The Periodic Table of Elements

The periodic table of elements exhibits many types of symmetry which we will try to understand better through careful consideration of examples. First, a word about the structure of the periodic table. The rows in the table represent the shells (roughly, see below) in which the different sets of electrons "live." The electrons in the higher shells, corresponding to heavier and more complex atoms, are further from the nucleus. One might ask why the periodic table does not go on and on and there are several possible explanations for this. Perhaps the best explanation would come from nuclear physics which studies the forces at work within the nucleus but we do not have the time or expertise to go into this.

Within each shell, the electrons come in pairs (assuming that there are enough of them to fill the shell) possessing opposite "spin." Spin is a magnetic phenomenon which, like the nuclear physics above, we also do not have the time or expertise to discuss. The first shell has only one pair of electrons and the unique pair is called 1s. The second shell has a 2s pair of electrons and 3 pairs labelled 2p. The third shell, like the second, has one 3s pair and three more 3p pairs. It also has a third series of orbitals, but they do not fill until entering the fourth row of the periodic table. These other orbitals are the *d* orbitals and there are five of them. In the fourth shell, there is one 4s pair, five 4d pairs (which do not fill until the fifth row) and nine 4f pairs (which do not fill until the sixth row!), and three 4p pairs. Of main importance to us will be the fact that the different electrons pairs within a given shell do not all possess the same energy and the gaps between the various energy levels are not evenly spaced. As far as increasing energy goes, the order of the electron pairs, for some of the lower shells, is roughly follows:

$$1s < 2s < 2p < 3s < 3p < 4s \sim 3d < 4p < 5s \sim 4d < 5p < 4f.$$

This sequence, plus the fact that new electrons will tend to go to the lowest available energy slot available, explain the structure of the periodic table.

Of central importance to us will be the way in which atoms bond together and how this influences the properties of the corresponding molecules. You will find some very insightful information in this regard in the two essays by Eugene Wigner, "On the structure of solid bodies" and "The Effects of Radiation on Solids." We will mainly be interested in studying the effects of ionic and covalent bonds. In an ionic bond, such as the one formed in salt, NaCl, one atom (the sodium atom) gives up an electron to the other atom (the chlorine atom): the corresponding molecule is stable because the chlorine atom has now filled its second shell while the sodium atom has emptied its third shell. The force holding the two atoms together is one of attraction, with the positively charged sodium ion being attracted to the negatively charged chlorine ion. In a covalent bond, such as that formed in carbon dioxide, CO_2, the atoms *share* electrons. Thus the carbon atom requires 4 electrons to fill its second shell while each oxygen atom requires two electrons to fill its second shell: there are just enough electrons in this configuration so that with the (total of) eight shared electrons all three atoms are stable. It is important to note that the notions of ionic and covalent bonds are simple conceptual models and that reality may be much more complex: in particular, a chemical bond can share both ionic and covalent characteristics.

The beauty of chemistry, from the point of view presented here, is that one can make predictions, based largely on symmetry, about which types of substances should be stable, which types of bonds should form between atoms, and even what properties different substances should have. Of course nature has lots of surprises in store but inevitably these surprises, when properly understood, involve some higher level of symmetry.

As you will find, there are difficulties with these theories of bonding, difficulties arising from the quantum nature of the particles involved. In particular, electrons are not localized in space and time and molecules are not rigid (except at temperatures approaching absolute zero). Molecules tend to alternate between different states: the more stable the state, the higher the probability that you will find the molecule in that state at a given time. The appropriate language for quantifying this behavior is that of quantum mechanics. One of the real triumphs of quantum mechanics is its ability to provide an accurate model for particle behavior. In quantum mechanics, roughly speaking, to an atom or molecule (or particle) is associated a state vector v which encodes the various (stable and unstable) configurations for the system, *along* with the probability that the system will be in that particular configuration at a given time.

One final note: molecular notation in chemistry is very much guided by symmetry considerations. When one writes H_2O for the water molecule, the fact that the two hydrogen atoms are not distinguished *means* that they must be in a symmetric position in the water molecule (at least in most of its stable states).

1. Looking at the periodic table, which atoms would you expect to have a “preference” for ionic bonding? Which would you expect to have a tendency to form covalent bonds?

a. Of all atoms, which do you think should have the greatest flexibility and variety in terms of the bonds they can form? Why?

b. Based on bonding considerations alone, which atoms do you think, together, have the greatest ability to form a large variety of stable, complex molecules?

c. How are the answers questions **a** and **b** related to living organisms?

2. Carrying problem **1** a little further, below is a list of *ionization energies*, the energy required to remove electrons from an atom, thereby creating a positively charged ion; the subscript indicates how many electrons are being removed (the units are kilojoules per mole):

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4560					
Mg	735	1445	7730				
Al	580	1815	2740	11600			
Si	780	1575	3220	4330	18100		
P	1060	1890	2905	4950	6270	21200	
S	1005	2260	3375	4565	6950	8490	27000
Cl	1255	2295	3850	5160	6560	9360	11000
Ar	1527	2665	3945	5770	7230	8780	12000

a. In each of the first six rows of the table there is a very large jump in the ionization energy at the end of the row. Why?

b. Why do you think the ionization energies tend to go up as you move down a column in the table?

c. Why do the ionization energies tend to *decrease* as one goes down a column of the *periodic table* (note: the above table does not give this information as it is a *row* of the periodic table)?

d. Why do you think that Phosphorous and Sulfur have comparable first ionization energies while the second ionization energy of phosphorous is less than that of sulfur?

e. Which quantum numbers do you think are associated to the sixth electron in a carbon atom? There are two natural, choices: it could either fill in the first of the three p–orbitals or it could go into one of the two empty p–orbitals.

3. Below is a list of bond strength for a variety of common molecular bonds (the units are again kilojoules per mole):

Bond	Strength
$O-O$	146
$O=O$	495
$C-O$	358
$C-N$	305
$C=N$	615
$C\equiv N$	891

a. Why do you think that the bond strength of $O=O$ is more than three times as strong as $O-O$? In what (molecular) form do you think oxygen is most often seen in our atmosphere?

b. In what molecular form do you think nitrogen is most often seen in our atmosphere? Do you think it is more or less stable than O_2?

c. Nitroglycerin has formula $C_3H_5N_3O_9$. It is of course extremely volatile, reacting in the following fashion:

$$4C_3H_5N_3O_9 \mapsto 6N_2 + 12CO_2 + 10H_2O + O_2 + \text{energy}.$$

Check that this equation is correct at the atomic level. Can you find the structure of the nitroglycerin molecule (Hint: there are exclusively single bonds)? Why do you think the energy term on the right is high? In the reaction, the left hand side is liquid while the terms on the right hand side are all gases. Why is nitroglycerin a powerful explosive? Nitroglycerin is the key ingredient in dynamite.

4. In a bicycling magazine, I found the following list of particularly offensive pollutants which one faces out there on the road:

a. ozone (O_3),

b. sulfur trioxide (SO_3),

c. carbon monoxide (CO).

For each of these gases, find and explain what you think the molecular structure might be, given the constituent atoms. What about carbon dioxide (a less noxious constituent of the air we breathe)? For ozone, we require the notion of *resonance*: this describes a situation where several different, more or less stable, molecular structures are possible, with the given constituent atoms. In the language of quantum mechanics, one could say that at any given time there is a certain probability of finding the molecule in one state or another. What are the different possible structures for the nitrate ion (NO_3^-) and the nitrite ion (NO_2^-)?

5. For each of the following molecules, describe the bonds and molecular structure you expect given the constituent atoms: sodium chloride (NaCl), methane (CH_4), ammonia (NH_3).

6. Suppose you have a solid substance which you find is a good conductor of electricity. Would you expect to find predominantly covalent bonds? What about ionic bonds? What type of struture do you think would be most favorable to conducting electricity?

a. Continuing this line of thought, do you expect the water molecule, H_2O, to have any "bond polarity," that is do you expect that one part of the molecule has a positive charge while another part has a negative charge?

b. What about the carbon dioxide molecule CO_2?