

## 15.8: Finding Equilibrium Concentrations

### Key Concept Video Finding Equilibrium Concentrations from Initial Concentrations

In [Section 15.6](#), we discussed how to calculate an equilibrium constant from the equilibrium concentrations of the reactants and products. Just as commonly, we will want to calculate equilibrium concentrations of reactants or products from the equilibrium constant. These kinds of calculations are important because they allow us to calculate the amount of a reactant or product at equilibrium. For example, in a synthesis reaction, we might want to know how much of the product forms when the reaction reaches equilibrium. Or for the hemoglobin–oxygen equilibrium discussed in [Section 15.1](#), we might want to know the concentration of oxygenated hemoglobin present under certain oxygen concentrations within the lungs or muscles.

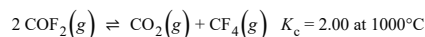
We can divide these types of problems into two categories: (1) finding equilibrium concentrations when we know the equilibrium constant and all but one of the equilibrium concentrations of the reactants and products, and (2) finding equilibrium concentrations when we know the equilibrium constant and only initial concentrations. The second category of problem is more difficult than the first. Let's examine each separately.

### Finding Equilibrium Concentrations from the Equilibrium Constant and All but One of the Equilibrium Concentrations of the Reactants and Products

We can use the equilibrium constant to calculate the equilibrium concentration of one of the reactants or products, given the equilibrium concentrations of the others. To solve this type of problem, we follow our general problem-solving procedure as demonstrated in [Example 15.8](#).

#### Example 15.8 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:

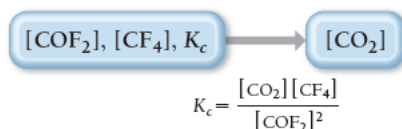


In an equilibrium mixture, the concentration of  $\text{COF}_2$  is 0.255 M and the concentration of  $\text{CF}_4$  is 0.118 M. What is the equilibrium concentration of  $\text{CO}_2$ ?

**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:**

$$\begin{aligned} [\text{COF}_2] &= 0.255 \text{ M} \\ [\text{CF}_4] &= 0.118 \text{ M} \\ K &= 2.00 \end{aligned}$$

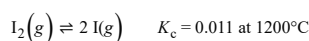
**FIND:**  $[\text{CO}_2]$ **STRATEGIZE** You can calculate the concentration of the product using the given quantities and the expression for  $K_c$ .**CONCEPTUAL PLAN****SOLVE** Solve the equilibrium expression for  $[\text{CO}_2]$  and substitute in the appropriate values to calculate it.**SOLUTION**

$$[\text{CO}_2] = K_c \frac{[\text{COF}_2]^2}{[\text{CF}_4]}$$

$$[\text{CO}_2] = 2.00 \left( \frac{(0.255)^2}{0.118} \right) = 1.10 \text{ M}$$

**CHECK** Check your answer by mentally substituting the given values of  $[\text{COF}_2]$  and  $[\text{CF}_4]$  as well as your calculated value for  $\text{CO}_2$  back into the equilibrium expression.

$$K_c = \frac{[\text{CO}_2][\text{CF}_4]}{[\text{COF}_2]^2}$$

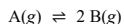
You found  $[\text{CO}_2]$  to be roughly equal to 1.  $[\text{COF}_2]^2 \approx 0.06$  and  $[\text{CF}_4] \approx 0.12$ . Therefore,  $K_c$  is approximately 2, as given in the problem.**FOR PRACTICE 15.8** Diatomic iodine  $[\text{I}_2]$  decomposes at high temperature to form I atoms according to the reaction:In an equilibrium mixture, the concentration of  $\text{I}_2$  is 0.10 M. What is the equilibrium concentration of I?**Interactive Worked Example 15.8 Finding Equilibrium Concentrations When You Know the Equilibrium Constant and All but One of the Equilibrium Concentrations of the Reactants and Products**

## Finding Equilibrium Concentrations from the Equilibrium Constant and Initial Concentrations or Pressures

More commonly, we know the equilibrium constant and only the initial concentrations of reactants, and we need to find the *equilibrium concentrations* of the reactants or products. These kinds of problems are generally

more involved than those we just examined and require a specific procedure to solve them. The procedure has some similarities to the one used in [Examples 15.5](#) and [15.6](#) in that we set up an ICE table showing the initial conditions, the changes, and the equilibrium conditions. However, unlike [Examples 15.5](#) and [15.6](#), here the changes in concentration are not known and are represented with the variable  $x$ .

For example, consider again the simple reaction:



Suppose that, as before (see [Section 15.6](#)), we have a reaction mixture in which the initial concentration of A is 1.0 M and the initial concentration of B is 0.00 M. However, now we know the equilibrium constant,  $K = 0.33$ , and want to find the equilibrium concentrations. We know that since  $Q = 0$ , the reaction proceeds to the right (toward the products).

We set up the ICE table with the given initial concentrations and *represent the unknown change in [A] with the variable  $x$*  as follows:

	[A]	[B]
Initial	1.0	0.00
Change	$-x$	$+2x$
Equil	$1.0 - x$	$2x$

Represent changes from initial conditions with the variable  $x$ .

Notice that, due to the stoichiometry of the reaction, the change in [B] must be  $+2x$ . As before, each *equilibrium* concentration is the sum of the two entries above it in the ICE table. To find the equilibrium concentrations of A and B, we must find the value of the variable  $x$ . Since we know the value of the equilibrium constant, we can use the equilibrium constant expression to set up an equation in which  $x$  is the only variable:

$$K_c = \frac{[\text{B}]^2}{[\text{A}]} = \frac{(2x)^2}{1.0 - x} = 0.33$$

or more simply:

$$\frac{4x^2}{1.0 - x} = 0.33$$

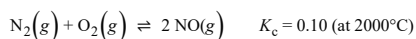
This equation is a *quadratic* equation—it contains the variable  $x$  raised to the second power. In general, we can solve quadratic equations with the quadratic formula, which we introduce in [Example 15.10](#). If the quadratic equation is a perfect square, however, we can solve it by simpler means, as shown in [Example 15.9](#). For these examples, we give the general procedure in the left column and apply the procedure to the two different example problems in the center and right columns. Later in this section, we see that quadratic equations can often be simplified by making some approximations based on our chemical knowledge.

### Example 15.9 Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

#### PROCEDURE FOR Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

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

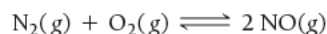
Consider the reaction:



A reaction mixture at  $2000^\circ\text{C}$  initially contains  $[\text{N}_2] = 0.200 \text{ M}$  and  $[\text{O}_2] = 0.200 \text{ M}$ . Find the equilibrium

concentrations of the reactants and product at this temperature.

- 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 <sub>2</sub> ]	[O <sub>2</sub> ]	[NO]
Initial	0.200	0.200	0.00
Change			
Equil			

- 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 will proceed.

$$Q_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(0.000)^2}{(0.200)(0.200)} = 0$$

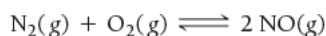
$Q < K$ ; therefore, the reaction will proceed to the right.

- 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 <sub>2</sub> ]	[O <sub>2</sub> ]	[NO]
Initial	0.200	0.200	0.00
Change	-x	-x	+2x
Equil			

- 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 <sub>2</sub> ]	[O <sub>2</sub> ]	[NO]
Initial	0.200	0.200	0.00
Change	-x	-x	+2x
Equil	0.200 - x	0.200 - x	2x

- 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, such as [Example 15.9](#), you can take the square root of both sides of the expression to solve for  $x$ . In other cases, such as [Example 15.10](#), you must solve a quadratic equation

to find  $x$ .

Remember the quadratic formula:

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

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

$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

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

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

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

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

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

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

$$0.063 = 2.3x$$

$$x = 0.027$$

**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.

$$[\text{NO}_2] = 0.200 - 0.027$$

$$= 0.172 \text{ M}$$

$$[\text{O}_2] = 0.200 - 0.027$$

$$= 0.173 \text{ M}$$

$$[\text{NO}] = 2(0.027)$$

$$= 0.054 \text{ M}$$

**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.

$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

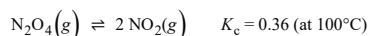
$$= \frac{(0.054)^2}{(0.173)(0.173)} = 0.097$$

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

**FOR PRACTICE 15.9** The reaction in [Example 15.9](#) is carried out at a different temperature at which  $K_c = 0.055$ . This time the reaction mixture starts with only the product,  $[\text{NO}] = 0.0100 \text{ M}$ , and no reactants. Find the equilibrium concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium.

### Example 15.10 Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

Consider the reaction:



A reaction mixture at 100°C initially contains  $[\text{NO}_2] = 0.100 \text{ M}$ . Find the equilibrium concentrations of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  at this temperature.

**PROCEDURE** Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

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

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.

$$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$$

	$[\text{N}_2\text{O}_4]$	$[\text{NO}_2]$
Initial	0.00	0.100
Change		
Equil		

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 will proceed.

$$Q_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.100)^2}{0.00} = \infty$$

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

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.

$$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$$

	$[\text{N}_2\text{O}_4]$	$[\text{NO}_2]$
Initial	0.00	0.100
Change	$+x$	$-2x$
Equil		

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

$$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$$

	$[\text{N}_2\text{O}_4]$	$[\text{NO}_2]$
Initial	0.00	0.100
Change	$+x$	$-2x$
Equil	$x$	$0.100 - 2x$

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, such as [Example 15.9](#), you can take the square root of both sides of the expression to solve for  $x$ . In other cases, such as [Example 15.10](#), you must solve a quadratic equation to find  $x$ .

Remember the quadratic formula:

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

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

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

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

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

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

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

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

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

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

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

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  $\text{NO}_2$ . Using  $x = 0.014$ , we get the following concentrations:

$$[\text{NO}_2] = 0.100 - 2x$$

$$= 0.100 - 2(0.014)$$

$$= 0.072 \text{ M}$$

$$[\text{N}_2\text{O}_4] = x$$

$$= 0.014 \text{ M}$$

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.


$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

$$= \frac{(0.072)^2}{0.014} = 0.37$$

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

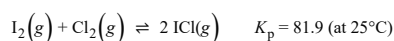
**FOR PRACTICE 15.10** The reaction in [Example 15.10](#) is carried out at the same temperature, but this time the reaction mixture initially contains only the reactant,  $[\text{N}_2\text{O}_4] = 0.0250 \text{ M}$ , and no  $\text{NO}_2$ . Find the equilibrium concentrations of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$ .

**Interactive Worked Example 15.9 Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant**

When the initial conditions are given in terms of partial pressures (instead of concentrations) and the equilibrium constant is given as  $K_p$  instead of  $K_c$ , use the same procedure, but substitute partial pressures for concentrations, as shown in [Example 15.11](#). 

**Example 15.11 Finding Equilibrium Partial Pressures When You Are Given the Equilibrium Constant and Initial Partial Pressures**

Consider the reaction:



A reaction mixture at  $25^\circ\text{C}$  initially contains  $P_{\text{I}_2} = 0.100 \text{ atm}$ ,  $P_{\text{Cl}_2} = 0.100$ , and  $P_{\text{ICl}} = 0.100 \text{ atm}$ . Find the equilibrium partial pressures of  $\text{I}_2$ ,  $\text{Cl}_2$ , and  $\text{ICl}$  at this temperature.

**SOLUTION** Follow the procedure used in [Examples 15.5](#)  and [15.6](#)  (using partial pressures in place of concentrations) to solve the problem.

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

$$\text{I}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{ICl}(\text{g})$$

	$P_{\text{I}_2}(\text{atm})$	$P_{\text{Cl}_2}(\text{atm})$	$P_{\text{ICl}}(\text{atm})$
Initial	0.100	0.100	0.100
Change			
Equil			

- 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.

$$Q_p = \frac{(P_{\text{ICl}})^2}{P_{\text{I}_2} P_{\text{Cl}_2}} = \frac{(0.100)^2}{(0.100)(0.100)} = 1$$

$$K_p = 81.9 \text{ (given)}$$

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

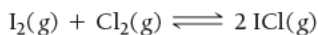
- Represent the change in the partial pressure of one of the reactants or products with the variable  $x$ . Define the changes in the partial pressures of the other reactants or products in terms of  $x$ .

$$\text{I}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{ICl}(\text{g})$$

	$P_{\text{I}_2}(\text{atm})$	$P_{\text{Cl}_2}(\text{atm})$	$P_{\text{ICl}}(\text{atm})$
Initial	0.100	0.100	0.100
Change	$-x$	$-x$	$+2x$
Equil			



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  $x$ .



	$P_{\text{I}_2}(\text{atm})$	$P_{\text{Cl}_2}(\text{atm})$	$P_{\text{ICl}}(\text{atm})$
Initial	0.100	0.100	0.100
Change	$-x$	$-x$	$+2x$
Equil	$0.100 - x$	$0.100 - x$	$0.100 + 2x$

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  $x$ .

$$K_p = \frac{(P_{\text{ICl}})^2}{P_{\text{I}_2} P_{\text{Cl}_2}} = \frac{(0.100 + 2x)^2}{(0.100 - x)(0.100 - x)}$$

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

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

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

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

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

$$0.805 = 11.05x$$

$$x = 0.0729$$

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

$$P_{\text{I}_2} = 0.100 - 0.0729 = 0.027 \text{ atm}$$

$$P_{\text{Cl}_2} = 0.100 - 0.0729 = 0.027 \text{ atm}$$

$$P_{\text{ICl}} = 0.100 + 2(0.0729) = 0.246 \text{ atm}$$

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  $K$ .

$$K_p = \frac{(P_{\text{ICl}})^2}{P_{\text{I}_2} P_{\text{Cl}_2}} = \frac{(0.246)^2}{(0.027)(0.027)} = 83$$

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

**FOR PRACTICE 15.11** The reaction between  $\text{I}_2$  and  $\text{Cl}_2$  in Example 15.11 is carried out at the same temperature, but with these initial partial pressures:  $P_{\text{I}_2} = 0.150 \text{ atm}$ ,  $P_{\text{Cl}_2} = 0.150 \text{ atm}$ ,  $P_{\text{ICl}} = 0.00 \text{ atm}$ . Find the equilibrium partial pressures of all three substances.

## Simplifying Approximations in Working Equilibrium

## Problems

For some equilibrium problems of the type shown in Examples 15.9, 15.10, and 15.11, we can make an approximation that simplifies the calculations without any significant loss of accuracy. For example, if the equilibrium constant is relatively small, the reaction will not proceed very far to the right. Therefore, if the initial reactant concentration is relatively large, we can make the assumption that  $x$  is small relative to the initial concentration of reactant.

To see how this approximation works, consider again the simple reaction  $A \rightleftharpoons 2B$ . Suppose that, as before, we have a reaction mixture in which the initial concentration of A is 1.0 M and the initial concentration of B is 0.0 M and that we want to find the equilibrium concentrations. However, suppose that in this case the equilibrium constant is much smaller, say  $K_c = 3.3 \times 10^{-5}$ . The ICE table is identical to the one we set up previously:

	[A]	[B]
Initial	1.0	0.0
Change	$-x$	$+2x$
Equil	$1.0 - x$	$2x$

Except for the value of  $K_c$ , we end up with the exact quadratic equation that we had before:

$$K_c = \frac{[B]^2}{[A]} = \frac{(2x)^2}{1.0 - x} = 3.3 \times 10^{-5}$$

or more simply:

$$\frac{4x^2}{1.0 - x} = 3.3 \times 10^{-5}$$

We can rearrange this quadratic equation into standard form and solve it using the quadratic formula. But because  $K_c$  is small, the reaction will not proceed very far toward products and, therefore,  $x$  will also be small. If  $x$  is much smaller than 1.0, then  $1.0 - x$  (the quantity in the denominator) can be approximated by 1.0:

$$\frac{4x^2}{1.0 - x} = 3.3 \times 10^{-5}$$

This approximation greatly simplifies the equation, which we can then solve for  $x$  as follows:

$$\begin{aligned} \frac{4x^2}{1.0} &= 3.3 \times 10^{-5} \\ 4x^2 &= 3.3 \times 10^{-5} \\ x &= \sqrt{\frac{3.3 \times 10^{-5}}{4}} = 0.0029 \end{aligned}$$

We can check the validity of this approximation by comparing the calculated value of  $x$  to the number from which it was subtracted. The ratio of  $x$  to the number it is subtracted from should be less than 0.05 (or 5%) for the approximation to be valid. In this case,  $x$  was subtracted from 1.0, and therefore we can calculate the ratio of the value of  $x$  to 1.0 as follows:

$$\frac{0.0029}{1.0} \times 100\% = 0.29\%$$

The approximation is less than 0.05 (or 5%) and is therefore valid.

In Examples 15.12 and 15.13, we treat two nearly identical problems—the only difference is the initial concentration of the reactant. In Example 15.12, the initial concentration of the reactant is relatively large, the equilibrium constant is small, and the  $x$  is small approximation works well. In Example 15.13, however, the initial concentration of the reactant is much smaller, and even though the equilibrium constant is the same, the  $x$  is small approximation does not work (because the initial concentration is also small). In cases such as this, we have a couple of options to solve the problem. We can either solve the equation exactly or use the method of

have a couple of options to solve the problem. We can either solve the equation exactly or use the *method of successive approximations*, which is introduced in [Example 15.13](#). In this method, we essentially solve for  $x$  as if it were small, and then substitute the value obtained back into the equation (where  $x$  was initially neglected) to solve for  $x$  again. This can be repeated until the calculated value of  $x$  stops changing with each iteration, an indication that we have arrived at an acceptable value for  $x$ .

Note that the  $x$  is *small* approximation does not imply that  $x$  is *zero*. If that were the case, the reactant and product concentrations would not change from their initial values. The  $x$  is *small* approximation just means that when  $x$  is added or subtracted to another number, it does not change that number by very much.

For example, we can calculate the value of the difference  $1.0 - x$  when  $x = 3.0 \times 10^{-4}$ :

$$1.0 - x = 1.0 - 3.0 \times 10^{-4} = 0.997 = 1.0$$

Since the value of 1.0 is known only to two significant figures, subtracting the small  $x$  does not change the value at all. This situation is similar to weighing yourself on a bathroom scale with and without a penny in your pocket. Unless your scale is unusually precise, removing the penny from your pocket does not change the reading on the scale. This does not imply that the penny is weightless, only that its weight is small compared to your body weight. You can neglect the weight of the penny in reading your weight with no detectable loss in accuracy.

### Example 15.12 Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

**PROCEDURE FOR** Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

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

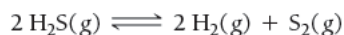
Consider the reaction for the decomposition of hydrogen disulfide:



A 0.500-L reaction vessel initially contains 0.0125 mol of  $\text{H}_2\text{S}$  at  $800^\circ\text{C}$ . Find the equilibrium concentrations of  $\text{H}_2$  and  $\text{S}_2$ .

- Using the balanced equation as a guide, prepare a table showing the known initial concentrations of the reactants and products. (In these examples, you must first calculate the concentration of  $\text{H}_2\text{S}$  from the given number of moles and volume.)

$$[\text{H}_2\text{S}] = \frac{0.0125 \text{ mol}}{0.500 \text{ L}} = 0.0250 \text{ M}$$



	$[\text{H}_2\text{S}]$	$[\text{H}_2]$	$[\text{S}_2]$
Initial	0.0250	0.00	0.00
Change			
Equil			

- Use the initial concentrations to calculate the reaction quotient ( $Q$ ). Compare  $Q$  to  $K$  to predict the direction in which the reaction will proceed.

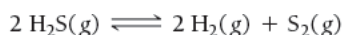
By inspection,  $Q_c = 0$ ; the reaction will proceed to the right.

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  $x$ .



	$[\text{H}_2\text{S}]$	$[\text{H}_2]$	$[\text{S}_2]$
Initial	0.0250	0.00	0.00
Change	$-2x$	$+2x$	$+x$
Equil			

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



	$[\text{H}_2\text{S}]$	$[\text{H}_2]$	$[\text{S}_2]$
Initial	0.0250	0.00	0.00
Change	$-2x$	$+2x$	$+x$
Equil	$0.0250 - 2x$	$2x$	$x$

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, you know that the reaction does not proceed very far to the right. Therefore,  $x$  will be 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).

Check whether your approximation was 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.

$$\begin{aligned}
 K_c &= \frac{[\text{H}_2]^2[\text{S}_2]}{[\text{H}_2\text{S}]^2} \\
 &= \frac{(2x)^2x}{(0.0250 - 2x)^2} \\
 1.67 \times 10^{-7} &= \frac{4x^3}{(0.0250 - 2x)^2} \\
 1.67 \times 10^{-7} &= \frac{4x^3}{(0.0250 - 2x)^2} \quad \text{\textcolor{red}{ $x$  is small.}} \\
 1.67 \times 10^{-7} &= \frac{4x^3}{6.25 \times 10^{-4}} \\
 6.25 \times 10^{-4}(1.67 \times 10^{-7}) &= 4x^3 \\
 x^3 &= \frac{6.25 \times 10^{-4}(1.67 \times 10^{-7})}{4} \\
 x &= 2.97 \times 10^{-4}
 \end{aligned}$$

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.

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 [Example 15.13](#), use the method of successive approximations.

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

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

$$\begin{aligned} [\text{H}_2\text{S}] &= 2.50 \times 10^{-4} - 2(1.28 \times 10^{-5}) \\ &= 2.24 \times 10^{-4} \text{ M} \\ [\text{H}_2] &= 2(1.28 \times 10^{-5}) \\ &= 2.56 \times 10^{-5} \text{ M} \\ [\text{S}_2] &= 1.28 \times 10^{-5} \text{ M} \end{aligned}$$

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.

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

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.

#### FOR PRACTICE 15.12

The reaction in [Example 15.12](#) is carried out at the same temperature with the following initial concentrations:

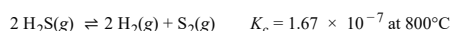
$[\text{H}_2\text{S}] = 0.100 \text{ M}$ ,  $[\text{H}_2] = 0.100 \text{ M}$ , and  $[\text{S}_2] = 0.000 \text{ M}$ . Find the equilibrium concentration of  $[\text{S}_2]$ .

### Example 15.13 Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

**PROCEDURE FOR** Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

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

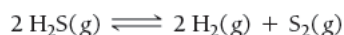
Consider the reaction for the decomposition of hydrogen disulfide:



A 0.500-L reaction vessel initially contains  $1.25 \times 10^{-4}$  of  $\text{H}_2\text{S}$  at  $800^\circ\text{C}$ . Find the equilibrium concentrations of  $\text{H}_2$  and  $\text{S}_2$ .

- Using the balanced equation as a guide, prepare a table showing the known initial concentrations of the reactants and products. (In these examples, you must first calculate the concentration of  $\text{H}_2\text{S}$  from the given number of moles and volume.)

$$[\text{H}_2\text{S}] = \frac{0.0125 \text{ mol}}{0.500 \text{ L}} = 0.0250 \text{ M}$$



	$[\text{H}_2\text{S}]$	$[\text{H}_2]$	$[\text{S}_2]$
Initial	0.0250	0.00	0.00
Change			
Equil			

- Use the initial concentrations to calculate the reaction quotient ( $Q$ ). Compare  $Q$  to  $K$  to predict the direction in which the reaction will proceed.

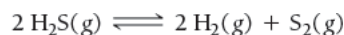
By inspection,  $Q_c = 0$ ; the reaction will proceed to the right.

- 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  $x$ .



	$[\text{H}_2\text{S}]$	$[\text{H}_2]$	$[\text{S}_2]$
Initial	$2.50 \times 10^{-4}$	0.00	0.00
Change	$-2x$	$+2x$	$+x$
Equil			

- Sum each column for each reactant and product to determine the equilibrium concentrations in terms of the initial concentrations and the variable  $x$ .



	$[\text{H}_2\text{S}]$	$[\text{H}_2]$	$[\text{S}_2]$
Initial	$2.50 \times 10^{-4}$	0.00	0.00
Change	$-2x$	$+2x$	$+x$
Equil	$2.50 \times 10^{-4} - 2x$	$2x$	$x$

- 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, you know that the reaction does not proceed very far to the right. Therefore,  $x$  will be 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).

Check whether your approximation was 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.

$$\begin{aligned}
 K_c &= \frac{[\text{H}_2]^2[\text{S}_2]}{[\text{H}_2\text{S}]^2} \\
 &= \frac{(2x)^2x}{(2.50 \times 10^{-4} - 2x)^2} \\
 1.67 \times 10^{-7} &= \frac{4x^3}{(2.50 \times 10^{-4} - 2x)^2} \\
 1.67 \times 10^{-7} &= \frac{4x^3}{(2.50 \times 10^{-4} - 2x)^2} \quad \text{\textcolor{red}{*x is small.*}} \\
 1.67 \times 10^{-7} &= \frac{4x^3}{6.25 \times 10^{-8}} \\
 6.25 \times 10^{-8}(1.67 \times 10^{-7}) &= 4x^3 \\
 x^3 &= \frac{6.25 \times 10^{-8}(1.67 \times 10^{-7})}{4} \\
 x &= 1.38 \times 10^{-5}
 \end{aligned}$$

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).

**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 [Example 15.13](#), use the method of successive approximations.

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

$$\begin{aligned}
 1.67 \times 10^{-7} &= \frac{4x^3}{(2.50 \times 10^{-4} - 2x)^2} \\
 x &= 1.38 \times 10^{-5} \\
 1.67 \times 10^{-7} &= \frac{4x^3}{(2.50 \times 10^{-4} - 2.76 \times 10^{-5})^2} \\
 x &= 1.27 \times 10^{-5}
 \end{aligned}$$

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

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

$$\begin{aligned}
 [\text{H}_2\text{S}] &= 2.50 \times 10^{-4} - 2(1.28 \times 10^{-5}) \\
 &= 2.24 \times 10^{-4} \text{ M}
 \end{aligned}$$

$$\begin{aligned}[\text{H}_2] &= 2(1.28 \times 10^{-5}) \\&= 2.56 \times 10^{-5} \text{ M} \\[\text{S}_2] &= 1.28 \times 10^{-5} \text{ M}\end{aligned}$$

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.

$$\begin{aligned}K_c &= \frac{(2.56 \times 10^{-5})^2 (1.28 \times 10^{-5})}{(2.24 \times 10^{-4})^2} \\&= 1.67 \times 10^{-7}\end{aligned}$$

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

### FOR PRACTICE 15.13

The reaction in [Example 15.13](#) is carried out at the same temperature with the following initial concentrations:  $[\text{H}_2\text{S}] = 1.00 \times 10^{-4} \text{ M}$ ,  $[\text{H}_2] = 0.00 \text{ M}$ , and  $[\text{S}_2] = 0.000 \text{ M}$ . Find the equilibrium concentration of  $[\text{S}_2]$ .

**Interactive Worked Example 15.12 Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant**

**Conceptual Connection 15.6 The  $x$  is small Approximation**

Interactive



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