Thermodynamics

Recall that **thermodynamics** is the study of the relationship between work and energy in chemical and physical processes.

Spontaneity

Thermodynamic favorability determines whether a process is **spontaneous**, occurs naturally under given conditions, or **non-spontaneous**, energy must be input into the system for the process to occur.

Entropy

A **reversible process** is one that occurs so slowly that it is always at equilibrium. Originally introduced to describe spontaneous heat flow, **entropy (S)** change was introduced as;

$$\Delta S = \frac{q_{rev}}{T}$$

Ludwig Boltzmann came up with a statistical formulation, having to do with the amount of *microstates(W)* possible for a system. A **microstate** is a specific microscopic configuration of energies and positions of a system. Boltzmann's entropy is defined as;

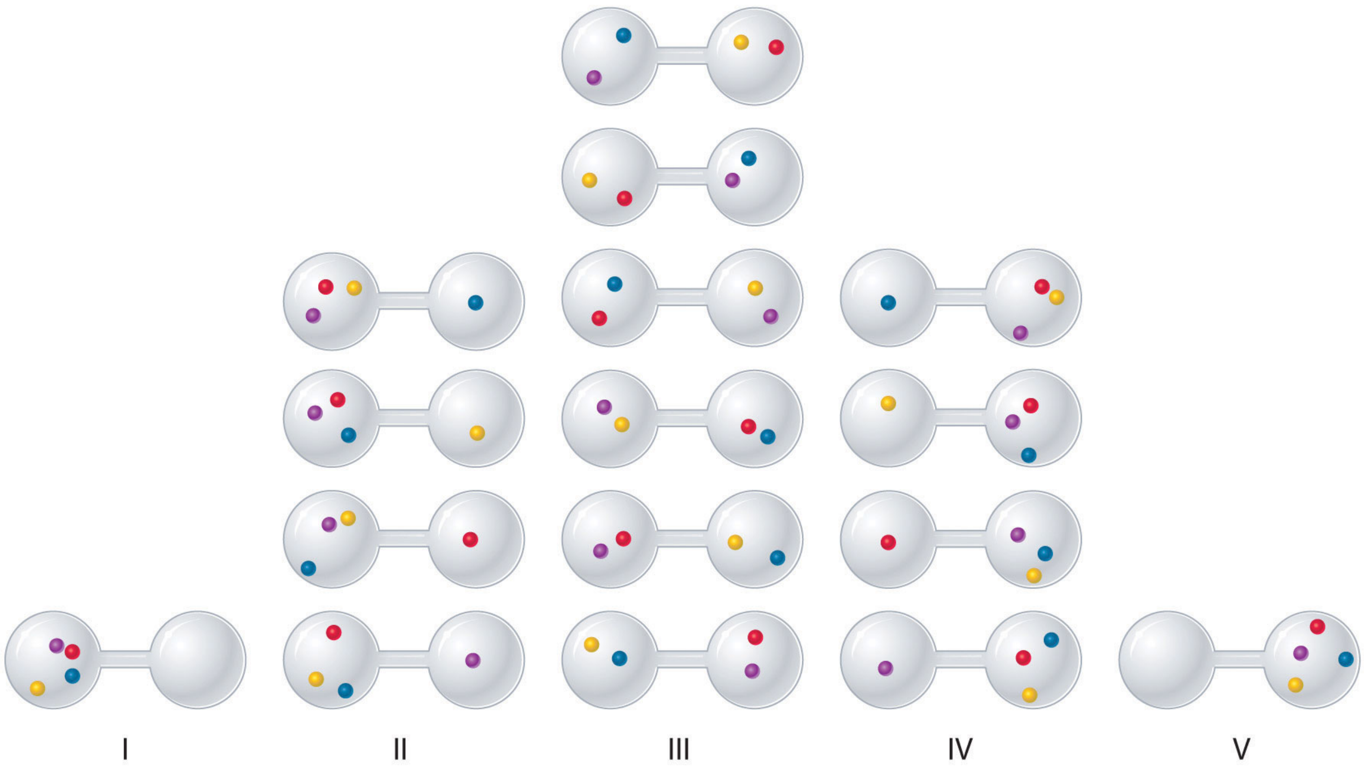
$$S = klnW$$

where k is Boltzmanns constant,$1.38 \times 10^-23\ J/K$. Since entropy is a state function, the entropy change can be defines as;

$$\Delta S = kln\frac{W_f}{W_i}$$

Where W_i and W_f are the respective initial and final number of microstates of a system.

Considering a system of N particles with n boxes, the amount of possible microstates would be n^N. Microstates with equivalent particle arrangements are called *distributions*, where the most probable distribution is the one with the largest entropy.



Second Law of Thermodynamics

For a spontaneous process, the entropy of the universe must increase.

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

Third Law of Thermodynamics

The entropy of a pure, crystalline solid a 0 K is 0.

Free Energy

The **Gibbs Free Energy (G)** is another thermodynamic property that allows us to define sponteneity only though consideration of the system.

$$G = H \ - TS$$

Again, the Gibbs free energy is a state function and as such can be described through changes in the respective enthalpy and entropy.

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

While maybe not immediatly straightforward, the Gibbs energy can be derived;

$$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{surr}$$
$$\Delta S_{uni} = \Delta S_{sys} + \frac{q_{surr}}{T}$$

recall that at q_{surr} = $-q_{sys}$ and at constant p, $\Delta H = q_{sys}$;

$$\Delta S_{uni} = \Delta S_{sys} - \frac{\Delta H}{T}$$
$$-T\Delta S_{uni} = \Delta H - T\Delta S_{sys}$$
$$\Delta G = \Delta H \ - T\Delta S$$

Thus, we can now use this new concept to define sponteneity in terms of the system.

ΔS_{uni}	ΔG	**Spont.?**
$\Delta S_{uni} > 0$	$\Delta G < 0$	yes
$\Delta S_{uni} < 0$	$\Delta G > 0$	no
$\Delta S_{uni} = 0$	$\Delta G = 0$	equilibrium

This difference in G could also be throught of as the summation of energy produced v. the energy lost to surroundings, the Gibbs energy is thus the energy available to do work.

Calculating Free Energies

Free energies can be calculated using Hess's law, as was done with enthalpy.