Chemistry Honors – Lesson 5 Thermochemistry

All chemical reactions are accompanied by changes. One such change is the change in energy. Thermal, chemical, potential and kinetic energies are all interconvertible as they must obey the **Law of Conservation of Energy**. The law states that total energy in a system is created nor destroyed but changes from one state to another. Energy changes determine whether reactions can occur and how easily they will do so. So understanding **thermodynamics** is essential in understanding chemistry. The application of thermodynamics to chemical reactions is called **thermochemistry**. Several thermodynamic definitions are useful in thermochemistry.

- 1. **System** is the particular part of the universe being studied; everything outside the system is considered the surroundings or environment. A system may be:
 - a. **Isolated** when it cannot exchange energy or matter with the surroundings, as with an insulated bomb reactor
 - b. **Closed** when it can exchange energy but not matter with the surroundings, as with a steam radiator
 - c. **Open** when it can exchange both matter and energy with the surroundings, as with a pot of boiling water
- 2. **Process** when one or more of a system's properties changes. A process is associated with a change of state
 - a. Isothermal occurs when the temperature of a system remains constant
 - b. Adiabatic occurs when no heat exchange occurs
 - c. Isobaric occurs when the pressure of the system remains constant

<u>Heat</u>

Heat is a form of energy which can easily transfer to or from a system, the result of which is a temperature difference between the system and its surroundings. This transfer will occur from a warmer system to a cooler system. When heat is absorbed from the surroundings, its is called **endothermic**. When a system releases heat to its surroundings its is called **exothermic**. By convention, the heat absorbed by the system is positive and heat lost to the environment is negative.

Calorimetry measures heat changes. The term **calorie** is a unit of measure equal the amount of heat required to raise the temperature of 1 gram of water by 1 degree Celsius. The heat absorbed or released in a given process is calculated from the equation:

$q = mc\Delta T$

where q is the heat, m is the mass, c is the **heat capacity** and ΔT is the change in temperature.

States and State Functions

The state of a system is described by the macroscopic properties of the system. Macroscopic properties include temperature (T), pressure (P), and volume (V). When the state of a system changes, the values of the properties change. Properties whose magnitude depends only on the initial and final states of the system and no ton the path of the change, are know as **state functions**. Pressure, temperature and volume are all important state functions. Other important state functions include **enthalpy (H), entropy** (S), and **free energy (G)**.

A set of standard conditions (25°C and 1 atm) is normally used when measuring enthalpy, entropy and free energy of a reaction. A substance in its most stable form under standard conditions is said to be in its standard state. The changes in enthalpy, entropy and free energy that occur under standard conditions are called standard enthalpy (Δ H°), standard entropy (Δ S°) and standard free energy (Δ G°).

1. Enthalpy – is the amount of energy in a system capable of doing mechanical work. This takes into the account the total internal energy of a system (including heat) as well as the effects of volume and pressure of the surroundings. At constant pressure, enthalpy is proportional to the heat absorbed or released by the system. The enthalpy of a process or reaction depends only on the initial and final state enthalpies. Thus to find the enthalpy change of a reaction, one must subtract the enthalpy of the reactants from the enthalpy of the products:

 $\Delta H_{rxn} = H_{products} - H_{reactants}$

A positive ΔH means its an endothermic process and a negative ΔH is an exothermic process. Unfortunately, it is not possible to measure H directly, only ΔH can be measured, and even then only certain processes. Thus there are several standard methods have been developed to calculate ΔH .

- a. Standard Heat of Formation the enthalpy of formation of a compound, ΔH°_{f} , is the enthalpy change that would occur if one mole of a compound were formed directly from its elements in their standard states. The ΔH°_{f} of most known substances are tabulated.
- b. Standard Heat of Reaction The standard heat of a reaction is the hypothetical enthalpy change that would occur if the reaction was carried out under standard conditions:

 $\Delta H^{\circ}_{rxn} = (sum of \Delta H^{\circ}_{f} products) - (sum of \Delta H^{\circ}_{f} reactants)$

- c. Hess's Law states that enthalpies of reactions are additive. When chemical reactions for which energy changes are known are added to give a net equation, the corresponding heats of reaction are also added to give the net heat of reaction.
- d. Bond Dissociation Energy heats or reactions are related to changes in energy associated with the break-down and formation of chemical bonds. Bond dissociation energy is an average of the energy required to break a particular type of bond in on mole.

2. Entropy – is a measure of the disorder, or randomness of a system. The unites of entropy are energy/temperature. The greater the order in the system, the lower the entropy; the greater the disorder of randomness, the higher the entropy. At any given temperature, a solid will have lower entropy than gas, because the molecules in the gas are moving more randomly than in the solid phase. Since entropy is a state function, its value depends only on the initial and final states:

$$\Delta S = S_{\rm final} - S_{\rm initial}$$

The **Second Law of Thermodynamics** states that all spontaneous processes (or processes that proceed on their own "naturally") proceed such that the entropy of the system plus its surroundings increases (ie the universe evolves toward a state of randomness). When $\Delta S > 0$, then the process is spontaneous. During **equilibrium** when no observable changes take place, then $\Delta S = 0$. A system will tend toward an equilibrium if left alone.

3. Gibbs Free Energy – combines the two factors which affect the spontaneity of a reaction – changes in enthalpy (Δ H) and changes in entropy (Δ S). The change in the free energy of a system (Δ G) represents the maximum amount of energy released by a process, occurring at a constant temperature and pressure, that is available to perform useful work. Δ G is defined:

$$\Delta G = \Delta H - T\Delta S$$

where T is the **absolute temperature** (in Kelvin) and $T\Delta S$ is the total amount of heat absorbed.

- a. If ΔG is negative, the reaction s spontaneous
- b. If ΔG is positive, the reaction is not spontaneous
- c. If ΔG is zero, the system is in a state of equilibrium; $\Delta G = 0$ and $\Delta H = T\Delta S$