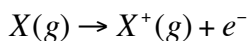


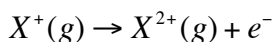
Thoughts for the Day
CH301 Fall 2010
09/02/10

We can now go into the lab and measure how much energy we need to put into an atom to get the electron to escape the potential of the nucleus. This is the ionization energy



This amount of energy needed to make this happen is the ionization energy. Strictly speaking it is the first ionization energy, generally written as IE_1 .

The energy to get the second electron off is IE_2 and is the energy for the following



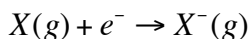
It always required more energy to get the 2nd electron off (the now positive particle). That is $IE_2 > IE_1$ for every element.

However there are large trends in the IE for the elements.

If we look at the trends we see that IE goes up as we go across the periodic table from left to right with the noble gases being the highest IE in each row. As we move up on Z unit from noble gas back to group 1 we see that the IE decreases dramatically.

This gives up the “idea” of “shells” of electrons. The reason that Na is so much easier to ionize than Ne must be because the electrons in Na don't feel the entire attraction of the nucleus (which has a higher charge). If they did, then the IE would be higher, but it is much lower. Therefore we come up with a picture in which there is a “core” of electrons in Na which “shields” the nucleus. Then the outer most electron feels a reduced pull from the nucleus. We can say that rather than using Z in the Coulomb equation we should instead use an effective Z_{eff} . This Z_{eff} will always be smaller than the true Z. It is as if the negative electrons of the core are “canceling” out some of the positive charge of the nucleus. (you should note: this is a completely classical picture of the electrons in an atom that is in fact not what is actually happening. However, it always us to get a hand wavy perspective on what is going on with periodic trends).

Finally, we discussed electron affinity. Some elements mostly group 6 & 7 release energy if they add another electron to the atom to form an anion (negative ion).



The amount of energy released in this reaction is the electron affinity.

You should note that even though IE and EA are tabulated as positive numbers you should think about them as having opposite sign. IE is energy IN. Therefore we use it as a positive number. EA is energy OUT. Therefore we should use it as a negative number. This is important when we look at ionic bonding and we are trying to figure out how much energy is required to form the cation and anion. We need to put energy in to make the cation. We get energy back (the EA) when the anion is formed. The total energy is then the $IE - EA$.

Electronegativity

In thinking about bonding we want to know where the electrons in a molecule reside. One way to think about this is to compare atoms one to another and decide if the electron would have a lower energy on one or another. This is the idea of electronegativity. This is the propensity of an element to attract electrons to itself compared to other elements.

We have two derivations of the same idea.

Mulliken's EN

$$EN \propto \frac{1}{2}(IE + EA)$$

This is very straight forward. An element will have a high EN if it has a high IE as it is unlikely to lose its electron to the other element. An element will have a high EN if it has a high EA as it is very favorable for the element to add another electron. (note: here we use both numbers as tabulated as their positive values)

Paulings Scale

Linus Pauling EN scale has to do with bonding. He looked at the energies required to break bonds and formulated the following idea.

A pure covalent bond (exactly equal sharing between the two elements) between two elements A & B should have a bond strength that is the average of the strength of the bonds of those two elements with themselves.

That is an A-B bond should be the average of a A-A bond and a B-B bond

He formulated this as a geometric average (the square root of the two multiplied by each other)

$$\Delta E_{A-B}^{\text{purecovalent}} = \sqrt{\Delta E_{A-A} \Delta E_{B-B}}$$

Where ΔE is the bond strength

Then he looked at the difference between the real bond strength for A-B and this hypothetical A-B covalent bond. If the two atoms did not “share” the electron equally this would add to the bond strength as there would be an added ionic coulomb attraction. The larger this ionic component, the larger the shifting of charge from one atom to another, the larger the difference between the actual and pure covalent bond strength. This difference he called Δ

$$\Delta = \Delta E_{A-B}^{actual} - \Delta E_{A-B}^{purecovalent}$$

Δ then depends on the electronegativity difference between the two elements. If they have identical electronegativities then Δ must be zero. The larger the difference the larger Δ . To quantify this the relationship is that the electronegativity difference is equal to a constant times the square root of Δ .

$$\chi_A - \chi_B = 0.102\Delta^{1/2}$$

Trend in EN

EN increases left to right in the periodic table.
EN decreased top to bottom

How should we think about bonds from a potential energy stand point. There are many forces at work. Electron-nucleus attraction, electron-electron repulsion, nucleus-nucleus repulsion. At many distances. We would like to simplify the problem to a single effective potential and a single coordinate, the distance between the two nuclei.

Percent ionic character

Diatomic molecules like this in the gas phase are generally not 100% ionic (which is a whole electron moving from one atom to another). This can be estimated by measuring particular properties of the molecule.

Dipole moments

A dipole is two equal but opposite charges (q) separated by a distance (R). The dipole moment is given by

$$\mu = qR$$

The dipole moment is typically measured in unit of Debye. 1 D is charges of +/- 1 electron at a distance of 0.2082 Å.

We can use what we measure in the lab to deduce the charges on the molecule and thus the % ionic character.

First we measure the bond length and then the dipole

$$\mu(D) = \frac{\text{bondlength}(\text{\AA})}{0.2082\text{\AA}} \times \delta$$

From this we can find the partial charges (or percent ionic character) of the bond. This is given by the lower case delta.