Spontaneity

One of the major goal of thermodynamics is to determine the spontaneity of a reaction, or if a reaction will complete on its own, without energy being constantly added. Spontaneity is unrelated to kinetics, so we can't determine the rate of reaction from thermodynamics, only the direction, as spontaneous reactions have a preferred direction.

Spontaneity is influenced by two factors:

- Energy (Enthalpy)
- Randomness (Entropy)

Entropy

Entropy is a measure of how energy is distributed to, from, and within a system as a function of temperature. In short, it is a measure of the randomness of the system.

$$S = k \ln(W)$$

- k is the Boltzmann constant
- W is the number of microstates

Microstates & Macrostates

What is a microstate? First, we need to understand macrostates. A macrostate is a state with constant pressure, temperature, volume and density, but which does not describe the exact behavior of the particles within the macrostate. A microstate is the number of different combinations a group of particles/molecules can be arranged in a given macrostate.

As the number of microstates increase, the number of ways that energy can be transmitted increases, so the entropy of the system increases as well.

The number of microstates will increase if:

1. The temperature increases

    - As the temperature increases, there will be more kinetic energy and therefore more particle motion, which translates to more disorder.

2. The reaction results in an increased number of particles

    - As the number of particles increases, there will be more disorder.

3. An increase in volume

    - This will give the particles more room to move, which means more disorder.

Changes in Entropy

Entropy change is favorable when the result is in a more random system.

$$\Delta S = S_f - S_i$$

$$\implies \Delta S = k \ln\left(\frac{W_f}{W_i}\right)$$

Based on this formula, we can see that if the reaction goes from a lower number of microstates to a higher number, the change in entropy will be postive ($W_f > W_i, \therefore \Delta S > 0$).

Entropy will change when:

- The products and the reactants are in a different state
- Temperature changes
- There are more moles in the products than the reactants
- Solids dissociate into ions

State Change

Note: all spontaneous endothermic processes require $\Delta S > 0$.

The increase in entropy with regard to space has to do with the freedom of motion of the molecule.

- For solids, the molecules just vibrate in place, so their entropy isn't very high as their range of motion is low.
- For liquids, the molecules can now move around and rotate, so their entropy increases.
- For gases, they have an even greater freedom of motion compared to liquids, so their entropy is the highest.

Quantitatively Determining Changes in Entropy

There are three changes in entropy that we need to find in order to determine a quantitave change in entropy. The relationship between these is formalized in the 2nd Law of Thermodynamics.

- ΔS_{sys} is the change in the system (reaction) itself
- ΔS_{surr} is the change in the environment surrounding the reaction
- ΔS_{univ} is the universal change in entropy, and is the sum of the other two

We can find the change in the system just like how we would find the change of enthalpy (ΔH):

$$\Delta S_{sys} = \sum n(S^{\circ}_{prod}) - \sum n(S^{\circ}_{reac})$$

2nd Law of Thermodynamics

The 2nd law of thermodynamics states that the total entropy change of the universe must be positive for a process to be spontaneous.

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

- A process is irreversible (spontaneous) when $\Delta S_{univ} > 0$
- A process is reversible (at equilibrium) when $\Delta S_{univ} = 0$

Heat Exchange and Surrounding Entropy

- When a system is exothermic, it adds heat to its surroundings, increasing the entropy of the surroundings.
- When a system is endothermic, it takes heat from its surroundings, decreasing the entropy of the surroundings.

The amount that ΔS_{surr} changes depends on the original temperature. The higher the original temperature, the less effect the addition or removal of heat will have.

Quantifying Entropy Changes in Surroundings

So, ΔS_{surr} is proportional to the amount of heat gained or lost:

$$q_{surr} = -q_{sys}$$

The entropy change of the surroundings is also inversely proportional to its temperature, so at constant pressure and temperature, we get:

$$\Delta S_{surr} = \frac{-q_{sys}}{T} = \frac{-\Delta H_{sys}}{T}$$

Calculating the Standard Entropy Change for a Reaction

ΔS°_{rxn} is the change in entropy for a process where all reactants and products are in their standard states. Recall that the standard state is when:

- Gases: $P = 1\ atm$
- Liquids & Solids: $T = 25°C$ and $P = 1\ atm$
- Solutions: $C = 1M$

3rd Law of Thermodynamics

The third Law of Thermodynamics states that the entropy of any perfect substance will be equal to zero at absolute zero ($0K$). Recall Boltzmann's equation:

$$S = k\ln(W)$$

At absolute zero, there is no kinetic energy, so there is only one possible microstate

$$\therefore W = 1, \rightarrow S = 0$$

It is impossible to lower the temperature of any system to absolute zero in a finite number of steps, so absolute zero can never actually be reached.

Absolute Entropy

Absolute entropy of a substance is the sum of entropy it would acquire from warming from absolute zero to any given temperature. As a result, the absolute entropy is always positive. This allows us to calculate the entropy change of a reaction like we can for enthalpy:

$$\Delta S_{rxn} = \sum nS_{prod} - \sum nS_{react}$$