Chapter 6 – Electronic Structure of the Atom

Visible light is a small portion of the electromagnetic spectrum which spans radio and microwaves, to infrared, visible, ultraviolet, and X-rays.

All electromagnetic radiation travels at the speed of light, c, which is 3×10^8 m/s

The frequency of EM radiation is the greek letter ν, (nu), and $\nu = c / \lambda$

Three experiments led to the theory of quantum mechanics:
1) Blackbody Radiation – the phenomenon that hot objects emit light
2) The photoelectric effect – that metals can emit electrons when light with a high enough frequency hits its surface
3) The emission spectra of hydrogen – with its sharp distinct lines

The energy of a photon of light is equal to $E = h\nu$, where h is Planck's constant.

The photoelectric effect had three important observations
1) Light of a certain threshold frequency was necessary to cause electrons to eject.
2) The more light used the more electrons came out
3) The higher the frequency of light used the faster the electrons came out

The photoelectric effect strongly supported the theory of light as a particle

The emission spectra of hydrogen was noticed to fit a pattern where the energy of the different colored lines was proportional to $(1 / n_f^2 - 1 / n_i^2)$. This led to Bohr's theory of quantized energy states for the electron in the atom.

It was proposed that if light could act like a particle, then maybe particles (matter) could act like a wave.

The Heisenberg uncertainty principle states that there is an inherent limit to the accuracy with which the position and momentum of a particle can be measured simultaneously.

The electrons go around the atom in orbitals, which are not like orbits because the position of the electron cannot be predicted (like a planet). Instead the orbital represents a probability region of finding an electron.

Orbitals are denoted with quantum numbers, n, l, and m_l. The principle quantum number, n, determines the energy level associated with an orbital. l indicates if the orbitals are s, p, d, or f, and m_l indicates which subdivision of p, d, or f it is (for example if it is p_x or p_y)

An electron shell is the set of orbitals with the same number n, such as 3s, 3p, 3d.

s orbitals are spherical, p orbitals are dumbbell shaped

Orbitals can contain nodes where the probability of finding an electron is zero.

If orbitals have the same energy, for example the 3 different p orbitals, they are said to be degenerate.

2 electrons fit into one orbital, and one will be spin up and the other will be spin down

When filling electrons into orbitals start with the lowest energy orbitals first. For degenerate orbitals fill the orbitals with spin up electrons before putting in spin down electrons (Hund's Rule).

Know how to use the periodic table to write the full and condensed electronic configuration for most atoms in the periodic table. (i.e. Na : [Ne] $3s^1$) The 'answer key' is on page 248, don't be concerned with atoms that have an anomalous configuration compared to what you would expect from their position in the table.

The noble gas 'core' electrons in a condensed electronic configuration enable one to clearly see that the other additional, non-core electrons, are valence. Valence electrons are responsible for chemical bonds.

Chapter 7 Periodic Properties of the Elements

Mendeleev is credited with organizing the 1st periodic table. One reason why he gets credit is because his table left holes for undiscovered elements like Ga and Ge whose properties he accurately predicted, before they were discovered.

Many trends in the periodic table are caused because core electrons act to shield valence electrons from the nucleus. The valence electrons in the largest orbitals of the atom therefore, do not experience the full electrostatic attraction that one might expect from a positively charge nucleus. Instead, they experience a lesser attraction or an "effective nuclear charge" which is always less than the real nuclear charge. The equation for $Z_{eff} = Z - S$, where Z is the number of protons in the nucleus (the atomic number) and S is the number of core electrons that are acting as a <u>S</u>hield.

Since the nuclear charge increases from left to right on the periodic table, but the number of core electrons does not change (the atoms in a row all have the same noble gas core), the Zeff increases from left to right (L to R).

Since Z_{eff} increases from L to R the atomic radius decrease from L to R because the valence e- are more attracted to the higher Z_{eff} and are pulled closer to the nucleus – resulting in a smaller atom.

Atomic Radius increases from the top down because higher energy orbitals, which are larger, get filled with each row lower on the periodic table.

Combining these last two trends – atoms are smallest in the top right of the periodic table (He is the smallest) and largest in the bottom left (Cs is one of the largest common elements)

If an electron or multiple electrons are added to an atom to make it an anion, it will always have a larger radius than the neutral atom.

If an electron or multiple electrons are removed from an atom to make a cation, it will always have a smaller radius than the neutral atom.

Ionization Energy is the energy required to take an electron away from a metal atom in the gas phase: $M_{(g)} \rightarrow M_{(g)}^{+} + e-$ ΔE = ionization energy. [where M is some generic atom] The 2nd ionization energy is what is needed to remove another electron : $M_{(g)}^{+} \rightarrow M_{(g)}^{+2} + e-$ DE = 2nd ionization energy.

The 2nd ionization energy is always greater than the 1st ionization energy because the 2nd electron is being pulled away from a positively charged species, which it is very attracted to.

Atoms in the bottom – left of the periodic table have very low ionization energy. The atoms are very large and Z_{eff} is low so the electrons are not tightly held, therefore they are easily removed. Conversely, ionization energy is very large in the top – right of the periodic table.

Electron affinity is a measure of the energy released / required to add an electron to a neutral atom in the gas phase. $M_{(g)} + e- \rightarrow M_{(g)}^{-}$ ΔE = electron affinity. Because of the trend in Z_{eff}, atoms in the top – right of the periodic table (ie fluorine) have high electron affinity (the energy is large in magnitude, but negative in sign because energy is released when the ion forms). High electron affinity = they really want electrons.

The first column, the alkali metals (Li, Na, K..), are stable when they lose 1 e- to get a noble gas configuration, and the 2nd column the alkali earth metals (Mg, Ca, Sr..) lose 2 e- to get a noble gas configuration.

Both alkali and alkali earth are soft and light (low density) metals, compared to most other metals in the periodic table. They are reactive because they have low ionization energy and readily give up electrons to other atoms. They are also more reactive than most other metals in the table, and some for instance react violently with water.

Halogens (F, Cl, Br, I) exist as diatomic species F_2, Cl_2, Br_2, I_2. F_2 and Cl_2 are gases, Br_2 is a liquid, and I_2 is a solid at room temperature. They are reactive because they have high electron affinity and will take electrons from many other atoms.

The noble gases (He, Ne, Ar, Kr..) are not reactive at all. Their electron shells are completely full. They neither want to give or receive electrons. Therefore, they don’t react with any other atoms.

Chapter 8 Chemical Bonding

There are 3 types of chemical bond: ionic bonds, metallic bonds, and covalent bonds.

Ionic bonds are an electrostatic attraction between negative and positive ions, which are always metal ions (ie Na^+) and nonmetal ions (ie Cl^-, or SO_4^{-2}). Ionic compounds form crystal lattices of cations and anions and this arrangement of + - + - greatly stabilizes the ions. The resulting stability arises from the lattice energy associated with the crystal. The lattice energy is defined as how much energy is require to pull the crystal apart, but it can also be thought of in reverse, as how much energy is 'gained' when the ions come together to form a crystal.

Metallic bonds are formed by the 'sea of electrons' which move between metallic nuclei in a piece of metal. Since each metal atom only holds its valence electrons loosely, the electrons on one atom readily change hands and move to other atoms. This flowing sea of electrons is why metals conduct electricity and heat, and also explains why they can be deformed (malleable, ductile) so easily.

The Covalent bond occurs when two atoms 'share' electrons. These bonds will occur between nonmetals, which are looking to gain another electron from somewhere. If a nonmetal can't take an electron completely (ie Cl^-, from a Na atom) then it may share an electron with another atom in the same situation. For example, Cl wants 1 e- to have the configuration of Ne, if two Cl atoms share one electron they can both have the configuration of Ne. So they'll form a Cl_2 molecule.

In addition to trying to attain noble gas configurations it is also stabilizing to have half full orbitals. For example, Cr has an anomalous electronic configuration. It should be Cr: [Ar] $4s^2$ $3d^4$, but it is actually Cr: [Ar] $4s^1$ $3d^5$. By promoting and s-electron it now has a half-full s orbital and a half-full d shell. These half full shells are stabilizing, compared to partially full orbitals.

Lewis structures indicate how many valence electrons an atom has and whether they are free to bond with something (single dots) or if they are nonbonding lone pairs (two dots). If two atoms have a single dot (electron) they may come together to share that dot (electron) and form a covalent bond, indicated by a single line. The dots can be thought to correspond to the arrows in the electronic configuration diagrams. (ie. N:[He] $2s^2$ $2p^3$, so it would have a 2s box with an up and a down arrow, and then three up arrows in the 2p group of boxes. The Lewis symbol for nitrogen has a pair of dots on one side, and three single dots on the other sides).

Multiple bonds (double or triple bonds) can be formed by sharing two or three pairs of electrons, respectively.

Triple bonds are shorter (in length) and stronger than double bonds, which are shorter and stronger than single bonds.

While all covalent bonds share electrons between atoms, not all of them share equally. Some atoms are more electronegative than others. Electronegativity is very much like electron affinity in that it is an indication of how much an atom ‘wants’ and electron. Like electron affinity, atoms in top right of the periodic table have high electronegativity. These atoms will therefore pull more strongly on shared electrons in a bond with an atom that is less electronegative. The result of this uneven pulling is a polar bond.

A polar bond means that electron density is higher on one side of the bond than the other. There is a net dipole. A dipole means there are two poles, a positive end and negative end. (like the N and S poles of the earth)

Procedure for Drawing Lewis Structures:
1) Count number of valence electrons from each atom
2) Place least electronegative atom in center (if formula is AB_2, usually A is central atom)
3) Place electrons around surrounding atoms to complete their octet
4) Put remaining electrons around central atom to complete its octet. If there are no enough electrons – try making double / triple bonds
5) Check the formal charge on all the atoms, the configuration with the lowest formal charges is best.
6) Indicate any resonance structures

Exceptions: S, P, Cl (and larger atoms) can have more than 8 e-

Note: basically all these rules can have exceptions except for #1.

The Lewis structure for ions should have the ion surrounded in brackets with the charge in the top right.

The formal charge is the # of valence electrons – the # assigned electrons in the structure.

Resonance structures are drawn if there are multiple configurations that satisfy all the rules. The alternate structures should be drawn next to one another with double headed arrows in between, indicating that the molecule can switch between those configurations. In reality molecules are neither one structure or the other, but are constantly switching.

There are 3 exceptions to the octet rule #1) having an odd number of electrons – which is very rare. #2) Having less than 8 electrons, typically only Be and B do this. #3) Overfilling the octet with 10 or 12 electrons. This is fairly common for larger atoms such as S, P, Cl and atoms below them in the periodic table.

General trends in Lewis structures to look for:

C – often makes 4 bonds (any combination of single, double, and triple to total 4). Rarely has lone pairs.

N – often makes 3 bonds with a lone pair (ie NH_3) or four bonds with +1 formal charge (ie NH_4^+)

O – often makes two bonds (two single or one double) and has two lone pairs (ie. H_2O). Another common way to find it is with one bond and three lone pairs, and a -1 formal charge (ie. OH^-)

Chapter 9 Molecular Geometry and Bonding Theories

The valence shell electron repulsion (VSEPR) model is based on the fact that electrons, both in bonds and nonbonding, will repel one another. Based on the number of electron domain basic shapes will form and then actual shapes of molecules can be predicted by taking into account how many nonbonding electron pairs there are.

An electron domain is a region of electron density around an atom. A bond with another atom (whether it is single, double, or triple, it doesn't matter) is an electron domain. Each lone pair of electrons is also an electron domain. By counting these, the basic shape around a central atom can be found. For example, if there are 4 domains, as in the case of the four bonds to hydrogen in CH_4, then the shape is going to be tetrahedral.

The shapes come from the table on page 349. 2 electron domains – linear, 3 – trigonal planar, 4 – tetrahedral, 5 – trigonal bipyramidal, 6 – octahedral
DO NOT MEMORIZE this entire table. Just be recognize and understand the basic shapes and be able to fill in a couple of blanks if some parts of the table were omitted.

Nonbonding pairs are slightly larger than bonding pairs and can act to compress some bond angles. For example, the normal angle for a tetrahedral bond is 109° (ie CH_4), but in NH_3 where one arm of the tetrahedron is a lone pair the other bonds are flexed a little closer so the angle is 107° (don't memorize the numbers, just understand the concept)

Just like bonds can be polar, an uneven sharing of electrons, so can entire molecules. If there are several polar bonds in a molecule the entire molecule will be polar unless each dipole associated with each polar bond cancels. Whether or not dipoles cancel depends mostly on symmetry. If electrons are pulled equally in multiple directions they may all cancel (ie CCl4, each bond is polar but because of the symmetry of the tetrahedron they all cancel). If they do not all cancel one end of the molecule will have a higher density of electrons than another end – this is said to be a polar molecule. Water is a polar molecule. Oil (most hydrocarbons) are nonpolar. Polar and nonpolar compounds do not mix.

The idea that valence electrons are shared to form covalent bonds doesn't in itself explain why VSEPR yields the correct predictions for a molecules shape.

The standard atomic orbitals, like s and p, do not look like tetrahedron or trigonal planar, so where do these shapes come from?

All the shapes in the VSEPR model can be obtained using the idea of hybrid orbitals. If an s orbital and a p orbital are mixed (hybridized) the result is two sp orbitals. Each sp orbital resembles a p orbital but it is asymmetric with one lobe being much larger and rounder than the other lobe. Combining the two sp orbitals results in two electronic domain which are linear (like the 1st row of the VSEPR shapes)

Combining s and two p orbitals results in three sp^2 obitals. Each sp^2 orbital is a large lobe and a small lobe and when the three sp^2 orbitals are put together they form a trigonal planar geometry.

Combining s and three p orbitals results in four sp^3 orbitals. Each sp^3 orbital is a large lobe and a small lobe and when the four sp^3 orbitals are put together they form a tetrahedron.

d orbitals may also be combined and sp^3d have the shape of a trigonal bipyriamid and sp^3d^2 has the shape on an octahedron.

For all hybrid orbitals the number of starting orbitals = the number hybrid orbitals.

To hybridize an orbital an electron must be promoted from a full s or p shell into an unfilled p or d shell respectively. The hybridized orbital is intermediate in terms of energy between the s and p orbitals that make it up. That is, the energy is $s < sp < p$.

Hybrid orbitals can be used to visualize how bonds look in 3-dimensions. Bonds involving s orbitals or s orbital hybrids (sp, sp^2, or sp^3) are sigma bonds (sigma is a greek 's'). Sigma, σ, bonds have 'head to head' overlap and have the electrons in the bond in the line between the two nuclei.

Pi, π, bonds are formed between p orbitals. They have side-to-side overlap, and the electrons are above and below the line between the nuclei.

All single bonds are sigma bonds. All double bonds are 1 sigma and 1 pi, and all triple bonds are 1 sigma and 2 pi bonds.

For resonance structures, the electrons are delocalized in the p-orbitals and are really spread across the entire molecule, such as in the nitrate ion (NO_3^{-2}) or in benzene C_6H_6.