Chemical Bonding

- Petrucci, Harwood and Herring: Chapters 10 and 11
- Aims:
  - To look at bonding and possible shapes of molecules
    - We will mainly do this through Lewis structures
  - To look at ionic and covalent bonds
  - Use valence shell electronic structure to predict shapes of molecules

Chemical Bonding

- The most important concepts here are:
  - Electrons, particularly valence electrons play a fundamental role in chemical bonding.
  - When elements combine to produce compounds they are attempting to achieve a valence shell like a noble gas

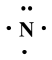
Chemical Bonding

- The driving force for the production of chemical bonds is the need for an atom to complete a valence shell (usually 8 electrons)
  - Often electrons can be transferred from one atom to another to make ions. The atoms are then held together by coulombic forces in an ionic bond
  - More often the only way an atom can gain electrons is by sharing. This sharing produces a covalent bond

Lewis Symbols

- This is a way of representing the valence electrons in an element
  - It does not include the inner shell electrons
  - It does not include the spin of an electron
  - e.g. Si ([Ne]$3s^2 3p^2$)

  - N ([He]$2s^2 2p^3$)

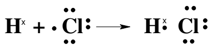


Lewis Structures

- These are the combination of Lewis symbols that represents the sharing or transfer of electrons in a molecule
  - Examples
  - Ionic bond

$Na^{x} + Cl \rightarrow [Na]^{+} [Cl]^{-}$

  - Covalent bond

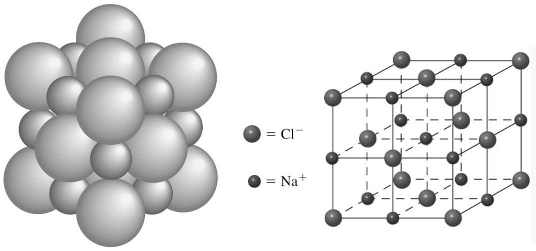


$H^{x} + Cl \rightarrow HCl$

Ionic Compounds

- We don’t usually see isolated ionic compounds
  - Normally they are in crystals where one anion (negative) is attached to several cations (positive) and vice versa. Electrical neutrality means the total number of each ion is the same.

Ionic Compounds

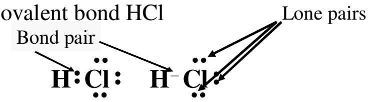


Covalent Compounds

- Here electrons are shared between two atoms.
  - (May actually be more than just a couple of shared electrons)
  - The electrons spend “time” around each atom in the covalent bond
  - The overall effect is that each atom has “more” (usually a full shell of) valence electrons.

Covalent Compounds

- Examples
  - Single covalent bond HCl



Note that there are 6 electrons around the Cl that are not involved in bonding. It is normal to talk about these as lone pairs, in contrast to bond pairs

Multiple Covalent Bonds

- Often the sharing of one electron does not "fill" the valence shell of an atom.
- e.g. N_2

Multiple Bonds

- We use a number of different ways to describe multiple bonds
- For 1 bond pair
  - Single bond
  - bond order =1
- For 3 bond pair
  - Triple bond
  - bond order =3
- For 2 bond pairs
  - Double bond
  - bond order =2

Bond Length

- Bond Length
  - The distance between two atoms joined by a covalent bond
  - As the bond order increases the bond length decreases

Bond	Length/pm	Bond	Length/pm
C-C	154	N-N	145
C=C	134	N=N	123
C≡C	120	N≡N	110

Bond Energy

- To separate two atoms that are joined by a covalent bond, energy must be supplied. This is the Bond Dissociation Energy (D).
- This is equal to the energy released when the bond is formed.

$H_2(g) \rightarrow 2H(g) \qquad \Delta H = D(H\text{-}H) = +435.93\ \text{kJ mol}^{-1}$

- Listed bond energies are usually an average over a number of compounds

Polarity of Bonds

In many molecules the electrons in the covalent bond are not shared equally between the two atoms.

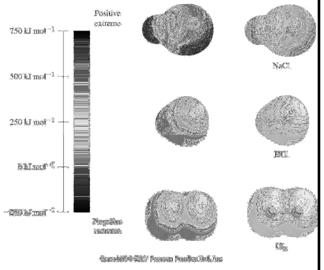
- They are associated more strongly with one of the atoms.
- This leads to a polar covalent bond.

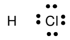
Polarity of Bonds

If the molecule is symmetric about a bond, the bonding electrons are equally shared and the bond is nonpolar.

If this molecule is not symmetric about a bond, the bonding electrons are not shared equally and are displaced towards the more electronegative element. This gives the molecule a permanent dipole, or dipole moment, and the bond is polar.

The magnitude of this dipole moment, or the polarity of the bond, is dependent upon the difference in the electronegativities of the elements in the bond. When the difference in electronegativities is very large, the bond is said to be ionic and not simply polar.





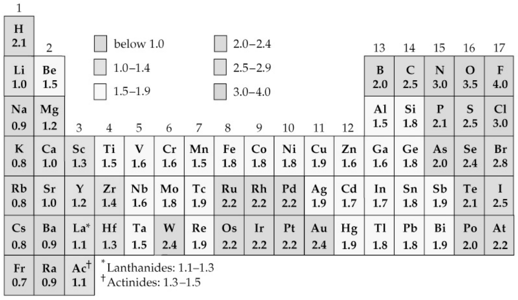
H − Cl

$\delta^+ \quad \delta^-$

Polarity of Bonds

- The ability to attract electrons in a bond appears to be related to electron affinity but we use a molecular property to describe it.
- Electronegativity is a quantitative measure of an atom's ability to compete for electrons with other atoms to which it is bonded.

Polarity of Bonds: Electronegativities



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
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 **0.8**	**Ba** **0.9**	**La*** **1.1**	**Hf** **1.3**	**Ta** **1.5**	**W** **2.4**	**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†** **1.1**														

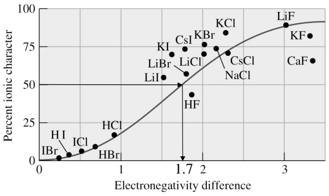
▨ below 1.0
▨ 1.0–1.4
☐ 1.5–1.9
▨ 2.0–2.4
▨ 2.5–2.9
▨ 3.0–4.0

*Lanthanides: 1.1–1.3
†Actinides: 1.3–1.5

Polarity of Bonds: Ionic Character

The larger the electronegativity difference between the atoms, the more ionic the bond.

If ΔEN > 1.7, bond is ionic.



Lewis Structures

- Lewis structures are useful it indicating the bonding in molecules.
- Rules:
  - All valence electrons must appear
  - The electrons are usually paired
  - The valence shells are usually filled (2 electrons for H, 8 for systems with s and p orbitals)
  - Multiple bonds are often needed, especially in C, N, O, P, S.

Lewis Structures

1. Check if the compound is ionic. If it is, treat each ion separately.
2. Add up the number of valence electrons (that's from all atoms). Add or subtract electrons to give the right charge. This is the available electrons A.
3. Draw a skeletal structure. The central atom will normally have the lowest electronegativity. Carbon is always a central atom. Hydrogen is always terminal.

Lewis Structures

4. Calculate the number of valence electrons needed to give all the atoms a full shell (2 or 8). This is the number of needed electrons N
5. Determine the number of electrons that must be shared S=N-A
6. Place single bonds in the skeletal structure (2 electrons per). Add extra bonds to satisfy S.
7. Place remaining electrons, in (lone) pairs to complete the octets for each atom.

Lewis Structures

Example C_2N_2

Carbon has 4 valence electrons, nitrogen 5. A=18

Each atom wants an octet, N=32

Shared electrons S= 32-18 =14 (7 bonds)

Skeleton: (Electronegativities C 2.5, N 3.0)

N-C-C-N : Still need 4 more bonds.

$N\equiv C-C\equiv N$ is the only way to add the 4 bonds without having more than 8 electrons around a carbon.

Lewis Structures

Example C_2N_2

This uses 14 of the 18 electrons, so there are only 4 left. The carbons have their octet, each nitrogen is 2 short so we must have one lone pair on each nitrogen.

$:N\equiv C-C\equiv N:$

Resonance

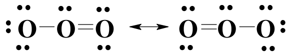
- Consider ozone O_3

$$:\ddot{\underset{..}{O}}-\ddot{O}=\ddot{\underset{..}{O}} \qquad \ddot{\underset{..}{O}}=\ddot{O}-\ddot{\underset{..}{O}}:$$

These are both reasonable Lewis structures BUT experimental evidence shows the bonds are the same length.

Resonance

- The real structure is a hybrid of these two

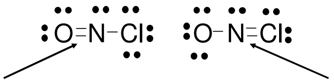


This is called resonance. The real structure is a resonance hybrid of these two structures.

The real structure has bonds which are between single and double bonds. So what is the bond order of the oxygen-oxygen bond in ozone?

Formal Charges

- The method of obtaining the Lewis structures can yield anomalous results, when the structure has atoms not contributing equal numbers of electrons.
- E.g. ONCl



Cl and N donate one electron each Cl donates 3 electrons to the bond
O and N donate 2 electrons each O donates 0 electrons to the bond
This seems more reasonable.

Formal Charges

- The formal charge is the apparent charge on an atom. It can be used to decide between possible structures.
- The formal charge is:

FC = # of valence electrons in free atom
- # of lone pair electrons
- ½ (# of bonding electrons)

Formal Charges

Rules for the most plausible Lewis structure:

1. The most plausible is the one where no atoms have a formal charge.
2. Where formal charges are required, they should be as small as possible.
3. Negative formal charges should be on the most electronegative atoms.
4. Same sign formal charges on adjacent atoms are unlikely.

Formal Charges

Example: HCN

H −C≡N: H− N≡ C:

Remembering that C has 4 valence electrons and N 5

FC(H) = 0	FC(H) = 0
FC(C) = 0	FC(C) = -1
FC(N) = 0	FC(N) = +1

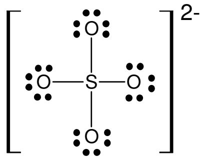
HCN is most likely.

Exceptions/Extensions

- Odd electron species: eg NO (11 electrons)
  - You can produce a Lewis structure but will have 1 electron left, it goes on the atom to minimize the formal charge.
- Incomplete octets.
  - Sometimes you just plain don’t have enough electrons. This usually leads to needing resonance structures.
- Expanded valence shells.
  - Sometimes it seems necessary to have more than 8 electrons in the valence shell. This can be done for third period elements by invoking the “d” orbitals.

Expanded Octet Example

Sulphate, SO_4^{2-}

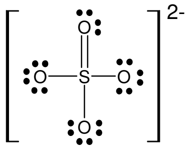


Octets are complete, but sulphur is in the 3rd period so d orbitals are available for expanding the octet to reduce formal charges.

FC(-O) = -1

FC(S) = +2

Expanded Octet Example (cont.)



FC(single bonded O) = -1

FC(double bonded O) = 0

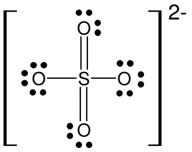
FC(S) = +1

The octet around the S has been expanded to hold 10.

On basis of formal charge this is better.

Would formal charges be further reduced by further expansion?

Expanded Octet Example (cont.)



FC(single bonded O) = -1

FC(double bonded O) = 0

FC(S) = 0

A second octet has been expanded.

Is this the best possible structure?

Try expanding another octet to see if the formal charges are further reduced.