7.4: Why Do Chemical Reactions Occur? Free Energy

Learning Outcomes

- Describe the meaning of a spontaneous reaction in terms of enthalpy and entropy changes.
- Define free energy.
- Determine the spontaneity of a reaction based on the value of its change in free energy at high and low temperatures.

Spontaneous Reactions

A **spontaneous reaction** *is a reaction that favors the formation of products at the conditions under which the reaction is occurring*. A roaring bonfire (see Figure $7.4.1$ below) is an example of a spontaneous reaction. A fire is *exothermic*, which means a decrease in the energy of the system as energy is released to the surroundings as heat. The products of a fire are composed mostly of gases such as carbon dioxide and water vapor, so the entropy of the system increases during most combustion reactions. This combination of a decrease in energy and an increase in entropy means that combustion reactions occur spontaneously.

Figure $7.4.1$: Combustion reactions, such as this fire, are spontaneous reactions. Once the reaction begins, it continues on its own until one of the reactants (fuel or oxygen) is gone.

A **nonspontaneous reaction** *is a reaction that does not favor the formation of products at the given set of conditions*. In order for a reaction to be nonspontaneous, one or both of the driving forces must favor the reactants over the products. In other words, the reaction is endothermic, is accompanied by a decrease in entropy, or both. Out atmosphere is composed primarily of a mixture of nitrogen and oxygen gases. One could write an equation showing these gases undergoing a chemical reaction to form nitrogen monoxide.

$$\mathrm{N_2}\left(g\right)+\mathrm{O_2}\left(g\right)\rightarrow 2\mathrm{NO}\left(g\right) \tag{7.4.1}$$

Fortunately, this reaction is nonspontaneous at normal temperatures and pressures, it is a highly endothermic reaction. However, nitrogen monoxide is capable of being produced at very high temperatures, and this reaction has been observed to occur as a result of lightning strikes.

One must be careful not to confuse the term spontaneous with the notion that a reaction occurs rapidly. A spontaneous reaction is one in which product formation is favored, even if the reaction is extremely slow. You do not have to worry about a piece of paper on your desk suddenly bursting into flames, although its combustion is a spontaneous reaction. What is missing is the required activation energy to get the reaction started. If the paper were to be heated to a high enough temperature, it would begin to burn, at which point the reaction would proceed spontaneously until completion.

Entropy as a Driving Force

An example of a very simple spontaneous process is that of a melting ice cube. Energy is transferred from the room to the ice cube, causing it to change from the solid to the liquid state.

$$\mathrm{H_2O}\left(s\right)+6.01\ \mathrm{kJ}\rightarrow \mathrm{H_2O}\left(l\right) \tag{7.4.2}$$

The solid state of water, ice, is highly *ordered* because its molecules are fixed in place. The melting process frees the water molecules from their hydrogen-bonded network and allows them a greater degree of movement. Water is more *disordered* than ice. The change from the solid to the liquid state of any substance corresponds to an increase in the disorder of the system.

The tendency in nature for systems to proceed toward a state of greater disorder or randomness is called **entropy**, which is symbolized by *S*, and expressed in units of Joules per mole-kelvin, $\text{J}/(\text{mol}\cdot\text{K})$. Larger values of *S* indicate that the particles in a substance have more disorder or randomness. In the example above, the particles in the ice cube (solid water) have lower freedom of motion, they are less random. As the ice melts to liquid water, the particles become more disordered and entropy increases. If the liquid water was heated further, the particles would even gain more freedom of motion, become more disordered, and eventually change to a gas, which has even higher entropy.

Chemical reactions also tend to proceed in such a way as to increase the total entropy of the system, measured by the **entropy change ($\boldsymbol{\Delta S}$)** between reactants and products. How can you tell if a certain reaction shows an increase or a decrease in entropy? The states of the reactants and produces provide certain clues. The general cases below illustrate entropy at the molecular level.

1. For a given substance, the entropy of the liquid state is greater than the entropy of the solid state. Likewise, the entropy of the gas is greater than the entropy of the liquid. Therefore, entropy increases in processes in which solid or liquid reactants form gaseous products. Entropy also increases when solid reactants form liquid products.
2. Entropy increases when a substance is broken up into multiple parts. The process of dissolving increases entropy because the solute particles become separated from one another when a solution is formed.
3. Entropy increases as temperature increases. An increase in temperature means that the particles of the substance have greater kinetic energy. The faster moving particles have more disorder than particles that are moving more slowly at a lower temperature.
4. Entropy generally increases in reactions in which the total number of product molecules is greater than the total number of reactant molecules. An exception to this rule is when nongaseous products are formed from gaseous reactants.

The examples below will serve to illustrate how the entropy change in a reaction can be predicted.

$$\text{Cl}_2\left(g\right) \rightarrow \text{Cl}_2\left(l\right) \tag{7.4.3}$$

The entropy is decreasing because a gas is becoming a liquid.

$$\text{CaCO}_3\left(s\right) \rightarrow \text{CaO}\left(s\right) + \text{CO}_2\left(g\right) \tag{7.4.4}$$

The entropy is increasing because a gas is being produced, and the number of molecules is increasing.

$$\text{N}_2\left(g\right) + 3\text{H}_2\left(g\right) \rightarrow 2\text{NH}_3\left(g\right) \tag{7.4.5}$$

The entropy is decreasing because four total reactant molecules are forming two total product molecules. All are gases.

$$\text{AgNO}_3\left(aq\right) + \text{NaCl}\left(aq\right) \rightarrow \text{NaNO}_3\left(aq\right) + \text{AgCl}\left(s\right) \tag{7.4.6}$$

The entropy is decreasing because a solid is formed from aqueous reactants.

$$\text{H}_2\left(g\right) + \text{Cl}_2\left(g\right) \rightarrow 2\text{HCl}\left(g\right) \tag{7.4.7}$$

The entropy change is unknown (but likely not zero) because there are equal numbers of molecules on both sides of the equation, and all are gases.

Gibbs Free Energy

Many chemical reactions and physical processes release energy that can be used to do other things. When the fuel in a car is burned, some of the released energy is used to power the vehicle. **Free energy** *is energy that is available to do work*. Spontaneous reactions release free energy as they proceed. The determining factors for spontaneity of a reaction depend on both the *enthalpy* and *entropy* changes that occur for the system. The **free energy change ($\boldsymbol{\Delta G}$)** of a reaction is a mathematical combination of the enthalpy change and the entropy change.

$$\Delta G^\text{o} = \Delta H^\text{o} - T\Delta S^\text{o} \tag{7.4.8}$$

The symbol for free energy is G, in honor of American scientist Josiah Gibbs (1839 - 1903), who made many contributions to thermodynamics. The change in Gibbs free energy is equal to the change in enthalpy minus the mathematical product of the change in entropy multiplied by the Kelvin temperature. Each thermodynamic quantity in the equation is for substances in their standard states, as indicated by the $^\text{o}$ superscripts.

A spontaneous reaction is one that releases free energy, and so the sign of ΔG must be negative. Since both ΔH and ΔS can be either positive or negative, depending on the characteristics of the particular reaction, there are four different possible combinations. The outcomes for ΔG based on the signs of ΔH and ΔS are outlined in the table below. Recall that $-\Delta \mathrm{H}$ indicates that the reaction is exothermic and a $+\Delta \mathrm{H}$ means the reaction is endothermic. For entropy, $+\Delta \mathrm{S}$ means the entropy is increasing and the system is becoming more disordered. A $-\Delta \mathrm{S}$ means that entropy is decreasing and the system is becoming less disordered (more ordered).

A process that releases free energy, $(-\Delta G)$, is said to be ***exergonic***. Processes that require free energy $(+\Delta G)$, are ***endergonic***. These terms are used when considering chemical reactions that occur in living systems.

Table 7.4.1: Enthalpy, Entropy, and Free Energy Changes.

ΔH	ΔS	ΔG
negative	positive	always negative
positive	positive	negative at higher temperatures, positive at lower temperatures
negative	negative	negative at lower temperatures, positive at higher temperatures
positive	negative	always positive

Keep in mind that the temperature in the Gibbs free energy equation is the Kelvin temperature, so it can only have a positive value. When ΔH is negative and ΔS is positive, the sign of ΔG will always be negative, and the reaction will be spontaneous at all temperatures. This corresponds to both driving forces being in favor of product formation. When ΔH is positive and ΔS is negative, the sign of ΔG will always be positive, and the reaction can never be spontaneous. This corresponds to both driving forces working against product formation.

When one driving force favors the reaction, but the other does not, it is the temperature that determines the sign of ΔG. Consider first an endothermic reaction (positive ΔH) that also displays an increase in entropy (positive ΔS). It is the entropy term that favors the reaction. Therefore, as the temperature increases, the $T \Delta S$ term in the Gibbs free energy equation will begin to predominate and ΔG will become negative. A common example of a process which falls into this category is the melting of ice (see figure below). At a relatively low temperature (below $273 \mathrm{~K}$), the melting is not spontaneous because the positive ΔH term "outweighs" the $T \Delta S$ term. When the temperature rises above $273 \mathrm{~K}$, the process becomes spontaneous because the larger T value has tipped the sign of ΔG over to being negative.

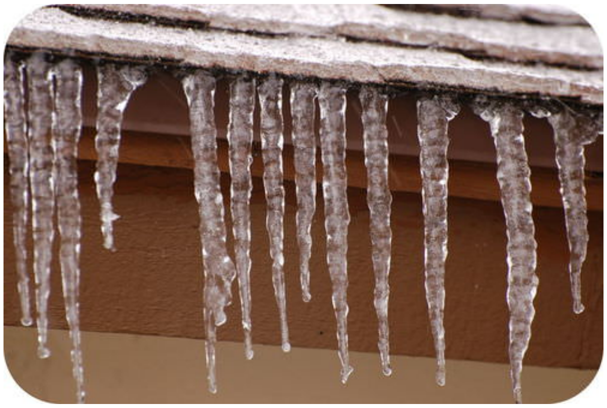

Figure 7.4.2: Ice melts spontaneously only when the temperature is above $0^{\circ} \mathrm{C}$. The increase in entropy is then able to drive the unfavorable endothermic process.

When the reaction is exothermic (negative ΔH) but undergoes a decrease in entropy (negative ΔS), it is the enthalpy term which favors the reaction. In this case, a spontaneous reaction is dependent upon the $T \Delta S$ term being small relative to the ΔH term, so that ΔG is negative. The freezing of water is an example of this type of process. It is spontaneous only at a relatively low temperature. Above $273 .\ \mathrm{K}$, the larger $T \Delta S$ value causes the sign of ΔG to be positive, and freezing does not occur.

Contributors and Attributions

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