

8.3: Le Chatelier's Principle

Learning Outcomes

- Define Le Chatelier's principle.
- Predict how the change in amounts of substances, temperature, or pressure will affect amounts of reactants and products present at equilibrium.

Le Chatelier's Principle

Chemical equilibrium was studied by the French chemist Henri Le Chatelier (1850 - 1936) and his description of how a system responds to a stress to equilibrium has become known as **Le Chatelier's principle**: When a chemical system that is at equilibrium is disturbed by a stress, the system will respond in order to relieve the stress. Stresses to a chemical system involve changes in the concentrations of reactants or products, changes in the temperature of the system, or changes in the pressure of the system. We will discuss each of these stresses separately. The change to the equilibrium position in every case is either a favoring of the forward reaction or a favoring of the reverse reaction. When the forward reaction is favored, the concentrations of products increase, while the concentrations of reactants decrease. When the reverse reaction is favored, the concentrations of the products decrease, while the concentrations of reactants increase.

Original Equilibrium	Favored Reaction	Result	
$A \rightleftharpoons B$	Forward: $A \rightarrow B$	$[A]$ decreases; $[B]$ increases	(8.3.1)
$A \rightleftharpoons B$	Reverse: $A \leftarrow B$	$[A]$ increases; $[B]$ decreases	



Figure 8.3.1: Henri Le Chatelier.

Effect of Concentration

A change in concentration of one of the substances in an equilibrium system typically involves either the addition or the removal of one of the reactants or products. Consider the Haber-Bosch process for the industrial production of ammonia from nitrogen and hydrogen gases.



If the concentration of one substance in a system is increased, the system will respond by favoring the reaction that removes that substance. When more N_2 is added, the forward reaction will be favored because the forward reaction uses up N_2 and converts it to NH_3 . The forward reaction speeds up temporarily as a result of the addition of a reactant. The position of equilibrium shifts as more NH_3 is produced. The concentration of NH_3 increases, while the concentrations of N_2 and H_2 decrease. After some time passes, equilibrium is reestablished with new concentrations of all three substance. As can be seen in the figure below, if more N_2 is added, a new equilibrium is achieved by the system. The new concentration of NH_3 is higher because of the favoring of the forward reaction. The new concentration of the H_2 is lower. The concentration of N_2 is higher than in the original equilibrium, but went down slightly following the addition of the N_2 that disturbed the original equilibrium. By responding in this way, the value of the equilibrium constant for the reaction, K_{eq} , does not change as a result of the stress to the system.

In other words, the amount of each substance is different but the ratio of the amount of each remains the same.

If more NH_3 were added, the reverse reaction would be favored. This "favoring" of a reaction means temporarily speeding up the reaction in that direction until equilibrium is reestablished. Recall that once equilibrium is reestablished, the rates of the forward and reverse reactions are again equal. The addition of NH_3 would result in increased formation of the reactants, N_2 and H_2 .

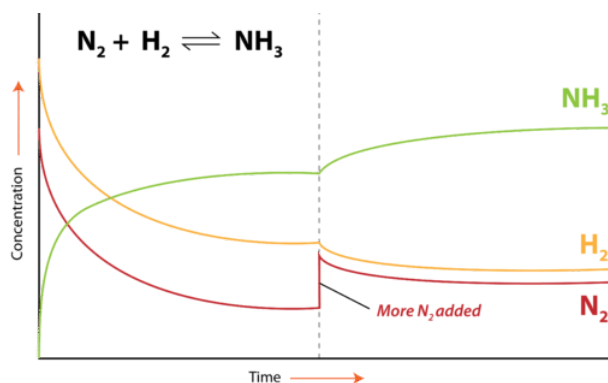


Figure 8.3.2: The Haber-Bosch process is an equilibrium between reactants N_2 and H_2 and product NH_3 .

An equilibrium can also be disrupted by the removal of one of the substances. If the concentration of a substance is decreased, the system will respond by favoring the reaction that replaces that substance. In the industrial Haber-Bosch process, NH_3 is removed from the equilibrium system as the reaction proceeds. As a result, the forward reaction is favored so that more NH_3 is produced. The concentrations of N_2 and H_2 decrease. Continued removal of NH_3 will eventually force the reaction to go to completion until all of the reactants are used up. If either N_2 or H_2 were removed from the equilibrium system, the reverse reaction would be favored and the concentration of NH_3 would decrease.

The effect of changes in concentration on an equilibrium system according to Le Chatelier's principle is summarized in the table below.

Table 8.3.1

Stress	Response
addition of reactant	forward reaction favored
addition of product	reverse reaction favored
removal of reactant	reverse reaction favored
removal of product	forward reaction favored

Effect of Temperature

Increasing or decreasing the temperature of a system at equilibrium is also a stress to the system. The equation for the Haber-Bosch process is written again below, as a thermochemical equation (i.e. it contains information about the energy gained or lost when the reaction occurs).



The forward reaction is the exothermic direction: the formation of NH_3 releases heat which is why that is shown as a product. The reverse reaction is the endothermic direction: as NH_3 decomposes to N_2 and H_2 , heat is absorbed. An increase in the temperature for this is like adding a product because heat is being released by the reaction. If we add a product then the reaction proceeds towards the formation of more reactants. Reducing the temperature for this system would be similar to removing a product which would favor the formation of more products. The amount of NH_3 will increase and the amount of N_2 and H_2 will decrease.

For changes in concentration, the system responds in such a way that the value of the equilibrium constant, K_{eq} is unchanged. However, a change in temperature shifts the equilibrium and the K_{eq} value either increases or decreases. As discussed in the previous section, values of K_{eq} are dependent on the temperature. When the temperature of the system for the Haber-Bosch process is increased, the resultant shift in equilibrium towards the reactants means that the K_{eq} value decreases. When the temperature is decreased, the shift in equilibrium towards the products means that the K_{eq} value increases.

Le Chatelier's principle as related to temperature changes can be illustrated easily by the reaction in which dinitrogen tetroxide is in equilibrium with nitrogen dioxide.



Dinitrogen tetroxide (N_2O_4) is colorless, while nitrogen dioxide (NO_2) is dark brown in color. When N_2O_4 breaks down into NO_2 , heat is absorbed (endothermic) according to the forward reaction above. Therefore, an increase in temperature (adding heat) of the system will favor the forward reaction. Conversely, a decrease in temperature (removing heat) will favor the reverse reaction.

Effect of Pressure

Changing the pressure of an equilibrium system in which gases are involved is also a stress to the system. A change in the pressure on a liquid or a solid has a negligible effect. We will return again the equilibrium for the Haber-Bosch process. Imagine the gases are contained in a closed system in which the volume of the system is controlled by an adjustable piston as shown in the figure below.

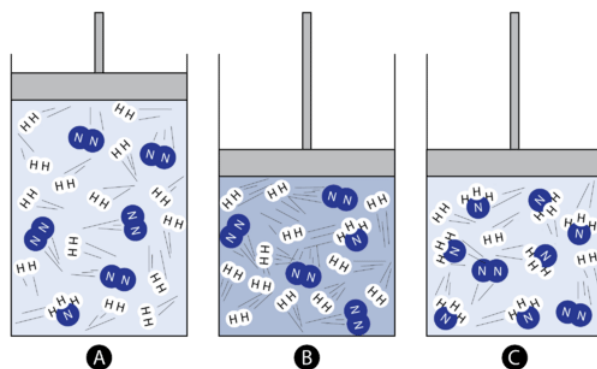


Figure 8.3.3: Effect of pressure on equilibrium. (A) is at equilibrium, (B) increase of pressure through decreased volume, and (C) equilibrium is reestablished.

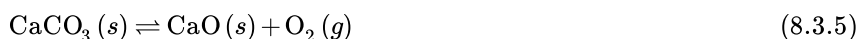
On the far left, the reaction system contains primarily N_2 and H_2 , with only one molecule of NH_3 present. As the piston is pushed inwards, the pressure of the system increases according to Boyle's law. This is a stress to the equilibrium. In the middle image, the same number of molecules is now confined in a smaller space and so the pressure has increased. According to Le Chatelier's principle, the system responds in order to relieve the stress. In the image on the right, the forward reaction has been favored and more NH_3 is produced. The overall result is a decrease in the number of gas molecules in the entire system. This in turn decreases the pressure and provides a relief to the original stress of a pressure increase. An increase in pressure on an equilibrium system favors the reaction which products fewer total moles of gas. In this case, it is the forward reaction that is favored.

A decrease in pressure on the above system could be achieved by pulling the piston outward, increasing the container volume. The equilibrium would respond by favoring the reverse reaction in which NH_3 decomposes to N_2 and H_2 . This is because the overall number of gas molecules would increase and so would the pressure. A decrease in pressure on an equilibrium system favors the reaction which produces more total moles of gas. This is summarized in the table below.

Table 8.3.2

Stress	Response
pressure increase	reaction produces fewer gas molecules
pressure decrease	reaction produces more gas molecules

Like changes in concentration, the K_{eq} value for a given reaction is unchanged by a change in pressure. The amounts of each substance will change but the ratio will not. It is important to remember when analyzing the effect of a pressure change on equilibrium that only gases are affected. If a certain reaction involves liquids or solids, they should be ignored. For example, calcium carbonate decomposes according to the equilibrium reaction:



Oxygen is the only gas in the system. An increase in the pressure of the system slows the rate of decomposition of CaCO_3 because the reverse reaction is favored. When a system contains equal moles of gas on both sides of the equation, pressure has no effect on the equilibrium position, as in the formation of HCl from H_2 and Cl_2 .



Contributors and Attributions

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