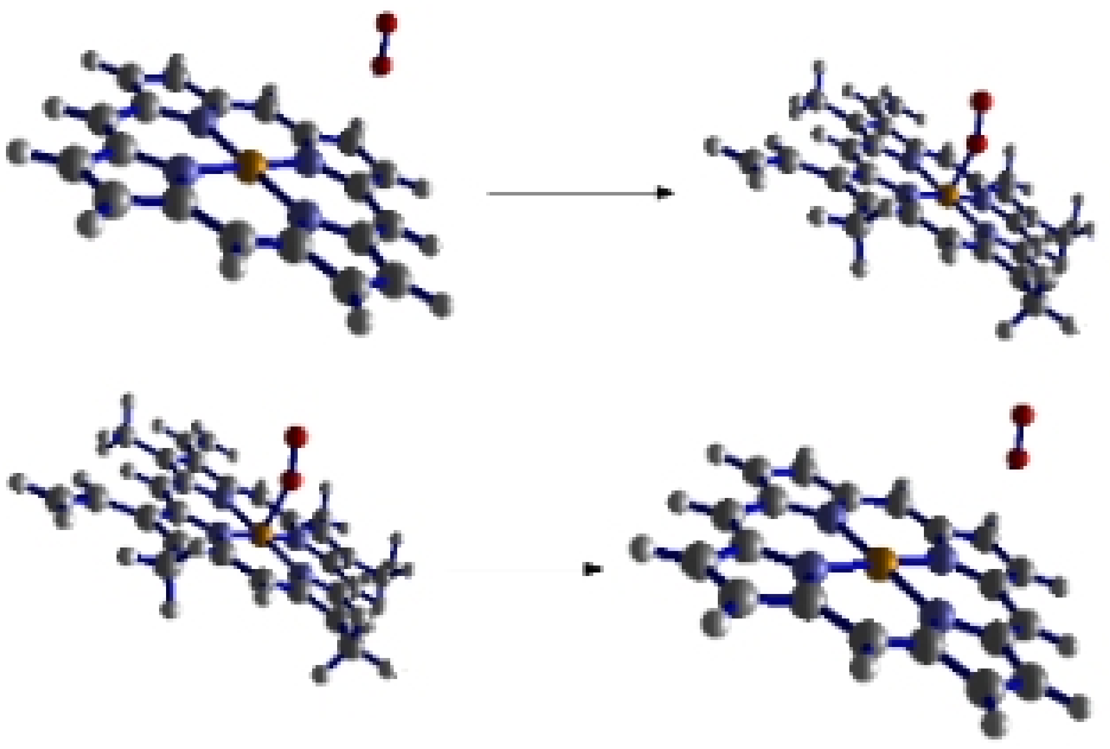
Chapter 15: Chemical Equilibrium

Figure to come

The heme/O_2 equilibrium, with image and models?



Caption to come

Chapter 15

Chapter Goals

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Chapter In Context

This chapter begins our coverage of chemical equilibria. The nature of a dynamic equilibrium was briefly introduced earlier in our description of phase equilibria (sections 12.X and 12.X). In the chapters that follow this one we will apply the concepts and tools learned in this chapter to acid-base equilibria and the chemistry of insoluble ionic compounds.

Chemical equilibrium and the reversibility of chemical reactions plays an important role in one of the most important chemical reactions in the human body, the binding of oxygen molecules to heme groups in the protein hemoglobin. When hemoglobin is exposed to oxygen in the lungs, oxygen molecules attach to the heme groups. When the oxygenated hemoglobin reaches oxygen-depleted cells, the oxygen is released. The process is reversible, and as you will see in this chapter, it is the reversible nature of chemical reactions that is the basis of chemical equilibrium. Reversibility is a central and important aspect of chemical activity in many areas of nature and commerce. For example,

- Biology: The oxygenation of heme is crucial to life, but so is the absorption and release of other gases, such as carbon dioxide, from body fluids. Other equilibrium processes that occur in the body include the reversible binding of metal ions by proteins and the acid-base balance of biochemical systems.
- Environment: The dissolution of toxic metal ions can be reversibly changed through changes in solution acidity brought on by acid rain or industrial acid discharge. These changes can allow for the transportation of normally insoluble harmful substances into natural water systems, affecting plants, fish, and other aquatic species.
- In Your World: The application and removal of floor wax depends on the reversible binding of Zn^{2+} ions to organic polymer materials. Also, soft drinks, beer and champagne all fizz when opened because of the reversible solubility of CO_2 in water.

15.1 The Nature of the Equilibrium State

OWL Opening Simulation
15.1 Microscopic Reversibility

In the previous chapter we learned that chemical reactions proceed in a series of steps called a reaction mechanism. The **principle of microscopic reversibility** tells us that any chemical reaction can proceed in the forward or reverse direction. Thus any series of chemical reactions, the elementary steps in a mechanism, for example, can proceed in either the forward or reverse direction.

Consider the two-step mechanism for the reaction of nitrogen dioxide with carbon monoxide.

Step 1: $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$

Step 2: $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$

Net reaction: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

The two elementary steps in the mechanism could also proceed in the reverse direction.

Step 1’ $NO_2(g) + CO_2(g) \rightarrow NO_3(g) + CO(g)$ (Step 2 reversed)

Step 2’ $NO_3(g) + NO(g) \rightarrow NO_2(g) + NO_2(g)$ (Step 1 reversed)

The new net reaction is the reverse of the original reaction.

New net reaction: $NO(g) + CO_2(g) \rightarrow NO_2(g) + CO(g)$

The equilibrium arrow (*Æ*) is used to indicate that a reaction is reversible.

$NO_2(g) + CO(g)$ *Æ* $NO(g) + CO_2(g)$

There are occasions when the use of an equilibrium arrow is not appropriate. For example, when hydrogen and oxygen react to form water vapor (Figure 15.X), product formation is very strongly favored and no noticeable amounts of reactants are formed by the reverse reaction. The chemical equation representing this reaction therefore uses a single reaction arrow (→). Also, if the reverse reaction cannot occur, such as when one of the reaction products is physically separated from a reaction mixture as a gas (the reaction of a metal carbonate with acid, for example, Figure 15.X), a single reaction arrow is used.

Figure 15.X

The Equilibrium State

In Chapter 12, we described the nature of a dynamic equilibrium between a liquid and its vapor in a sealed flask. When equilibrium was reached in the flask, the amount of liquid did not change, but the vaporization and condensation processes continued. When the rate of vaporization is equal to the rate of condensation, a state of dynamic equilibrium between the two phases is reached. We can apply this concept to reversible chemical reactions and use it to describe the nature of a dynamic chemical equilibrium.

Flashback
12.X Vapor Pressure

Consider the reversible reaction between Fe^{3+} and the thiocyanate ion.

$Fe^{3+}(aq) + SCN^{-}(aq)$ *Æ* $FeSCN^{2+}(aq)$

When the two reactants are mixed, they react in the forward direction to form $FeSCN^{2+}$ in a second order process.

$Fe^{3+}(aq) + SCN^{-}(aq) \rightarrow FeSCN^{2+}(aq)$ Rate (forward) = $k_{forward}[Fe^{3+}][SCN^{-}]$

As the reaction proceeds, the product concentration increases and the reverse reaction begins to take place.

$$FeSCN^{2+}(aq) \rightarrow Fe^{3+}(aq) + SCN^{-}(aq) \qquad \text{Rate (reverse)} = k_{reverse}[FeSCN^{2+}]$$

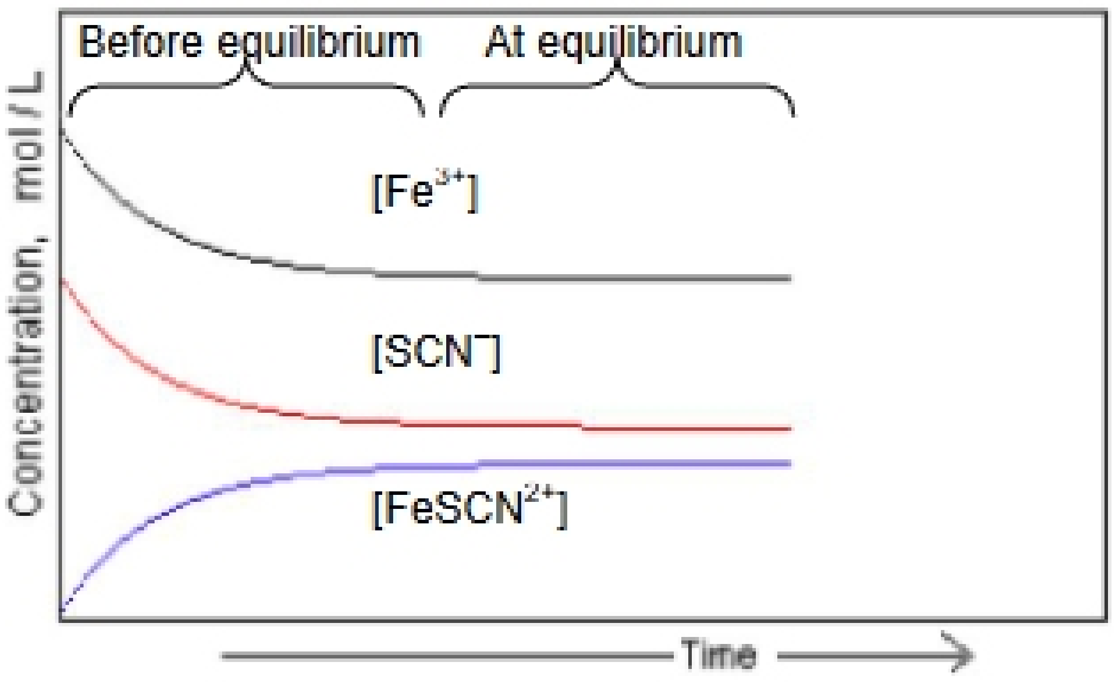
As the reaction continues, the rate of the forward reaction decreases (because $[Fe^{3+}]$ and $[SCN^{-}]$ decrease) and the rate of the reverse reaction increases (because $[FeSCN^{2+}]$ increases). Eventually, a state of **chemical equilibrium** is reached where the rate of the forward reaction is equal to the rate of the reverse reaction:

$$\text{Rate (forward)} = \text{Rate (reverse)}$$

$$k_{forward}[Fe^{3+}][SCN^{-}] = k_{reverse}[FeSCN^{2+}]$$

When this equilibrium state is achieved, the concentrations of all the species in solution are constant, even though the forward and reverse reactions continue to take place.

The equilibrium state can be represented graphically by plotting the concentration of reactants and products over time (Figure 15.X). Notice that during the first stage of the reaction, the forward reaction is faster than the reverse reaction and reactant concentrations decrease while the product concentration increases. When the system reaches equilibrium, the forward and reverse rates are equal and concentrations of reactants and product do not change.



Note: We will use shading to indicate when reaction is at equilibrium

Figure 15.X Graphical representation of progression towards chemical equilibrium in the $Fe^{3+}/SCN^{-}/FeSCN^{2+}$ system

OWL Concept Exploration
15.3 The Equilibrium State: Simulation
15.4 The Equilibrium State

15.2. The Equilibrium Constant, *K*

OWL Opening Exploration
15.5 The Equilibrium Constant

The relationship between forward and reverse rate constants for an equilibrium system is shown in an **equilibrium constant expression** and quantified by an **equilibrium constant (*K*)**. An equilibrium constant expression is written by rearranging the equation relating forward and reverse reaction rates. When the rate of forward and reverse reaction rates is equal, the chemical system is at equilibrium and the ratio of forward and reverse rate constants is equal to the **equilibrium constant, *K***. For the $Fe^{3+}/SCN^{-}/Fe(SCN)^{2+}$ equilibrium system, for example,

Rate constants are symbolized by a lower-case *k* and equilibrium constants are symbolized by a capital *K*.