Bonding in Compounds

Ionic and Covalent Bonds

Ionic Bonds

- ***Ionic bonds*** form from the electrostatic attraction between positive and negative ions
  - Formation of ions
    - Metals lose electrons
      - $Na \rightarrow Na^+ + e^-$
      - $[Ne]\ 3s^1 \rightarrow [He]\ 2s^2\ 2p^6 + e^-$
    - Non-metals gain electrons
      - $Cl + e^- \rightarrow Cl^-$
      - $[Ne]\ 3s^2\ 3p^5 + e^- \rightarrow [Ne]\ 3s^2\ 3p^6$
    - Note that both ions formed are isoelectronic with a noble gas (8 valence electrons).

Formation of ions continued

- Main group elements
  - Cations from groups IA to IIIA that are isoelectronic with noble gases have a charge equal to the group number. Mg^{2+} or Na^+
  - Cations from groups IIIA to VA that have ns^2 electrons have a charge equal to the group number minus 2. Tl^+ or Pb^{2+}
  - Anions from groups VA to VIIA that are isoelectronic with noble gases have a charge equal to the group number minus 8. N^{3-} or F^-

Formation of ions continued

- Transition metal ions
  - Transition metals lose their *ns* electrons first.
  - Then 1 or more (*n*-1)d electrons if necessary.
    - Fe^{2+} $[Ar]\ 4s^2\ 3d^6 \rightarrow [Ar]\ 3d^6$
    - Fe^{3+} $[Ar]\ 4s^2\ 3d^6 \rightarrow [Ar]\ 3d^5$

Ionic radii

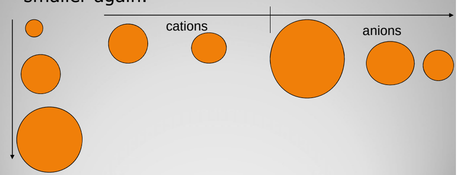
- When metals lose electrons they lose them from the outer most energy level.
- This results in the ion having one less energy level than the neutral atom.
- Ions of metals are smaller than the neutral atoms from which they came.

Ionic radii

- Non-metals gain electrons in their valence shell.
- The repulsion between the original electrons and the added electrons causes them to move farther apart.
- Ions of non-metals are larger than the neutral atoms from which they came.

Ionic radii

- Trends
  - Down a group the ions get larger because of the extra shells.
  - Across a period the ions get smaller then increase suddenly at the anions and get smaller again.



Energetics of ionic bond formation

- Why do we always form Na^+Cl^- and not Na^-Cl^+?
  - Energy!
    - Let's look at the energy involved in forming each of these compounds.

Na^+Cl^-

- Start with 1 mol Na atoms and 1 mol Cl atoms
  - We need to remove the electrons from the sodium atoms. This involves the ionization energy (496 kJ/mol)
  - We need to add those electrons to the chlorine atoms. This is the electron affinity energy (-349 kJ/mol)
  - Next we need to put them together to form the compound (-786 kJ/mol)
  - This is a total energy change of -639 kJ/mol. A net lowering of energy.

Na^-Cl^+

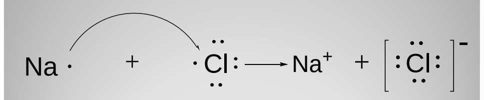
- Start with 1 mol Na atoms and 1 mol Cl atoms
  - We need to remove the electrons from the chlorine atoms. This involves the ionization energy (1250 kJ/mol)
  - We need to add those electrons to the sodium atoms. This is the electron affinity energy (-53 kJ/mol)
  - Next we need to put them together to form the compound (-786 kJ/mol)
  - This is a total energy change of +411 kJ/mol. A net increase of energy.

Properties of ionic solids

- High melting points.
  - This can be explained by the fact that the ions are relatively small.
  - They are also charged.
    - the smaller the ions the higher the melting point.
    - the higher the charge on the ions the higher the melting point.

Lewis electron-dot symbols

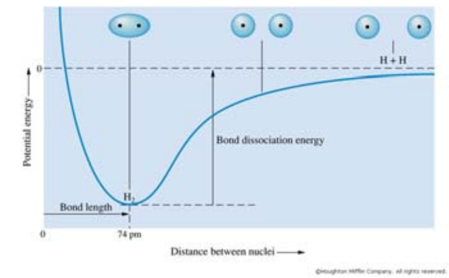
- ***Lewis electron dot-symbols*** are a way of representing the elements with their valence electrons.
- Examples
  - H· 1 valence electron
  - ·C̈· (with dots above and below) 4 valence electrons
- Notice that the electrons are not yet paired.



Ionic compound formation with Lewis electron-dot symbols

- ***Covalent bonds*** arise when atoms share electrons.
- Formation of covalent bonds
  - Separated atoms move close to each other. Because of van der Waals forces the potential energy decreases.
  - As they get closer, eventually, their valence shells overlap which results in a sharp decrease in the potential energy.
  - If they get too close the nuclei repel one another which causes the potential energy to increase again.

Covalent bonds



- Because the electrons in covalent compounds are shared, we have to represent them differently in their Lewis structures.
- We will use single (–), double (=) and triple (≡) lines to represent the shared electrons in the compound.

Lewis Formulas for Covalent Compounds

- Another kind of bond that can form is a ***coordinate covalent bond***.
  - Both electrons in the bond come from one atom.
  - The bond formed is no different from a normal covalent bond.

Lewis Formulas for Covalent Compounds

- Most compound will follow the ***octet rule***.
  - All atoms, except for hydrogen, will have 8 electrons around them (hydrogen will have 2).
  - Some compounds (usually with a central atom from the 3rd period or higher) can form what is called an ***expanded octet***. (10 or 12 electrons).
  - Some compounds, notably with boron, will form compound with only 6 electron around the central atom.

Octet Rule

Polar bonds

- Not all bonds share the electrons equally.
  - These are referred to as ***polar bonds***.
  - The difference in share comes from a difference in ***electronegativity***.
- ***Electronegativity*** is the tendency of an atom to pull electrons toward itself when it is in a bond.

Electronegativity

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB	VIIIB	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														

How to draw Lewis structures for covalent compounds

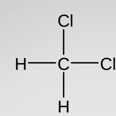
- Calculate the total number of valence electrons in the compound.
  - Add electrons for each negative charge.
  - Subtract electrons for each positive charge.
- Write the skeletal structure of the compound.
  - The central atom, in general, will be the least electronegative atom.
  - All the outer atoms will be connected to the central atom initially by single bonds.

How to draw Lewis structures for covalent compounds

- Give all the outer atoms an octet by adding pairs of electrons.
- Any electrons left over should go on the central atom.
- If, after distributing all the electrons, the central atoms does not have an octet, shift electrons from the outer atoms to make double or triple bonds as needed to give it an octet.

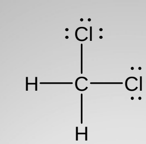
Example: CH_2Cl_2

- Count all of the valence electrons
  - 4+2(1)+2(7)=20
    C H Cl
- Draw skeletal structure



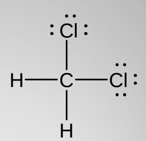
Example: CH_2Cl_2

- Give outer atoms (except H) an octet.



Example: CH_2Cl_2

- Check for octets:
- All the atoms that need octets have them.
- The structure is complete.



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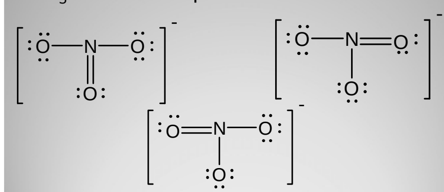
Resonance structures

- Sometimes there is more than one possible way of drawing a Lewis structure.
- NO_3^- is an example



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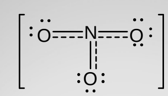
Resonance structures

- The structure can be represented as having ***delocalized electrons***.
- Delocalized electrons are electrons that are shared across the whole molecule.



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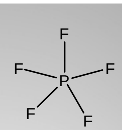
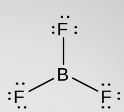
Exceptions to the octet rule

- Central element from period three or higher



- Central element is electron deficient



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Formal Charge

- ***Formal charge*** is a way of determining which of several possible structure is likely.

$$FC = (\text{valence electrons on free atom}) - \tfrac{1}{2}(\text{number of electrons in bonds}) - (\text{number of lone pair electrons})$$

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Formal charge: the rules

- Lower FC values on all atoms is usually best
- Negative FC should be on the more electronegative atom.
- Sum of all the FC's should equal the overall charge.

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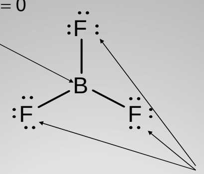
$FC = 3 - \frac{1}{2}(6) - 0 = 0$



This shows why BF_3 does not obey the octet rule.

$FC = 7 - \frac{1}{2}(2) - 6 = 0$

BF_3 and formal charges

- ***Bond order*** is the number of pairs of electrons in a bond.
- ***Bond length*** is the distance between the nuclei in a bond.
- Bond length and bond order are related

Bond order	Bond length
1	longest
2	shorter
3	shortest

Bond order and length

- ***Bond energy*** is the energy contained in a chemical bond.
  - The energy is released when the bond is formed (negative value)
  - The energy is absorbed when the bond is broken (positive value).
- Bond energies are listed in your textbook and on the back of the periodic table used for your exam.

Bond energy

- We can use bond energies to estimate the reaction enthalpy of a reaction.
- We subtract the energy of any bonds formed and add the energy of any bonds broken.

$$\Delta H \approx BE(\text{broken}) - BE(\text{formed})$$

Bond energy and reaction enthalpy

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$$

Broken
- 4 C-H (411 kJ)
- 2 O=O (494 kJ)

Formed
- 2 C=O (799 kJ)
- 4 H-O (459 kJ)

$$\Delta H \approx [(4)(411\text{ kJ}) + (2)(494\text{ kJ})] - [(2)(799\text{ kJ}) + (4)(459\text{ kJ})] = -802\text{ kJ}$$

Example