

## 15.4: Non-equilibrium Conditions

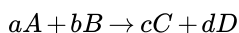
### Learning Objectives

- To predict in which direction a reaction will proceed.

In [Section 15.3](#), we saw that knowing the magnitude of the equilibrium constant under a given set of conditions allows chemists to predict the extent of a reaction. Often, however, chemists must decide whether a system has reached equilibrium or if the composition of the mixture will continue to change with time. In this section, we describe how to quantitatively analyze the composition of a reaction mixture to make this determination.

### The Reaction Quotient

To determine whether a system has reached equilibrium, chemists use a quantity called the reaction quotient ( $Q$ ). A quantity derived from a set of values measured at any time during the reaction of any mixture of reactants and products, regardless of whether the system is at equilibrium:  $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$  for the general balanced chemical equation  $aA + bB \rightleftharpoons cC + dD$ . The expression for the reaction quotient has precisely the same form as the equilibrium constant expression, except that  $Q$  may be derived from a set of values measured at *any* time during the reaction of *any* mixture of the reactants and the products, regardless of whether the system is at equilibrium. Therefore, for the following general reaction:

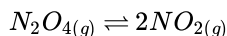


the reaction quotient is defined as follows:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (15.4.1)$$

The reaction quotient  $Q_p$  analogous to  $K_p$ , can be written for any reaction that involves gases by using the partial pressures of the components.

To understand how information is obtained using a reaction quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide,



for which  $K = 4.65 \times 10^{-3}$  at 298 K. We can write  $Q$  for this reaction as follows:

$$Q = \frac{[NO_2]^2}{[N_2O_4]} \quad (15.4.2)$$

The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of  $Q$  were calculated for each. Each experiment begins with different proportions of product and reactant:

Experiment	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$Q = [NO_2]^2/[N_2O_4]$
1	0	0.0400	$\frac{0^2}{0.0400} = 0$
2	0.0600	0	$\frac{(0.0600)^2}{0} = \text{undefined}$
3	0.0200	0.0600	$\frac{(0.0200)^2}{0.0600} = 6.67 \times 10^{-3}$

As these calculations demonstrate,  $Q$  can have any numerical value between 0 and infinity (undefined); that is,  $Q$  can be greater than, less than, or equal to  $K$ .

Comparing the magnitudes of  $Q$  and  $K$  enables us to determine whether a reaction mixture is already at equilibrium and, if it is not, predict how its composition will change with time to reach equilibrium (i.e., whether the reaction will proceed to the right or to the

left as written). All you need to remember is that the composition of a system not at equilibrium will change in a way that makes  $Q$  approach  $K$ . If  $Q = K$ , for example, then the system is already at equilibrium, and no further change in the composition of the system will occur unless the conditions are changed. If  $Q < K$ , then the ratio of the concentrations of products to the concentrations of reactants is *less* than the ratio at equilibrium. Therefore, the reaction will proceed to the right as written, forming products at the expense of reactants. Conversely, if  $Q > K$ , then the ratio of the concentrations of products to the concentrations of reactants is *greater* than at equilibrium, so the reaction will proceed to the left as written, forming reactants at the expense of products. These points are illustrated graphically in Figure 15.4.1

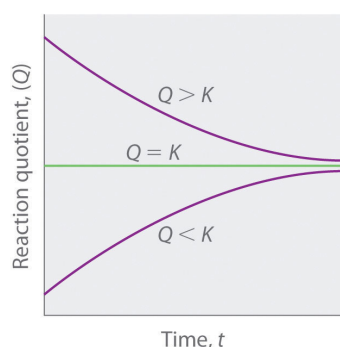
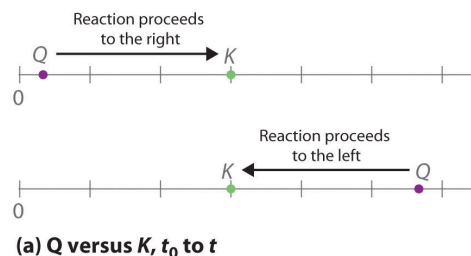


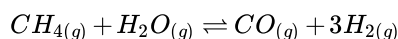
Figure 15.4.1 Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of  $Q$  and  $K$ (a) Both  $Q$  and  $K$  are plotted as points along a number line: the system will always react in the way that causes  $Q$  to approach  $K$ . (b) The change in the composition of a system with time is illustrated for systems with initial values of  $Q > K$ ,  $Q < K$ , and  $Q = K$ .

### Note the Pattern

If  $Q < K$ , the reaction will proceed to the right as written. If  $Q > K$ , the reaction will proceed to the left as written. If  $Q = K$ , then the system is at equilibrium.

### Example 15.4.1

At elevated temperatures, methane ( $\text{CH}_4$ ) reacts with water to produce hydrogen and carbon monoxide in what is known as a *steam-reforming* reaction:



$K = 2.4 \times 10^{-4}$  at 900 K. Huge amounts of hydrogen are produced from natural gas in this way and are then used for the industrial synthesis of ammonia. If  $1.2 \times 10^{-2}$  mol of  $\text{CH}_4$ ,  $8.0 \times 10^{-3}$  mol of  $\text{H}_2\text{O}$ ,  $1.6 \times 10^{-2}$  mol of  $\text{CO}$ , and  $6.0 \times 10^{-3}$  mol of  $\text{H}_2$  are placed in a 2.0 L steel reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce  $\text{CO}$  and  $\text{H}_2$  or to the left to form  $\text{CH}_4$  and  $\text{H}_2\text{O}$ ?

**Given:** balanced chemical equation,  $K$ , amounts of reactants and products, and volume

**Asked for:** direction of reaction

**Strategy:**

**A** Calculate the molar concentrations of the reactants and the products.

**B** Use Equation 15.4.1 to determine  $Q$ . Compare  $Q$  and  $K$  to determine in which direction the reaction will proceed.

### Solution:

**A** We must first find the initial concentrations of the substances present. For example, we have  $1.2 \times 10^{-2}$  mol of  $\text{CH}_4$  in a 2.0 L container, so

$$[\text{CH}_4] = \frac{1.2 \times 10^{-2} \text{ mol}}{2.0 \text{ L}} = 6.0 \times 10^{-3} \text{ M}$$

We can calculate the other concentrations in a similar way:

- $[\text{H}_2\text{O}] = 4.0 \times 10^{-3} \text{ M}$ ,
- $[\text{CO}] = 8.0 \times 10^{-3} \text{ M}$ , and
- $[\text{H}_2] = 3.0 \times 10^{-3} \text{ M}$ .

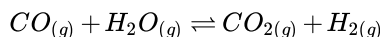
**B** We now compute  $Q$  and compare it with  $K$ :

$$Q = \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4][\text{H}_2\text{O}]} = \frac{(8.0 \times 10^{-3})(3.0 \times 10^{-3})^3}{(6.0 \times 10^{-3})(4.0 \times 10^{-3})} = 9.0 \times 10^{-6}$$

Because  $K = 2.4 \times 10^{-4}$ , we see that  $Q < K$ . Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming  $\text{H}_2$  and  $\text{CO}$  at the expense of  $\text{H}_2\text{O}$  and  $\text{CH}_4$ .

### Exercise

In the water–gas shift reaction introduced in Example 10, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:



$K = 0.64$  at 900 K. If 0.010 mol of both  $\text{CO}$  and  $\text{H}_2\text{O}$ , 0.0080 mol of  $\text{CO}_2$ , and 0.012 mol of  $\text{H}_2$  are injected into a 4.0 L reactor and heated to 900 K, will the reaction proceed to the left or to the right as written?

**Answer:**  $Q = 0.96$  ( $Q > K$ ), so the reaction will proceed to the left, and  $\text{CO}$  and  $\text{H}_2\text{O}$  will form.

## Predicting the Direction of a Reaction with a Graph

By graphing a few equilibrium concentrations for a system at a given temperature and pressure, we can readily see the range of reactant and product concentrations that correspond to equilibrium conditions, for which  $Q = K$ . Such a graph allows us to predict what will happen to a reaction when conditions change so that  $Q$  no longer equals  $K$ , such as when a reactant concentration or a product concentration is increased or decreased.

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:



Because  $\text{PbCO}_3$  and  $\text{PbO}$  are solids, the equilibrium constant is simply  $K = [\text{CO}_2]$ . At a given temperature, therefore, any system that contains solid  $\text{PbCO}_3$  and solid  $\text{PbO}$  will have exactly the same concentration of  $\text{CO}_2$  at equilibrium, regardless of the ratio or the amounts of the solids present. This situation is represented in [Figure 15.4.2](#), which shows a plot of  $[\text{CO}_2]$  versus the amount of  $\text{PbCO}_3$  added. Initially, the added  $\text{PbCO}_3$  decomposes completely to  $\text{CO}_2$  because the amount of  $\text{PbCO}_3$  is not sufficient to give a  $\text{CO}_2$  concentration equal to  $K$ . Thus the left portion of the graph represents a system that is *not* at equilibrium because it contains only  $\text{CO}_{2(g)}$  and  $\text{PbO}_{(s)}$ . In contrast, when just enough  $\text{PbCO}_3$  has been added to give  $[\text{CO}_2] = K$ , the system has reached equilibrium, and adding more  $\text{PbCO}_3$  has no effect on the  $\text{CO}_2$  concentration: the graph is a horizontal line. Thus any  $\text{CO}_2$  concentration that is not on the horizontal line represents a nonequilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough  $\text{PbCO}_3$  and  $\text{PbO}$  are present. For example, the point labeled A in [Figure 15.4.2](#) lies above the horizontal line, so it corresponds to a  $[\text{CO}_2]$  that is greater than the equilibrium concentration of  $\text{CO}_2$  ( $Q > K$ ). To reach equilibrium, the system must decrease  $[\text{CO}_2]$ , which it can do only by reacting  $\text{CO}_2$  with solid  $\text{PbO}$  to form solid  $\text{PbCO}_3$ . Thus the reaction in [Equation 15.4.3](#) will proceed to the left as written, until  $[\text{CO}_2] = K$ . Conversely, the point labeled B in [Figure 15.4.2](#) lies below the horizontal line, so it corresponds to a  $[\text{CO}_2]$  that is less than the equilibrium concentration of  $\text{CO}_2$  ( $Q < K$ ). To reach equilibrium, the system must increase  $[\text{CO}_2]$ , which it can do only by decomposing solid  $\text{PbCO}_3$  to form  $\text{CO}_2$  and solid  $\text{PbO}$ . The reaction in [Equation 15.4.2](#) will therefore proceed to the right as written, until  $[\text{CO}_2] = K$ .

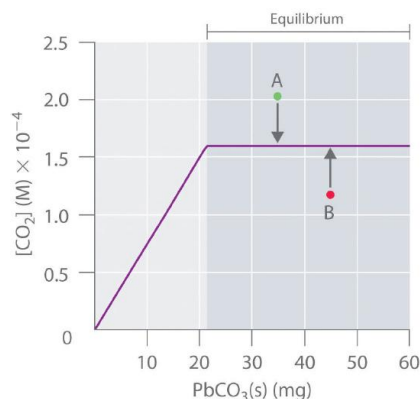


Figure 15.4.2 The Concentration of Gaseous  $\text{CO}_2$  in a Closed System at Equilibrium as a Function of the Amount of Solid  $\text{PbCO}_3$  Added Initially the concentration of  $\text{CO}_2(\text{g})$  increases linearly with the amount of solid  $\text{PbCO}_3$  added, as  $\text{PbCO}_3$  decomposes to  $\text{CO}_2(\text{g})$  and solid  $\text{PbO}$ . Once the  $\text{CO}_2$  concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid  $\text{PbCO}_3$  has no effect on  $[\text{CO}_2]$ , as long as the temperature remains constant.

In contrast, the reduction of cadmium oxide by hydrogen gives metallic cadmium and water vapor:



and the equilibrium constant  $K$  is  $[\text{H}_2\text{O}]/[\text{H}_2]$ . If  $[\text{H}_2\text{O}]$  is doubled at equilibrium, then  $[\text{H}_2]$  must also be doubled for the system to remain at equilibrium. A plot of  $[\text{H}_2\text{O}]$  versus  $[\text{H}_2]$  at equilibrium is a straight line with a slope of  $K$  (Figure 15.4.3). Again, only those pairs of concentrations of  $\text{H}_2\text{O}$  and  $\text{H}_2$  that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line corresponds to a nonequilibrium state. In such cases, the reaction in Equation 15.4.4 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point A in Figure 15.4.3 lies below the line, indicating that the  $[\text{H}_2\text{O}]/[\text{H}_2]$  ratio is less than the ratio of an equilibrium mixture ( $Q < K$ ). Thus the reaction in Equation 15.4.3 will proceed to the right as written, consuming  $\text{H}_2$  and producing  $\text{H}_2\text{O}$ , which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point B in Figure 15.4.3 lies above the line, indicating that the  $[\text{H}_2\text{O}]/[\text{H}_2]$  ratio is greater than the ratio of an equilibrium mixture ( $Q > K$ ). Thus the reaction in Equation 15.4.3 will proceed to the left as written, consuming  $\text{H}_2\text{O}$  and producing  $\text{H}_2$ , which causes the concentration ratio to move down and to the right toward the equilibrium line.

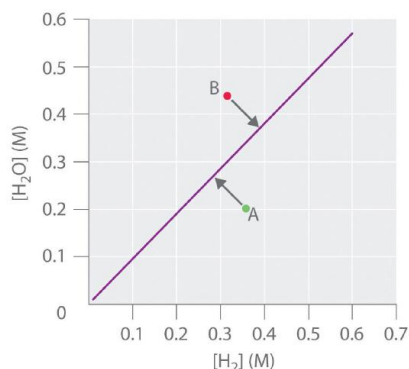


Figure 15.4.3 The Concentration of Water Vapor versus the Concentration of Hydrogen for the  $\text{CdO}_{(s)} + \text{H}_{2(g)} \rightleftharpoons \text{Cd}_{(s)} + \text{H}_2\text{O}_{(g)}$  System at **Equilibrium** For any equilibrium concentration of  $\text{H}_2\text{O}(\text{g})$ , there is only one equilibrium concentration of  $\text{H}_2(\text{g})$ . Because the magnitudes of the two concentrations are directly proportional, a large  $[\text{H}_2\text{O}]$  at equilibrium requires a large  $[\text{H}_2]$  and vice versa. In this case, the slope of the line is equal to  $K$ .

In another example, solid ammonium iodide dissociates to gaseous ammonia and hydrogen iodide at elevated temperatures:



For this system,  $K$  is equal to the product of the concentrations of the two products:  $[\text{NH}_3][\text{HI}]$ . If we double the concentration of  $\text{NH}_3$ , the concentration of  $\text{HI}$  must decrease by approximately a factor of 2 to maintain equilibrium, as shown in Figure 15.4.4. As a result, for a given concentration of either  $\text{HI}$  or  $\text{NH}_3$ , only a *single* equilibrium composition that contains equal concentrations of both  $\text{NH}_3$  and  $\text{HI}$  is possible, for which  $[\text{NH}_3] = [\text{HI}] = K^{1/2}$ . Any point that lies below and to the left of the equilibrium curve (such

as point A in Figure 15.4.4) corresponds to  $Q < K$ , and the reaction in Equation 15.4.4 will therefore proceed to the right as written, causing the composition of the system to move toward the equilibrium line. Conversely, any point that lies above and to the right of the equilibrium curve (such as point B in Figure 15.4.3) corresponds to  $Q > K$ , and the reaction in Equation 15.4.4 will therefore proceed to the left as written, again causing the composition of the system to move toward the equilibrium line. By graphing equilibrium concentrations for a given system at a given temperature and pressure, we can predict the direction of reaction of that mixture when the system is not at equilibrium.

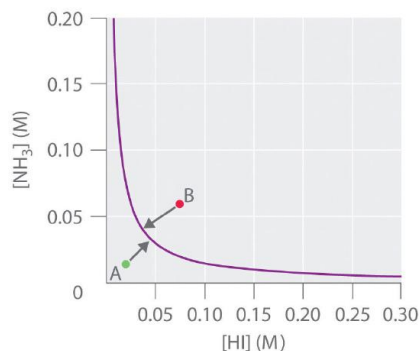


Figure 15.4.4 The Concentration of  $\text{NH}_3(\text{g})$  versus the Concentration of  $\text{HI}(\text{g})$  for the  $\text{NH}_4\text{I}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HI}(\text{g})$  System at **Equilibrium** Only one equilibrium concentration of  $\text{NH}_3(\text{g})$  is possible for any given equilibrium concentration of  $\text{HI}(\text{g})$ . In this case, the two are inversely proportional. Thus a large  $[\text{HI}]$  at equilibrium requires a small  $[\text{NH}_3]$  at equilibrium and vice versa.

## Le Chatelier's Principle

When a system at equilibrium is perturbed in some way, the effects of the perturbation can be predicted qualitatively using Le Chatelier's principle. If a stress is applied to a system at equilibrium, the composition of the system will change to relieve the applied stress. (named after the French chemist Henri Louis Le Chatelier, 1850–1936). The name is pronounced “Luh SHOT-lee-ay.” This principle can be stated as follows: *if a stress is applied to a system at equilibrium, the composition of the system will change to counteract the applied stress*. Stress occurs when any change in a system affects the magnitude of  $Q$  or  $K$ . In Equation 15.4.4, for example, increasing  $[\text{NH}_3]$  produces a stress on the system that requires a decrease in  $[\text{HI}]$  for the system to return to equilibrium. As a further example, consider esters, which are one of the products of an equilibrium reaction between a carboxylic acid and an alcohol. (For more information on this type of reaction, see Section 7.5.) Esters are responsible for the scents we associate with fruits (such as oranges and bananas), and they are also used as scents in perfumes. Applying a stress to the reaction of a carboxylic acid and an alcohol will change the composition of the system, leading to an increase or a decrease in the amount of ester produced. In Section 15.5 and Section 15.6, we explore how chemists control reactions conditions to affect equilibrium concentrations.

### Note the Pattern

In all reactions, if a stress is applied to a system at equilibrium, the composition of the system will change to counteract the applied stress (Le Chatelier's principle).

### Example 15.4.2

Write an equilibrium constant expression for each reaction and use this expression to predict what will happen to the concentration of the substance in bold when the indicated change is made if the system is to maintain equilibrium.

- $2\text{HgO}(\text{s}) \rightleftharpoons 2\text{Hg}(\text{l}) + \text{O}_2(\text{g})$ : the amount of  $\text{HgO}$  is doubled.
- $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$ : the concentration of  $\text{H}_2\text{S}$  is tripled.
- $n\text{-butane}(\text{g}) \rightleftharpoons \text{isobutane}(\text{g})$ : the concentration of isobutane is halved.

**Given:** equilibrium systems and changes

**Asked for:** equilibrium constant expressions and effects of changes

**Strategy:**

Write the equilibrium constant expression, remembering that pure liquids and solids do not appear in the expression. From this expression, predict the change that must occur to maintain equilibrium when the indicated changes are made.

**Solution:**

1. Because  $\text{HgO(s)}$  and  $\text{Hg(l)}$  are pure substances, they do not appear in the equilibrium constant expression. Thus, for this reaction,  $K = [\text{O}_2]$ . The equilibrium concentration of  $\text{O}_2$  is a constant and does not depend on the amount of  $\text{HgO}$  present. Hence adding more  $\text{HgO}$  will not affect the equilibrium concentration of  $\text{O}_2$ , so no compensatory change is necessary.
2.  $\text{NH}_4\text{HS}$  does not appear in the equilibrium constant expression because it is a solid. Thus  $K = [\text{NH}_3][\text{H}_2\text{S}]$ , which means that the concentrations of the products are inversely proportional. If adding  $\text{H}_2\text{S}$  triples the  $\text{H}_2\text{S}$  concentration, for example, then the  $\text{NH}_3$  concentration must decrease by about a factor of 3 for the system to remain at equilibrium so that the product of the concentrations equals  $K$ .
3. For this reaction,  $K = [\text{isobutane}]/[\text{n-butane}]$ , so halving the concentration of isobutane means that the  $\text{n-butane}$  concentration must also decrease by about half if the system is to maintain equilibrium.

#### Exercise

Write an equilibrium constant expression for each reaction. What must happen to the concentration of the substance in bold when the indicated change occurs if the system is to maintain equilibrium?

1.  $\text{HBr(g)} + \text{NaH(s)} \rightleftharpoons \text{NaBr(s)} + \text{H}_2\text{(g)}$ : the concentration of  $\text{HBr}$  is decreased by a factor of 3.
2.  $6\text{Li(s)} + \text{N}_2\text{(g)} \rightleftharpoons 2\text{Li}_3\text{N(s)}$ : the amount of  $\text{Li}$  is tripled.
3.  $\text{SO}_2\text{(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons \text{SO}_2\text{Cl}_2\text{(l)}$ : the concentration of  $\text{Cl}_2$  is doubled.

#### Answer

1.  $K = [\text{H}_2]/[\text{HBr}]$ ;  $[\text{H}_2]$  must decrease by about a factor of 3.
2.  $K = 1/[\text{N}_2]$ ; solid lithium does not appear in the equilibrium constant expression, so no compensatory change is necessary.
3.  $K = 1/[\text{SO}_2][\text{Cl}_2]$ ;  $[\text{SO}_2]$  must decrease by about half.

#### Summary

The **reaction quotient** ( $Q$  or  $Q_p$ ) has the same form as the equilibrium constant expression, but it is derived from concentrations obtained at any time. When a reaction system is at equilibrium,  $Q = K$ . Graphs derived by plotting a few equilibrium concentrations for a system at a given temperature and pressure can be used to predict the direction in which a reaction will proceed. Points that do not lie on the line or curve represent nonequilibrium states, and the system will adjust, if it can, to achieve equilibrium. **Le Chatelier's principle** states that if a stress is applied to a system at equilibrium, the composition of the system will adjust to counteract the stress.

#### Key Takeaway

- The reaction quotient ( $Q$ ) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction.

#### Key Equation

##### Reaction quotient

Equation 15.4.1:

$$Q = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \quad (15.4.1)$$

#### Conceptual Problems

1. During a set of experiments, graphs were drawn of [reactants] versus [products] at equilibrium. Using [Figure 15.4.4](#) and [Figure 15.4.4](#) as your guides, sketch the shape of each graph using appropriate labels.
  1.  $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{O(g)}$
  2.  $2\text{MgO(s)} \rightleftharpoons 2\text{Mg(s)} + \text{O}_{2\text{(g)}}$
  3.  $2\text{O}_{3\text{(g)}} \rightleftharpoons 3\text{O}_{2\text{(g)}}$
  4.  $2\text{PbS(s)} + 3\text{O}_{2\text{(g)}} \rightleftharpoons 2\text{PbO(s)} + 2\text{SO}_{2\text{(g)}}$
2. Write an equilibrium constant expression for each reaction system. Given the indicated changes, how must the concentration of the species in bold change if the system is to maintain equilibrium?
  1.  $2\text{NaHCO}_3\text{(s)} \rightleftharpoons \text{Na}_2\text{CO}_3\text{(s)} + \text{CO}_2\text{(g)} + \text{H}_2\text{O(g)}$ :  $[\text{CO}_2]$  is doubled.
  2.  $\text{N}_2\text{F}_4\text{(g)} \rightleftharpoons 2\text{NF}_2\text{(g)}$ :  $[\text{NF}_2]$  is decreased by a factor of 2.

3.  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ :  $[\text{I}_2]$  is doubled.

3. Write an equilibrium constant expression for each reaction system. Given the indicated changes, how must the concentration of the species in bold change if the system is to maintain equilibrium?

1.  $\text{CS}_2(\text{g}) + 4\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + 2\text{H}_2\text{S}(\text{g})$ :  $[\text{CS}_2]$  is doubled.

2.  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ :  $[\text{Cl}_2]$  is decreased by a factor of 2.

3.  $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$ :  $[\text{NO}]$  is doubled.

### Answer

1.

2.

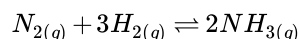
3. 1.  $K = \frac{[\text{CH}_4][\text{H}_2\text{S}]^2}{[\text{CS}_2][\text{H}_2]^4}$ ; doubling  $[\text{CS}_2]$  would require decreasing  $[\text{H}_2]$  by a factor of  $2^{1/4} \approx 1.189$ .

2.  $K = \frac{[\text{PCl}_3]}{[\text{Cl}_2][\text{PCl}_5]}$ ; if  $[\text{Cl}_2]$  is halved,  $[\text{PCl}_5]$  must also be halved.

3.  $K = \frac{[\text{NO}]^4[\text{H}_2\text{O}]^6}{[\text{NH}_3]^4[\text{O}_2]^5}$ ; if  $[\text{NO}]$  is doubled,  $[\text{H}_2\text{O}]$  is multiplied by  $2^{2/3} \approx 1.587$ .

### Numerical Problems

1. The data in the following table were collected at 450°C for the reaction



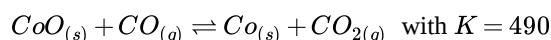
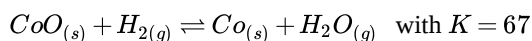
P (atm)	Equilibrium Partial Pressure (atm)		
	$\text{NH}_3$	$\text{N}_2$	$\text{H}_2$
30 (equilibrium)	1.740	6.588	21.58
100	15.20	19.17	65.13
600	321.6	56.74	220.8

The reaction equilibrates at a pressure of 30 atm. The pressure on the system is first increased to 100 atm and then to 600 atm. Is the system at equilibrium at each of these higher pressures? If not, in which direction will the reaction proceed to reach equilibrium?

2. For the reaction  $2\text{A} \rightleftharpoons \text{B} + 3\text{C}$ ,  $K$  at 200°C is 2.0. A 6.00 L flask was used to carry out the reaction at this temperature. Given the experimental data in the following table, all at 200°C, when the data for each experiment were collected, was the reaction at equilibrium? If it was not at equilibrium, in which direction will the reaction proceed?

Experiment	A	B	C
1	2.50 M	2.50 M	2.50 M
2	1.30 atm	1.75 atm	14.15 atm
3	12.61 mol	18.72 mol	6.51 mol

3. The following two reactions are carried out at 823 K:



1. Write the equilibrium expression for each reaction.

2. Calculate the partial pressure of both gaseous components at equilibrium in each reaction if a 1.00 L reaction vessel initially contains 0.316 mol of  $\text{H}_2$  or  $\text{CO}$  plus 0.500 mol  $\text{CoO}$ .

3. Using the information provided, calculate  $K_p$  for the following reaction:  $\text{H}_{2(\text{g})} + \text{CO}_{2(\text{g})} \rightleftharpoons \text{CO}_{(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$

4. Describe the shape of the graphs of [reactants] versus [products] as the amount of  $\text{CoO}$  changes.

4. Hydrogen iodide (HI) is synthesized via  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ , for which  $K_p = 54.5$  at  $425^\circ\text{C}$ . Given a 2.0 L vessel containing  $1.12 \times 10^{-2}$  mol of  $\text{H}_2$  and  $1.8 \times 10^{-3}$  mol of  $\text{I}_2$  at equilibrium, what is the concentration of HI? Excess hydrogen is added to the vessel so that the vessel now contains  $3.64 \times 10^{-1}$  mol of  $\text{H}_2$ . Calculate  $Q$  and then predict the direction in which the reaction will proceed. What are the new equilibrium concentrations?

### Answers

1. Not at equilibrium; in both cases, the sum of the equilibrium partial pressures is *less* than the total pressure, so the reaction will proceed to the right to decrease the pressure.
- 2.
3.
  1.  $K = [\text{H}_2\text{O}][\text{H}_2]$ ;  $K = [\text{CO}_2][\text{CO}]$
  2.  $P_{\text{H}_2\text{O}} = 21.0 \text{ atm}$ ;  $P_{\text{H}_2} = 0.27 \text{ atm}$ ;  $P_{\text{CO}_2} = 21.3 \text{ atm}$ ;  $P_{\text{CO}} = 0.07 \text{ atm}$
  3.  $K_p = 0.14$
4. The amount of CoO has no effect on the shape of a graph of products versus reactants *as long as some solid CoO is present*.
- 4.

### Contributors

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Modified by Joshua B. Halpern

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