Thermodynamics

Thermodynamics is the study of energy and its inter-conversions.

For this class we will define energy as the ability to do work or produce heat.

The first law of thermodynamics is the law of conservation of energy. That is, the total energy of the universe is constant. Energy is neither created nor destroyed, simply transferred from one form to another.

There are two types of energy:

Kinetic Energy is the energy of motion, and depends on the mass and velocity of the object.

Potential energy is the energy an object has due to it's position.

We are generally much more interested in the change in the energy an object has than the absolute amount of energy the object has.

Energy Changes

There are two ways that energy changes can take place in the chemical reactions we will be looking at:

Work is defined as a force acting over a distance.

Heat is the transfer of energy between two objects due to temperature differences.

To determine how energy is flowing we need to define the system and the surroundings.

The system is the thing (chemical reaction) that we are interested in.

The surroundings are everything else in the universe.

Energy conversions are know as state functions, that is, only the starting and ending points in the change are important. How the change takes place, or the pathway, is unimportant.

The total internal energy (E) of the system would be the sum of the kinetic and potential energy of the system. The energy of the system can be changed by work or heat or both.

$$\Delta E = q + w$$

Calculating ΔE

In general measuring the value of E is difficult, while measuring ΔE is easy. We will generally only deal with measuring ΔE.

Changes to heat we can measure with temperature and the most common type of work for a chemical system is changes to volume of a gas at a constant pressure.

$$w = -P\Delta V$$

$$\Delta E = q - P\Delta V$$

Endo- and Exo- thermic

When heat (energy) flows out of the system in to the surroundings we say the change is exothermic and the energy would be written on the right side of the equation.

$$2\mathrm{H}_{2(g)} + \mathrm{O}_{2(g)} \rightarrow 2\mathrm{H}_2\mathrm{O}_{(g)} + \mathrm{energy(heat)}$$

When heat (energy) flows in to the system from the surroundings we say the change is endothermic and the energy term would be written on the left side of the equation.

$$2\mathrm{H}_{2(g)} + \mathrm{CO}_{(g)} + \mathrm{energy(heat)} \rightarrow \mathrm{CH}_3\mathrm{OH}_{(l)}$$

Calorimetry

Clearly the change in temperature is directly related to the heat flow, however it is not the only factor. The mass of substance that is changing temperature is also very important, as well different substances change temperature different amounts with the addition of the same amount of energy. We need an equation to combine all of these factors.

$$q = m \cdot s \cdot \Delta T$$

The heat capacity is defined as the amount of heat absorbed divided by the increase in temperature. It is a way to relate how much energy it takes to raise the temperature of a substance. The heat capacity can also be expressed per gram and per mole, giving us the specific heat capacity and the molar heat capacity respectively.

$$C = \frac{\text{heat absorbed}}{\text{increase in temperature}}$$

$$q = 250\mathrm{g} \cdot 4.18\frac{\mathrm{J}}{\mathrm{g \cdot C}} \cdot -25\mathrm{C}$$

Calorimeters

The most common type of calorimeter in chemistry is know as a coffee-cup calorimeter and functions at constant pressure. This allows us to calculate q by knowing the specific heat capacity, mass and temperature change.

Ex:

The other commonly used calorimeter is know as a bomb calorimeter, because it functions at constant volume and is frequently used for combustion reactions. Because the bomb calorimeter does not function at constant pressure we can not relate it to ΔH in the same way as we did for the coffee-cup calorimeter. We can however, relate ΔE directly to q at constant volume.