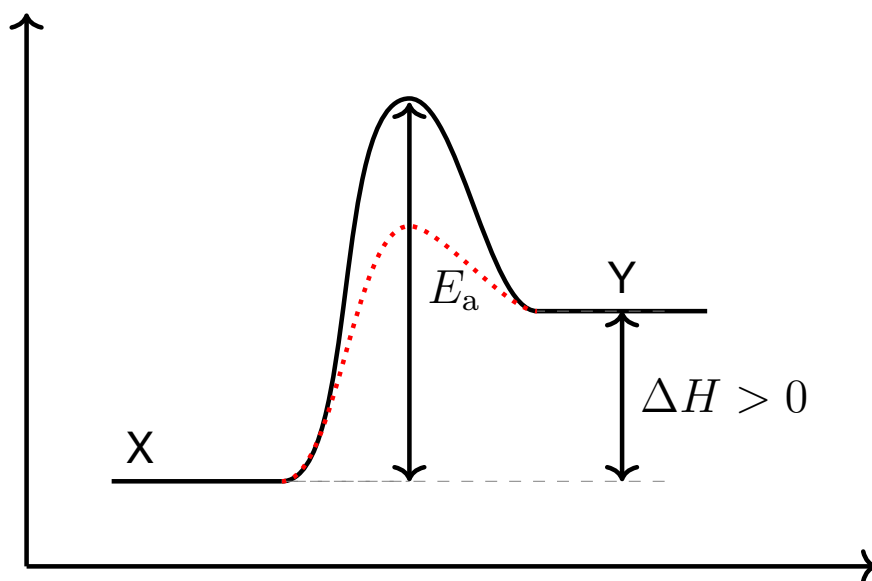# Physical Chemistry

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

Chapters 5 to 7

Contents

I Gibbs Free Energy and Entropy

1 Entropy and Spontaneity

The Second Law of Thermodynamics states that for a process to be spontaneous, the total entropy of the system must increase. Entropy, represented by *S*, is a measure of the number of ways energy can be distributed in a given system. This is often manifested through the motion of particles.

In a solid, movement is restricted and the kinetic energy of particles can only have so many permutations. Entropy is the smallest in the solid state.

In a gas, movement is almost unrestricted, and the possible range of kinetic energies for particles within the system is huge. Thus, entropy is the greatest. The difference in entropy between a gas and a liquid is much greater than that between a solid and a liquid.

1.1 Change in Entropy (ΔS)

The entropy change of a given reaction or action is determined mainly by the effect on the number of ways to distribute energy in the system. The ways in which entropy is changed include changing the *temperature*, *number of moles of gas*, or the *state* of one or more compounds present in the system.

Throughout this terrible, tedious chapter, it is important to note that S $\neq \Delta S$. The units of ΔS are typically $J\,mol^{-1}$ (joules per mole).

1.1.1 Change in Temperature

Increasing the temperature of a system of molecules increases their average kinetic energy, and hence the range of possible energies within the system.

As such, the amount of ways to distribute energy in the system increases, resulting in greater entropy. ($\Delta S > 0$)
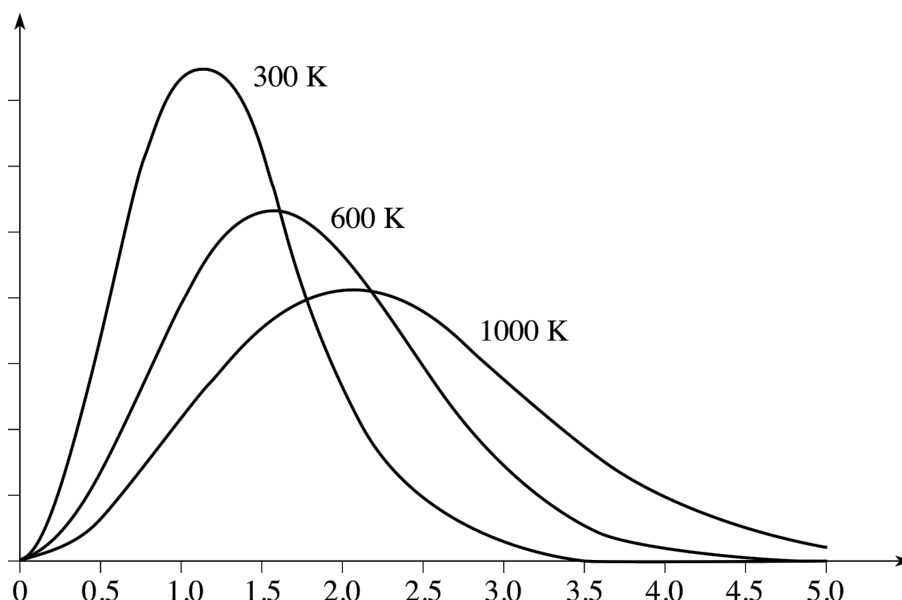

The Maxwell-Boltzmann curve above shows that as temperature increases, the possible range of kinetic energies of the system also increases, thus increasing entropy.

1.1.2 Change in Number of Gas Particles

From the diagram above, it should be obvious that, since gaseous molecules have a much greater entropy, an increase in the number of gas particles will also result in an increase in the entropy of the system ($\Delta S > 0$).

Simply put, if the reaction results in a greater number of gaseous products than reactants, then there will be a net increase in entropy. For example:

$$2\,NaN_{3\,(s)} \longrightarrow 2\,Na_{(s)} + 3\,N_{2\,(g)}$$
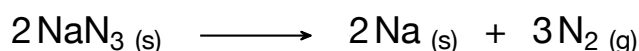
Here, the number of moles of gas *increased* from 0 to 3, hence $\Delta S > 0$. The reverse is also true, naturally — if the number of moles of gas decreases, then the entropy change will be negative.

1.1.3 Change in Phase

When a particular substance melts, boils, condenses or freezes, the entropy of the system changes accordingly. The diagram below aptly illustrates this.
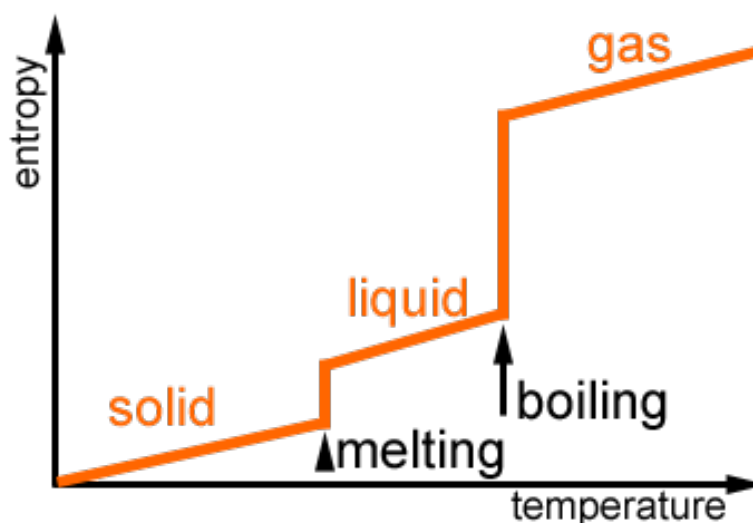
As a substance melts, its molecules are no longer constrained by the structure of the solid state; average kinetic energy increases, and $\Delta S > 0$. As the substance boils, the molecules are completely free to move; naturally, the change in entropy is much greater than for melting. $\Delta S > 0$, obviously.

1.1.4 Change in Volume

If the available volume of a gas increases (at a constant temperature, which implies a decrease in pressure), then the entropy of the system will also increase. The possible distributions of each molecule of gas increases, and hence entropy increases ($\Delta S > 0$). Naturally, the opposite is also true; if the pressure of a system increases at a constant temperature, then the entropy will decrease ($\Delta S < 0$).

Note that when two containers containing two different gases are mixed, the entropy of the system also increases — the total volume that each gas occupies is increased as well.

1.1.5 Dissolution of Ionic Solids

When solid ionic compounds are dissolved in water (or another polar solvent), the total entropy of the system will also change. However, it depends on the interposition of two separate factors; when the ionic compound is dissolved, the constituent ions are able to move around, thus increasing the entropy.

However, the water molecules that are interacting with the dissolved ions are now restricted in movement, and hence entropy decreases as well. Thus, the net change in entropy of the system depends on which of the above factors is more significant. For singly-charged ions, the net change in entropy is usually an increase ($\Delta S > 0$).

1.2 Gibbs Free Energy

Since the enthalpy change (ΔH) and the change in entropy (ΔS) are both crucial in determining whether a given reaction will be spontaneous (occurring without external energy input), they are used together to calculate the change in Gibbs free energy, ΔG. If you paid attention to the cover page, then this equation should be familiar to you:

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

In short, the change in Gibbs energy of a given reaction is determined by the temperature, and the changes in both enthalpy and entropy, of the reaction. The units of ΔG are typically kJ mol^{-1} (kilojoules per mole), and that for temperature is K (kelvins).

Exergonic reactions, where ΔG < 0, are said to be energetically feasible, and take place spontaneously. Conversely, endergonic reactions where $\Delta G > 0$ are energetically infeasible, and do not take place spontaneously. ΔG can be 0, for example during melting or boiling.

1.2.1 Effect of Gibbs Free Energy

Given the sign (positive or negative, duh) of both ΔH and ΔS, it is possible to determine if ΔG will increase or decrease with temperature. Thus, it is possible to predict if the reaction will be more or less spontaneous (and thus energetically feasible) with a change in temperature.

A *disgusting* and *abhorrent* table below summarises the four possible scenarios:

ΔH	ΔS	ΔG	Feasibility
< 0	< 0	always < 0	All temperatures
< 0	> 0	always > 0	Never
> 0	< 0	depends	Low temperatures
> 0	> 0	depends	High temperatures

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