Thoughts of the Day

11/23/10

Covered three main ideas today
The first Law of thermodynamics, heat, and work.

Introduced the idea of internal energy. All of the energy of the system. Discussed that the internal energy is a state function. That is that it only depends on the state of the system (its particular properties T,V,P, ...) not how the system arrived in this state.

Changes in internal energy are then associated with any energy that flows into or out of the system.

We discussed two forms of energy flow: heat and temperature

Heat. Heat is not temperature. Can't say this enough. Heat is not temperature. Heat is energy flow. We will show with the second law that heat must flow from high temperature to low temperature, but for now we'll just accept this. We looked at heat flow that we all know intuitively. Take a hot pan on the stove and touch it. Heat (energy) flows from the hot pan into your hand and the temperature of your finger rises. Heat capacity is the proportionality constant that relates heat and temperature change. It is extensive. Big things have big heat capacities. If you flow the same amount of heat into two objects (this can be done with a calibrated resistive heater) the one with the lower heat capacity will have a higher temperature change. Imagine try heat a glass of water (low heat capacity) with a blow torch versus heating up the Atlantic ocean (big heat capacity). There are also important circumstances in which heat does not lead to temperature change. The energy is not lost it simply "goes" somewhere else. For example melting ice or chemistry.

Work. Force acting over a distance. We will deal mostly with pressure volume work. We looked at how expansion of a gas leads to a loss of energy from work (energy out is negative work). Compression is work in. In these situations, the force that is of interest is the one "acting" on the system. This is the external pressure (or pressure of the surroundings). The work is the integral of the external pressure times the change in volume integrated from the initial to the final volume. In the case of a constant external pressure this gives simply the negative of the external pressure times the volume change. No volume change. No PV work.

Final and most importantly. Changes in internal energy (U) are the sum of the energy in and energy out in the form of heat (q) and work (w). $\Delta U = q + w$

The sign matters. Engery in is positive change. Energy out is negative. This is because we define the change as final minus initial.

Enthalpy.

We are interested in the heat as it is straight forward to measure and can be related to entropy change.

Thus we need a state function that is related to the heat. At constant volume this is the total energy (no work). At constant pressure we invent the enthalpy, H. The change in enthalpy at constant pressure is equal to the heat. This is why we invented the idea. For systems with minimal or no work the change in enthalpy is simply the change in energy. This a reasonable way to think about it.

Heat.

We divided heat up into two distinct version. One with temperature change and no chemistry and no phase transition. Or alternatively no temperature change but with chemistry (phase transition). Anything that is both can be thought of in two steps where they are divided up.

First temperature change.

This is straight forward. The amount of temperature change that occurs for a given amount of energy flow depends on the heat capacity.

$$q = C\Delta T$$

q is the heat, C is the heat capacity, deltaT is the temperature change.

The heat capacity is extensive. Therefore it depends on the amount of stuff. You may have seen other formulas for heat and temperature change such as

$$q = mC\Delta T$$
$$q = nC\Delta T$$

where m is the mass or n is the number of moles. These are the same as the previous formula except that in the first the heat capacity is the "specific heat" or heat capacity per mass. The second equation uses the molar heat capacity. They are all the same. You simply have to be careful with the units. The first equation (no m or n) uses the extensive heat capacity (no per gram or per mole). The second equations use the intensive version (the per gram or per mole version) thus the need to multiply the mass or the number of moles.

Heat with no temperature change involves either chemistry or phase change. For a phase change we simply have to measure the heat and tabulate it. Thus we can look up deltaH of fusion for water or ethanol or whatever substance we are interested in.

Additional we tabulate the heat of vaporization and sublimation. The opposite phase transition as the same but the opposite sign. For example condensation of water is exothermic. The heat is simply the negative of the enthalpy of vaporization.

For heat of reactions we can simply measure them all. Or we can devise a scheme by which they can be calculated. This is the approach we imagine getting from the reactant molecules to the product molecules by first converting all them to their elemental form. If we know the enthalpy associated in going from the elements to the molecules (and we have these tabulated), then we can calculate the heat for any reaction. There is a very nice section of the book that covers this (along with phase transition).

Section 12.5 Thermochemistry is a must read.