LECTURE 1

STRUCTURE DETERMINES PROPERTIES

1. Atomic Structure.
   - Nucleus and electrons. Nucleus consists of protons and neutrons. Atomic (Z) and mass (M) numbers. Isotopes.
2. Electronic Structure.
   - The element's properties are determined by the # of protons, and thus by the number of electrons;
   - According to the *De Broglie*'s concept, electrons have wave-like properties;
   - *Schrödinger*'s equation derives particular energy states for the electrons in atoms. In other words, energy states (levels) are quantized. To each energy state corresponds a particular wave function or orbital.
   - *Heisenberg*'s uncertainty principle states that electrons cannot be found with 100% accuracy at any point in space. Rather, there is a certain higher probability for finding them in particular regions of space – orbitals.
   - Orbitals differ in shape and energy, they are arranged in shells, according to the so-called principal quantum number *n*. For *n* = 1, only *1s* orbital. For n = 2, one *2s* and three *2p* orbitals. Show shapes of *s* and *p*-orbitals. Discuss nodes! The *p*-orbitals are degenerate, i.e. of equal energy, but differently directed in space.
   - Electrons have spins and spin quantum numbers. The spin quantum number has two values: +1/2 or –1/2.
   - *Pauli*'s exclusion principle states that any orbital can be occupied by a maximum of two electrons, with opposite spins.
   - *Hund*'s rule states that degenmerate orbitals are first all singly occupied, before any of them is double occupied.
   - The filling of shells. Valence electrons.
   - The octet rule of *G. Lewis* – atoms transfer OR share electrons, with the end goal of achieving octets (i.e. filled shells) of valence electrons. This is the electronic configuration of a noble gas.
3. Bonding and types of bonds. Ionic and Covalent bonds.
   A. Ionic Bond: One way to achieve an octet configuration is via a complete transfer of a certain # of electrons. This is the ionic bonding. Neutral atoms are converted to ions, which attract each other.

   B. Covalent Bond: Much more applicable to organic chemistry. Give first example with a "same-element molecule", such as hydrogen or chlorine. Then show methane, ethane – how to draw Lewis structures in general. Some more examples with unshared pairs – methanol, ethylamine. Unshared pairs (or lone pairs) are very important. The number of bonds that an atom forms corresponds to its ***valence***.

   C. Multiple Bonds: The multiplicity of the bond is directly determined by the # of electron pairs that two atoms have to share. Double bond, triple bond. Give examples.

   D. Non-polar vs. Polar Bonds: If elements are the same, as in hydrogen or chlorine molecule, then non-polar, but if different, then there is an electronegativity factor. Roughly speaking, it reflects the element's ability to attract electrons. Most useful scale is that of Pauling. Some general trends in ***electronegativity***. A more electronegative element will tend to attract more strongly the shared electrons of a covalent bond, making it polar. This leads to the creation of partial charges, δ+/–, at the corresponding centers.

   E. Quantitative measure – the dipole moment (charge δ times the distance between charges). Some times dipole moment in a bond means a dipole moment in a molecule, sometimes it doesn't – depends on the molecular structure. Examples!!

   F. Formal and Real Charges: As discussed with the polar bonds, this leads to the creation of some real charges δ+/–. In chemistry exists the term formal charge, which is easily determined:

   Formal Charge = group # - lone pair electrons – ½(shared electrons)

   Examples: methanol, $BF_3.H_2O$, ammonium ion (here also show ionic bond to Cl^- in ammonium chloride), methyleneimine. Formal charges do not necessarily correspond to real charges.

G. How to write a Lewis structure: The rules are as follows:

   a. Count the total number of electrons available **(A)**;
   b. Calculate the total number of necessary electrons **(B)**, in order for each atom to achieve an octet (Hydrogen needs only two electrons!!);
   c. Subtract and divide: **(B – A)/2 = number of bonds**;
   d. Construct a meaningful structure with the above calculated number of bonds;
   e. If electrons remain, first assign lone pairs to the terminal atoms, then to the central atoms, wherever necessary;
   f. Assign formal charges, if applicable;

      Do not forget: Hydrogens are ALWAYS terminal!

4. Structural Formulas of Organic Molecules – the conventional structural formulas are often a tedious way to depict organic molecules, particularly large ones. Thus two ways have been introduced for a more concise representation of molecules:

   A. Condensed structural formulas – molecules are represented with majority (or all) bonds being omitted.

   B. Bond–line formulas – bonds are represented by lines and carbon atoms are the crossing points of lines. Hydrogens at carbons are not explicitly shown. Heteroatoms and hydrogens at Heteroatoms ARE explicitly shown.

5. Constitutional Isomers – often, for given molecular formula, one can write more than one plausible Lewis structure, and as it turns out, they could correspond to real molecules. Obviously such molecules will have the same count of atoms for each element, i.e. they would be isomers. The difference is in the way the atoms are connected to ach other, i.e. these are constitutional (or structural) isomers.

6. Resonance – certain molecules or ions cannot be properly described by a single Lewis structure, but as a combination of several, RESONANCE structures. Please remember always: Resonance structures ARE NOT real structures but only formal descriptions of a single molecule. The double-headed resonance arrow DOES NOT signify equilibrium between structures. There are certain rules for writing and assigning importance to resonance structures:

   A resonance structure is acceptable if:

   - It is a meaningful Lewis structure (Please refer to rules for writing Lewis structures!)
   - Electrons are moved but the skeleton of the molecule is retained

   A resonance structure has a greater importance if:

   - It contains a greater number of bonds and atom octets
   - It has minimum charge separation
   - The negative charge resides on a more electronegative atom

7. Acids and Bases.

   A. The *Arrhenius* Theory – according to *Arrhenius* theory, acids are compounds, which dissociate in water to give hydrogen ions (protons); bases are compounds, which dissociate in water to give hydroxide anions.

   B. The *Brønsted – Lowry* theory – according to *Brønsted* and *Lowry*, acids are compounds that donate protons, while bases are compounds that accept protons. Thus any acid-base reaction leads to a proton exchange, and the end result is another acid-base pair, known as the conjugate base and conjugate acid of the original acid and base. In water, one of the partners (serving as either acid or base) is the water molecule. Since an acid-base interaction leads to another acid or base, the overall result is an equilibrium, shifted towards the weaker acid-weaker base pair. The equilibrium is quantitatively defined via equilibrium constant K_a (if acid) or K_b (if base). Practically results are reported as pK_a or pK_b. pK_b can be avoided altogether, since one can compare the pK_a's of the conjugate acids (the stronger the conjugate acid, the weaker the corresponding base!!).

   C. Factors affecting the strength of acids (See separate handout!!).

D. *Lewis* theory – according to *G. Lewis*, acids are compounds that can accept electron pairs; bases are compounds that donate electron pairs. *Lewis* theory expands the notion of acids and bases, as it eliminates the hydrogen ion (proton) as a mediator for acid-base interaction. Lewis acid-base reactions are extremely common in organic chemistry. In organic terminology, Lewis bases are often called nucleophiles, while Lewis acids are known as electrophiles.

After this lecture you should know and be confident on the following topics:

- Writing Lewis structures, including the determination of formal charges;
- Writing proper resonance structures and capable of qualitatively evaluating their stability and relative contribution;
- Be capable of representing a molecule by using the abbreviated notations, such as condensed structural formulas and ESPECIALLY the bond-line formulas;
- Have firm knowledge about acids and bases. Particularly the *Brønsted-Lowry* and the *Lewis* theories. I assure you that we will be mentioning and working with *Brønsted* and *Lewis* acids and bases throughout this entire course;