalization)

- Resonance occurs where more than one correct dot structure is possible.
- Show all of the dot structures with ↔ between each of them.



Ex 9.09 Resonance Dot Structures for Carbonate Anion (CO<sub>3</sub><sup>-2</sup>)

- CO<sub>3</sub><sup>-2</sup> has 4 + 3(6) + 2 = 24 e<sup>-1</sup>'s.
- All 24 e<sup>-1</sup>'s are needed for the O's octets.
- Also, one double bond is needed for C's octet.



Delocalized Bonding

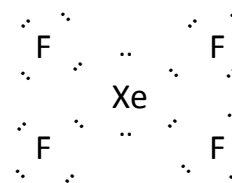
- Delocalized bonding is a type of bonding where a bonding e<sup>-1</sup> pair is spread over > 2 atoms.
- The result of averaging the resonance forms is called a resonance hybrid.
- With O<sub>3</sub>, the two bonds between O's are averaged to appear like 1.5 e<sup>-1</sup> pairs per bond.

Exceptions to Octet Rule with more than 8 e<sup>-1</sup>'s

- [Phosphorus pentafluoride](#) (PF<sub>5</sub>) has 5 pairs (or 10 e<sup>-1</sup>'s) surrounding the central P atom.
- This results from using one of phosphorus' 3d orbitals in addition to its 3s and 3p orbitals.

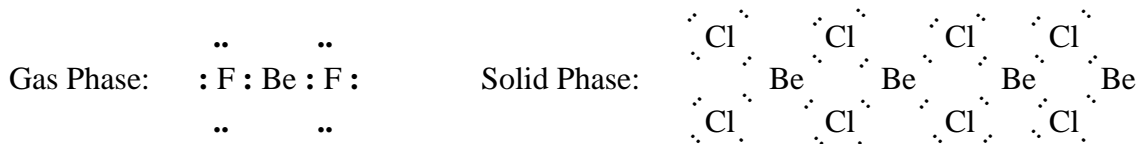
Ex 9.10 Dot Structure for Xenon Tetrafluoride (XeF<sub>4</sub>)

- Xe already has an octet with eight e<sup>-1</sup> combined from 5s and 5p.
- Each F adds one more e<sup>-1</sup> to the total with a shared e<sup>-1</sup> pair.
- This gives Xe a total of twelve valence e<sup>-1</sup> in XeF<sub>4</sub>.
- The extra four e<sup>-1</sup>'s use two of Xe's 5d orbitals.
- Four e<sup>-1</sup> pairs are shared with the F's.
- So, there are four more e<sup>-1</sup>'s in two nonbonding e<sup>-1</sup> pairs.

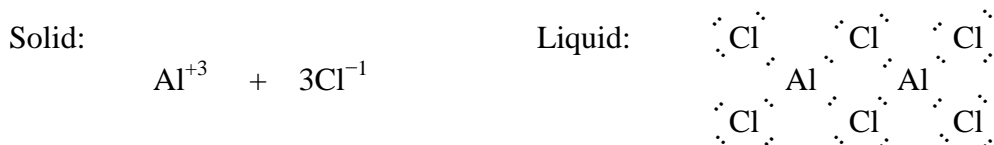


### Exceptions to Octet Rule with less than 8 e<sup>-1</sup>'s

- BF<sub>3</sub> only has 3 pairs (or 6 e<sup>-1</sup>'s) surrounding the central B atom.
- A normal covalent bond has two shared e<sup>-1</sup>'s, with one e<sup>-1</sup> from each of the two atoms.
- Since B only has three valence e<sup>-1</sup>'s, it can only form three normal covalent bonds.
- BF<sub>3</sub> can, however, accept an e<sup>-1</sup> pair from an atom which has a nonbonding e<sup>-1</sup> pair. So, it reacts with :NH<sub>3</sub>, to form the complex F<sub>3</sub>B:NH<sub>3</sub>. The new bond gives B its octet.
- Similarly, BeF<sub>2(g)</sub> has only two pairs around Be, which has two valence e<sup>-1</sup>'s.
- However, BeF<sub>2(s)</sub> and BeCl<sub>2(s)</sub> form molecules that are long chains of BeX<sub>2</sub> formula units. This allows Be to use e<sup>-1</sup> pairs from neighboring F and Cl atoms in order to obtain its octet.



- AlCl<sub>3(s)</sub> is ionic, but melts at 192 °C to form covalently bonded Al<sub>2</sub>Cl<sub>6(L)</sub> molecules.



### Formal Charge

- Formal charge is a hypothetical charge on an atom that results if the bonding e<sup>-1</sup>'s are all shared equally between atoms.
- Formal charges are eliminated, where possible, in the Lewis dot structures of neutral compounds.
- If the formal charges cannot be completely eliminated, such as with polyatomic ions, then they are at least minimized.
- Assign valence e<sup>-1</sup>'s to a particular atom as follows:
  - o Half of the two e<sup>-1</sup>'s in a bond (i.e., one e<sup>-1</sup> each) belong to each of the two atoms.
  - o Both e<sup>-1</sup>'s in a (nonbonding) lone pair belong to the atom that they are attached to.
- For example, N owns 2 + 3(1) = 5 e<sup>-1</sup>'s of the surrounding octet in :NH<sub>3</sub>. This is the same as N's original number of valence e<sup>-1</sup>'s, so this N has no formal charge.
- Write the Lewis dot structures to minimize formal charges as follows:
  - o Choose the dot formula with the lowest values on formal charges.
  - o Place the negative charge on the more electronegative atom.
  - o Don't put like charges on adjacent atoms.

### Ex 9.11 Formal Charges on [H<sub>2</sub>SO<sub>4</sub>](#)

- With all single bonds, each atom has an octet, but S is + 2 and two oxygens are - 1.
- Formal charges are eliminated if S uses two d orbitals, and becomes an exception to the octet rule, so that it can have double bonds with the two free O's.

## Bond Length

- Bond length is the distance between the nuclei of two single-bonded atoms.
- Bond length approximately equals the sum of the [covalent radii](#) for each atom.
- [This chart](#) predicts the bond length for a C-Cl bond as  $77 + 99 = 176$  pm.

## Bond Order

- Bond Order is the number of shared  $e^{-1}$  pairs:
  - o 1 for single bonds ( $H_3C:CH_3$ ).
  - o 2 for double bonds ( $H_2C::CH_2$ ).
  - o 3 for triple bonds ( $HC:::CH$ ).
- Increasing the bond order will increase the bond strength and the decrease bond length. More shared  $e^{-1}$  pairs makes the bond shorter and stronger.

## Ex 9.12 Bond Lengths for Carbon-Carbon Bonds in $C_2H_2$ , $C_2H_4$ , and $C_2H_6$

- The bond length trend is as follows:  $\text{triple} < \text{double} < \text{single}$  (longest)  
 $H:C:::C:H < H_2C::CH_2 < H_3C:CH_3$
- The strength trend is the reverse:  $\text{triple} > \text{double} > \text{single}$  (weakest)

## Bond Energy

- [Bond energy](#) is the average  $\Delta H$  input needed to break a bond in a gas phase molecule.
- $CH_{4(g)} \rightarrow C_{(g)} + 4H_{(g)}$  has  $\Delta H = +1662$  kJ and four C-H bonds are broken. So, the experimental C-H bond strength is  $(+1662) \div 4 = 415.5$  kJ.
- The average bond energy value for the C-H bond in Table 7.2 is 415 kJ.
- Note that bond energy for double and triple bonds in the table is generally much higher than for single bonds.
- Bond energy of  $CH_4$  reactant is  $4 \times 415$  kJ according to the table, and the bond energy for the product is 0 kJ (no bonds).
- The enthalpy of a reaction can be found by:  
$$\Delta H = (\text{bond energy of reactants}) - (\text{bond energy of products})$$
- To break  $CH_4$  down completely into its atoms using the table's values we get:  
$$\Delta H = (4 \times 415) - (0) = 1660$$
 kJ

## Ex 9.13 Forming Polyethylene from Ethylene $n[H_2C=CH_2] \rightarrow [-H_2C-CH_2-]_n$

- Polyethylene is a polymer, and its molecular structure is a chain of repeating ethylene units.
- The product's "n" subscript is the number of connected [repeating unit]'s in the chain.
- One C=C (double bond) is broken and is replaced with two C-C single bonds.
- One C-C is between the C's inside the repeating unit (product).
- The bonds on the left and right of that unit connect it to other repeating units, so each of those counts as only half of a bond inside the repeating unit. So,  $\frac{1}{2} + 1 + \frac{1}{2} = 2$  bonds total.

$$\Delta H = [C=C + (4 \text{ C-H})] - [(2 \text{ C-C}) + (4 \text{ C-H})] \text{ for } n = 1 \text{ mole of } H_2C=CH_2$$

$$\Delta H = [611 + (4 \times 415)] - [(2 \times 345) + (4 \times 415)] = -79 \text{ kJ per mole of } H_2C=CH_2$$