Quantitative Changes in Equilibrium Systems

Carbon dioxide gas can dissolve in liquid water, $H_2O(l)$, to form a solution of carbonic acid, $H_2CO_3(aq)$, in a reversible reaction. This equilibrium system is involved in maintaining the pH of your blood. If your blood pH falls outside a narrow range of values—lower than 7.35 or higher than 7.45—you can suffer life-threatening symptoms. Cellular respiration produces aqueous carbon dioxide and liquid water. When these products are transferred from the cells to the blood, they can combine to produce aqueous carbonic acid, which lowers blood pH. This chemical reaction system can be represented by this equation:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

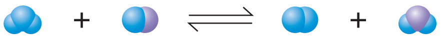
In critical cases of low blood pH, a doctor may administer a solution of hydrogen carbonate ions, HCO_3^- (aq), intravenously to raise the pH to normal range (**Figure 1**). We can think of carbonic acid as an ionic compound that decomposes readily to aqueous hydrogen carbonate ions and hydrogen ions, $H^+(aq)$. Administering aqueous hydrogen carbonate will cause the equilibrium system in the equation above to shift away from carbonic acid to the left, toward the reactants. This reduces the acid concentration and so raises blood pH. Knowing how much hydrogen carbonate produces the desired shift can have life-or-death implications. Fortunately, the equilibrium law equation allows us to predict equilibrium shifts quantitatively.

Figure 1 People with type 1 diabetes that is not well controlled are at higher risk for low blood pH.

We know that the equilibrium constant does not change with concentration. However, adjusting any concentration of an entity in this expression will disturb the equilibrium. This will force the equilibrium to shift through changes in the concentrations of other entities until the equilibrium constant is re-established at its original value, indicating that the system is again at equilibrium.

What happens at the level of the chemical entities to restore the equilibrium constant in a disturbed equilibrium? To answer this, imagine a reaction involving entities composed of two different hypothetical atoms, which we will represent as ● and ●.

The chemical reaction between these entities is reversible and the chemical reaction system has an equilibrium constant, K, of 25. We can represent this chemical reaction system as



Now, assume we place 12  and 12  in a closed reaction chamber and allow them to react. **Figure 2** depicts the entities in the reaction vessel before any chemical reactions have occurred.

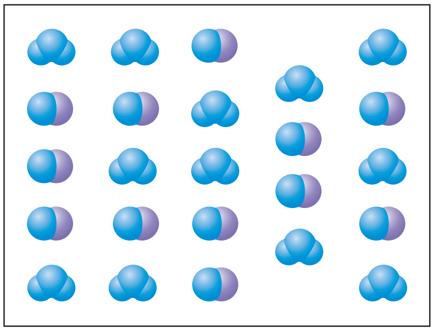
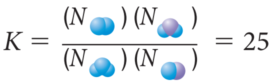


Figure 2 At the start of the reaction, 24 reactant molecules are mixed together in a reaction chamber in a 1:1 ratio.

Suppose that we allow the chemical reaction to reach equilibrium. Since we know the value of the equilibrium constant is 25, the equilibrium law equation for this reaction can be represented graphically as



In this equation, N represents the number of each entity. Since the equilibrium constant is not reported with units, the ratio of numbers (of entities) to numbers will yield the same value as the ratio of concentrations to concentrations. Therefore, we can use actual numbers of entities in the equilibrium law equation. We want to determine how many  and  entities will be present when this chemical system reaches equilibrium. How can we do this?

One strategy we can try is trial and error. Suppose we start by guessing that 5  will have reacted when the system reaches equilibrium. Since we know from the balanced equation that equal numbers of  and  react, then 5  must also have reacted and produced 5  and 5  (see **Table 1**).

Table 1 Number of Entities at Initial and New Conditions for a Reaction where K is 25; Numbers Determined by Trial and Error

				
Initial number of entities	12	12	0	0
Guessed change in number of entities	12 − 5 = 7	12 − 5 = 7	0 + 5 = 5	0 + 5 = 5
Equilibrium number of entities	?	?	?	?

We can check if the distribution in Table 1 forms a valid equilibrium for this chemical reaction system by substituting the numbers in the table into the equilibrium expression to see if we get a value of 25 (the given equilibrium constant value).

$K =$ (N ) (N ) / (N ) (N )

$$= \frac{(5)(5)}{(7)(7)}$$

$$K = 0.51$$

Since the calculated value using the numbers from Table 1 is not 25, we know that our guess was incorrect. The value that we calculated is less than 25, so we also know that the correct distribution must have a larger numerator (products) relative to the denominator (reactants).

Clearly, we underestimated by guessing that only 5 of the original reactants would need to react to reach equilibrium. How can we find the correct number? We might instead use a variable, such as x, to represent the number of entities that react and then analyze the distribution using an ICE table, as shown in **Table 2**.

Table 2 Initial, Change, Equilibrium Table for Hypothetical Equilibrium System

		+ 	$\rightleftharpoons$ 	+ 
Initial number of entities	12	12	0	0
Change in number of entities	$-x$	$-x$	$+x$	$+x$
Equilibrium number of entities	$12-x$	$12-x$	$+x$	$+x$

Rewriting the equilibrium expression for this algebraic representation gives

$K =$ (N ) (N ) / (N ) (N )

$$K = \frac{(x)(x)}{(12 - x)(12 - x)}$$

Since we know that the equilibrium constant, K, is equal to 25, we can solve this equation for x.

$$\begin{aligned}\frac{(x)(x)}{(12-x)(12-x)} &= 25\\ \frac{x^2}{(12-x)^2} &= 25\\ \frac{\sqrt{x^2}}{\sqrt{(12-x)^2}} &= \sqrt{25}\\ \frac{x}{12-x} &= \pm 5\\ x &= (\pm 5)(12-x)\end{aligned}$$

The square root of a number may be positive or negative. If $\sqrt{25} = +5$, then

$$\begin{aligned} x &= (5)(12-x)\\ x &= 60 - 5x\\ 6x &= 60\\ x &= 10\end{aligned}$$

If $\sqrt{25} = -5$, then

$$\begin{aligned} x &= (-5)(12-x)\\ x &= -60 + 5x\\ 4x &= 60\\ x &= 15\end{aligned}$$

We started with 12 entities of each reactant, so a value of 15 for x would give us a negative number of atoms, which is not possible. Therefore, the solution is that x is equal to 10. To check this, we substitute 10 for x in our algebraic equation for the equilibrium constant:

$$\begin{aligned} K &= \frac{(x)(x)}{(12-x)(12-x)}\\ &= \frac{(10)(10)}{(12-10)(12-10)}\\ K &= 25\end{aligned}$$

Figure 3 depicts this distribution of entities at equilibrium.

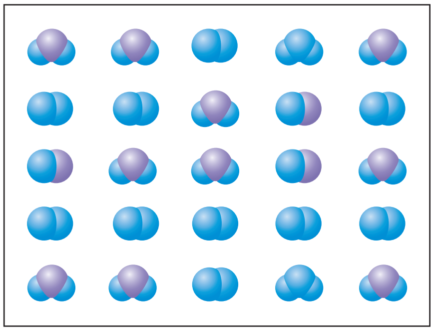


Figure 3 At equilibrium, the system contains 10 , 10 , 2 , and 2 .

The Reaction Quotient (*Q*)

reaction quotient (*Q*) the product of the concentrations of the products, divided by the product of the concentrations of the reactants, for a chemical reaction that is not necessarily at equilibrium

The **reaction quotient (*Q*)** is the ratio of the product of the concentrations of the products to the product of the concentrations of the reactants. Like the equilibrium constant, this ratio can be used to analyze an equilibrium system. However, the

instantaneous concentrations concentrations that occur together at a particular instant in time in the progress of a chemical reaction

reaction quotient can be calculated for a chemical reaction that is not at equilibrium. To obtain the reaction quotient, the equilibrium law equation is applied using instantaneous concentrations. **Instantaneous concentrations** are a set of concentrations that correspond to a particular instant in time. The specific instant in time does not matter, as long as the concentrations of all reactants and products are measured at the same instant. If the concentrations of reactants and products are measured when a system is at equilibrium, then the reaction quotient, Q, will have the same value as the equilibrium constant, K. CAREER LINK

It is often convenient to measure concentrations at the beginning of a reaction, when all product concentrations are zero. For example, consider the synthesis of ammonia gas, $NH_3(g)$, from gaseous nitrogen, $N_2(g)$, and hydrogen, $H_2(g)$. You may recall that Fritz Haber's explorations of this reaction system won him the Nobel Prize in Chemistry (Section 7.3). The balanced chemical equation for this reaction is

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

The reaction quotient equation for this reaction system at any time is

$$Q = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$$

When the concentration of any reactant or product is zero, the chemical equilibrium system will shift in the direction that produces the missing substance. What happens at a point when none of the concentrations are zero? To predict the direction in which the chemical equilibrium system will shift, we can compare the values of the reaction quotient, Q, to the equilibrium constant, K. The relative sizes of Q and K can give three possible predictions:

1. Q is less than K. The ratio of the concentrations of products to the concentrations of reactants is smaller than when the chemical system is at equilibrium. To move Q toward K, the concentrations of products must increase while the concentration of the reactants decreases. The chemical equilibrium system shifts to the right, consuming reactants and forming products until equilibrium is reached and Q equals K.
2. Q is equal to K. The chemical system is at equilibrium, so no shift will occur.
3. Q is greater than K. The ratio of the concentrations of products to the concentrations of reactants is larger than when the chemical system is at equilibrium. To move Q toward K, the concentrations of products must decrease and that of reactants must increase. The chemical equilibrium system shifts to the left and converts products into reactants until it achieves equilibrium and Q equals K.

These predictions are summarized graphically in **Figure 4**. WEB LINK

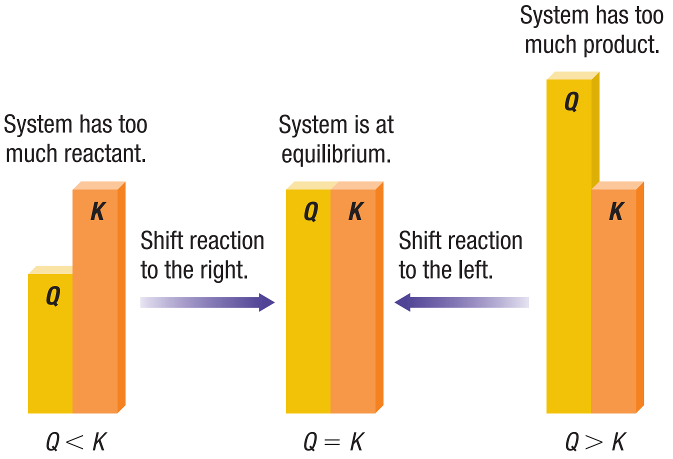


Figure 4 The relationship between reaction quotient, Q, and the equilibrium constant, K.

Tutorial 1 Using the Reaction Quotient

It is useful to think of the reaction quotient as just that—a quotient (i.e., the result of a mathematical division) of the products over the reactants. If the reaction quotient is larger than *K*, then the concentrations of the products are high and the concentrations of the reactants are low compared to their equilibrium values. If the quotient is less than *K*, then products are low and reactants are high. Once we know which of these cases applies, it is clear in which direction a reaction will proceed to reach equilibrium.

Sample Problem 1: Using *Q* to Determine if a Chemical Reaction System Is at Equilibrium

For the synthesis of ammonia gas at 500 °C in a closed vessel from gaseous nitrogen and hydrogen, the equilibrium constant, *K*, is 6.01×10^{-2}. The balanced chemical equation for this reaction is

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

For each of the following initial conditions, determine if the given concentrations represent an equilibrium. If not, predict the direction in which the reaction will proceed to reach equilibrium.

(a) $[NH_3(g)]_{initial} = 1.00 \times 10^{-3}$ mol/L;
$[N_2(g)]_{initial} = 1.00 \times 10^{-5}$ mol/L;
$[H_2(g)]_{initial} = 2.00 \times 10^{-3}$ mol/L

(b) $[NH_3(g)]_{initial} = 2.00 \times 10^{-4}$ mol/L;
$[N_2(g)]_{initial} = 1.50 \times 10^{-5}$ mol/L;
$[H_2(g)]_{initial} = 3.54 \times 10^{-1}$ mol/L

(c) $[NH_3(g)]_{initial} = 1.00 \times 10^{-4}$ mol/L;
$[N_2(g)]_{initial} = 5.00$ mol/L;
$[H_2(g)]_{initial} = 1.00 \times 10^{-2}$ mol/L

(a) **Given:** $[NH_3(g)]_{initial} = 1.00 \times 10^{-3}$ mol/L;
$[N_2(g)]_{initial} = 1.00 \times 10^{-5}$ mol/L;
$[H_2(g)]_{initial} = 2.00 \times 10^{-3}$ mol/L; $K = 6.01 \times 10^{-2}$

Required: *Q*

Solution:

Step 1. Write the equilibrium constant equation for the reaction system and calculate *Q* from the given concentrations:

$$Q = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$$

$$= \frac{(1.00 \times 10^{-3})^2}{(1.00 \times 10^{-5})(2.00 \times 10^{-3})^3}$$

$$Q = 1.25 \times 10^7$$

Since $K = 6.01 \times 10^{-2}$, *Q* is greater than *K*, and the system is not at equilibrium.

Step 2. Since *Q* is greater than *K*, the system has more of the product now than it would have at equilibrium. To reach equilibrium, the equilibrium system must shift to the left (toward the reactants).

Statement: At the given initial conditions, this chemical reaction system must shift to the left, toward reactants, to reach equilibrium.

(b) **Given:** $[NH_3(g)]_{initial} = 2.00 \times 10^{-4}$ mol/L;
$[N_2(g)]_{initial} = 1.50 \times 10^{-5}$ mol/L;
$[H_2(g)]_{initial} = 3.54 \times 10^{-1}$ mol/L; $K = 6.01 \times 10^{-2}$

Required: *Q*

Solution: Calculate *Q*, and compare its value to the value of *K*.

$$Q = \frac{(2.00 \times 10^{-4})^2}{(1.50 \times 10^{-5})(3.54 \times 10^{-1})^3}$$

$$Q = 6.01 \times 10^{-2}$$

Since $K = 6.01 \times 10^{-2}$, *Q* is equal to *K* and the system is at equilibrium.

Statement: Since the chemical reaction system is at equilibrium at the given initial conditions, it will not shift.

(c) **Given:** $[NH_3(g)]_{initial} = 1.00 \times 10^{-4}$ mol/L;
$[N_2(g)]_{initial} = 5.00$ mol/L;
$[H_2(g)]_{initial} = 1.00 \times 10^{-2}$ mol/L; $K = 6.01 \times 10^{-2}$

Required: *Q*

Solution:

Step 1. Calculate *Q*, and compare its value to the value of *K*.

$$Q = \frac{(1.00 \times 10^{-4})^2}{(5.00)(1.00 \times 10^{-2})^3}$$

$$Q = 2.00 \times 10^{-3}$$

Step 2. *Q* is less than *K*, so the system is not at equilibrium. To reach equilibrium, the equilibrium system must shift to the right, toward the product.

Statement: At the given initial conditions, this chemical equilibrium system will shift to the right (toward the product) to achieve equilibrium.

Practice

1. The equilibrium constant, K, is 0.020 when the chemical reaction system given by the following balanced chemical equation is carried out in a closed container at 445 °C:

   $2\ HI(g) \rightleftharpoons H_2(g) + I_2(g)$

   Determine the value of Q to establish whether this chemical reaction system is at equilibrium when reactants and products have the following concentrations. If the system is not at equilibrium, predict the direction in which the reaction will proceed to reach equilibrium. T/I

   (a) $[HI(g)] = 0.14$ mol/L, $[H_2(g)] = 0.040$ mol/L, and $[I_2(g)] = 0.010$ mol/L. [ans: $Q = 0.020$]

   (b) $[HI(g)] = 0.20$ mol/L, $[H_2(g)] = 0.15$ mol/L, and $[I_2(g)] = 0.090$ mol/L. [ans: $Q = 0.34$; left]

2. In a closed container, dinitrogen tetroxide gas, $N_2O_4(g)$, decomposes to nitrogen dioxide gas, $NO_2(g)$. The equilibrium constant, K, for this reaction is 0.87 at 55 °C. A chemist fills a vessel with dinitrogen tetroxide gas at 55 °C. He then analyzes the contents twice as the reaction is proceeding, and finds that it contains the following concentrations:
   Time 1: $[N_2O_4(g)] = 0.80$ mol/L, $[NO_2(g)] = 1.55$ mol/L
   Time 2: $[N_2O_4(g)] = 1.66$ mol/L, $[NO_2(g)] = 1.2$ mol/L

   For each time, determine whether the system was in equilibrium. If it was not, predict the direction in which the reaction would proceed to achieve equilibrium. [ans: Time 1: no, left; Time 2: yes] T/I

3. When heated, solid silver oxide, $Ag_2O(s)$, will decompose into silver metal, $Ag(s)$, and oxygen gas, $O_2(g)$. In a sealed vessel, the chemical system will form an equilibrium with an equilibrium constant, K, of 2.5×10^{-3}.

   $2\ Ag_2O(s) \rightleftharpoons 4\ Ag(s) + O_2(g)$

   (a) Write the equilibrium constant equation. K/U

   (b) When the instantaneous concentration of oxygen gas is 5.0×10^{-2} mol/L, is the chemical system at equilibrium? If not, in what direction will it shift to reach equilibrium? [ans: no; left] T/I

Calculating Equilibrium Concentrations

We can calculate the value of the equilibrium constant if we are given the initial concentrations of all reactants and products and at least one equilibrium concentration. We can also calculate the equilibrium concentrations from the equilibrium constant and the initial concentrations.

Tutorial 2 Calculating Equilibrium Concentrations

One strategy to find equilibrium concentrations of reactants and products is to work with the initial concentrations. You can then modify these initial concentrations appropriately to find the equilibrium concentrations.

Sample Problem 1: Determining Equilibrium Concentrations and K from All Initial Concentrations and One Equilibrium Concentration

Phosphorus pentachloride gas, $PCl_5(g)$, decomposes to form phosphorus trichloride gas, $PCl_3(g)$, and chlorine gas, $Cl_2(g)$:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

A 2.00 L sealed flask at 30 °C initially contains 0.298 mol of phosphorus trichloride gas, 8.70×10^{-3} mol of phosphorus pentachloride gas, and no chlorine gas. At equilibrium, the flask contains 2.00×10^{-3} mol of chlorine gas. Calculate the equilibrium concentrations of all entities and the value of K.

Given: Volume, $V = 2.00$ L;
$n_{\text{initial }PCl_5(g)} = 8.70 \times 10^{-3}$ mol;
$n_{\text{initial }PCl_3(g)} = 0.298$ mol; $n_{\text{initial }Cl_2(g)} = 0$ mol;
$n_{\text{equilibrium }Cl_2(g)} = 2.00 \times 10^{-3}$ mol

Required: $[PCl_5(g)]_{\text{equilibrium}}$; $[PCl_3(g)]_{\text{equilibrium}}$; K

Analysis: $c = \dfrac{n}{V}$

Solution:

Step 1. Calculate concentrations, c, in mol/L from the given amounts of all entities.

$$[PCl_5(g)]_{initial};\ c = \frac{n_{initial}}{V}$$

$$= \frac{8.70 \times 10^{-3}\ \text{mol}}{2.00\ \text{L}}$$

$$[PCl_5(g)]_{initial} = 4.35 \times 10^{-3}\ \text{mol/L}$$

Using the same formula,

$$[PCl_3(g)]_{initial} = 0.149\ \text{mol/L}$$

Since there is no chlorine gas initially, $[Cl_2(g)]_{initial}$ is 0 mol/L. The equilibrium concentration of $Cl_2(g)$ is

$$[Cl_2(g)]_{equilibrium};\ c = \frac{n_{equilibrium}}{V}$$

$$= \frac{2.00 \times 10^{-3}\ \text{mol}}{2.00\ \text{L}}$$

$$[Cl_2(g)]_{equilibrium} = 1.00 \times 10^{-3}\ \text{mol/L}$$

Step 2. Use an ICE table to determine the required equilibrium concentrations.

According to the balanced chemical equation for the chemical reaction system, the mole ratio is 1:1:1. The initial concentration of $Cl_2(g)$ was 0 mol/L, and 1.00×10^{-3} mol/L of $Cl_2(g)$ is present at equilibrium, so there is a decrease in the concentration of $PCl_5(g)$ and an increase $PCl_3(g)$ of 1.00×10^{-3} mol/L. Since all the coefficients in the balanced equation are 1, the magnitude of the change is the same for all entities. Organize this information in an ICE table, similar to **Table 3**.

Table 3 ICE Table for Calculating Equilibrium Concentrations

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
I	4.35×10^{-3}		0.149		0
C	$-(1.00 \times 10^{-3})$		$+(1.00 \times 10^{-3})$		$+(1.00 \times 10^{-3})$
E	3.35×10^{-3}		0.150		1.00×10^{-3}

Step 3. Calculate the equilibrium constant, K, by substituting the equilibrium concentrations into the equilibrium constant equation.

$$K = \frac{[Cl_2(g)][PCl_3(g)]}{[PCl_5(g)]}$$

$$= \frac{(1.00 \times 10^{-3})(0.150)}{(3.35 \times 10^{-3})}$$

$$K = 4.48 \times 10^{-2}$$

Statement: The equilibrium concentration of the reactant, phosphorus pentachloride gas, $PCl_5(g)$, is 3.35×10^{-3} mol/L. The equilibrium concentrations of the products are 0.150 mol/L for phosphorus trichloride gas, $PCl_3(g)$, and 1.00×10^{-3} mol/L for chlorine gas, $Cl_2(g)$. The equilibrium constant for the equilibrium system is 4.48×10^{-2}.

Sample Problem 2: Determining Equilibrium Concentrations from *K* and Initial Concentrations Only

Carbon monoxide gas, $CO(g)$, reacts with steam, $H_2O(g)$, to produce carbon dioxide, $CO_2(g)$, and hydrogen, $H_2(g)$. At 700 K, the equilibrium constant is 5.10. Calculate all equilibrium concentrations if 1.250 mol of each entity is initially placed in a 500.0 mL sealed flask.

Given: $V = 500.0$ mL; $n_{initial\ CO(g)} = 1.250$ mol; $n_{initial\ H_2O(g)} = 1.250$ mol; $n_{initial\ H_2(g)} = 1.250$ mol; $n_{initial\ CO_2(g)} = 1.250$ mol; $K = 5.10$

Required: $[CO(g)]_{equilibrium}$; $[H_2O(g)]_{equilibrium}$; $[H_2(g)]_{equilibrium}$; $[CO_2(g)]_{equilibrium}$

Solution:

Step 1. Convert the given amounts to concentrations in mol/L by dividing by the volume.

$$[CO(g)]_{initial} = \frac{1.250\ \text{mol}}{0.5000\ \text{L}}$$

$$[CO(g)]_{initial} = 2.500\ \text{mol/L}$$

Since $n_{initial}$ is the same for all products and reactants, and $[CO(g)]_{initial} = 2.500$ mol/L, you know that $[H_2O(g)]_{initial} = 2.500$ mol/L, $[CO_2(g)]_{initial} = 2.500$ mol/L, and $[H_2(g)]_{initial} = 2.500$ mol/L.

Step 2. Write the balanced equation for the equilibrium reaction system.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Step 3. Calculate the reaction quotient, Q, for the initial concentrations and compare its value with the given value of K.

$$Q = \frac{[CO_2(g)][H_2(g)]}{[CO(g)][H_2O(g)]}$$

$$= \frac{(2.500)(2.500)}{(2.500)(2.500)}$$

$$Q = 1.000$$

Since this Q is less than the given value of 5.10 for K, the system is not at equilibrium. For Q to be equal to K (5.10), the chemical reaction system must shift to the right (toward products).

Step 4. Use an ICE table to determine the required changes to the equilibrium concentrations. Use a variable for unknowns. Your table should look similar to **Table 4**.

Table 4 ICE Table for Calculating Equilibrium Concentrations

	$CO(g)$ +	$H_2O(g)$ ⇌	$CO_2(g)$ +	$H_2(g)$
I	2.500	2.500	2.500	2.500
C	$-x$	$-x$	$+x$	$+x$
E	$2.500-x$	$2.500-x$	$2.500+x$	$2.500+x$

Step 5. Calculate the value of x by substituting the given value of K and the concentrations from the ICE table into the equilibrium constant equation. Note that all concentrations have units of mol/L, but we have omitted the units to simplify the calculation.

$$\frac{[CO_2(g)][H_2(g)]}{[CO(g)][H_2O(g)]} = 5.10$$

$$\frac{(2.500 + x)(2.500 + x)}{(2.500 - x)(2.500 - x)} = 5.10$$

$$\frac{\sqrt{(2.500 + x)^2}}{\sqrt{(2.500 - x)^2}} = \sqrt{5.10}$$

$$\frac{2.500 + x}{2.500 - x} = \pm 2.258$$

$$2.500 + x = (\pm 2.258)(2.500 - x)$$

$$x = \pm 2.258(2.500 - x) - 2.500$$

Solve for x for the positive root.

$$\begin{aligned} x &= 2.258(2.500 - x) - 2.500 \\ x &= 5.645 - 2.258x - 2.500 \\ 3.258x &= 3.145 \\ x &= 0.965 \end{aligned}$$

Solve for x for the negative root.

$$\begin{aligned} x &= -2.258(2.500 - x) - 2.500 \\ x &= -5.645 + 2.258x - 2.500 \\ 8.145 &= 1.258x \\ x &= 6.475 \end{aligned}$$

Substituting this value of x into the expressions for equilibrium concentrations in the ICE table results in negative concentration values, which are not possible in the real world. Therefore, use $x = 0.965$ mol/L in the equilibrium concentration calculations.

Step 6. Calculate the equilibrium concentrations.

Reactants:

$$\begin{aligned} [CO(g)]_{\text{equilibrium}} \text{ and } [H_2O(g)]_{\text{equilibrium}} &= 2.500 - x \\ &= 2.500 - 0.965 \\ [CO(g)]_{\text{equilibrium}} \text{ and } [H_2O(g)]_{\text{equilibrium}} &= 1.535 \text{ mol/L} \end{aligned}$$

Products:

$$\begin{aligned} [CO_2(g)]_{\text{equilibrium}} \text{ and } [H_2(g)]_{\text{equilibrium}} &= 2.500 + x \\ &= 2.500 + 0.965 \\ [CO_2(g)]_{\text{equilibrium}} \text{ and } [H_2(g)]_{\text{equilibrium}} &= 3.465 \text{ mol/L} \end{aligned}$$

Check these values by substituting them into the equilibrium law equation.

$$\begin{aligned} K &= \frac{[CO_2(g)][H_2(g)]}{[CO(g)][H_2O(g)]} \\ &= \frac{(3.465)^2}{(1.535)^2} \\ K &= 5.096 \end{aligned}$$

This result is the same as the given value of K (5.10), within rounding error.

Statement: The equilibrium concentration for both carbon monoxide gas and steam is 3.47 mol/L. The equilibrium concentration for both carbon dioxide gas and hydrogen gas is 1.54 mol/L.

Practice

1. In a 250 mL sealed container at 150 °C, 0.50 mol of both iodine gas, $I_2(g)$, and bromine gas, $Br_2(g)$, are mixed and allowed to react until they form an equilibrium with iodine monobromide gas, IBr(g). The equilibrium constant for this reaction is 1.2×10^2. What are the equilibrium concentrations for iodine gas and bromine gas? T/I [ans: $[I_2] = 0.3$ mol/L; $[Br_2] = 0.3$ mol/L]
2. In a 2.00 L reaction vessel at 440 °C, hydrogen gas and iodine vapour form gaseous hydrogen iodide. The equilibrium constant, K, is 49.7. Determine the equilibrium concentrations for all entities if 4.00 mol of hydrogen gas and 1.99 mol of iodine vapour are combined and the equilibrium concentration of hydrogen gas is 1.07 mol/L. T/I [ans: $[H_2(g)] = 1.07$ mol/L; $[I_2(g)] = 0.06$ mol/L; and $[HI(g)] = 1.86$ mol/L.]
3. At a temperature of 500 K, carbon dioxide gas, $CO_2(g)$, and solid carbon, C(s), will react to form an equilibrium.

   $$CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)$$

   When 0.250 mol of carbon dioxide gas was placed in a 0.500 L flask with carbon powder and reacted until equilibrium was reached, the concentration of carbon monoxide gas at equilibrium was 0.0157 mol/L. Determine the value of the equilibrium constant, K, and the concentration of carbon dioxide gas at equilibrium. T/I [ans: $K = 5.01 \times 10^{-4}$, $[CO_2(g)]_{\text{equilibrium}} = 0.492$ mol/L]

Solving More Complex Equilibrium Problems

So far, we have worked only with problems in which the initial concentrations and stoichiometry gave us polynomials that were easily reduced to simple linear equations. Concentrations, temperatures, and equilibrium constants were carefully chosen so that you could follow the logic of the solutions more easily. However, in the real world, problem-solving for chemical equilibria will rarely involve linear equations. Instead, equilibrium problems often require working with higher-order polynomials. In Tutorial 3, you will see how and when to use the same strategy we have used thus far to solve these more complex problems.

Tutorial 3 Solving More Complex Equilibrium Problems

The general strategy to solve more complex equilibrium problems is the same as for the simpler problems. You will either be given or be expected to know the following: the balanced equation for the reaction, the equilibrium law equation for the reaction, the equilibrium constant for the equilibrium system, and the initial concentrations of the entities in the reaction.

Sample Problem 1: Using Assumptions about the Magnitude of *x*

Carbon monoxide gas, CO(g), is a primary starting material in the synthesis of many organic compounds, including methanol, $CH_3OH(l)$. At 2000 °C, K is 6.40×10^{-7} for the decomposition of carbon dioxide gas, $CO_2(g)$, into carbon monoxide and oxygen, $O_2(g)$. Calculate the concentrations of all entities at equilibrium if 0.250 mol of $CO_2(g)$ is placed in a 1.000 L closed container and heated to 2000 °C.

Given: $V = 1.000$ L; $n_{CO_2(g)} = 0.250$ mol; $K = 6.40 \times 10^{-7}$

Required: $[CO_2(g)]_{[equilibrium]}$; $[O_2(g)]_{equilibrium}$; $[CO(g)]_{equilibrium}$

Solution:

Step 1. Determine initial concentrations of substances in mol/L, using any given amounts and volumes.

Since the reaction has not yet started, the initial concentration of $CO_2(g)$ and $O_2(g)$ is 0 mol/L. Since V is 1.000 L,

$$[CO_2(g)]_{initial};\ c = \frac{n}{V}$$

$$[CO_2(g)]_{initial} = 0.250 \text{ mol/L}$$

Step 2. Calculate Q and compare it to K.

Since there are initially no products, you also know that Q is 0. Q is therefore less than K and the equilibrium system will shift to the right, toward the products.

Step 3. Use an ICE table to determine the equilibrium concentrations.

Write the balanced chemical equation for the reaction

$$2\ CO_2(g) \rightleftharpoons 2\ CO(g) + O_2(g)$$

Use a variable for unknowns, using coefficients according to the stoichiometry of the balanced equation. Your table should look similar to **Table 5**.

Table 5 ICE Table for Calculating Equilibrium Concentrations

	$2\ CO_2(g)$ $\rightleftharpoons$	$2\ CO(g)$ +	$O_2(g)$
I	0.250	0.00	0.00
C	$-2x$	$+2x$	$+x$
E	$0.250 - 2x$	$2x$	x

Step 4. Substitute the equilibrium concentrations into the equilibrium constant equation, and solve for the unknown.

$$K = \frac{[CO(g)]^2[O_2(g)]}{[CO_2(g)]^2} = 6.40 \times 10^{-7}$$

$$\frac{(2x)^2(x)}{(0.250 - 2x)^2} = 6.40 \times 10^{-7}$$

$$\frac{4x^3}{(0.250 - 2x)^2} = 6.40 \times 10^{-7}$$

There is not an easy way to solve a cubic equation. However, you can simplify it by making some reasonable assumptions. Notice that the equilibrium constant value is very small compared to the initial concentration of carbon dioxide gas. Therefore, very little carbon dioxide gas will decompose at this temperature. From this, you can assume that the value of x will also be so small as to be negligible.

If x is negligible, then $2x$ will be a very small number. Therefore,

$$[CO_2(g)]_{equilibrium} = [CO_2(g)]_{initial} - 2x$$

$$= 0.250 \text{ mol/L} - (\text{very small number})$$

$$[CO_2(g)]_{equilibrium} \approx 0.250 \text{ mol/L}$$

At equilibrium, then, the cubic equation for *K* can be simplified and solved.

$$\frac{4x^3}{(0.250 - 2x)^2} = 6.40 \times 10^{-7}$$

$$\frac{4x^3}{(0.250)^2} \approx 6.40 \times 10^{-7}$$

$$4x^3 \approx (6.40 \times 10^{-7})(0.250)^2$$

$$x^3 \approx \frac{4.00 \times 10^{-8}}{4}$$

$$x \approx \sqrt[3]{1.00 \times 10^{-8}}$$

$$x \approx 2.15 \times 10^{-3}$$

Now, use this value to test the validity of your earlier assumption.

$$\begin{aligned}[CO_2(g)]_{\text{equilibrium}} &= [CO_2(g)]_{\text{initial}} - 2x \\ &= 0.250\ \text{mol/L} - 2(2.15\ \text{mol/L} \times 10^{-3}) \\ &= 0.250\ \text{mol/L} - 0.00430\ \text{mol/L} \\ [CO_2(g)]_{\text{equilibrium}} &= 0.246\ \text{mol/L}\end{aligned}$$

The difference between 0.250 mol/L and 0.246 mol/L is 0.004, or 1.6 %. This very small discrepancy will have little effect on calculations of equilibrium concentrations. In general, a difference of less than 5 % justifies the simplifying assumption. It can be shown that, if the concentration to which *x* is added or subtracted is at least 100 times the value of *K*, the simplifying assumption will give an error of less than 5 %. We will call this the "hundred rule." The hundred rule can determine if a simplifying assumption is warranted in a complex calculation and so should be used before the calculation is made.

$$\frac{[CO_2(g)]_{\text{initial}}}{K} = \frac{0.250}{6.40 \times 10^{-7}}$$

$$\frac{[CO_2(g)]_{\text{initial}}}{K} = 3.91 \times 10^5$$

The ratio of 3.91×10^5 is much greater than 100, which shows that the assumption $0.250 - 2x = 0.250$ was warranted.

Now that you have a good approximation of *x*, you can use it to solve for the equilibrium concentrations by substituting it in the expressions in the ICE table. This will give you the following concentrations:

$[CO_2(g)]_{\text{equilibrium}} = 0.246$ mol/L

$[CO(g)]_{\text{equilibrium}} = 4.30 \times 10^{-3}$ mol/L

$[O_2(g)]_{\text{equilibrium}} = 2.15 \times 10^{-3}$ mol/L

Step 5. Check your work by determining *K* from the equilibrium concentrations you calculated, and comparing the value to the standard value of *K*. If they are within 5 %, you can be confident that your calculations are correct.

$$K = \frac{[CO(g)]^2[O_2(g)]}{[CO_2(g)]^2}$$

$$= \frac{(4.30 \times 10^{-3})^2(2.15 \times 10^{-3})}{(0.246)^2}$$

$$K = 6.57 \times 10^{-7}$$

The calculated value of *K* (6.57×10^{-7}) is within 3 % of the given value (6.40×10^{-7}).

Statement: The equilibrium concentrations for gaseous carbon dioxide, carbon monoxide, and oxygen are 0.246 mol/L, 4.30×10^{-3} mol/L, and 2.15×10^{-3} mol/L, respectively.

Sample Problem 2: Rejecting an Assumption about the Magnitude of *x*

If 0.500 mol of dinitrogen tetroxide gas, $N_2O_4(g)$, is placed in a 1.00 L closed container at 150 °C, what will be the concentrations of dinitrogen tetroxide gas and nitrogen dioxide gas, $NO_2(g)$, at equilibrium? The equilibrium constant, *K*, is 4.50 under these conditions.

Given: $V = 1.00$ L; $n_{N_2O_4} = 0.500$ mol; $K = 4.50$

Required: all equilibrium concentrations in mol/L

Solution:

Step 1. Since initially there are no products, *Q* is 0, which is smaller than *K*. The equilibrium system will shift to the right, in the direction of products.

Step 2. Using the balanced chemical equation, construct an ICE table similar to **Table 6**.

Table 6 ICE Table for Calculating Equilibrium Concentrations

	$N_2O_4(g)$ $\rightleftharpoons$	$2\ NO_2(g)$
I	0.500	0.00
C	$-x$	$+2x$
E	$0.500 - x$	$2x$

Step 3. Substitute the expressions from the ICE table into the equilibrium constant equation. The equilibrium law for this reaction is

$$\frac{[NO_2(g)]^2}{[N_2O_4(g)]} = 4.50$$

$$\frac{(2x)^2}{(0.500 - x)} = 4.50$$

This equation cannot be solved by taking the square root of both sides. Apply the hundred rule to see if x can be assumed to be negligible.

$$\frac{[N_2O_4(g)]_{\text{initial}}}{K} = \frac{0.500}{4.50}$$

$$\frac{[N_2O_4(g)]_{\text{initial}}}{K} = 0.111$$

Since 0.111 is much less than 100, the assumption that $0.500 + x \approx 0.500$ is not warranted. Therefore, you must solve the equation.

Step 4. Solve the equation.

$$\frac{(2x)^2}{(0.500 - x)} = 4.50$$

$$(2x)^2 = (0.500 - x)4.50$$

$$4x^2 = 2.250 - 4.50x$$

$$4x^2 + 4.50x - 2.250 = 0$$

You can see that this is a quadratic equation of the general form

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

You can get the root of a quadratic equation by using the quadratic formula.

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

$$= \frac{-4.50 \pm \sqrt{(4.50)^2 - 4(4)(-2.250)}}{2(4)}$$

$$= \frac{-4.50 \pm 7.50}{8}$$

$$x = -1.50$$

or

$$x = 0.375$$

The negative root would result in a negative concentration for $NO_2(g)$, so $x = 0.375$ is the only acceptable solution to the quadratic equation. Use this value to calculate the equilibrium concentrations for $NO_2(g)$ and $N_2O_4(g)$ from the expressions in your ICE table.

$$[N_2O_4(g)]_{\text{equilibrium}} = 0.125 \text{ mol/L}$$

$$[NO_2(g)]_{\text{equilibrium}} = 0.750 \text{ mol/L}$$

Step 5. Check your results by calculating K to see if it equals the given value of 4.50.

The calculated value of 4.50 for K is equal to the given value of 4.50.

Statement: The solution is at equilibrium when the concentration of dinitrogen tetroxide is 0.125 mol/L and the concentration of nitrogen dioxide is 0.750 mol/L.

Sample Problem 3: Rejecting an Assumption about the Magnitude of x

Suppose that hydrogen fluoride gas, $HF(g)$, is synthesized by combining 3.000 mol of hydrogen gas, $H_2(g)$, and 6.000 mol of fluorine gas, $F_2(g)$, in a 3.000 L sealed flask. Assume that the equilibrium constant for the synthesis reaction at this temperature is 1.15×10^2. What are the concentrations for each gas at equilibrium?

Given: $V = 3.000$ L; $n_{H_2(g)} = 3.000$ mol; $n_{F_2(g)} = 6.000$ mol;
$K = 1.15 \times 10^2$

Required: $[H_2(g)]_{\text{equilibrium}}$; $[F_2(g)]_{\text{equilibrium}}$; and $[HF(g)]_{\text{equilibrium}}$

Solution:

Step 1. Convert the given amounts to concentrations in mol/L.

$$[H_2(g)]_{\text{initial}} = 1.000 \text{ mol/L}$$

$$[F_2(g)]_{\text{initial}} = 2.000 \text{ mol/L}$$

$$[HF(g)]_{\text{initial}} = 0 \text{ mol/L}$$

Step 2. Calculate Q and compare it to K.

At the start of the reaction Q is 0, which is less than K. The chemical reaction system must shift to the right, toward the products.

Step 3. Use an ICE table to determine the required equilibrium concentrations, similar to **Table 7**.

Table 7 ICE Table for Calculating Equilibrium Concentrations

	$H_2(g)$	+	$F_2(g)$	$\rightleftharpoons$	$2\ HF(g)$
I	1.000		2.000		0
C	$-x$		$-x$		$+2x$
E	$1.000 - x$		$2.000 - x$		$2x$

Step 4. Write the equilibrium constant equation.

$$K = \frac{[HF(g)]^2}{[H_2(g)][F_2(g)]} = 1.15 \times 10^2$$

$$\frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 1.15 \times 10^2$$

Step 5. Apply the hundred rule to see if x can be assumed to be negligible.

$$\frac{[F_2(g)]_{\text{initial}}}{K} = \frac{2.00}{1.15 \times 10^2}$$

$$\frac{[F_2(g)]_{\text{initial}}}{K} = 0.017$$

Since 0.017 is much less than 100, the simplification assumption that $2.00 - x \approx 2.00$ is not warranted.

Therefore, you must solve the equation. Rearrange the equation into the form of a quadratic equation, $ax^2 + bx + c = 0$.

$$\frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 1.15 \times 10^2$$

$$(2x)^2 = (1.15 \times 10^2)(1.000 - x)(2.000 - x)$$

$$4x^2 = (1.15 \times 10^2)(2.000 - 2.000x - 1.000x + x^2)$$

$$4x^2 = 2.30 \times 10^2 - (4.45 \times 10^2)x + (1.15 \times 10^2)x^2$$

$$(1.11 \times 10^2)x^2 - (4.45 \times 10^2)x + 2.30 \times 10^2 = 0$$

Solve the quadratic equation.

$$x = \frac{4.45 \times 10^2 \pm \sqrt{(-4.45 \times 10^2)^2 - 4(1.11 \times 10^2)(2.30 \times 10^2)}}{2(1.11 \times 10^2)}$$

$$x = 2.14 \text{ mol/L or } x = 0.968 \text{ mol/L}$$

Since the value of 2.14 for x would give a negative value for the equilibrium concentration of hydrogen gas ($[H_2(g)] = 1.000 \text{ mol/L} - x$), this value is not valid. The correct value for x therefore is 0.968 mol/L. Substituting this value in the expressions in the ICE table gives the following concentrations:

$$[H_2(g)]_{\text{equilibrium}} = 3.20 \times 10^{-2} \text{ mol/L}$$

$$[F_2(g)]_{\text{equilibrium}} = 1.03 \text{ mol/L}$$

$$[HF(g)]_{\text{equilibrium}} = 1.94 \text{ mol/L}$$

Step 6. Check these concentrations by substituting them into the equilibrium expression.

The calculated value of 1.14×10^2 is in close agreement with the given value for K (1.15×10^2).

Statement: The equilibrium concentrations for this chemical reaction system are 3.20×10^{-2} mol/L for hydrogen, 1.03 mol/L for fluorine, and 1.94 mol/L for hydrogen fluoride.

Practice

1. Cyclopropane gas will spontaneously undergo isomerization to form propene gas. If 2.50 mol of cyclopropane is placed in a sealed 0.500 L container, it will come to equilibrium with its isomer, propene. The value of the equilibrium constant, K, for this chemical system is 5.6. Determine the concentration of each of gas at equilibrium. T/I

   [ans: [cyclopropane] = 0.76 mol/L, [propene] = 4.24 mol/L]

2. If 0.200 mol of hydrogen gas, $H_2(g)$, and 0.200 mol of iodine gas, $I_2(g)$, are placed in a 1.00 L sealed flask, an equilibrium system will be established with hydrogen iodide gas, HI(g). Determine the concentration of all gases at SATP, given that the equilibrium constant, K, is 49.5. T/I

   [ans: $[HI(g)] = 0.311$ mol/L, $[H_2(g)] = 0.044$ mol/L, $[I_2(g)] = 0.044$ mol/L]

3. In a sealed vessel, a chemist allowed the decomposition of hydrogen chloride gas, HCl(g), to hydrogen gas, $H_2(g)$, and chlorine gas, $Cl_2(g)$, until equilibrium was reached. The balanced equation for this chemical reaction system is

   $$2\,HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$$

   If the chemist started the reaction with 0.500 mol of hydrogen chloride gas at 25 °C in a sealed 250.0 mL vessel, what was the concentration of all the gases at equilibrium, given that the equilibrium constant has a value of 3.2×10^{-34} at this temperature? T/I

   [ans: $[HCl(g)] = 2.00$ mol/L; $[H_2(g)] = 3.6 \times 10^{-17}$ mol/L; $[Cl_2(g)] = 3.6 \times 10^{-17}$ mol/L]

7.5 Review

Summary

- The magnitude of the equilibrium constant for a reaction, K, is directly proportional to the extent of that reaction.
- The reaction quotient, Q, is the product of the concentrations of the products, divided by the product of the concentrations of the reactants, for a chemical reaction that is not necessarily at equilibrium.
- Comparing the values of Q and K indicates whether a chemical reaction system is at equilibrium and, if not, the direction it will shift.

Questions

1. A chemist places a mixture of 2.00 mol of hydrogen gas, $H_2(g)$; 1.00 mol of nitrogen gas, $N_2(g)$; and 2.00 mol of ammonia gas, $NH_3(g)$, in a sealed, rigid 1.00 L flask at 750 K.

   The equilibrium constant for this reaction is 1.05×10^{21} at 750 K. T/I C

   (a) Write the balanced chemical equation for the synthesis of ammonia gas.
   (b) Calculate Q from the initial amounts of gases.
   (c) Determine whether the chemical system is at equilibrium. If the system is not at equilibrium, in which direction will the equilibrium shift?

2. The equilibrium constant is 0.0900 at 25 °C for the chemical reaction system represented by

   $$H_2O(g) + Cl_2O(g) \rightleftharpoons 2\ HOCl(g)$$

   For which sets of conditions below is the system at equilibrium? For those that are not at equilibrium, in which direction will the system shift? All flasks are rigid and sealed. T/I

   (a) A 1.0 L flask contains 1.0 mol $HOCl(g)$, 0.10 mol $Cl_2O(g)$, and 0.10 mol $H_2O(g)$.
   (b) A 2.0 L flask contains 0.084 mol $HOCl(g)$, 0.080 mol $Cl_2O(g)$, and 0.98 mol $H_2O(g)$.
   (c) A 3.0 L flask contains 0.25 mol $HOCl(g)$, 0.0010 mol $Cl_2O(g)$, and 0.56 mol $H_2O(g)$.

3. In a sealed, rigid container, nitrogen dioxide gas, $NO_2(g)$, is in equilibrium with dinitrogen tetroxide gas, $N_2O_4(g)$:

   $$2\ NO_2(g) \rightleftharpoons N_2O_4(g) \quad K = 1.15 \text{ at } 55\ °C$$

   Find the equilibrium concentration of gaseous nitrogen dioxide and dinitrogen tetroxide if the initial concentration of nitrogen dioxide gas is 0.850 mol/L. T/I

4. A rigid, sealed 1.00 L flask was filled with 2.00 mol carbon monoxide and 2.00 mol water vapour. After equilibrium was reached, it was found that 1.30 mol of each of carbon dioxide and hydrogen was present. Calculate the value of the equilibrium constant, K, for this reaction, assuming all substances are in the gas phase. T/I

5. A lab technician places 12.0 mol of sulfur trioxide gas, $SO_3(g)$, into a 3.0 L sealed, rigid container. The sulfur trioxide gas dissociates into gaseous sulfur dioxide, $SO_2(g)$, and oxygen, $O_2(g)$, until equilibrium is reached and 3.0 mol of sulfur dioxide is present. Calculate the equilibrium constant, K.

   $$2\ SO_3(g) \rightleftharpoons 2\ SO_2(g) + O_2(g)$$ T/I

6. At a particular temperature, the gases sulfur dioxide, $SO_2(g)$, and nitrogen dioxide, $NO_2(g)$, react in a closed vessel to form the gases sulfur trioxide, $SO_3(g)$ and nitric oxide, $NO(g)$:

   $$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

   If the equilibrium constant, K, is 3.75 and the initial concentration of all four gases was 0.800 mol/L, calculate the equilibrium concentrations of all these gases. T/I

7. The equilibrium constant, K, has a value of 2.4×10^{-3} at a given temperature, for the reaction represented by the balanced equation

   $$2\ H_2O(g) \rightleftharpoons 2\ H_2(g) + O_2(g)$$

   At equilibrium, the concentrations of water vapour and hydrogen gas were 1.1×10^{-1} mol/L and 1.2×10^{-2}, respectively. What was the equilibrium concentration of oxygen gas? T/I

8. The creation of shells by mollusc species is a fascinating process. By using calcium from their food and aqueous environment and some complex equilibrium processes, these animals produce a hard calcium carbonate shell. One important equilibrium reaction in this process is

   $$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

   $$K = 5.6 \times 10^{-11}$$

   If 0.16 mol of HCO_3^- is placed into 1.00 L of solution, what will the equilibrium concentration of CO_3^{2-} be? T/I