Expressing Equilibrium Constants for Chemical Equations

Express the equilibrium constant for the chemical equation:

$$CH_3OH(g) \rightleftharpoons CO(g) + 2\ H_2(g)$$

Solution

The equilibrium constant is the equilibrium concentrations of the products raised to their stoichiometric coefficients divided by the equilibrium concentrations of the reactants raised to their stoichiometric coefficients.

$$K = \frac{[CO][H_2]^2}{[CH_3OH]}$$

For Practice

Express the equilibrium constant for the combustion of propane:

$$C_3H_8(g) + 5\ O_2(g) \rightleftharpoons 3\ CO_2(g) + 4\ H_2O(g)$$

Manipulating the Equilibrium Constant to Reflect Changes in the Chemical Equation

Consider the chemical equation and equilibrium constant for the synthesis of ammonia at 25 °C:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad K = 5.6 \times 10^5$$

Calculate the equilibrium constant for the following reaction at 25 °C :

$$NH_3(g) \rightleftharpoons \tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \qquad K' = ?$$

Solution

You want to manipulate the given reaction and value of *K* to obtain the desired reaction and value of *K*. You can see that the given reaction is the reverse of the desired reaction, and its coefficients are twice those of the desired reaction.

Begin by reversing the given reaction and taking the inverse of the value of *K*.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad K = 5.6 \times 10^5$$

$$2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \qquad K_{\text{reverse}} = \frac{1}{5.6 \times 10^5}$$

Next, multiply the reaction by $\frac{1}{2}$ and raise the equilibrium constant to the $\frac{1}{2}$ power.

$$NH_3(g) \rightleftharpoons \tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g)$$

$$K' = K_{\text{reverse}}^{1/2} = \left(\frac{1}{5.6 \times 10^5}\right)^{1/2}$$

Calculate the value of *K*′.

$$K' = 1.3 \times 10^{-3}$$

Manipulating the Equilibrium Constant to Reflect Changes in the Chemical Equation

Continued

For Practice

Consider the following chemical equation and equilibrium constant at 25 °C:

$$2\ COF_2(g) \rightleftharpoons CO_2(g) + CF_4(g) \qquad K = 2.2 \times 10^6$$

Calculate the equilibrium constant for the following reaction at 25 °C:

$$2\ CO_2(g) + 2\ CF_4(g) \rightleftharpoons 4\ COF_2(g) \qquad K' = ?$$

Predict the equilibrium constant for the first reaction shown here given the equilibrium constants for the second and third reactions:

$$\begin{array}{lll} CO_2(g) + 3\ H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g) & & K_1 = ? \\ CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) & & K_2 = 1.0 \times 10^5 \\ CO(g) + 2\ H_2(g) \rightleftharpoons CH_3OH(g) & & K_3 = 1.4 \times 10^7 \end{array}$$

Relating K_p and K_c

Nitrogen monoxide, a pollutant in automobile exhaust, is oxidized to nitrogen dioxide in the atmosphere according to the equation:

$$2\ NO(g) + O_2(g) \rightleftharpoons 2\ NO_2(g) \qquad K_p = 2.2 \times 10^{12} \text{ at } 25\ °C$$

Find K_c for this reaction.

Sort

You are given K_p for the reaction and asked to find K_c.

Given: $K_p = 2.2 \times 10^{12}$

Find: K_c

Strategize

Use Equation 16.2 to relate K_p and K_c.

Equation

$K_p = K_c(RT)^{\Delta n}$

Solve

Solve the equation for K_c.

Calculate Δn.

Substitute the required quantities to calculate K_c. The temperature must be in kelvins. The units are dropped when reporting K_c, asdescribed later in this section.

Relating K_p and K_c

Continued

Solution

$$K_c = \frac{K_p}{(RT)^{\Delta n}}$$

$$\Delta n = 2 - 3 = -1$$

$$K_c = \frac{2.2 \times 10^{12}}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \cancel{\text{K}}} \times 298\ \cancel{\text{K}}\right)^{-1}}$$

$$= 5.4 \times 10^{13}$$

Check

The easiest way to check this answer is to substitute it back and confirm that you get the original value for K_p.

$$K_p = K_c(RT)^{\Delta n}$$

$$= 5.4 \times 10^{13}\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \cancel{\text{K}}} \times 298\ \cancel{\text{K}}\right)^{-1}$$

$$= 2.2 \times 10^{12}$$

For Practice

Consider the following reaction and corresponding value of K_c :

$$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g) \qquad K_c = 6.2 \times 10^2 \text{ at } 25\ °C$$

What is the value of K_p at this temperature?

Writing Equilibrium Expressions for Reactions Involving a Solid or a Liquid

Write an expression for the equilibrium constant (K_c) for this chemical equation:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Solution

Since $CaCO_3(s)$ and $CaO(s)$ are both solids, omit them from the equilibrium expression.

$$K_c = [CO_2]$$

For More Practice

Write an equilibrium expression (K_c) for the equation:

$$4\ HCl(g) + O_2(g) \rightleftharpoons 2\ H_2O(\ell) + 2\ Cl_2(g)$$

Finding Equilibrium Constants from Experimental Concentration Measurements

Consider the following reaction:

$$CO(g) + 2\ H_2(g) \rightleftharpoons CH_3OH(g)$$

A reaction mixture at 780 °C initially contains [CO] = 0.500 M and [H_2] = 1.00 M. At equilibrium, the CO concentration is found to be 0.15 M. What is the value of the equilibrium constant?

How To

Find Equilibrium Constants from Experimental Concentration Measurements

To solve these types of problems, follow the given procedure.

Step 1 **Using the balanced equation as a guide, prepare an ICE table showing the known initial concentrations and equilibrium concentrations of the reactants and products.** Leave space in the middle of the table for determining the changes in concentration that occur during the reaction.

$$CO(g) + 2\ H_2(g) \rightleftharpoons CH_3OH(g)$$

	[CO]	[H_2]	[CH_3OH]
Initial	0.500	1.00	0.00
Change			
Equil	0.15		

Finding Equilibrium Constants from Experimental Concentration Measurements

Continued

Step 2 **For the reactant or product whose concentration is known both initially and at equilibrium, calculate the change in concentration that occurs.**

$$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$$

	[CO]	$[H_2]$	$[CH_3OH]$
Initial	0.500	1.00	0.00
Change	−0.35		
Equil	0.15		

Step 3 **Use the change you calculated in step 2 and the stoichiometric relationships from the balanced chemical equation to determine the changes in concentration of all other reactants and products.** Since reactants are consumed during the reaction, the changes in their concentrations are negative. Since products are formed, the changes in their concentrations are positive .

$$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$$

	[CO]	$[H_2]$	$[CH_3OH]$
Initial	0.500	1.00	0.00
Change	−0.35	−2(0.35)	+0.35
Equil	0.15		

Finding Equilibrium Constants from Experimental Concentration Measurements

Continued

Step 4 **Sum each column for each reactant and product to determine the equilibrium concentrations.**

	[CO]	$[H_2]$	$[CH_3OH]$
Initial	0.500	1.00	0.00
Change	−0.35	−0.70	+0.35
Equil	0.15	0.30	0.35

Step 5 **Use the balanced equation to write an expression for the equilibrium constant and substitute the equilibrium concentrations to calculate *K*.**

$$\begin{aligned} K_c &= \frac{[CH_3OH]}{[CO][H_2]^2} \\ &= \frac{0.35}{(0.15)(0.30)^2} \\ &= 26 \end{aligned}$$

Finding Equilibrium Constants from Experimental Concentration Measurements

Continued

For Practice

The reaction between CO and H_2 is carried out at a different temperature with initial concentrations of [CO] = 0.27 M and [H_2] = 0.49 M. At equilibrium, the concentration of CH_3OH is 0.11 M. Find the equilibrium constant at this temperature

Finding Equilibrium Constants from Experimental Concentration Measurements

Consider the following reaction:

$$2\ CH_4(g) \rightleftharpoons C_2H_2(g) + 3\ H_2(g)$$

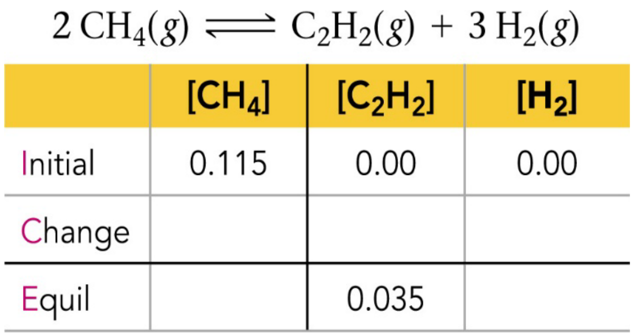
A reaction mixture at 1700 °C initially contains $[CH_4] = 0.115$ M. At equilibrium, the mixture contains $[C_2H_2] = 0.035$ M. What is the value of the equilibrium constant?

How To

Find Equilibrium Constants from Experimental Concentration Measurements

To solve these types of problems, follow the given procedure.

Step 1 **Using the balanced equation as a guide, prepare an ICE table showing the known initial concentrations and equilibrium concentrations of the reactants and products.** Leave space in the middle of the table for determining the changes in concentration that occur during the reaction.



$$2\ CH_4(g) \rightleftharpoons C_2H_2(g) + 3\ H_2(g)$$

	$[CH_4]$	$[C_2H_2]$	$[H_2]$
Initial	0.115	0.00	0.00
Change			
Equil		0.035	

Finding Equilibrium Constants from Experimental Concentration Measurements

Continued

Step 2 **For the reactant or product whose concentration is known both initially and at equilibrium, calculate the change in concentration that occurs.**

$$2\,CH_4(g) \rightleftharpoons C_2H_2(g) + 3\,H_2(g)$$

	$[CH_4]$	$[C_2H_2]$	$[H_2]$
Initial	0.115	0.00	0.00
Change		+0.035	
Equil		0.035	

Step 3 **Use the change you calculated in step 2 and the stoichiometric relationships from the balanced chemical equation to determine the changes in concentration of all other reactants and products.** Since reactants are consumed during the reaction, the changes in their concentrations are negative. Since products are formed, the changes in their concentrations are positive .

$$2\,CH_4(g) \rightleftharpoons C_2H_2(g) + 3\,H_2(g)$$

	$[CH_4]$	$[C_2H_2]$	$[H_2]$
Initial	0.115	0.00	0.00
Change	−2(0.035)	+0.035	+3(0.035)
Equil		0.035	

Finding Equilibrium Constants from Experimental Concentration Measurements

Continued

Step 4 **Sum each column for each reactant and product to determine the equilibrium concentrations.**

	$[CH_4]$	$[C_2H_2]$	$[H_2]$
Initial	0.115	0.00	0.00
Change	−0.070	+0.035	+0.105
Equil	0.045	0.035	0.105

Step 5 **Use the balanced equation to write an expression for the equilibrium constant and substitute the equilibrium concentrations to calculate *K*.**

$$\begin{aligned} K_c &= \frac{[C_2H_2][H_2]^3}{[CH_4]^2} \\ &= \frac{(0.035)(0.105)^3}{(0.045)^2} \\ &= 0.020 \end{aligned}$$

Finding Equilibrium Constants from Experimental Concentration Measurements

Continued

For Practice

The reaction of CH_4 is carried out at a different temperature with an initial concentration of $[CH_4] = 0.087$ M. At equilibrium, the concentration of H_2 is 0.012 M. Find the equilibrium constant at this temperature.

Predicting the Direction of a Reaction by Comparing *Q* and *K*

Consider the reaction and its equilibrium constant at 25.0 °C:

$$I_2(g) + Cl_2(g) \rightleftharpoons 2\ ICl(g) \qquad K_p = 81.9$$

A reaction mixture contains $P_{I_2} = 0.114$ atm, $P_{Cl_2} = 0.102$ atm, and $P_{ICl} = 0.355$ atm. Is the reaction mixture at equilibrium? If not, in which direction will the reaction proceed?

Solution

To determine the progress of the reaction relative to the equilibrium state, first calculate Q.

$$\begin{aligned} Q_p &= \left(\frac{P^2_{ICl}}{P_{I_2}P_{Cl_2}}\right) \\ &= \frac{(0.355)^2}{(0.114)(0.102)} \\ &= 10.8 \end{aligned}$$

Compare *Q* to *K*.

$$Q_p = 10.8;\ K_p = 81.9$$

Since $Q_p < K_p$, the reaction is not at equilibrium and will proceed to the right.

Predicting the Direction of a Reaction by Comparing *Q* and *K*

Continued

For Practice

Consider the reaction and its equilibrium constant:

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g) \quad K_c = 5.85 \times 10^{-3} \text{ (at some temperature)}$$

A reaction mixture contains $[NO_2] = 0.0255$ M and $[N_2O_4] = 0.0331$ M. Calculate Q_c and determine the direction in which the reaction will proceed.

Finding Equilibrium Concentrations When You Know the Equilibrium Constant and All but One of the Equilibrium Concentrations of the Reactants and Products

Consider the following reaction:

$$2\ COF_2(g) \rightleftharpoons CO_2(g) + CF_4(g) \qquad K_c = 2.00 \text{ at } 1000\ °C$$

In an equilibrium mixture, the concentration of COF_2 is 0.255 M and the concentration of CF_4 is 0.118 M. What is the equilibrium concentration of CO_2?

Sort

You are given the equilibrium constant of a chemical reaction, together with the equilibrium concentrations of the reactant and one product. You are asked to find the equilibrium concentration of the other product.

Given: $[COF_2] = 0.255\ M$

$[CF_4] = 0.118\ M$

$K_c = 2.00$

Find: $[CO_2]$

Strategize

Calculate the concentration of the product using the given quantities and the expression for K_c.

Finding Equilibrium Concentrations When You Know the Equilibrium Constant and All but One of the Equilibrium Concentrations of the Reactants and Products

Continued

Conceptual Plan

$$[\mathrm{COF_2}], [\mathrm{CF_4}], K_c \longrightarrow [\mathrm{CO_2}]$$

$$K_c = \frac{[\mathrm{CO_2}][\mathrm{CF_4}]}{[\mathrm{COF_2}]^2}$$

Solve

Solve the equilibrium expression for $[\mathrm{CO_2}]$ and then substitute in the appropriate values to calculate it.

Solution

$$[\mathrm{CO_2}] = K_c \frac{[\mathrm{COF_2}]^2}{[\mathrm{CF_4}]}$$

$$[\mathrm{CO_2}] = 2.00\left(\frac{(0.255)^2}{0.118}\right) = 1.10\ \mathrm{M}$$

Finding Equilibrium Concentrations When You Know the Equilibrium Constant and All but One of the Equilibrium Concentrations of the Reactants and Products

Continued

Check

Check your answer by mentally substituting the given values of $[COF_2]$ and $[CF_4]$ as well as your calculated value for CO_2 back into the equilibrium expression:

$$K_c = \frac{[CO_2][CF_4]}{[COF_2]^2}$$

$[CO_2]$ is roughly equal to 1. $[COF_2]^2 \approx 0.06$ and $[CF_4] \approx 0.12$. Therefore, K_c is approximately 2, as given in the problem.

For Practice 16.8

Diatomic iodine $[I_2]$ decomposes at high temperature to form I atoms according to the reaction:

$$I_2(g) \rightleftharpoons 2\ I(g) \qquad K_c = 0.011 \text{ at } 1200\ °C$$

In an equilibrium mixture, the concentration of I_2 is 0.10 M. What is the equilibrium concentration of I?

Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

Consider the reaction:

$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$

$K_c = 0.10$ (at 2000 °C)

A reaction mixture at 2000 °C initially contains $[N_2] = 0.200$ M and $[O_2] = 0.200$ M. Find the equilibrium concentrations of the reactants and product at this temperature.

How To

Find Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

To solve these types of problems, follow the given procedure.

Step 1 **Using the balanced equation as a guide, prepare a table showing the known initial concentrations of the reactants and products.** Leave room in the table for the changes in concentrations and for the equilibrium concentrations.

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$

	$[N_2]$	$[O_2]$	$[NO]$
Initial	0.200	0.200	0.00
Change			
Equil			

Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

Continued

Step 2 **Use the initial concentrations to calculate the reaction quotient (*Q*) for the initial concentrations. Compare *Q* to *K* to predict the direction in which the reaction proceeds.**

$$Q_c = \frac{[NO]^2}{[N_2][O_2]} = \frac{(0.00)^2}{(0.200)(0.200)}$$
$$= 0$$

$Q < K$; therefore, the reaction will proceed to the right.

Step 3 **Represent the change in the concentration of one of the reactants or products with the variable *x*. Define the changes in the concentrations of the other reactants or products in terms of *x*.** It is usually most convenient to let *x* represent the change in concentration of the reactant or product with the smallest stoichiometric coefficient.

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$

	$[N_2]$	$[O_2]$	$[NO]$
Initial	0.200	0.200	0.00
Change	$-x$	$-x$	$+2x$
Equil			

Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

Continued

Step 4 **Sum each column for each reactant and each product to determine the equilibrium concentrations in terms of the initial concentrations and the variable *x*.**

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$

	$[N_2]$	$[O_2]$	$[NO]$
Initial	0.200	0.200	0.00
Change	$-x$	$-x$	$+2x$
Equil	$0.200 - x$	$0.200 - x$	$2x$

Step 5 **Substitute the expressions for the equilibrium concentrations (from step 4) into the expression for the equilibrium constant. Using the given value of the equilibrium constant, solve the expression for the variable *x*.** In some cases, you can take the square root of both sides of the expression to solve for *x*. In other cases, you must solve a quadratic equation to find *x*.

Remember the quadratic formula:

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

Continued

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

$$= \frac{(2x)^2}{(0.200 - x)(0.200 - x)}$$

$$0.10 = \frac{(2x)^2}{(0.200 - x)^2}$$

$$\sqrt{0.10} = \frac{2x}{0.200 - x}$$

$$\sqrt{0.10}\,(0.200 - x) = 2x$$

$$\sqrt{0.10}\,(0.200) - \sqrt{0.10}\,x = 2x$$

$$0.063 = 2x + \sqrt{0.10}\,x$$

$$0.063 = 2.3x$$

$$x = 0.027$$

Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

Continued

Step 6 **Substitute x into the expressions for the equilibrium concentrations of the reactants and products (from step 4) and calculate the concentrations.** In cases where you solved a quadratic and have two values for *x*, choose the value for *x* that gives a physically realistic answer. For example, reject the value of *x* that results in any negative concentrations.

$$\begin{aligned}[N_2] &= 0.200 - 0.027 \\ &= 0.173\text{ M} \\ [O_2] &= 0.200 - 0.027 \\ &= 0.173\text{ M} \\ [NO] &= 2(0.027) \\ &= 0.054\text{ M}\end{aligned}$$

Step 7 **Check your answer by substituting the calculated equilibrium values into the equilibrium expression. The calculated value of *K* should match the given value of *K*.** Note that rounding errors could cause a difference in the least significant digit when comparing values of the equilibrium constant.

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

$$= \frac{(0.054)^2}{(0.173)(0.173)} = 0.097$$

Since the calculated value of K_c matches the given value (to within one digit in the least significant figure), the answer is valid.

Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

Continued

For Practice

The reaction is carried out at a different temperature at which $K_c = 0.055$. This time, however, the reaction mixture starts with only the product, [NO] = 0.0100 M, and no reactants. Find the equilibrium concentrations of N_2, O_2, and NO at equilibrium.

Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

Consider the reaction:

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$

$$K_c = 0.36 \text{ (at 100 °C)}$$

A reaction mixture at 100 °C initially contains $[NO_2] = 0.100$ M. Find the equilibrium concentrations of NO_2 and N_2O_4 at this temperature

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How To

Find Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

To solve these types of problems, follow the given procedure.

Step 1 **Using the balanced equation as a guide, prepare a table showing the known initial concentrations of the reactants and products.** Leave room in the table for the changes in concentrations and for the equilibrium concentrations.

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$

	$[N_2O_4]$	$[NO_2]$
Initial	0.00	0.100
Change		
Equil		

Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

Continued

Step 2 **Use the initial concentrations to calculate the reaction quotient (*Q*) for the initial concentrations. Compare *Q* to *K* to predict the direction in which the reaction proceeds.**

$$Q_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.100)^2}{0.00}$$
$$= \infty$$

$Q > K$; therefore, the reaction will proceed to the left.

Step 3 **Represent the change in the concentration of one of the reactants or products with the variable *x*. Define the changes in the concentrations of the other reactants or products in terms of *x*.** It is usually most convenient to let *x* represent the change in concentration of the reactant or product with the smallest stoichiometric coefficient.

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

	$[N_2O_4]$	$[NO_2]$
Initial	0.00	0.100
Change	$+x$	$-2x$
Equil		

Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

Continued

Step 4 **Sum each column for each reactant and each product to determine the equilibrium concentrations in terms of the initial concentrations and the variable *x*.**

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

	$[N_2O_4]$	$[NO_2]$
Initial	0.00	0.100
Change	$+x$	$-2x$
Equil	x	$0.100 - 2x$

Step 5 **Substitute the expressions for the equilibrium concentrations (from step 4) into the expression for the equilibrium constant. Using the given value of the equilibrium constant, solve the expression for the variable *x*.** In some cases, you can take the square root of both sides of the expression to solve for *x*. In other cases, you must solve a quadratic equation to find *x*.

Remember the quadratic formula:

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

Continued

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$= \frac{(0.100 - 2x)^2}{x}$$

$$0.36 = \frac{0.0100 - 0.400x + 4x^2}{x}$$

$$0.36x = 0.0100 - 0.400x + 4x^2$$

$$4x^2 - 0.76x + 0.0100 = 0 \; (\textit{quadratic})$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-(-0.76) \pm \sqrt{(-0.76)^2 - 4(4)(0.0100)}}{2(4)}$$

$$= \frac{0.76 \pm 0.65}{8}$$

$$x = 0.176 \quad \text{or} \quad x = 0.014$$

Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

Continued

Step 6 **Substitute x into the expressions for the equilibrium concentrations of the reactants and products (from step 4) and calculate the concentrations.** In cases where you solved a quadratic and have two values for x, choose the value for x that gives a physically realistic answer. For example, reject the value of x that results in any negative concentrations.

We reject the root $x = 0.176$ because it gives a negative concentration for NO_2. Using $x = 0.014$, we get the following concentrations:

$$\begin{aligned}[NO_2] &= 0.100 - 2x \\ &= 0.100 - 2(0.014) = 0.072\ \text{M} \\ [N_2O_4] &= x \\ &= 0.014\ \text{M}\end{aligned}$$

Step 7 **Check your answer by substituting the calculated equilibrium values into the equilibrium expression. The calculated value of *K* should match the given value of *K*.** Note that rounding errors could cause a difference in the least significant digit when comparing values of the equilibrium constant.

$$\begin{aligned}K_c &= \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.072)^2}{0.014} \\ &= 0.37\end{aligned}$$

Since the calculated value of K_c matches the given value (to within one digit in the least significant figure), the answer is valid.

Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

Continued

For Practice

The reaction in Example 16.10 is carried out at the same temperature, but this time the reaction mixture initially contains only the reactant, $[N_2O_4] = 0.0250$ M, and no NO_2. Find the equilibrium concentrations of N_2O_4 and NO_2.

Finding Equilibrium Partial Pressures When You Are Given the Equilibrium Constant and Initial Partial Pressures

Consider the reaction:

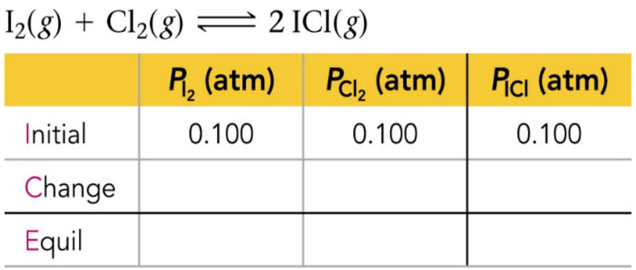
$$I_2(g) + Cl_2(g) \rightleftharpoons 2\ ICl(g) \qquad K_p = 81.9 \text{ (at 25 °C)}$$

A reaction mixture at 25 °C initially contains $P_{I_2} = 0.100$ atm, $P_{Cl_2} = 0.100$ atm, and $P_{ICl} = 0.100$ atm. Find the equilibrium partial pressures of I_2, Cl_2, and ICl at this temperature.

Solution

Follow the procedure (using partial pressures in place of concentrations) to solve the problem.

Step 1 Using the balanced equation as a guide, prepare an ICE table showing the known initial partial pressures of the reactants and products.



$$I_2(g) + Cl_2(g) \rightleftharpoons 2\ ICl(g)$$

	P_{I_2} (atm)	P_{Cl_2} (atm)	P_{ICl} (atm)
Initial	0.100	0.100	0.100
Change			
Equil			

Finding Equilibrium Partial Pressures When You Are Given the Equilibrium Constant and Initial Partial Pressures

Continued

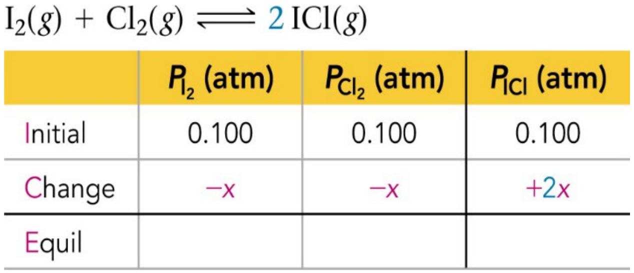
Step 2 Use the initial partial pressures to calculate the reaction quotient (*Q*). Compare *Q* to *K* to predict the direction in which the reaction will proceed.

$$Q_p = \frac{(P_{ICl})^2}{P_{I_2}P_{Cl_2}} = \frac{(0.100)^2}{(0.100)(0.100)} = 1$$

$K_p = 81.9$ (given)

$Q < K$; therefore, the reaction will proceed to the right.

Step 3 Represent the change in the partial pressure of one of the reactants or products with the variable *x*. Define the changes in the partial pressures of the other reactants or products in terms of *x*.



$$I_2(g) + Cl_2(g) \rightleftharpoons 2\,ICl(g)$$

	P_{I_2} (atm)	P_{Cl_2} (atm)	P_{ICl} (atm)
Initial	0.100	0.100	0.100
Change	$-x$	$-x$	$+2x$
Equil			

Finding Equilibrium Partial Pressures When You Are Given the Equilibrium Constant and Initial Partial Pressures

Continued

Step 4 Sum each column for each reactant and product to determine the equilibrium partial pressures in terms of the initial partial pressures and the variable *x*.

$$I_2(g) + Cl_2(g) \rightleftharpoons 2\,ICl(g)$$

	P_{I_2} (atm)	P_{Cl_2} (atm)	P_{ICl} (atm)
Initial	0.100	0.100	0.100
Change	$-x$	$-x$	$+2x$
Equil	$0.100 - x$	$0.100 - x$	$0.100 + 2x$

Finding Equilibrium Partial Pressures When You Are Given the Equilibrium Constant and Initial Partial Pressures

Continued

Step 5 Substitute the expressions for the equilibrium partial pressures (from step 4) into the expression for the equilibrium constant. Use the given value of the equilibrium constant to solve the expression for the variable *x*.

$$K_p = \frac{(P_{ICl})^2}{P_{I_2}P_{Cl_2}} = \frac{(0.100 + 2x)^2}{(0.100 - x)(0.100 - x)}$$

$$81.9 = \frac{(0.100 + 2x)^2}{(0.100 - x)^2} \quad \text{(perfect square)}$$

$$\sqrt{81.9} = \frac{(0.100 + 2x)}{(0.100 - x)}$$

$$\sqrt{81.9}\,(0.100 - x) = 0.100 + 2x$$

$$\sqrt{81.9}\,(0.100) - \sqrt{81.9}\,x = 0.100 + 2x$$

$$\sqrt{81.9}\,(0.100) - 0.100 = 2x + \sqrt{81.9}\,x$$

$$0.805 = 11.05x$$

$$x = 0.0729$$

Finding Equilibrium Partial Pressures When You Are Given the Equilibrium Constant and Initial Partial Pressures

Continued

Step 6 Substitute *x* into the expressions for the equilibrium partial pressures of the reactants and products (from step 4) and calculate the partial pressures.

$$\begin{aligned} PI_2 &= 0.100 - 0.0729 = 0.027 \text{ atm} \\ P_{Cl_2} &= 0.100 - 0.0729 = 0.027 \text{ atm} \\ P_{ICl} &= 0.100 + 2(0.0729) = 0.246 \text{ atm} \end{aligned}$$

Step 7 Check your answer by substituting the calculated equilibrium partial pressures into the equilibrium expression. The calculated value of *K* should match the given value of *K*.

$$K_p = \frac{(P_{ICl})^2}{P_{I_2}P_{Cl_2}} = \frac{(0.246)^2}{(0.027)(0.027)} = 83$$

Since the calculated value of Kp matches the given value (within the uncertainty indicated by the significant figures), the answer is valid.

For Practice

The reaction between I_2 and Cl_2 is carried out at the same temperature, but with these initial partial pressures: P_{I_2} = 0.150 atm, P_{Cl_2} = 0.150 atm, P_{ICl} = 0.00 atm. Find the equilibrium partial pressures of all three substances.

Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

Consider the reaction for the decomposition of hydrogen disulfide:

$$2\ H_2S(g) \rightleftharpoons 2\ H_2(g) + S_2(g)$$

$$K_c = 1.67 \times 10^{-7} \text{ at } 800\ °C$$

A 0.500-L reaction vessel initially contains 0.0125 mol of H_2S at 800 °C. Find the equilibrium concentrations of H_2 and S_2.

How To

Determine Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

To solve these types of problems, follow the given procedure.

Step 1 Using the balanced equation as a guide, prepare a table showing the known initial concentrations of the reactants and products. (In these examples, you first calculate the concentration of H_2S from the given number of moles and volume.)

$$[H_2S] = \frac{0.0125\ \text{mol}}{0.500\ \text{L}} = 0.0250\ \text{M}$$

$$2\ H_2S(g) \rightleftharpoons 2\ H_2(g) + S_2(g)$$

	$[H_2S]$	$[H_2]$	$[S_2]$
Initial	0.0250	0.00	0.00
Change			
Equil			

Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

Continued

Step 2 Use the initial concentrations to calculate the reaction quotient (Q). Compare Q to K to predict the direction in which the reaction proceeds.

By inspection, $Q = 0$; the reaction proceeds to the right.

Step 3 Represent the change in the concentration of one of the reactants or products with the variable x. Define the changes in the concentrations of the other reactants or products with respect to x.

$$2\,H_2S(g) \rightleftharpoons 2\,H_2(g) + S_2(g)$$

	$[H_2S]$	$[H_2]$	$[S_2]$
Initial	0.0250	0.00	0.00
Change	$-2x$	$+2x$	$+x$
Equil			

Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

Continued

Step 4 Sum each column for each reactant and product to determine the equilibrium concentrations in terms of the initial concentrations and the variable *x*.

$$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$$

	$[H_2S]$	$[H_2]$	$[S_2]$
Initial	0.0250	0.00	0.00
Change	$-2x$	$+2x$	$+x$
Equil	$0.0250 - 2x$	$2x$	x

Step 5 Substitute the expressions for the equilibrium concentrations (from step 4) into the expression for the equilibrium constant. Use the given value of the equilibrium constant to solve the resulting equation for the variable *x*. In this case, the resulting equation is cubic in *x*. Although cubic equations can be solved, the solutions are not usually simple. However, since the equilibrium constant is small, we know that the reaction does not proceed very far to the right. Therefore, *x* is a small number and can be dropped from any quantities in which it is added to or subtracted from another number (as long as the number itself is not too small).

Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

Continued

Check whether your approximation is valid by comparing the calculated value of x to the number it was added to or subtracted from. The ratio of the two numbers should be less than 0.05 (or 5%) for the approximation to be valid. If the approximation is not valid, proceed to step 5a.

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2}$$

$$= \frac{(2x)^2x}{(0.0250 - 2x)^2}$$

$$1.67 \times 10^{-7} = \frac{4x^3}{(0.0250 - 2x)^2}$$

x is small.

$$1.67 \times 10^{-7} = \frac{4x^3}{(0.0250 - \cancel{2x})^2}$$

$$1.67 \times 10^{-7} = \frac{4x^3}{6.25 \times 10^{-4}}$$

$$6.25 \times 10^{-4}(1.67 \times 10^{-7}) = 4x^3$$

$$x^3 = \frac{6.25 \times 10^{-4}(1.67 \times 10^{-7})}{4}$$

$$x = 2.97 \times 10^{-4}$$

Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

Continued

Checking the x *is small* approximation:

$$\frac{2.97 \times 10^{-4}}{0.0250} \times 100\% = 1.19\%$$

The x *is small* approximation is valid; proceed to step 6.

Step 5a If the approximation is not valid, you can either solve the equation exactly (by hand or with your calculator), or use the method of successive approximations. In this example, the method of successive approximations is used.

Substitute the value obtained for x in step 5 back into the original cubic equation, but only at the exact spot where you assumed x was negligible, and then solve the equation for x again. Continue this procedure until the value of x you obtain from solving the equation is the same as the one that you substituted into the equation.

Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

Continued

Step 6 Substitute *x* into the expressions for the equilibrium concentrations of the reactants and products (from step 4) and calculate the concentrations.

$$[H_2S] = 0.0250 - 2(2.97 \times 10^{-4})$$
$$= 0.0244\ M$$

$$[H_2] = 2(2.97 \times 10^{-4})$$
$$= 5.94 \times 10^{-4}\ M$$

$$[S_2] = 2.97 \times 10^{-4}\ M$$

Step 7 Check your answer by substituting the calculated equilibrium values into the equilibrium expression. The calculated value of *K* should match the given value of *K*. Note that the approximation method and rounding errors could cause a difference of up to about 5% when comparing values of the equilibrium constant.

$$K_c = \frac{(5.94 \times 10^{-4})^2(2.97 \times 10^{-4})}{(0.0244)^2}$$
$$= 1.76 \times 10^{-7}$$

The calculated value of *K* is close enough to the given value when you consider the uncertainty introduced by the approximation. Therefore, the answer is valid.

Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

Continued

For Practice

The reaction is carried out at the same temperature with the following initial concentrations: $[H_2S] = 0.100$ M, $[H_2] = 0.100$ M, and $[S_2] = 0.00$ M. Find the equilibrium concentration of $[S_2]$.

Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

Consider the reaction for the decomposition of hydrogen disulfide:

$$2\ H_2S(g) \rightleftharpoons 2\ H_2(g) + S_2(g)$$

$$K_c = 1.67 \times 10^{-7} \text{ at } 800\ °C$$

A 0.500-L reaction vessel initially contains 1.25×10^{-4} mol of H_2S at 800 °C. Find the equilibrium concentrations of H_2 and S_2.

How To

Determine Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

To solve these types of problems, follow the given procedure.

Step 1 Using the balanced equation as a guide, prepare a table showing the known initial concentrations of the reactants and products. (In these examples, you first calculate the concentration of H_2S from the given number of moles and volume.)

$$[H_2S] = \frac{1.25 \times 10^{-4}\ \text{mol}}{0.500\ \text{L}} = 2.50 \times 10^{-4}\ \text{M}$$

$$2\ H_2S(g) \rightleftharpoons 2\ H_2(g) + S_2(g)$$

	$[H_2S]$	$[H_2]$	$[S_2]$
Initial	2.50×10^{-4}	0.00	0.00
Change			
Equil			

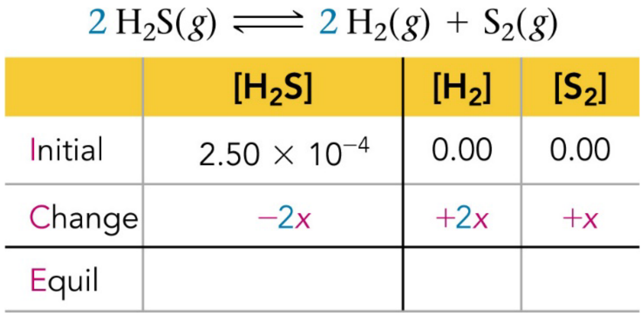
Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

Continued

Step 2 Use the initial concentrations to calculate the reaction quotient (*Q*). Compare *Q* to *K* to predict the direction in which the reaction proceeds.

By inspection, $Q = 0$; the reaction proceeds to the right.

Step 3 Represent the change in the concentration of one of the reactants or products with the variable *x*. Define the changes in the concentrations of the other reactants or products with respect to *x*.



$$2\,H_2S(g) \rightleftharpoons 2\,H_2(g) + S_2(g)$$

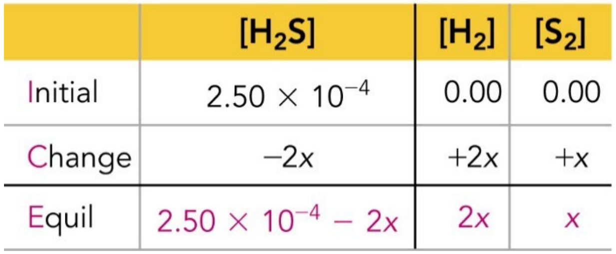
	$[H_2S]$	$[H_2]$	$[S_2]$
Initial	2.50×10^{-4}	0.00	0.00
Change	$-2x$	$+2x$	$+x$
Equil			

Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

Continued

Step 4 Sum each column for each reactant and product to determine the equilibrium concentrations in terms of the initial concentrations and the variable *x*.

$$2\mathrm{H_2S}(g) \rightleftharpoons 2\mathrm{H_2}(g) + \mathrm{S_2}(g)$$



	$[H_2S]$	$[H_2]$	$[S_2]$
Initial	2.50×10^{-4}	0.00	0.00
Change	$-2x$	$+2x$	$+x$
Equil	$2.50 \times 10^{-4} - 2x$	$2x$	x

Step 5 Substitute the expressions for the equilibrium concentrations (from step 4) into the expression for the equilibrium constant. Use the given value of the equilibrium constant to solve the resulting equation for the variable *x*. In this case, the resulting equation is cubic in *x*. Although cubic equations can be solved, the solutions are not usually simple. However, since the equilibrium constant is small, we know that the reaction does not proceed very far to the right. Therefore, *x* is a small number and can be dropped from any quantities in which it is added to or subtracted from another number (as long as the number itself is not too small).

Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

Continued

Check whether your approximation is valid by comparing the calculated value of x to the number it was added to or subtracted from. The ratio of the two numbers should be less than 0.05 (or 5%) for the approximation to be valid. If the approximation is not valid, proceed to step 5a.

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2}$$

$$= \frac{(2x)^2x}{(2.50 \times 10^{-4} - 2x)^2}$$

$$1.67 \times 10^{-7} = \frac{4x^3}{(2.50 \times 10^{-4} - 2x)^2}$$

x is small.

$$1.67 \times 10^{-7} = \frac{4x^3}{(2.50 \times 10^{-4} - \cancel{2x})^2}$$

$$1.67 \times 10^{-7} = \frac{4x^3}{6.25 \times 10^{-8}}$$

$$6.25 \times 10^{-8}(1.67 \times 10^{-7}) = 4x^3$$

$$x^3 = \frac{6.25 \times 10^{-8}(1.67 \times 10^{-7})}{4}$$

$$x = 1.38 \times 10^{-5}$$

Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

Continued

Checking the x is *small* approximation:

$$\frac{1.38 \times 10^{-5}}{2.50 \times 10^{-4}} \times 100\% = 5.52\%$$

The approximation does not satisfy the <5% rule (although it is close).

Step 5a If the approximation is not valid, you can either solve the equation exactly (by hand or with your calculator), or use the method of successive approximations. In this example, the method of successive approximations is used.

Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

Continued

Substitute the value obtained for *x* in step 5 back into the original cubic equation, but only at the exact spot where you assumed *x* was negligible, and then solve the equation for *x* again. Continue this procedure until the value of *x* you obtain from solving the equation is the same as the one that you substituted into the equation.

$$1.67 \times 10^{-7} = \frac{4x^3}{(2.50 \times 10^{-4} - \underset{\underset{x = 1.38 \times 10^{-5}}{\uparrow}}{2x})^2}$$

$$1.67 \times 10^{-7} = \frac{4x^3}{(2.50 \times 10^{-4} - 2.76 \times 10^{-5})^2}$$

$$x = 1.27 \times 10^{-5}$$

If we substitute this value of x back into the cubic equation and solve it, we get $x = 1.28 \times 10^{-5}$, which is nearly identical to 1.27×10^{-5}. Therefore, we have arrived at the best approximation for *x*.

Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

Continued

Step 6 Substitute *x* into the expressions for the equilibrium concentrations of the reactants and products (from step 4) and calculate the concentrations.

$$[H_2S] = 2.50 \times 10^{-4} - 2(1.28 \times 10^{-5})$$

$$= 2.24 \times 10^{-4}\ M$$

$$[H_2] = 2(1.28 \times 10^{-5})$$

$$= 2.56 \times 10^{-5}\ M$$

$$[S_2] = 1.28 \times 10^{-5}\ M$$

Step 7 Check your answer by substituting the calculated equilibrium values into the equilibrium expression. The calculated value of *K* should match the given value of *K*. Note that the approximation method and rounding errors could cause a difference of up to about 5% when comparing values of the equilibrium constant.

$$K_c = \frac{(2.56 \times 10^{-5})^2(1.28 \times 10^{-5})}{(2.24 \times 10^{-4})^2}$$

$$= 1.67 \times 10^{-7}$$

The calculated value of *K* is equal to the given value. Therefore, the answer is valid.

Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

Continued

For Practice

The reaction is carried out at the same temperature with the following initial concentrations: $[H_2S] = 1.00 \times 10^{-4}$ M, $[H_2] = 0.00$ M, and $[S_2] = 0.00$ M. Find the equilibrium concentration of $[S_2]$.

The Effect of a Concentration Change on Equilibrium

Consider the following reaction at equilibrium:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

What is the effect of adding additional CO_2 to the reaction mixture? What is the effect of adding additional $CaCO_3$?

Solution

Adding additional CO_2 increases the concentration of CO_2 and causes the reaction to shift to the left. Adding additional $CaCO_3$, however, does *not* increase the concentration of $CaCO_3$ because $CaCO_3$ is a solid and therefore has a constant concentration. Thus, adding additional $CaCO_3$ has no effect on the position of the equilibrium. (Note that, as we saw in Section 16.5, solids are not included in the equilibrium expression.)

For Practice

Consider the following reaction in chemical equilibrium:

$$2\ BrNO(g) \rightleftharpoons 2\ NO(g) + Br_2(g)$$

What is the effect of adding additional Br_2 to the reaction mixture? What is the effect of adding additional BrNO?

The Effect of a Volume Change on Equilibrium

Consider the following reaction at chemical equilibrium:

$$2\ KClO_3(s) \rightleftharpoons 2\ KCl(s) + 3\ O_2(g)$$

What is the effect of decreasing the volume of the reaction mixture? Increasing the volume of the reaction mixture? Adding an inert gas at constant volume?

Solution

The chemical equation has 3 mol of gas on the right and zero moles of gas on the left. Decreasing the volume of the reaction mixture increases the pressure and causes the reaction to shift to the left (toward the side with fewer moles of gas particles). Increasing the volume of the reaction mixture decreases the pressure and causes the reaction to shift to the right (toward the side with more moles of gas particles.) Adding an inert gas has no effect.

For Practice

Consider the following reaction at chemical equilibrium:

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$

What is the effect of decreasing the volume of the reaction mixture? Increasing the volume of the reaction mixture?

The Effect of a Temperature Change on Equilibrium

The following reaction is endothermic:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

What is the effect of increasing the temperature of the reaction mixture? Decreasing the temperature?

Solution

Since the reaction is endothermic, we can think of heat as a reactant:

$$\text{Heat} + CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Raising the temperature is like adding a reactant, causing the reaction to shift to the right. Lowering the temperature is equivalent to removing a reactant, causing the reaction to shift to the left.

For Practice

The following reaction is exothermic:

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$

What is the effect of increasing the temperature of the reaction mixture? Decreasing the temperature?