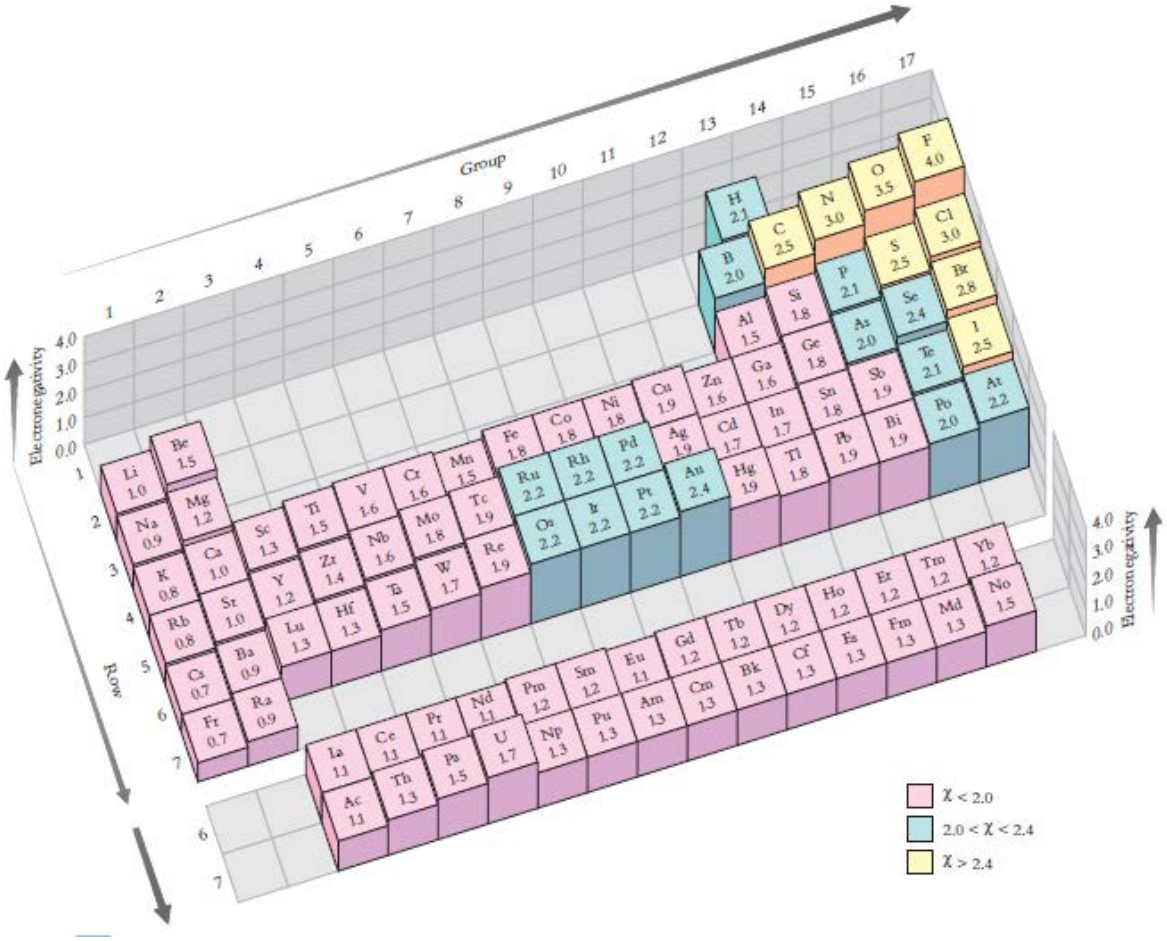
1. Ionic vs. Covalent Bonds

The basis for the decision of whether a bond is ionic or covalent is how much each atom in the bond attracts electrons to itself. You might think we would use the electron affinity for this, but a slightly different scale, the electronegativity (χ), expresses the ability of an atom involved in a bond to attract electrons to itself. Electronegativities are given in Figure 6–7 of the textbook, which is reproduced below:



Electronegativity (which is dimensionless), increases going up a group or L to R across a period. Thus, F has the highest electronegativity (4.0) and Fr the lowest (0.7).

If the difference in electronegativity ($\Delta\chi$) of the two atoms involved in a bond is <0.5, the bond is said to be non-polar covalent. This usually only happens for identical atoms, e.g. the H atoms in H_2.

If $0.5 \leq \Delta\chi \leq 1.7$, the bond is said to be polar covalent. In this case the atom with the higher χ has the greater share of the electrons involved in the bond. For example, each O–H bond in water is polar covalent, since $\chi(O) = 3.5$, and $\chi(H) = 2.1$ and $\Delta\chi = 1.4$.

Finally, if $\Delta\chi$ >1.7, the bond is ionic. We expect that the more electronegative atom completely steals the electron away from the less electronegative one, creating a positive and a negative ion, which then are attracted to each other creating an ionic compound. e.g. KBr is ionic, since χ(K) = 0.8, χ(Br) = 2.8; $\Delta\chi$ = 2.8, and the compound must be ionic.

e.g. Arrange the following in increasing order of bond polarity, and predict whether each is non-polar covalent, polar covalent or ioinc:

C-Cl, C-H, C-Mg, C-O and C-S

The calculated differences are:

C-Cl: $\Delta\chi$ = 3.0-2.5 = 0.5 (polar covalent)

C-H: $\Delta\chi$ = 2.5 - 2.1 = 0.4 (non-polar covalent)

C-Mg: $\Delta\chi$ = 2.5 - 1.2 = 1.3 (polar covalent)

C-O: $\Delta\chi$ = 3.5 - 2.5 = 1.0 (polar covalent)

C-S: $\Delta\chi$ = 3.5 - 2.5 = 1.0 (polar covalent)

Order: C-H < C-Cl < C-O < C-S < C-Mg

Note that you cannot make an ionic compound with carbon!

2. Lewis Structures and VSEPR

To predict the shape of a molecule using VSEPR, follow the following rules. If you don't use the rules, you will probably get it wrong!

1. Draw the Lewis structure

(i) Count the valence electrons
(ii) Write a skeletal structure, putting the least electronegative element at the centre.
(iii) Put single bonds to each terminal atom (2 electrons each)
(iv) Complete the octets around the terminal atoms, where applicable (i.e. not for H)
(v) Put any remaining pairs of electrons or single electrons on the central atom
(vi) make double bonds where necessary
(vii) Write the shorthand notation of the structure as, e.g. AX_3E_2, where A is the central atom, there are three X terminal atoms and two lone pairs (E), also on the central atom.

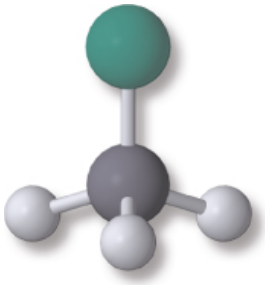
2. Predict the shape based on the shorthand notation developed above. See Table 6–2 in the text for a complete list of possible shapes.

The only way to learn this is by practicing it:

(a) predict the shape and polarity of CH_4.
Count the valence electrons: 4 for the C, 4 x 1 for the H's = 8
The structure thus has 4 bonds to the carbon, using all 8 electrons. The shorthand notation is AX_4. Must be tetrahedral. All bond angles are 109.5°.

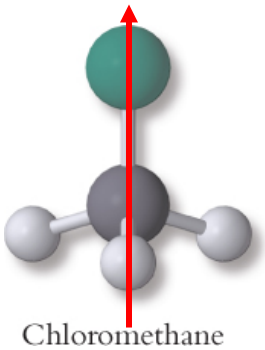
Each of the C– H bonds is slightly polar ($\Delta\chi = 0.4$). But note that these four individual dipole cancel each other out in three–dimensional space, so the molecule as a whole is non– polar.

(b) predict the shape and polarity of CH_3Cl.
Count the valence electrons: 4 for the C, 3 x 1 for the H's, 7 for the Cl = 14
The four bonds use 8, leaving six to be placed as lone pairs on the Cl. The shorthand notation is AX_3E. Must be tetrahedral as well. A first approximation is that all bond angles are 109.5°.



Chloromethane

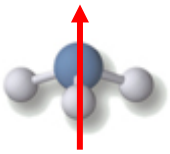
The three C– H bonds are slightly polar, with the negative ends on the C atom. The C– Cl bond is also polar, with the negative end of the Cl. The net dipole is therefore up through the C atom towards the Cl atom as shown:



Chloromethane

(c) predict the shape and polarity of NH_3.
5 + 3 x 1 = 8 valence electrons
The three bonds use 6 of them, leaving a lone pair on the N atom. The shorthand notation is thus AX_3E. Must be a trigonal pyramid.

$\Delta\chi = 3.0 - 2.1 = 0.9$ for each bond. In this case however, the three dipoles add up to one larger one overall, so ammonia is polar with the negative end near the N atom and the positive end in between the three H atoms. The H– N– H bond angle is less than 109.5^o because of the lone pair on top.

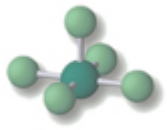


(d) predict the shape and polarity of PCl_5.
5 + 5 x 7 = 40 valence electrons
Five single bonds = 10 electrons. Six more around each Cl to complete the octets uses 30 more.
The shorthand notation is thus AX_5. Shape is a trigonal bipyramid.

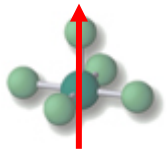
Each bind is polar, but the (vector) sum of these five dipoles is zero because the molecule is symmetrical. There are two bond angles: 120^o in the plane containing three Cl atoms, and 90^o perpendicular to this plane.

(e) predict the shape of and polarity IF_5.
7 + 5 x 7 = 42 valence electrons.

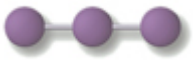
As above, the bonds plus the completed octets use 40 electrons. The two extra go on the central I atom. Must be AX_5E. Shape is a square pyramid. All bond angles are 90^o.



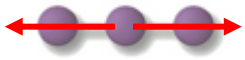
The four dipoles in the plane cancel each other out, but the vertical one is not cancelled out. F has a greater electronegativity than I, so the dipole looks like:



(f) predict the shape of and polarity IF_2^- .
7 + 2 x 7 + 1 = 22 valence electrons.
Two bonds use 4 electrons. Completing the octets on the terminal F atoms use another 12. This leaves 6 electrons to be placed as three lone pairs on the central I atom. Must be AX_2E_3. Shape is linear (180^o).



Although each I– F bond is polar, they point in opposite directions and cancel each other out. The molecule is therefore non–polar:



(g) predict the bond angles and polarities in the molecule methyl isocyanate, CH_3NCO.
Here, there are three "central" atoms - the C, the N and the other C. The shape around each can be predicted using VSEPR. Then the bond angles are obvious.

Valence electrons = 8 from the two C atoms, 5 from the N, 3 from the H's and 6 from the O for a total of 22.

The skeletal structure is:
H3C - N - C - O (where there is a single bond between the C and each H) This has used only 12 electrons. We can put 3 lone pairs on the O resulting in:

H3C - N - C - O:::

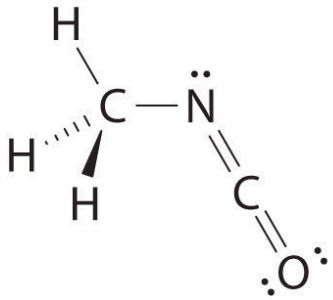
and put the last two pairs on the middle C and the N atom:

H3C - N: - C: - O::: which uses all 22 electrons. However, the N and the middle C do not have complete octets. We can therefore make double bonds by shifting the lone pair on the middle C to the left, and one lone pair on the O atom to the left as well:

H3C - N: = C = O::

Now look at each of the central atoms. The carbon at the left has four pairs of electrons around it, all bonding pairs. The shape around this C atom is therefore tetrahedral, with an ideal angle of 109.5 degrees.
The N atom has two bonds and a lone pair. The shape is therefore bent (120 degrees ideally).
The middle C atom has two bonding groups around it and no lone pairs. Bond angle must be 180 degrees.

The final shape looks like:



3. Resonance Structures

Sometimes there is more than one possible Lewis structure. The "correct" one is chosen based on the formal charges of the atoms in the molecules. In general, the correct structure:

a. has formal charges that sum up to the charge on the molecule
b. has formal charges on each atom that are as close to zero as possible

Which of the two structures of the cyanate ion, NCO^-, (A or B) is more likely [1], based on formal charges [2]? Why [2]?

A B

In structure A, the formal charges on the N, C and O atoms are -1, 0 and 0 respectively. In structure B, they are -2, +1 and 0. Thus, structure A is more likely because the formal charges are closer to zero.