Qualitative Changes in Equilibrium Systems

Imagine that your friend is trying to stay in the same place while walking up an escalator that is moving down. She will be able to maintain her location if the rate at which she walks up equals the rate at which the escalator moves down. As long as the rate your friend walks up is the same as the rate that the escalator moves down, this system is in a state of dynamic equilibrium. However, should the escalator begin to move faster while your friend maintains the same rate of walking up, the dynamic equilibrium will be disturbed and the location of your friend on the escalator will shift down. To re-establish equilibrium, she must increase her stepping rate to match the new rate of motion of the escalator. However, when dynamic equilibrium is re-established, she will be at a new location, lower on the escalator. As we will see, the changes in this dynamic equilibrium are analogous to what happens in a chemical equilibrium system when it is disturbed.

What do we mean when we say a chemical system at equilibrium is disturbed? Previously in this chapter, we saw that changes in temperature can shift the position of an equilibrium in a closed system. These changes are examples of disturbances in a chemical equilibrium system. In general, chemical systems at equilibrium may be disturbed by changes in pressure, temperature, concentration, or a combination of these.

Figure 1 Henry-Louis Le Châtelier (1850–1936), a chemist and engineer, is best known for his generalization about the nature of disturbance to chemical equilibria.

Le Châtelier's Principle

In 1884, the French chemist Henry-Louis Le Châtelier (**Figure 1**) was best known for his work in analyzing chemical reaction systems at equilibrium. Le Châtelier started with a well-defined initial equilibrium state, then changed one property of the system. He observed that there would be a temporary "non-equilibrium" state in the chemical reaction system, and then a new equilibrium state would become established. The goal behind Le Châtelier's investigations was to maximize the yield of products from equilibrium systems, using this systematic process of trial and error. As he gathered data, he saw a pattern emerge. He communicated this pattern to the scientific community as the generalization now known as **Le Châtelier's principle**. WEB LINK

Le Châtelier's principle a generalization that states that chemical systems at equilibrium shift to restore equilibrium when a change occurs that disturbs the equilibrium

> When a chemical system at equilibrium is disturbed by a change in a property, the system adjusts in a way that opposes the change.

Le Châtelier's principle allows chemists to predict the qualitative effects of changes in concentration, pressure, and temperature on a chemical reaction system at equilibrium. Since Le Châtelier's time, this generalization has been supported through extensive evidence. It is regularly applied by chemical engineers who want to maximize the yield of a desired product to make industrial-scale chemical processes more efficient. In fact, Fritz Haber and Carl Bosch used Le Châtelier's principle in their work to devise a process for the economical production of ammonia gas from atmospheric nitrogen (Section 7.3.) CAREER LINK

Le Châtelier's Principle and Changes in Concentration

An adjustment by a system at equilibrium that results in a change in the concentrations of reactants and products is called an **equilibrium shift**. One way to cause an equilibrium shift is to add additional reactant to the reaction vessel. By applying Le Châtelier's principle, we can predict that increasing the concentration of a reactant will shift the equilibrium to the right, to oppose this change. This prediction can be tested by investigation. For example, when a light yellow solution of iron(III) ions, $Fe^{3+}(aq)$, is mixed

equilibrium shift a change in concentrations of reactants and products in order to restore an equilibrium state with a colourless solution of thiocyanate ions, $SCN^-(aq)$, an equilibrium is reached with the product, iron thiocyanate ions, $FeSCN^{2+}(aq)$. The balanced chemical equation for this chemical reaction system is

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

Note that there are two reactants and one product in the forward reaction of this equilibrium system. **Figure 2** shows the concentrations of the reactants and products over time. At the zero time point, the two solutions are mixed. Notice how the concentrations of reactants fall as the concentration of the product increases. When the reaction system reaches equilibrium, all three concentrations remain constant and all three lines on the graph are horizontal. At the point marked by the first dotted vertical line, more thiocyanate ions are added to the equilibrium. This causes the solution to change colour (**Figure 3**). After the addition, the concentration of thiocyanate briefly increases, then it decreases again. The decrease is the result of some of these ions being used to form more product, the iron thiocyanate ions. Similarly, the concentration of aqueous iron(III) ions decreases as some of them are used also in product formation. However, eventually equilibrium is re-established at a new position.

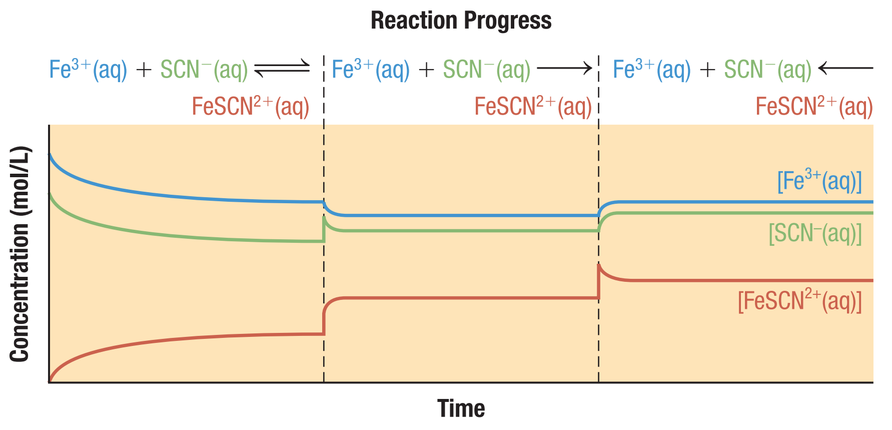

Figure 2 When yellow aqueous iron(III) ions, $Fe^{3+}(aq)$, initially mix with colourless aqueous thiocyanate ions, $SCN^-(aq)$, a portion of the ions combine to form red aqueous iron thiocyanate ions, $FeSCN^{2+}(aq)$. As the reaction progresses, the concentrations of reactants fall as the concentration of the product rises, until equilibrium is reached. When more thiocyanate ions are added at the point indicated by the dashed line, the aqueous thiocyanate ion concentration increases momentarily but then falls off as additional aqueous iron thiocyanate ions are produced. Can you identify what change was made to the system at the second dashed line?

Figure 3 The deep red colour of the equilibrium system changes when more aqueous thiocyanate ions are added, indicating an equilibrium shift.

This experiment verifies the prediction made by Le Châtelier's principle, that increasing the concentration of a reactant will shift the equilibrium to the right. Notice that the concentrations of reactants and products at this new equilibrium position are different from their concentrations in the original equilibrium. When additional reactant is added, the equilibrium concentration of the added reactant in the new equilibrium is usually higher than was its equilibrium concentration in the original equilibrium.

Le Châtelier's principle also predicts that removing some of a reactant in a chemical system at equilibrium will shift the equilibrium to the left (toward reactants), to partially counteract the lower reactant concentration. We will look at these predictions more closely by considering an investigation of the chemical reaction system represented by the following chemical equation:

$$2\,CO_2(g) \rightleftharpoons 2\,CO(g) + O_2(g)$$

When more carbon dioxide gas was added to the system at equilibrium, its concentration first spiked, then immediately started to decrease as the concentrations of the products increased. The concentrations of gaseous carbon dioxide, carbon monoxide, and oxygen at the new equilibrium position are higher than they were in the original equilibrium (**Figure 4(a)**). When one of the products, carbon monoxide gas, was removed from the system at equilibrium, more reactant was converted to products to compensate for the change (**Figure 4(b)**). The equilibrium shifts to the right: the concentration of oxygen gas increases while the concentration of carbon dioxide gas decreases, until a new equilibrium is established.

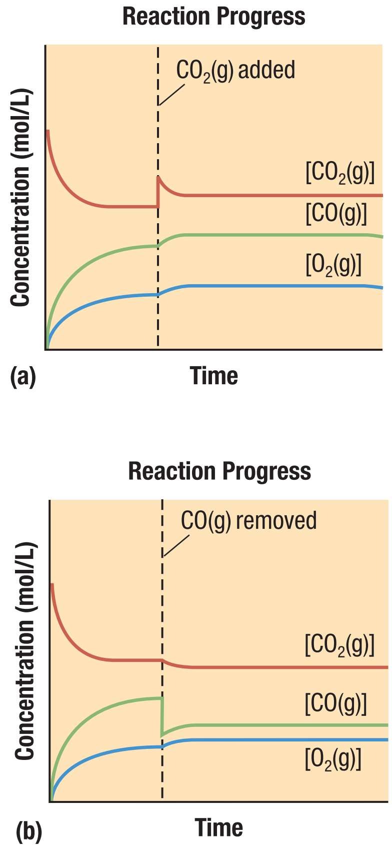

Figure 4 (a) At the dotted line, when the system was at equilibrium, more carbon dioxide gas (reactant) was added to the system. The equilibrium responded by shifting to the right (in the direction of products). The concentration of the reactant at the new equilibrium is also higher. (b) At the dotted line, when the system was at equilibrium, carbon monoxide gas (product) was removed from the system. As in (a), the equilibrium responded by shifting to the right, converting more reactant to products.

Collision Theory and Concentration Changes in an Equilibrium System

According to collision theory, entities in a chemical system must collide to react. When the concentration of an entity in a chemical reaction system is increased, it is more likely that that entity will collide with other entities. There are simply more of them present. However, only collisions between reactant entities can potentially contribute to a chemical reaction. Even so, the more frequently collisions occur overall, the more likely it is that a chemical reaction will take place.

Collision theory explains the response of a chemical reaction system at equilibrium to a change in concentration as the result of random collisions and probability. When we add more reactant entities in an equilibrium system, the equilibrium shifts to the right because the number of successful collisions for the forward reaction increases. If, instead, we add more product entities, then the number of successive collisions for the reverse reaction will increase and the equilibrium will shift to the left. WEB LINK

The rate of a chemical reaction reflects how often reacting entities collide, be they products or reactants. Therefore, when we add a reactant to an equilibrium system, the resulting higher concentration increases the rate of the forward reaction to which it contributes. The higher rate, in turn, decreases the concentration of that substance, so the forward reaction rate then decreases. Conversely, the product(s) of the forward reaction increase in concentration and so become more likely to collide, causing the rate of the reverse reaction to increase. Once the rates of the forward and reverse reactions become equal, a new equilibrium is established. The rates of the forward and reverse reactions will not be the same as in the original equilibrium, however.

Applications of Le Châtelier's Principle and Concentration Changes

Chemical engineers may apply Le Châtelier's principle when designing industrial processes based on reversible reactions. Often the production process involves continuous addition of reactants or removal of products. This prevents the chemical reaction system from ever reaching equilibrium, so that the formation of products will always be favoured. One example of this is in the industrial production of aqueous nitric acid, HNO_3(aq):

$$3\ NO_2(g) + H_2O(l) \rightleftharpoons 2\ HNO_3(aq) + NO(g)$$

Nitric acid has many uses, such as in the synthesis of fertilizers, explosives, dyes, and perfumes. Nitric oxide is not as useful. In the industrial production of aqueous nitric acid, the nitric oxide gas is removed from the chemical reaction system by reacting it with oxygen gas. As the nitric acid product is removed, the equilibrium shifts to the right to compensate, so more reactants form products. This has the desired result of increasing the yield of nitric acid.

Another example is the gasification of carbon. This chemical reaction system is an important part of the conversion of biomass to usable hydrogen gas fuel. At high temperatures, elemental carbon, C(s), reacts with water vapour to produce hydrogen gas and carbon monoxide gas. The balanced equation for the gasification of carbon is

$$C(s) + H_2O(g) \rightleftharpoons H_2(g) + CO(g)$$

Carbon monoxide gas then reacts with water vapour to produce gaseous carbon dioxide and hydrogen in a reaction known as the water–gas shift reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

As fast as the gasification reaction produces gaseous carbon monoxide (and hydrogen), it is used up as a reactant in the water–gas shift reaction. Thus, the water-gas shift reaction constantly forces the equilibrium position of the gasification reaction to the right, producing more products. This has the effect of increasing the yield of hydrogen.

Le Châtelier's principle also applies to biological processes. For example, hemoglobin in your blood, Hb(aq), binds to dissolved oxygen, O_2(aq), in a reversible reaction represented by this balanced equation:

$$Hb(aq) + O_2(aq) \rightleftharpoons HbO_2(aq)$$

Oxygen is first absorbed into your lungs. The concentration of oxygen (a reactant) in the lungs is high, so the equilibrium position is to the right, toward the product, hemoglobin–oxygen complex, HbO_2(aq). The hemoglobin–oxygen complex in the blood is then pumped to your body cells, where the oxygen concentration is relatively low. In other words, the concentration of this reactant is low in your body cells. To compensate, the equilibrium shifts to the left, in favour of the reactants. As a result, oxygen is released from hemoglobin, and it is then available for use by your body cells. CAREER LINK

Le Châtelier's Principle and Changes in Energy

A system at equilibrium will also shift when it is disturbed by the addition or removal of energy. For example, an equilibrium will shift when the temperature is increased or decreased (a change in thermal energy). To apply Le Châtelier's principle and predict how a change in energy will affect a chemical system at equilibrium, we can think of energy as a reactant or a product. For example, energy is absorbed in an endothermic reaction. If we consider energy to be a reactant, we can write the word equation

$$\text{reactants} + \text{energy} \rightleftharpoons \text{products}$$

Similarly, since energy is released during an exothermic reaction, we can consider energy to be a reactant and write

$$\text{reactants} \rightleftharpoons \text{products} + \text{energy}$$

To use Le Châtelier's principle to predict how an equilibrium will shift in response to a change in energy, consider how the system can counteract this shift.

Endothermic Reactions

If an endothermic reaction is cooled (thermal energy removed), we can consider that the quantity of one of the reactants has been decreased. We can therefore predict that the equilibrium will shift to the left (toward the reactants), and energy will be released. For example, the decomposition of dinitrogen tetroxide gas, N_2O_4(g), to nitrogen dioxide gas, NO_2(g), is an endothermic process. We can represent the reaction by this balanced equation:

$$\underset{\text{colourless}}{N_2O_4(g)} + \text{energy} \rightleftharpoons \underset{\text{reddish brown}}{2\,NO_2(g)}$$

If thermal energy were added to this equilibrium system by heating, the equilibrium would likely shift to the right. The additional energy would be absorbed to create more product, nitrogen dioxide gas. Since dinitrogen tetroxide gas is colourless and nitrogen dioxide gas is reddish brown, such a shift would make the gas mixture a darker colour. **Figure 5** shows the visible changes in this chemical reaction system when the temperature was changed from room temperature to 0 °C or to 85 °C.

Figure 5 The room-temperature sample in the centre contains a mix of both gases. Changing the temperature shifts the endothermic reaction equilibrium. The sample on the left, at 0 °C, is shifted toward the formation of colourless dinitrogen tetroxide gas. The darker colour of the sample sample on the right, at 85 °C, is due to a shift toward the formation of reddish brown nitrogen dioxide gas.

Exothermic Reactions

If thermal energy is removed from an exothermic reaction—where energy is a product—then the equilibrium will shift to the right (toward the products), and energy will be released to counteract the change. If energy is added to an exothermic reaction, the equilibrium will shift to the left to compensate for the change, and the energy will be used as products are converted to reactants. An example of an exothermic reaction is the forward reaction in the reversible reaction in which sulfur trioxide gas, $SO_3(g)$, is produced from gaseous oxygen and sulfur dioxide, $SO_2(g)$. The balanced chemical equation for this reaction, including energy, is

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g) + \text{energy}$$

From Le Châtelier's principle, we can predict that removing energy will shift the equilibrium to the right. When the reaction vessel is cooled, more energy will be released and more sulfur trioxide gas will be produced (**Figure 6**).

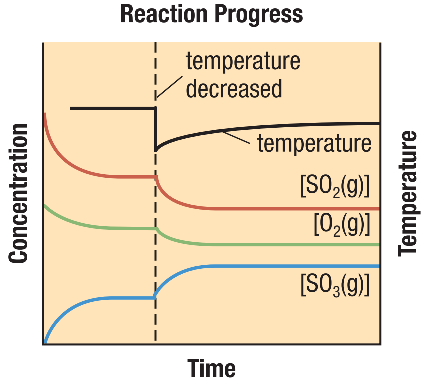

Figure 6 Cooling this system after it has reached equilibrium results in a new equilibrium being established at a lower temperature.

UNIT TASK **BOOKMARK**

How could you use information about Le Châtelier's principle as you work on the Unit Task on page 582?

In summary, if energy is added to or removed from a chemical reaction system at equilibrium, the equilibrium shifts in the direction that will compensate for the change in energy.

Le Châtelier's Principle and Changes in Gas Volume

If you have ever used a manual bicycle pump, you know that changing the volume of a sealed container of gas changes the pressure of the gas in the container. Changing the volume of a container of gas also changes the concentrations of the gases in the container. To understand how pressure relates to concentration in gases, first consider what happens to pressure when the volume of a gas changes. We will assume that our gas behaves as an **ideal gas**, which is a hypothetical gas that obeys all gas laws. According to Boyle's law, the pressure exerted on a container by a certain amount of an ideal gas held at a constant temperature varies inversely with the volume of the gas. This means that, as the volume of a gas changes, its pressure changes too. In the case of a bicycle pump, decreasing the volume of the cylinder to one-third its original volume would increase the pressure threefold.

ideal gas a hypothetical gas composed of entities that have no size, travel in straight lines, and have no attraction to each other (no intermolecular forces); a gas that obeys all gas laws

Boyle's law holds true whether the container holds a pure gas or a mixture of gases. However, when a container holds a gas mixture, each gas exerts its own partial pressure. The **partial pressure** of a gas is the pressure exerted by any one gas in a mixture, and is the same pressure as it would exert alone. The total pressure is simply the sum of all the partial pressures. When the volume of a container is changed, each gas in the mixture contributes its new partial pressure to the new total pressure. When the volume of a gas mixture decreases, the concentration (number of entities per unit volume) increases proportionally to the increase of their partial pressures.

partial pressure the pressure that a gas, in a mixture of gases, would exert if it alone occupied the whole volume occupied by the mixture

Figure 7 illustrates the changes that take place in a container of gas when the volume decreases by half. The container is holding a mixture of gases that react according to the equation

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

By Boyle's law, we know that reducing the volume of the container by one-half will double the total pressure of the gases in the container. Since the partial pressure of each gas will double, the number of molecules of each gas per unit volume will also double. According to the balanced chemical equation, there are 4 reactant entities—1 $N_2(g)$ and 3 $H_2(g)$—per unit volume for every 2 product entities—2 $NH_3(g)$ (**Figure 7(a)**). The total partial pressure of the reactants is twice that of the products, so, when the volume of the container is reduced, the change in concentrations of the reactants will be greater than the change in concentration of the product (**Figure 7(b)**). Le Châtelier's principle predicts that the equilibrium reaction will shift to the right to reduce the total number of entities per unit volume in the container from 4 entities—1 $N_2(g)$ and 3 $H_2(g)$—to 2 entities—2 $NH_3(g)$, which reduces the total pressure of the system (**Figure 7(c)**).

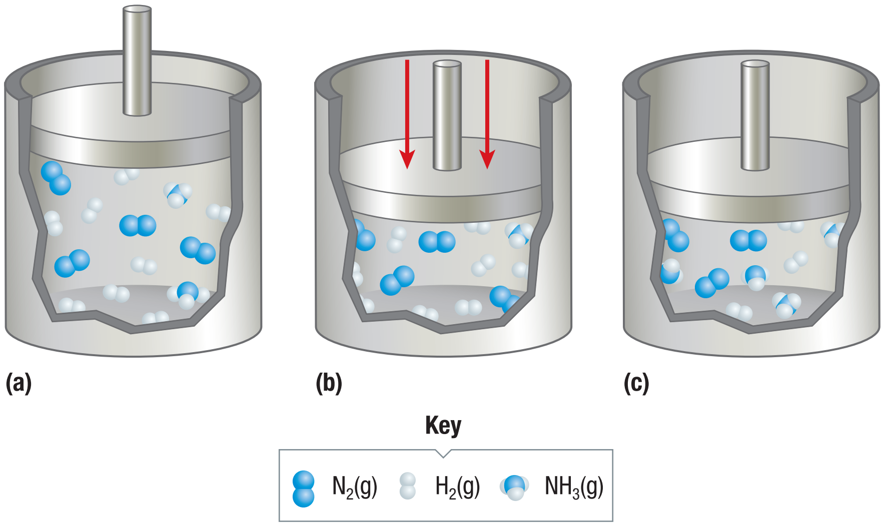

Figure 7 (a) The container holds the equilibrium reaction $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$. (b) The volume of the container is decreased by half, which doubles the total pressure of the system. (c) The reaction shifts to the right, which decreases the total number of particles in the container and the total pressure by producing more ammonia, $NH_3(g)$.

Investigation 7.4.1

Testing Le Châtelier's Principle (page 474)

In this investigation, you will use Le Châtelier's principle to make predictions about how some chemical equilibrium systems will respond to particular chemical and physical changes, and then make observations to see if your predictions are correct.

Changing an Equilibrium System without Affecting Equilibrium Position

As chemists and chemical engineers strive for ever higher efficiency and productivity in equilibrium systems, they may be limited by how much they can change concentration, pressure, and temperature. However, it is possible to modify the amount of reactants and products using methods that do not change the equilibrium position. These methods include using a catalyst, adding an inert gas, and changing the state of the reactants. We will take a brief look at some examples of these methods and see how they work.

Catalysts

Earlier in your studies, you learned that a catalyst provides an alternative path for a chemical reaction that has a lower activation energy barrier (**Figure 8**). In a reversible reaction, catalysts increase the reaction rates of the forward and reverse reactions equally, since both reactants and products can form by the lower-energy path.

Therefore, a catalyst does not change the equilibrium position, and the final equilibrium concentrations of reactants and products are not altered. However, the reaction reaches equilibrium much faster, which can be very useful.

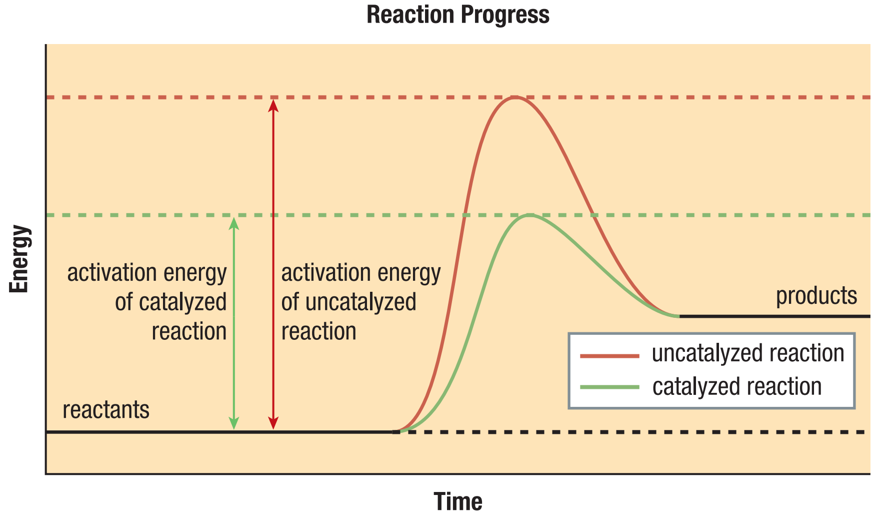

Figure 8 The effect of a catalyst is to lower the activation energy of a reaction. It does not change the energy levels of the reactants and products, so the overall energy change is not affected. As a result, the position of the equilibrium is not affected.

Inert Gas

An inert gas is a gas that is not reactive, and so will not enter into a chemical reaction. If an inert gas is added to an equilibrium system involving a gas mixture and the volume of the container is kept constant, the total number of entities in the volume and therefore the total pressure will increase. However, the partial pressures of the reactant and product entities remain the same. Since there are more entities there are more collisions, but collisions involving the inert gas will not result in a chemical reaction. These collisions can, however, redirect the movement of any entity involved. Imagine that the inert gas entities are fixed obstacles placed randomly in the container, like bumpers in a pinball game. The number and frequency of collisions between reactants and products remain the same. The obstacles redirect reactant and product entities when hit, but do not change the frequency with which reactants and/or product entities collide with each other. As long as the collision frequency for both forward and reverse reactions is unchanged, equilibrium will not shift (**Figure 9**).

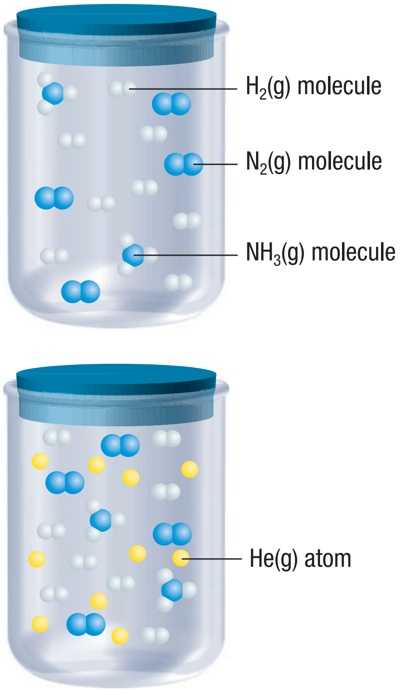

Figure 9 Adding an inert gas, He(g), to a container increases the total pressure of the system but has no effect on the equilibrium concentrations of reactants and products since their partial pressures did not change.

State of Reactants

When a chemical system involves entities in more than one state of matter, equilibrium is affected only by changes in concentration of entities that are in the same state of matter as the substances involved in the chemical reaction system. For example, consider the reaction of solid iodine vapour with hydrogen gas:

$$H_2(g) + I_2(s) \rightleftharpoons 2\,HI(g)$$

Solid iodine is placed in the reaction vessel with hydrogen gas. The solid iodine sublimes (passes directly to gas from the solid phase) before reacting with hydrogen. Once the system has come to equilibrium, the reaction vessel holds a mixture of hydrogen gas, iodine gas, hydrogen iodide gas, and solid iodine. Provided there is some solid iodine present at equilibrium, the gas phase will be saturated with iodine (that is, a second equilibrium will have been established between the solid and gaseous forms of iodine). Adding more solid iodine at that point cannot change the amount of gaseous iodine and, consequently, changing the amount of solid iodine does not affect equilibrium.

7.4 Review

Summary

- Le Châtelier's principle states that any system at equilibrium will respond to a disturbance by shifting to oppose the disturbance.
- Equilibrium position can be affected in predictable ways by changes in concentration of reactants or products, energy, or pressure.
- A catalyst may increase the rate at which a chemical reaction system comes to equilibrium but does not affect the equilibrium position.
- A chemical system at equilibrium will not be disturbed by adding an inert gas or a substance in a different state of matter from that in which the chemical reaction is occurring.

Questions

1. The following balanced chemical equation represents a reaction at equilibrium:

$$C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g) + \text{energy}$$

Predict how the equilibrium might respond to the following changes. Explain your answers. K/U T/I

(a) The volume of the container is decreased.
(b) The temperature of the container is increased.
(c) The concentration of $C_2H_6(g)$ is decreased by removing the product.
(d) More hydrogen gas is added.

2. A pair of students conducted an investigation using the equilibrium system represented by the balanced chemical equation below. So far, their notes include the testable question, the experimental design, and the evidence. Answer the questions in parts (a) to (c) to complete the prediction, analysis, and evaluation for this investigation.

$$\underset{\text{blue}}{Cu^{2+}(aq)} + 4\,Cl^-(aq) \rightleftharpoons \underset{\text{green}}{CuCl_4^{2-}(aq)}$$

Testable Question

What effect does the addition of chloride ions have on the equilibrium position of the system?

Experimental Design

Test tubes containing 10 mL each of copper(II) chloride solution, $CuCl_2(aq)$, were combined with 1.0, 2.0, and 5.0 mol/L hydrochloric acid, HCl(aq), in a total volume of 15 mL. All test tubes were stoppered, shaken, and allowed to reach equilibrium. The colour at equilibrium was observed and recorded.

Evidence

Table 1 Observations K/U T/I

Test tube number	Concentration of HCl(aq) added (mol/L)	Colour at equilibrium
1	1.0	blue
2	2.0	blue-green
3	5.0	green

(a) Write a prediction for this investigation.
(b) Analyze the evidence to answer the testable question.
(c) Identify the independent variable, the dependent variable, and the controls used.

3. Old-fashioned "smelling salts" consist of solid ammonium carbonate, $(NH_4)_2CO_3(s)$. Smelling salts could bring a person out of a faint by undergoing the following reaction. The released ammonia gas has a distinct smell.

$$(NH_4)_2CO_3(s) \rightleftharpoons 2\,NH_3(g) + CO_2(g) + H_2O(g)$$

This decomposition reaction is endothermic. Would the smell of ammonia increase or decrease as the temperature is increased? K/U

4. The only "stress" (change) that changes the value of the equilibrium constant, *K*, is a change in temperature. K/U

(a) For an exothermic reaction, in what direction will the equilibrium position shift as temperature increases? What happens to the value of *K*?
(b) Answer Part (a) for an endothermic reaction.
(c) If the value of *K* increases with a decrease in temperature, is the reaction exothermic or endothermic? Explain.