13.2: Chemical Equilibria

Learning Objectives

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium

A chemical reaction is usually written in a way that suggests it proceeds in one direction, the direction in which we read, but all chemical reactions are reversible, and both the forward and reverse reaction occur to one degree or another depending on conditions. In a chemical equilibrium, the forward and reverse reactions occur at equal rates, and the concentrations of products and reactants remain constant. If we run a reaction in a closed system so that the products cannot escape, we often find the reaction does not give a 100% yield of products. Instead, some reactants remain after the concentrations stop changing. At this point, when there is no further change in concentrations of reactants and products, we say the reaction is at equilibrium. A mixture of reactants and products is found at equilibrium.

For example, when we place a sample of dinitrogen tetroxide (N_2O_4, a colorless gas) in a glass tube, it forms nitrogen dioxide ($\mathrm{NO_2}$, a brown gas) by the reaction

$$\mathrm{N_2O_4(g) \rightleftharpoons 2\,NO_2(g)} \tag{13.2.1}$$

The color becomes darker as $\mathrm{N_2O_4}$ is converted to $\mathrm{NO_2}$. When the system reaches equilibrium, both $\mathrm{N_2O_4}$ and $\mathrm{NO_2}$ are present (Figure $13.2.1$).

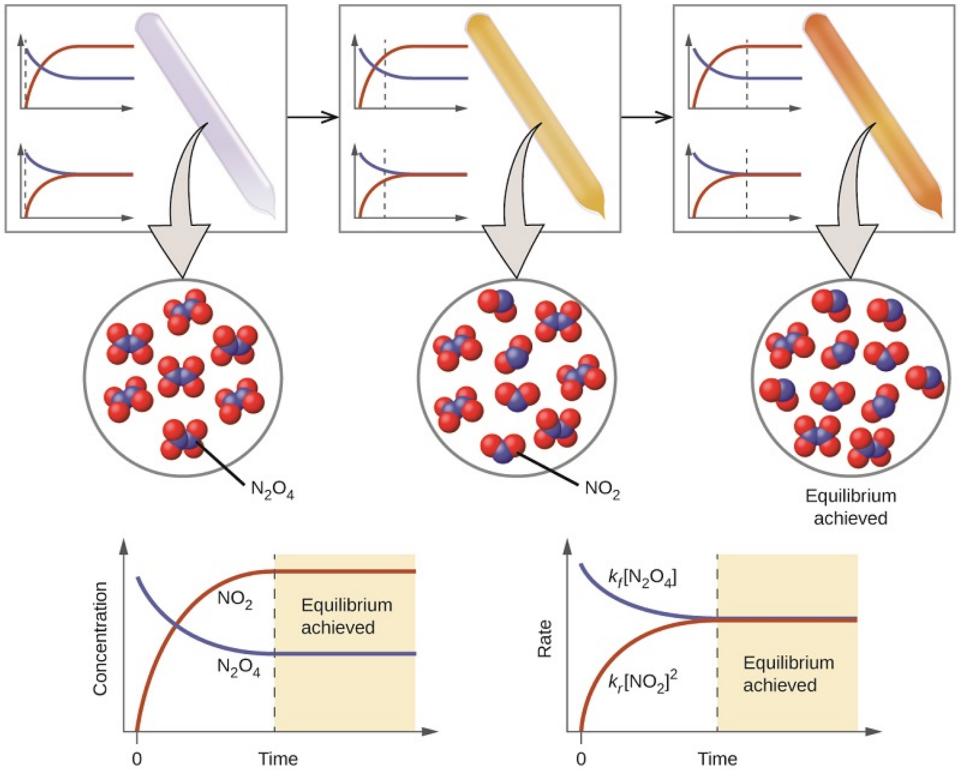

Figure 13.2.1: A mixture of NO_2 and N_2O_4 moves toward equilibrium. Colorless N_2O_4 reacts to form brown NO_2. As the reaction proceeds toward equilibrium, the color of the mixture darkens due to the increasing concentration of NO_2.

A three-part diagram is shown. At the top of the diagram, three beakers are shown, and each one contains a sealed tube. The tube in the left beaker is full of a colorless gas which is connected to a zoom-in view of the particles in the tube by a downward-facing arrow. This particle view shows seven particles, each composed of two connected blue spheres. Each blue sphere is connected to two red spheres. The tube in the middle beaker is full of a light brown gas which is connected to a zoom-in view of the particles in the tube by a downward-facing arrow. This particle view shows nine particles, five of which are composed of two connected blue spheres. Each blue sphere is connected to two red spheres. The remaining four are composed of two red spheres connected to a blue sphere. The tube in the right beaker is full of a brown gas which is connected to a zoom-in view of the particles in the tube by a downward-facing arrow. This particle view shows eleven particles, three of which are composed of two connected blue spheres. Each blue sphere is connected to two red spheres. The remaining eight are composed of two red spheres connected to a blue sphere. At the bottom of the image are two graphs. The left graph has a y-axis labeled, "Concentration," and an x-axis labeled, "Time." A red line labeled, "N O subscript 2," begins in the bottom left corner of the graph at a point labeled, "0," and rises near the highest point on the y-axis before it levels off and becomes horizontal. A blue line labeled, "N subscript 2 O subscript 4," begins near the highest point on the y-axis and drops below the midpoint of the y-axis before leveling off. The right graph has a y-axis labeled, "Rate," and an x-axis labeled, "Time." A red line labeled, "k subscript f, [N subscript 2 O subscript 4]," begins in the bottom left corner of the graph at a point labeled, "0," and rises near the middle of the y-axis before it levels off and becomes horizontal. A blue line labeled, "k subscript f, [N O subscript 2] superscript 2," begins near the highest point on the y-axis and drops to the same point on the y-axis as the red line before leveling off. The point where both lines become horizontal is labeled, "Equilibrium achieved."

The formation of NO_2 from N_2O_4 is a reversible reaction, which is identified by the equilibrium arrow ($\rightleftharpoons$). All reactions are reversible, but many reactions, for all practical purposes, proceed in one direction until the reactants are exhausted and will reverse only under certain conditions. Such reactions are often depicted with a one-way arrow from reactants to products. Many other reactions, such as the formation of NO_2 from N_2O_4, are reversible under more easily obtainable conditions and, therefore, are named as such. In a reversible reaction, the reactants can combine to form products and the products can react to form the reactants. Thus, not only can N_2O_4 decompose to form NO_2, but the NO_2 produced can react to form N_2O_4. As soon as the forward reaction produces any NO_2, the reverse reaction begins and NO_2 starts to react to form N_2O_4. At equilibrium, the concentrations of N_2O_4 and NO_2 no longer change because the rate of formation of NO_2 is exactly equal to the rate of consumption of NO_2, and the rate of formation of N_2O_4 is exactly equal to the rate of consumption of N_2O_4. *Chemical equilibrium is a dynamic process*: As with the swimmers and the sunbathers, the numbers of each remain constant, yet there is a flux back and forth between them (Figure 13.2.2).

Figure 13.2.2: These jugglers provide an illustration of dynamic equilibrium. Each throws clubs to the other at the same rate at which he receives clubs from that person. Because clubs are thrown continuously in both directions, the number of clubs moving in each direction is constant, and the number of clubs each juggler has at a given time remains (roughly) constant.

In a chemical equilibrium, the forward and reverse reactions do not stop, rather they continue to occur at the same rate, leading to constant concentrations of the reactants and the products. Plots showing how the reaction rates and concentrations change with respect to time are shown in Figure $13.2.1$.

We can detect a state of equilibrium because the concentrations of reactants and products do not appear to change. However, it is important that we verify that the absence of change is due to equilibrium and not to a reaction rate that is so slow that changes in concentration are difficult to detect.

We use a double arrow when writing an equation for a reversible reaction. Such a reaction may or may not be at equilibrium. For example, Figure $13.2.1$ shows the reaction:

$$\mathrm{N_2O_4(g) \rightleftharpoons 2\,NO_2(g)} \tag{13.2.2}$$

When we wish to speak about one particular component of a reversible reaction, we use a single arrow. For example, in the equilibrium shown in Figure $13.2.1$, the rate of the forward reaction

$$\mathrm{2\,NO_2(g) \rightarrow N_2O_4(g)} \tag{13.2.3}$$

is equal to the rate of the backward reaction

$$\mathrm{N_2O_4(g) \rightarrow 2\,NO_2(g)} \tag{13.2.4}$$

Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804; mostly known today for his role in the discovery and identification of oxygen) discovered a method of infusing water with carbon dioxide to make carbonated water. In 1772, Priestly published a paper entitled “Impregnating Water with Fixed Air.” The paper describes dripping oil of vitriol (today we call this sulfuric acid, but what a great way to describe sulfuric acid: “oil of vitriol” literally means “liquid nastiness”) onto chalk (calcium carbonate). The resulting CO_2 falls into the container of water beneath the vessel in which the initial reaction takes place; agitation helps the gaseous CO_2 mix into the liquid water.

$$\mathrm{H_2SO_4(l) + CaCO_3(s) \rightarrow CO_2(g) + H_2O(l) + CaSO_4(aq)}$$

Carbon dioxide is slightly soluble in water. There is an equilibrium reaction that occurs as the carbon dioxide reacts with the water to form carbonic acid (H_2CO_3). Since carbonic acid is a weak acid, it can dissociate into protons (H^+) and hydrogen carbonate ions (HCO_3^-).

$$\mathrm{CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)}$$

Today, $\mathrm{CO_2}$ can be pressurized into soft drinks, establishing the equilibrium shown above. Once you open the beverage container, however, a cascade of equilibrium shifts occurs. First, the $\mathrm{CO_2}$ gas in the air space on top of the bottle escapes, causing the equilibrium between gas-phase $\mathrm{CO_2}$ and dissolved or aqueous $\mathrm{CO_2}$ to shift, lowering the concentration of $\mathrm{CO_2}$ in the soft drink. Less $\mathrm{CO_2}$ dissolved in the liquid leads to carbonic acid decomposing to dissolved $\mathrm{CO_2}$ and H_2O. The lowered carbonic acid concentration causes a shift of the final equilibrium. As long as the soft drink is in an open container, the $\mathrm{CO_2}$

bubbles up out of the beverage, releasing the gas into the air (Figure $13.2.3$). With the lid off the bottle, the CO_2 reactions are no longer at equilibrium and will continue until no more of the reactants remain. This results in a soft drink with a much lowered CO_2 concentration, often referred to as "flat."

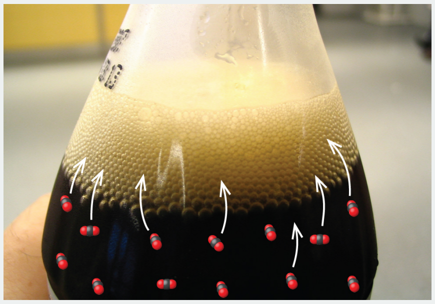

Figure $13.2.3$: When a soft drink is opened, several equilibrium shifts occur. (credit: modification of work by "D Coetzee"/Flickr)

A bottle of soda sitting on the ground is shown with a large amount of fizz-filled liquid spewing out of the top.

Sublimation of Bromine

Let us consider the evaporation of bromine as a second example of a system at equilibrium.

$$Br_2(l) \rightleftharpoons Br_2(g)$$

An equilibrium can be established for a physical change—like this liquid to gas transition—as well as for a chemical reaction. Figure $13.2.4$ shows a sample of liquid bromine at equilibrium with bromine vapor in a closed container. When we pour liquid bromine into an empty bottle in which there is no bromine vapor, some liquid evaporates, the amount of liquid decreases, and the amount of vapor increases. If we cap the bottle so no vapor escapes, the amount of liquid and vapor will eventually stop changing and an equilibrium between the liquid and the vapor will be established. If the bottle were not capped, the bromine vapor would escape and no equilibrium would be reached.

Figure $13.2.4$: An equilibrium is pictured between liquid bromine, $Br_2(l)$, the dark liquid, and bromine vapor, $Br_2(g)$, the orange gas. Because the container is sealed, bromine vapor cannot escape and equilibrium is maintained. (credit: Bromine [images-of-elements.com]).

A glass container is shown that is filled with an orange-brown gas and a small amount of dark orange liquid.

Summary

A reaction is at equilibrium when the amounts of reactants or products no longer change. Chemical equilibrium is a dynamic process, meaning the rate of formation of products by the forward reaction is equal to the rate at which the products re-form reactants by the reverse reaction.

Glossary

equilibrium

in chemical reactions, the state in which the conversion of reactants into products and the conversion of products back into reactants occur simultaneously at the same rate; state of balance

reversible reaction

chemical reaction that can proceed in both the forward and reverse directions under given conditions

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