15.1: The Concept of Chemical Equilibrium

Learning Objectives

- To understand what is meant by chemical equilibrium.

Chemical equilibrium is a dynamic process that consists of a forward reaction, in which reactants are converted to products, and a reverse reaction, in which products are converted to reactants. At equilibrium, the forward and reverse reactions proceed at equal rates. Consider, for example, a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide (N_2O_4) to nitrogen dioxide (NO_2). You may recall from Chapter 14 that NO_2 is responsible for the brown color we associate with smog. When a sealed tube containing solid N_2O_4 (mp = −9.3°C; bp = 21.2°C) is heated from −78.4°C to 25°C, the red-brown color of NO_2 appears (Figure 15.1.1). The reaction can be followed visually because the product (NO_2) is colored, whereas the reactant (N_2O_4) is colorless:

$$N_2O_4(g) colorless \rightleftharpoons 2NO_{2(g)}\ red-brown \tag{15.1.1}$$

The double arrow indicates that both the forward and reverse reactions are occurring simultaneously; it is read “is in equilibrium with.”

Figure 15.1.1 The **$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ System at Different Temperatures** (left) At dry ice temperature (−78.4°C), the system contains essentially pure solid N_2O_4, which is colorless. (center) As the system is warmed above the melting point of N_2O_4 (−9.3°C), the N_2O_4 melts and then evaporates, and some of the vapor dissociates to red-brown NO_2. (right) Eventually the sample reaches room temperature, and a mixture of gaseous N_2O_4 and NO_2 is present. The composition of the mixture and hence the color do not change further with time: the system has reached equilibrium at the new temperature.

Figure 15.1.2shows how the composition of this system would vary as a function of time at a constant temperature. If the initial concentration of NO_2 were zero, then it increases as the concentration of N_2O_4 decreases. Eventually the composition of the system stops changing with time, and chemical equilibrium is achieved. Conversely, if we start with a sample that contains no N_2O_4 but an initial NO_2 concentration twice the initial concentration of N_2O_4 in part (a) in Figure 15.1.2, in accordance with the stoichiometry of the reaction, we reach exactly the same equilibrium composition, as shown in part (b) in Figure 15.1.2. Thus equilibrium can be approached from *either direction* in a chemical reaction.

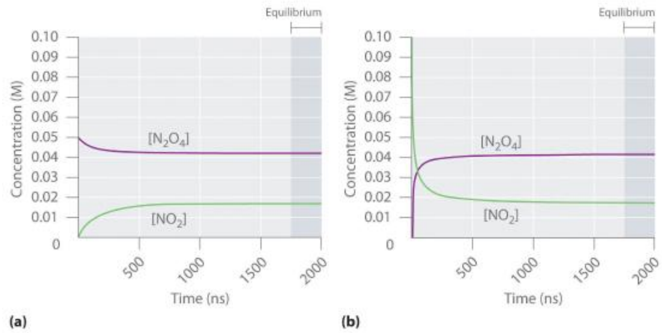


Figure 15.1.2 The Composition of N_2O_4/NO_2 Mixtures as a Function of Time at Room Temperature (a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2. The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system contains 0.1000 M NO_2 and no N_2O_4. The concentration of NO_2 decreases with time as the concentration of N_2O_4 increases. In both cases, the final concentrations of the substances are the same: $[N_2O_4]$ = 0.0422 M and $[NO_2]$ = 0.0156 M at equilibrium.

Figure 15.1.3 shows the forward and reverse reaction rates for a sample that initially contains pure NO_2. Because the initial concentration of N_2O_4 is zero, the forward reaction rate (dissociation of N_2O_4) is initially zero as well. In contrast, the reverse reaction rate (dimerization of NO_2) is initially very high (2.0×10^6 M/s), but it decreases rapidly as the concentration of NO_2 decreases. (Recall from Chapter 14 that the reaction rate of the dimerization reaction is expected to decrease rapidly because the reaction is second order in NO_2: rate = $k_r[NO_2]^2$, where k_r is the rate constant for the reverse reaction shown in Equation 15.1.1.) As the concentration of N_2O_4 increases, the rate of dissociation of N_2O_4 increases—but more slowly than the dimerization of NO_2—because the reaction is only first order in N_2O_4 (rate = $k_f[N_2O_4]$, where k_f is the rate constant for the forward reaction in Equation 15.1.1). Eventually, the forward and reverse reaction rates become identical, $k_F = k_r$, and the system has reached chemical equilibrium. If the forward and reverse reactions occur at *different* rates, then the system is *not* at equilibrium.

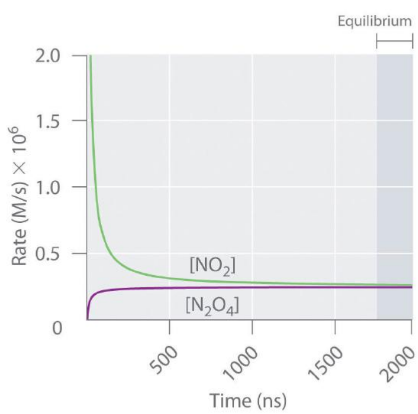


Figure 15.1.2

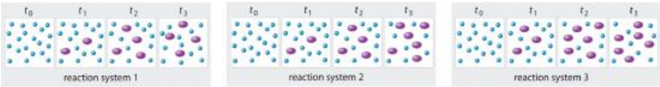
The rate of dimerization of NO_2 (reverse reaction) decreases rapidly with time, as expected for a second-order reaction. Because the initial concentration of N_2O_4 is zero, the rate of the dissociation reaction (forward reaction) at t = 0 is also zero. As the dimerization reaction proceeds, the N_2O_4 concentration increases, and its rate of dissociation also increases. Eventually the rates of the two reactions are equal: chemical equilibrium has been reached, and the concentrations of N_2O_4 and NO_2 no longer change.

Note the Pattern

At equilibrium, the forward reaction rate is equal to the reverse reaction rate.

Example 15.1.1

The three reaction systems (1, 2, and 3) depicted in the accompanying illustration can all be described by the equation <math display="inline" xml:id="av_1.0-15_m004"><semantics><mrow><mn>2</mn><mtext>A</mtext><mo>⇌</mo><mtext>B,</mtext></mrow></semantics></math> where the blue circles are A and the purple ovals are B. Each set of panels shows the changing composition of one of the three reaction mixtures as a function of time. Which system took the longest to reach chemical equilibrium?



Given: three reaction systems

Asked for: relative time to reach chemical equilibrium

Strategy:

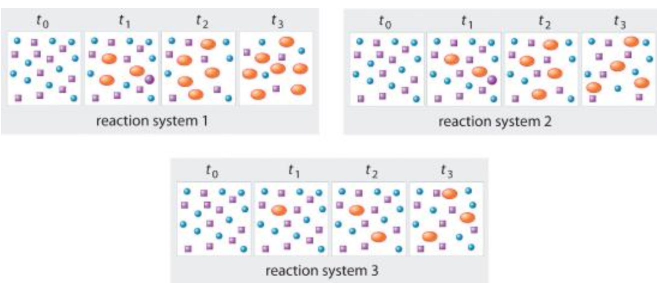
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

Solution:

In systems 1 and 3, the concentration of A decreases from t_0 through t_2 but is the same at both t_2 and t_3. Thus systems 1 and 3 are at equilibrium by t_3. In system 2, the concentrations of A and B are still changing between t_2 and t_3, so system 2 may not yet have reached equilibrium by t_3. Thus system 2 took the longest to reach chemical equilibrium.

Exercise

In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is A + B ⇌ C. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown has reached equilibrium?



Answer: system 2

Summary

Chemical equilibrium is a dynamic process consisting of forward and reverse reactions that proceed at equal rates. At equilibrium, the composition of the system no longer changes with time. The composition of an equilibrium mixture is independent of the direction from which equilibrium is approached.

Key Takeaway

- At equilibrium, the forward and reverse reactions of a system proceed at equal rates.

Conceptual Problems

1. What is meant when a reaction is described as “having reached equilibrium”? What does this statement mean regarding the forward and reverse reaction rates? What does this statement mean regarding the concentrations or amounts of the reactants and the products?
2. Is it correct to say that the reaction has “stopped” when it has reached equilibrium? Explain your answer and support it with a specific example.
3. Why is chemical equilibrium described as a dynamic process? Describe this process in the context of a saturated solution of NaCl in water. What is occurring on a microscopic level? What is happening on a macroscopic level?
4. Which of these systems exists in a state of chemical equilibrium?
    1. oxygen and hemoglobin in the human circulatory system
    2. iodine crystals in an open beaker
    3. the combustion of wood
    4. the amount of ^{14}C in a decomposing organism

Answer

1.
2.
3. Both forward and reverse reactions occur but at the same rate. Na^+ and Cl^- ions continuously leave the surface of an NaCl crystal to enter solution, while at the same time Na^+ and Cl^- ions in solution precipitate on the surface of the crystal.
4.

- Anonymous
