Spontaneity

A process or reaction is spontaneous if it happens without external intervention. There are two factors that determine if a process will be spontaneous or not:

Enthalpy- Reactions that give off energy tend to be spontaneous.

Entropy- Entropy is a measure of the randomness or disorder in a system. Generally reactions that increase the randomness of the system are spontaneous.

To understand if a reaction will be spontaneous we need to consider both of these factors.

Entropy

Entropy(S) is a function that describes the possible ways that a system can be arranged. It is possible to calculate the absolute entropy of a system by calculating all the possible microstates of a system. While entropy can be calculated directly we generally are more interested in determining the change in entropy ΔS. Most often we are not going to calculate the actual value for ΔS. We will only need to determine the sign for ΔS. We need to think most about positional entropy.

The Second Law

The second law of thermodynamics states that for any spontaneous process the entropy of the universe increases.

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

We want to be able to deal with reactions from the point of view of the system. We can do this because the ΔS of the surroundings depends on the heat flow and the temperature the surroundings are at.

$$\Delta S_{surr} = -\frac{\Delta H}{T}$$

To determine if a process is going to be spontaneous or not we need to determine if the ΔS of the universe is positive. We generally do this by looking at a function known as Gibb's free energy.

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

Ex:

ΔS and Chemical Reactions

There are just a few things we need to consider when we are trying to predict the change in entropy of a chemical reaction. In General:

Reactions that produce more particles have a positive entropy change.

Gasses have much greater entropy than liquids and liquids have greater entropy than solids.

Mixtures have greater entropy than pure substances.

Larger molecules have greater entropy than smaller molecules.

Calculating ΔS°

We can calculate the change in entropy by subtracting the entropy of the reactants from the entropy of the products.

$$\Delta S^o_{reaction} = \sum n_p S^o_{products} - \sum n_r S^o_{reactants}$$

We need to define a 0 point for entropy so we can calculate the entropy of other molecules based on that zero points. The third law of thermodynamics states that the entropy of a perfect crystal at 0 K is zero. Using this we can calculate standard entropy values.

Ex:

Calculating $\Delta G°$

Much as we defined the standard enthalpy and entropy change we can define standard conditions for the change in Gibb's free energy. We can calculate $\Delta G°$ in a couple of different ways. We can use the Gibb's equation:

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

We can use standard ΔG values from a table.

We can use a procedure like Hess's law.