11.4: Entropy and Enthalpy

Learning Outcomes

- Recall the meaning of exothermic and endothermic.
- Define entropy.
- Predict whether entropy change for a reaction is increasing or decreasing.

Previously, you learned that chemical reactions either absorb or release energy as they occur. The change in energy is one factor that allows chemists to predict whether a certain reaction will occur. In this lesson, you will learn about a second driving force for chemical reactions called entropy.

Enthalpy as a Driving Forces

The vast majority of naturally occurring reactions are exothermic. In an exothermic reaction, the reactants have a relatively high quantity of energy compared to the products. As the reaction proceeds, energy is released into the surroundings. Low energy can be thought of as providing a greater degree of stability to a chemical system. Since the energy of the system decreases during an exothermic reaction, the products of the system are more stable than the reactants. We can say that an exothermic reaction is an energetically favorable reaction.

If the drive toward lower energy were the only consideration for whether a reaction is able to occur, we would expect that endothermic reactions could never occur spontaneously. In an endothermic reaction, energy is absorbed during the reaction, and the products thus have a larger quantity of energy than the reactants. This means that the products are less stable than the reactants. Therefore, the reaction would not occur without some outside influence such as persistent heating. However, endothermic reactions do occur spontaneously, or naturally. There must be another driving force besides enthalpy change which helps promote spontaneous chemical reaction.

Entropy as a Driving Force

A very simple endothermic 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.

$$\mathrm{H_2O}\left(s\right) + 6.01 \text{ kJ} \rightarrow \mathrm{H_2O}\left(l\right) \tag{11.4.1}$$

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.

There is a tendency in nature for systems to proceed toward a state of greater disorder or randomness. **Entropy** *is a measure of the degree of randomness or disorder of a system*. Entropy is an easy concept to understand when thinking about everyday situations. When the pieces of a jigsaw puzzle are dumped from the box, the pieces naturally hit the table in a very random state. In order to put the puzzle together, a great deal of work must be dome in order to overcome the natural entropy of the pieces. The entropy of a room that has been recently cleaned and organized is low. As time goes by, it likely will become more disordered, and thus its entropy will increase (see figure below). The natural tendency of a system is for its entropy to increase.

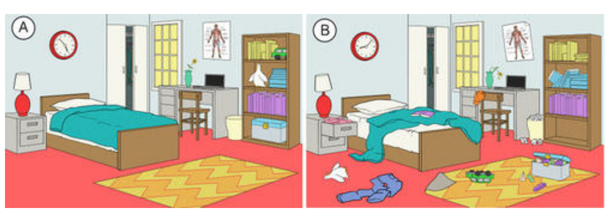

Figure 11.4.1: The messy room on the right has more entropy than the highly ordered room on the left. The drive toward an increase in entropy is the natural direction for all processes.

Chemical reactions also tend to proceed in such a way as to increase the total entropy of the system. 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.

$$\mathrm{Cl_2}\,(g) \rightarrow \mathrm{Cl_2}\,(l) \tag{11.4.2}$$

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

$$\mathrm{CaCO_3}\,(s) \rightarrow \mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g) \tag{11.4.3}$$

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

$$\mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g) \rightarrow 2\mathrm{NH_3}\,(g) \tag{11.4.4}$$

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

$$\mathrm{AgNO_3}\,(aq) + \mathrm{NaCl}\,(aq) \rightarrow \mathrm{NaNO_3}\,(aq) + \mathrm{AgCl}\,(s) \tag{11.4.5}$$

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

$$\mathrm{H_2}\,(g) + \mathrm{Cl_2}\,(g) \rightarrow 2\mathrm{HCl}\,(g) \tag{11.4.6}$$

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.

Contributors and Attributions

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