

The products are a solid and a gas. Because both CaCO_3 and CaO are solids, they are not in the equilibrium constant expression. This leads to the following expression for the equilibrium constant.

$$K = [\text{CO}_2]$$

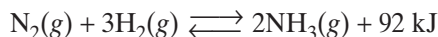
Carbon dioxide is the only substance in the system that appears in the equilibrium expression. Because the total number of moles of gas on the left side of the equation is different from the total number of moles on the right side of the equation, pressure changes will affect the equilibrium. High pressure favors the reverse reaction, which causes CO_2 molecules to react with the solid CaO to form solid CaCO_3 . Low pressure favors the formation of CO_2 from the decomposition of CaCO_3 . Because both CaO and CaCO_3 are solids, changing their amounts will not change the equilibrium concentration of CO_2 .

Changes in Temperature

Reversible reactions are exothermic in one direction and endothermic in the other. The effect of changing the temperature of an equilibrium mixture depends on which of the opposing reactions is endothermic and which is exothermic.

According to Le Châtelier's principle, the addition of energy in the form of heat shifts the equilibrium so that energy is absorbed. This favors the endothermic reaction. The removal of energy favors the exothermic reaction. A rise in temperature increases the rate of any reaction. In an equilibrium system, however, the rates of the opposing reactions are raised unequally. Thus, the value of the equilibrium constant for a given system is affected by the temperature.

The synthesis of ammonia by the Haber process is exothermic, as indicated by the energy as heat shown on the product side of the equation.



A high temperature favors the decomposition of ammonia, the endothermic reaction. But at low temperatures, the forward reaction is too slow to be commercially useful. The temperature used represents a compromise between kinetic and equilibrium requirements. It is high enough that equilibrium is established rapidly but low enough that the equilibrium concentration of ammonia is significant. Moderate temperature (about 500°C) and very high pressure (700–1000 atm) produce a satisfactory yield of ammonia.

The production of colorless dinitrogen tetroxide gas, N_2O_4 , from dark brown NO_2 gas is also an exothermic reaction. **Figure 5** shows how temperature affects the equilibrium of this system. **Figure 5b** shows the $\text{NO}_2/\text{N}_2\text{O}_4$ equilibrium mixture at 25°C . When the temperature of the system is lowered to 0°C , the system experiences a stress (removal of energy as heat). To counteract this stress, the system shifts to the right, or in the direction of the exothermic reaction. This shift increases the amount of colorless N_2O_4 gas and decreases the amount of brown NO_2 gas, as shown in **Figure 5a**. Because more N_2O_4 is present, K is increased. When the system is heated to 100°C , the added energy is the stress, and