

V25.0109: General Chemistry I (Honors)

Notes for Lecture 10

In this part of the course, we will set aside quantum mechanics briefly and discuss the so-called classical theory of chemical bonding. In our crude classical picture, electrons are viewed as point particles that move in stable classical orbits determined by Newton's second law around the atoms in a molecule. Because the nuclei are several thousand times more massive than electrons, we regard the nuclei as fixed on the time scale of significant "classical" electron motion.

Despite our crude classical picture, however, a conceptually useful definition of chemical bonding can be stated that relies on the relatively high mobility of the electrons compared to the nuclei:

Chemical bonds are formed either by one atom's transferring electrons to another atom or by two atoms' sharing electrons between them, or something in between these two situations.

I. ENERGETIC CONSIDERATIONS OF CHEMICAL BONDING

Based on our crude, conceptual definition of chemical bonding, it is clear that an important issue concerns the ability of atoms to give up electrons to or accept electrons from other atoms.

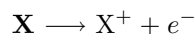
In order to quantify this notion, there are two energies that are relevant. These are:

1. **Ionization energy** – Measures the ability of a neutral atom to lose an electron.
2. **Electron affinity** – Measures the ability of a neutral atom to gain an electron.

Let us examine these in greater detail:

A. Ionization energy and the shell model of the atom

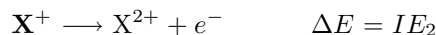
Consider the reaction describing the loss of an electron by a neutral atom:



Note that the new element of charge balance has come into chemical equations: the total charge on both sides is the same, zero in this case. The energy required for this reaction to occur is the change in energy ΔE between the products and reactants:

$$\Delta E = E(\text{products}) - E(\text{reactants}) = IE_1$$

where IE_1 stands for the first ionization energy. The term "first" or the "1" subscript is to distinguish this energy from the second ionization energy, which is the energy to remove an electron from the *ionized* species \mathbf{X}^+ :



The energies IE_1 and IE_2 are always positive and measure the stability of so called "outer shell" electrons of an atom. The higher the ionization energy, the greater the energy "cost" to remove an electron, hence the lower the tendency for such an atom to act as an electron donor in a chemical bond.

In general, IE_n is the n th ionization energy. The first ionization energy IE_1 tends to increase across each period, with the highest value occurring for the inert gases. This suggests that in this group, the elements have an especially high stability. On the other hand, if we look at the trend in IE_n as a function of n for a given element, an interesting phenomenon occurs. Consider the element sodium (Na). In units of MJ/mol, the first 10 ionization energies are $IE_1 = 0.5$, $IE_2 = 4.56$, $IE_3 = 6.91$, $IE_4 = 9.54$, $IE_5 = 13.35$, $IE_6 = 16.61$, $IE_7 = 20.11$, $IE_8 = 25.49$, $IE_9 = 28.93$, $IE_{10} = 141.37$. If we plot the log base 10 of these values vs. n , the plot appears as shown below:

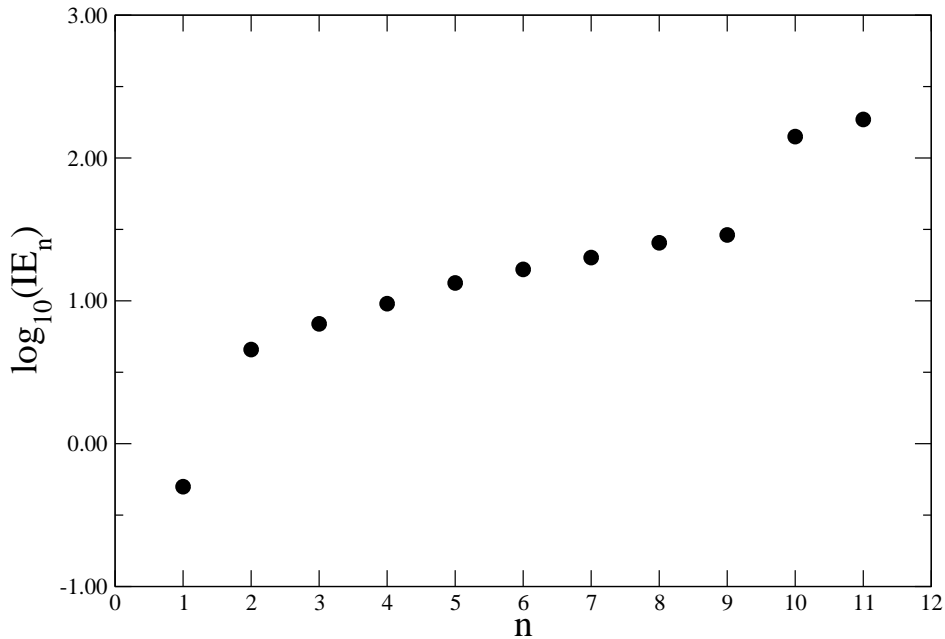


FIG. 1. Plot of ionization energies for Na.

From the plot, one sees three regions of stability. The first electron is removed easily, electrons 2-9 fall into an intermediate range, while electrons 10 and 11 are especially difficult to remove. In an attempt to explain this “shell”-like structure, we next consider the so-called classical *shell model* of the atom.

In order to appreciate how the shell structure arises, we must start by writing down the total energy of a molecule, viewed classically simply as a set of positive and negative charges. Suppose a molecule is composed of N nuclei at positions $\mathbf{R}_1, \dots, \mathbf{R}_N$ with charges Z_1e, \dots, Z_Ne and masses M_1, \dots, M_N and M electrons at positions $\mathbf{r}_1, \dots, \mathbf{r}_M$. If the nuclei at these positions have instantaneous momenta $\mathbf{P}_1, \dots, \mathbf{P}_N$ and the electrons have momenta $\mathbf{p}_1, \dots, \mathbf{p}_M$, then the total energy is

$$E = K + V$$

Considering the kinetic energy of the nuclei and the electrons, the Coulomb repulsion between the electrons, the Coulomb repulsion between the nuclei, and the Coulomb attraction between the electrons and nuclei, the total energy can be written as

$$E = \sum_{I=1}^N \frac{P_I^2}{2M_I} + \sum_{i=1}^M \frac{p_i^2}{2m_e} + \sum_{i>j} \frac{ke^2}{r_{ij}} + \sum_{I>J} \frac{kZ_I Z_J e^2}{R_{IJ}} - \sum_{i=1}^M \sum_{I=1}^N \frac{kZ_I e^2}{R_{iI}}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, $R_{IJ} = |\mathbf{R}_I - \mathbf{R}_J|$ and $R_{iI} = |\mathbf{r}_i - \mathbf{R}_I|$. This energy is a universal that describes all of ordinary matter. Since any chemical system, from proteins, cells, organisms, semiconductors, computer chips, polymers,... can all be considered as collections of nuclei and electrons, this energy is *always* the starting point for a microscopic description. The only parameters that distinguish one system from another are the numbers and types of nuclei and the number of electrons.

Let us apply the potential energy formula above to a single atom with nuclear with charge Ze and M electrons. Since there is only one nucleus (only one positive charge), there is no nuclear-nuclear repulsion term so that $V_{nn} = 0$. If the nucleus is fixed at the origin, then the potential energy V can be written simply as

$$V = -\frac{Ze^2}{4\pi\epsilon_0} \sum_{i=1}^M \frac{1}{r_i} + \frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{M-1} \sum_{j=i+1}^M \frac{1}{r_{ij}}$$

where we have used $k = 1/(4\pi\epsilon_0)$. Here $r_i = |\mathbf{r}_i|$ is simply the distance of each electron from the origin. If we consider the case of the Li atom, for example, for which $Z = 3$ and $M = 3$, the formula becomes

$$V = -\frac{3e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3} \right) + \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \right)$$

The formula requires knowing the distances of each of the 3 electrons from the origin as well as the three distances $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, $r_{13} = |\mathbf{r}_1 - \mathbf{r}_3|$ and $r_{23} = |\mathbf{r}_2 - \mathbf{r}_3|$ between the three electrons.

The potential energy, even for lithium, is a complicated function of the electron position variables. As a consequence, we cannot solve for the stable orbits of the electrons using classical mechanics. However, a simple approximation serves to explain why some electrons are more stable than others. In the shell model, we imagine fixing one of the electrons, say electron 1, and then letting all of the other electrons move around classically. The effect of the moving electrons on the fixed electron is then taken into account in an average sense, averaging over a long time period. The fixed electron will then see an *effective* potential that is a simple Coulomb form given by

$$V_{\text{eff}}(r) = -\frac{Z_{\text{eff}}e^2}{4\pi\epsilon_0 r}$$

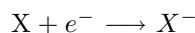
where Z_{eff} is an effective charge that results from the nucleus and the averaged motion of the electrons we did not fix. We can now generate an effective potential for electron 2 by first removing electron 1 entirely, fixing electron 2 and letting the remaining electrons move around to generate an effective potential. It is clear from this idea of successively removing electrons and generating effective potentials for one of the remaining electrons that *each electron will have a different effective potential!*

So now let's consider what happens for the case of sodium (Na), for which $Z = 11$. If we consider the effective potential of electron 1 by averaging over the motion of the remaining 10 electrons (this can be done relatively easily using a computer), we obtain a value of $Z_{\text{eff}} \approx 1$. It's not exactly 1, but close enough to 1 that we will call it 1. For electron 2, we now remove electron 1, and compute an effective potential by averaging over the motion of the remaining 9 electrons, and we obtain a value of $Z_{\text{eff}} \approx 5$. It's not exactly 5 but pretty close. Repeating this procedure for electrons 3, 4, 5,... up to 9, we find that Z_{eff} does not change much from 5. It's a little different for each electron, but the value for electrons 2-9 is fairly close to 5. However, if we now consider electrons 10, the value of Z_{eff} changes suddenly to a value quite close to 11. Obviously, for electron 11, the value of $Z_{\text{eff}} = 11$ exactly because the only charge electron 11 sees is the nuclear charge (which is exactly 11). Thus, we see very roughly, that three effective charge values $Z_{\text{eff}} = 1, 5, 11$ emerge from the shell model, and these values correspond to the shells observed in the energy plot above.

Electrons in the innermost shells with the highest values of Z_{eff} are called *core electrons*, and they tend to be unimportant for chemical reactivity. Electrons in the outermost shells, with low values of Z_{eff} are called *valence electrons*, and these are the most important in chemical reactions. The importance of electrons in shells with intermediate values of Z_{eff} in chemical reactions depends on the chemical process under consideration. Their role is likely to be important but indirect in that they can affect the distributions of valence electrons and influence their role in chemical bonding without, themselves, participating in chemical bonds.

B. Electron affinity

The electron affinity measure the ability of a neutral atom to gain an electron, as described by the reaction:



The electron affinity, EA is defined to be the negative of ΔE for this reaction:

$$EA = -\Delta E = E(\text{reactants}) - E(\text{products})$$

EA can be either positive or negative. If $EA > 0$, attachment is stable. If $EA < 0$, attachment is unstable, and the electron must be forced to stick to the atom.

C. Electronegativity scale

The electronegativity measures the ability of an atom to draw electrons to itself in a chemical bond. While it is reported as an atomic property, it is concerned with bonding within a molecule. One definition of electronegativity that was proposed by Mulliken in 1934 is particularly simple, being a simple arithmetical average:

$$\text{electronegativity} \propto \frac{1}{2}(IE_1 + EA)$$

The larger the electronegativity, the greater the tendency for an atom to draw electrons to itself in a chemical bond.

In general,

if IE_1 and EA are both large, giving up an electron is unlikely, but gaining an electron is likely, and the atom tends to act as an *electron acceptor*, or is “electronegative.”

if IE_1 is small, and EA is small or negative, giving up an electron is likely, but gaining an electron is unlikely, and the atom tends to act as an *electron donor*, or is “electropositive.”

Elements toward the left of the periodic table have low electron affinities, so they tend to act as electron donors, while atoms to the right of the periodic table have high electronegativities, and they tend to act as electron acceptors.

II. THE LEWIS DOT MODEL

When atoms are brought into some arrangement, the problem of determining the chemical bonding pattern amounts to figuring out where the electrons are and what they look like. The solution of this problem is known as *electronic structure theory* and is a quantum mechanical problem. All of chemical bonding can be explained by solving the Schrödinger wave equation, which we will discuss in the next chapter.

A simple model, developed by Lewis in 1916, exists that can be used to gain a qualitative understanding of chemical bonding and electronic structure. This is the Lewis dot model.

The Lewis model involves recognizing that not all electrons in an atom play a role in chemical bonding. Electrons that are closest to the nucleus for a set called the *core* electrons. These are generally chemically inert and not important for chemical bonding.

The outermost electrons of an atom, called the *valence electrons* are chemically, important, however, and are treated within the Lewis model.

It is worth noting that for quantitative accuracy, the effects of core electrons does need to be included in some approximate way. This can amount to a particularly difficult problem, especially in heavier elements, where the charge on the nucleus is large, and hence the forces on core electrons cause them to move at speeds near light speed. In that case, a fully relativistic treatment of core electrons is necessary, so if you thought your study of relativity theory in physics was useless, think again.

For elements in groups I-VIII in the periodic table,

$$\# \text{ valence electrons} = \text{group \# in periodic table}$$

Helium is an exception to this rule, having only 2 valence electrons.

Note that the group VIII elements, known as the noble gases, have 8 valence electrons (except He, which has only 2) and are highly non-reactive. We can surmise that 8 valence electrons is a kind of magic number giving special stability to the electronic structure of the atom. We call this an *octet*, which plays an important role in the Lewis model.

As an example of identifying the number of valence electrons, consider the second period:

