SCH4U-C

15

Introduction to Equilibrium

Introduction

So far in this unit, you have learned a number of fundamental concepts about chemical reactions. Chemical reactions occur because reactant particles collide together to become product particles. These collisions have to happen with sufficient energy and with proper orientation. The rate of a reaction is determined by both the number of collisions and the percentage of effective collisions. Different reactions occur at different rates. Even the same reaction can proceed at different rates if concentration, temperature, or surface area is changed, or if a catalyst is used. Some reactions are one-step, turning reactants directly into products, but most reactions are multi-step, requiring two or more steps. The series of steps is called a reaction mechanism.

Another major concept involving reactions is that reactions can proceed in both forward and reverse directions. Reactant particles will collide to form product particles, but the product particles can also collide and return to reactant particles. Eventually, the rate of the forward reaction and rate of the reverse reaction become equal, resulting in no net change in any concentration, reactant, or product. This is known as equilibrium, which is the focus of this lesson and the next one.

Planning Your Study

You may find this time grid helpful in planning when and how you will work through this lesson.

Suggested Timing for This Lesson (Hours)	
Equilibrium in Chemical Reactions	½
Equilibrium Constants	¾
ICE Charts and Equilibrium Concentrations	1½
Key Questions	1

What You Will Learn

After completing this lesson, you will be able to

- describe and explain equilibrium in chemical reactions
- write equilibrium expressions, calculate equilibrium constants (K_{eq}) from equilibrium concentrations, and determine whether a reaction is at equilibrium or not
- calculate equilibrium concentrations from initial concentrations and K_{eq}

Equilibrium in Chemical Reactions

Some reactions proceed until all of the reactants are turned into products. In this case, we would say that the reaction "goes to completion." In Grade 11 Chemistry, it was assumed that in all reactions, one or both of the reactants was totally consumed. Equilibrium reactions, however, do not simply proceed from reactants to products until all of the reactants are used up and only products remain. Equilibrium is reached when the forward rate of reaction (reactants $\rightarrow$ products) equals the reverse rate of reaction (products $\rightarrow$ reactants) and the reaction seems to have stopped. The forward and reverse reactions are combined together using a double-headed arrow:

reactants $\rightleftharpoons$ *products*

Equilibrium does **not** mean that the quantity of reactants equals the quantity of products when the reaction seems to have stopped. Sometimes, the quantities are close to being the same, but in other reactions, the amount of product is much greater than the amount of reactant or the amount of reactant is much greater than the product.

In past chemistry courses, you may have calculated percentage yield. Percentage yield tells you (the chemist) how effective the reaction was in turning reactants into products. If your percentage yield was low, you may have assumed that something had gone wrong when you performed the reaction. However, the reaction you were studying may have reached equilibrium with a greater amount of reactants than products. Even if you performed the reaction carefully again and again, you would always end up with the same low percentage yield. In other words, the low yield was the fault of the reaction, not of you, the chemist.

Industrial chemists use their understanding of equilibrium to maximize the yield of chemical reactions. Maximum yield and maximum rate are not the same. Yield describes how much product is obtained; rate describes how fast the product was created.

At equilibrium, the quantities of reactants and products do not change. When you observe a reaction at equilibrium, it appears that the reaction has stopped. The visible or macroscopic properties remain the same. But if you could see the reaction at the particle level (atoms and molecules are too small to see, even with the most powerful microscope), you would see the same number of reactant particles becoming products as product particles changing into reactants. This is called dynamic equilibrium. The particles do not stop moving or reacting when equilibrium is reached.

Equilibrium usually requires a closed system. No materials can enter or escape from a closed system. If the closed system has some sort of input or output (that is, it becomes an open system), the reaction will no longer be at equilibrium.

A familiar example of equilibrium exists with sealed bottles of carbonated beverages. There is an air space at the top of each bottle between the bottle cap and the level of the liquid drink. At the bottling factory, carbon dioxide is forced into the liquid under high pressure. Since carbonated beverages are mostly water, they can be thought of as carbon dioxide solutions ($CO_{2(aq)}$). Some of the carbon dioxide escapes from the liquid into this space ($CO_{2(g)}$). Equilibrium exists between the carbon dioxide dissolved in the liquid and the carbon dioxide gas in the space.

Support Questions

Be sure to try the Support Questions on your own before looking at the suggested answers provided.

27. Answer the following questions based on the carbonated beverage example just described.

a) Write an equation that describes dissolved carbon dioxide escaping from the liquid.

b) Write an equation to describe carbon dioxide from the space, above the liquid, dissolving into the liquid.

c) Combine the two equations together, using a double-headed arrow.

d) As you observe the sealed bottle, what would indicate that the system was at equilibrium?

e) What would you observe if you could actually see the carbon dioxide molecules?

f) Describe what happens to the carbon dioxide molecules (gaseous and dissolved) when the bottle is opened and then resealed.

g) Why do carbonated beverages go flatter and flatter each time they are opened?

Suggested answer

28. Why is the double-headed arrow a good symbol to use to show an equilibrium reaction?

Suggested answer

Equilibrium Constants

At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction. This is symbolized by:

reactants $\rightleftharpoons$ *products*

The quantities of reactants and products do not change, once a reaction has reached equilibrium. Concentration is used to measure the quantity of reactants and products in units of mol/L. Square brackets, [ ], are used to represent concentration.

In our study of equilibrium systems, we will restrict our cases to those dealing with homogeneous mixtures (solutions). These solutions could involve two scenarios:

i) Where the reactants and products in the equilibrium system are all gaseous. The system is a homogeneous mixture of gaseous reactants and products existing in a closed container. An example of such a system would be

$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$

The vessel containing this equilibrium would be a closed (sealed) container. Inside the vessel, we would find all three gases, NH_3, H_2, and N_2, in various concentrations.

ii) Where reactants and products exist in aqueous solutions (dissolved in water). An example of such a system would be one involving the ionization of an acid in water.

$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-{}_{(aq)} + H3O^+{}_{(aq)}$

Acetic acid acetate ion hydronium ion

Acid systems such as this will be studied in detail in Unit 5.

We now know that when the forward reaction rate becomes equal to the reverse reaction rate, we have reached a state of dynamic equilibrium. When equilibrium is achieved, the concentration of all chemicals (reactants and products) will remain constant. The term "dynamic" means that the forward and reverse processes continue to occur (at the same rate). The opposite of "dynamic" is "static." If the system were static, then nothing would be occurring.

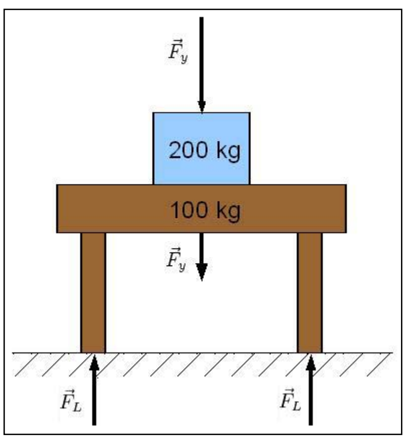

Figure 15.1: Illustration of a static equilibrium

Source: http://commons.wikimedia.org/wiki/File:Equilibrium.JPG

Scientists have determined that at equilibrium, there is a special relationship between the product concentrations and the reactant concentrations. This relationship can be illustrated with the equilibrium involving ammonia.

$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$

A ratio of product concentrations to reactant concentrations is written as follows:

$$\frac{[\text{"products"}]}{[\text{"reactants"}]} = \frac{[NH_{3(g)}]^2}{[H_{2(g)}]^3[N_{2(g)}]}$$ (called the **equilibrium expression**)

Note that:

a) the product concentrations are in the numerator (the top)

b) the reactant concentrations are in the denominator (the bottom)

c) the coefficients from the equation form exponents (similar to the rate law seen earlier)

d) the concentrations are multiplied

In general, if an equilibrium equation reads:

$aA + bB \quad cC + dD$

where A, B, C, and D are all gases or are all dissolved in water(aq), the **equilibrium expression** is written as

$$\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

At a certain temperature, this ratio (the equilibrium expression) will always have a constant value called the equilibrium constant, K_{eq} or just K. This tells us that the equilibrium constant is calculated as

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Example

Write the equilibrium constant expression for each of the following equilibrium systems:

a) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

b) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

c) $2NOBr_{(g)} \rightleftharpoons 2NO_{(g)} + Br_{2(g)}$

Solution

a) $K_{eq} = \dfrac{[HI]^2}{[H_2][I_2]}$

b) $K_{eq} = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

c) $K = \dfrac{[NO]^2[Br_2]}{[NOBr]^2}$

When writing equilibrium expressions, only certain reactants and products are included. Gases (g) and solutions (aq) are included. Solids (s) and pure liquids (l) are not. The reason for this is that concentrations of gases and solutions are variable, while concentrations of solids and pure liquids are not. The occurrence of solids and liquids in the equilibrium system will not be seen until later.

K_{eq} values vary with temperature. When K_{eq} values are listed, the temperature is often specified. You may see the same reaction with different K_{eq} values if the reaction has taken place at different temperatures.

K_{eq} values can be calculated if you know the concentration of all reactants and products when the reaction is at equilibrium. In the example above (which shows the synthesis of ammonia gas from hydrogen gas and nitrogen gas), the concentrations of each of the gases at equilibrium at a specified temperature are as follows:

$[H_2] = 0.400$ mol/L, $[N_2] = 0.200$ mol/L, and $[NH_3] = 0.100$ mol/L

The K_{eq} value is found by substituting the concentrations into the equilibrium expression and solving for K_{eq}. When the substitution is completed, the numbers are surrounded by round brackets ( ). The square brackets surround the concentration. You recorded the actual concentration, so you no longer need to use the square brackets. K_{eq} values do not have units.

$$K_{eq} = \frac{[NH_3]^2}{[H_2]^3[N_2]} = \frac{(0.100\text{ mol/L})^2}{(0.400\text{ mol/L})^3(0.200\text{ mol/L})} = 0.78125 = 0.781$$ (rounded to the correct number of significant figures)

What Does the Equilibrium Expression Tell You?

The value of the equilibrium expression can tell you if a chemical reaction (system) is at equilibrium or not. Reference tables are available that list the value of the equilibrium expression for reactions at equilibrium. These would be equilibrium constants, *K*, for various chemical reactions at a given temperature.

Example

For the following chemical reaction, at 485°C, the *K* value is 49.8.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

This means that if this system is at equilibrium, then the equilibrium expression will produce the value 49.8. That is, at equilibrium

$$\frac{[HI]^2}{[H_2][I_2]} = 49.8$$

At a certain time after the reaction began, the concentrations of the three chemicals were determined to be $[HI] = 2.98$ M, $[H_2] = 0.45$ M, and $[I_2] = 0.45$ M. Use these concentrations and the equilibrium expression to decide if the system had come to equilibrium when those concentrations were measured.

Solution

To do this, we will evaluate the expression to see if it has reached the value of 49.8. If it has, then the system has reached equilibrium. In the process of doing this, we will call the expression *Q* (some "Quotient"). We are not finding *K*. That is known to be 49.8. We are trying to find the value of the quotient (the expression) to determine if has reached the value of 49.8 yet.

$$Q = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2.98)^2}{(0.450)(0.450)} = 43.9$$

The quotient, *Q*, currently has a value below the *K* value of 49.8. The ratio of products/reactants is too low at this time, indicating that the system has not yet come to equilibrium.

Example

For the following situations involving the ammonia system, determine if the system is at equilibrium.

(1) $[H_2]$ = 0.200 mol/L, $[N_2]$ = 0.300 mol/L, and $[NH_3]$ = 0.500 mol/L

(2) $[H_2]$ = 0.800 mol/L, $[N_2]$ = 0.800 mol/L, and $[NH_3]$ = 0.100 mol/L

(3) $[H_2]$ = 0.300 mol/L, $[N_2]$ = 0.300 mol/L, and $[NH_3]$ = 0.07955 mol/L

Solution

(1) $$Q = \frac{[\mathrm{NH_3}]^2}{[\mathrm{H_2}]^3[\mathrm{N_2}]} = \frac{(0.500\ \mathrm{mol/L})^2}{(0.200\ \mathrm{mol/L})^3(0.300\ \mathrm{mol/L})} = 104.1667 = 104$$

(2) $$Q = \frac{[\mathrm{NH_3}]^2}{[\mathrm{H_2}]^3[\mathrm{N_2}]} = \frac{(0.100\ \mathrm{mol/L})^2}{(0.800\ \mathrm{mol/L})^3(0.800\ \mathrm{mol/L})} = 0.0244140 = 0.0244$$

(3) $$Q = \frac{[\mathrm{NH_3}]^2}{[\mathrm{H_2}]^3[\mathrm{N_2}]} = \frac{(0.07955\ \mathrm{mol/L})^2}{(0.300\ \mathrm{mol/L})^3(0.300\ \mathrm{mol/L})} = 0.781259 = 0.781$$

The first two sets of concentrations show that the reactions are not at equilibrium. The *Q* value that is calculated using both sets of concentrations does not equal 0.781, the actual K_{eq} value. However, the third set of concentrations does show that the reaction has reached equilibrium because the calculated *Q* value is equal to the accepted K_{eq} value.

In the first set of concentrations, the *Q* is higher than the accepted K_{eq} value. This means that the concentration of the product is too high, and the concentrations of the reactants are too low. In order to reach equilibrium, some of the product will have to become reactants.

In the second set of concentrations, the *Q* is lower than the accepted K_{eq} value. This means that the concentrations of the reactants are too high, and the concentration of the product is too low. Some of the reactants will have to become product in order to reach equilibrium.

What Does the Magnitude of *K* Indicate About the Equilibrium System?

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]}$$

The value of K is a ratio or comparison. It compares the "amount" of products to the "amount" of reactants in the system at equilibrium.

Example

Suppose that K_{eq} =10 for some system. Let's write this K value as a more obvious ratio:

$$K = \frac{(10)}{(1)}$$

This is saying that the ratio $\frac{[\text{products}]}{[\text{reactants}]} = \frac{(10)}{(1)}$

Looking at that ratio, which would you say is in greater abundance at equilibrium, the products or the reactants? This ratio is showing that, at equilibrium, the "amount" of products is 10 times greater than the "amount" of reactants.

Example

What if $K_{eq} = 1 \times 10^8$ (very large value) for a general system $A + B \rightleftharpoons C + D$?

The ratio of products/reactants now is $(1 \times 10^8)/1$. At equilibrium, this system will have mostly products (C and D) and very little reactants (A and B). When this system has reached equilibrium, most of the reactants have been consumed.

Example

What if a system, $X + Y \rightleftharpoons M + N$, has a $K = 1 \times 10^{-10}$ (a very small K value)? How do the products (M and N) compare to the reactants (X and Y) at equilibrium?

Here the ratio $\frac{[\text{products}]}{[\text{reactants}]} = \frac{1\times10^{-10}}{1}$ = (a very small value)/(comparatively large value)

This system, with a very small K value, will have very small “amounts” of products compared to relatively large “amounts” of reactants when the system comes to equilibrium. When this reaction occurs and the system moves to an equilibrium condition, very little of the reactant is consumed.

Summary

K_{eq} **very small:** [product]/[reactant] ratio is very small; at equilibrium, there will be very little of the product present.

K_{eq} **near 1 in value:** at equilibrium, this system would have comparatively similar amounts of product and reactant present.

K_{eq} **very large:** at equilibrium, the system will have mostly products in the container, and comparatively very little of the reactants. The system may have almost reached completion.

Support Questions

29. Write equilibrium expressions for the following reactions. Keep in mind that only gases and solutions appear in equilibrium expressions.

a) $O_{2(g)} + 2SO_{2(g)} \rightleftharpoons 2SO_{3(g)}$

b) $2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)}$

c) $CO_{2(g)} + 4H_{2(g)} \rightleftharpoons CH_{4(g)} + 2H_2O_{(g)}$

d) $2NaHCO_{3(s)} \rightleftharpoons Na_2CO_{3(s)} + H_2O_{(l)} + CO_{2(g)}$ Suggested answer

30. The equilibrium constant for $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ is 12.7. For each of the following sets of concentrations, determine whether or not the system is at equilibrium, and if not, describe what has to happen to have the reaction reach equilibrium.

a) $[N_2O_{4(g)}] = 0.125$ mol/L $[NO_{2(g)}] = 0.895$ mol/L

b) $[N_2O_{4(g)}] = 0.345$ mol/L $[NO_{2(g)}] = 2.09$ mol/L

c) $[N_2O_{4(g)}] = 0.0675$ mol/L $[NO_{2(g)}] = 1.27$ mol/L Suggested answer

31. Given a general system, $A+B \rightleftharpoons M+N$. If the $K = 4.5 \times 10^{-9}$, describe, in general terms, how the products and reactants would compare in concentrations. Suggested answer

ICE Charts and Equilibrium Concentrations

In the previous section of the lesson, you were asked to calculate K_{eq} values and determine if a reaction had reached equilibrium or not. But what if you didn't know the equilibrium concentrations? What if you only knew the concentrations at the start of the reaction and the K_{eq} value? Could you calculate the concentrations at equilibrium?

You are going to look at four different examples of how you calculate the concentrations at equilibrium. Each one has a slightly different focus, but, in each case, you will be following the same strategy, which involves making an ICE chart. ICE stands for **i**nitial, **c**hange, and **e**quilibrium concentrations. The following steps should be followed when you are asked to find the concentrations of reactants or products of equilibrium reactions.

The initial–change–equilibrium (ICE) strategy

1. Write the equilibrium expression for the reaction given in the question.
2. Record the initial concentrations using an ICE chart.
3. Use the balanced equation and the ICE chart to determine the changes in concentrations of reactants and products.
4. Substitute the equilibrium concentrations into the equilibrium expression.
5. Solve for unknown values.

Take your time working through each of the following examples. The given information or "set-up" is essential for solving equilibrium problems. Also, go through each of the example's calculations carefully. The ICE strategy that you are learning in this lesson will be used in the next five lessons.

Example

Take a look at the first example.

Nitrous oxide is formed by reacting nitrogen gas with oxygen gas, according to the following balanced equation:

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

If 0.50 moles of each reactant gas is placed in a 2.0 L container at the start of the reaction, determine both the concentration and the number of moles of each gas when the reaction is at equilibrium. The K_{eq} for this reaction is 0.0025.

Solution

Follow the steps of the five-step ICE strategy.

Step 1: Start by writing the equilibrium expression.

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

Step 2: Next, set up the ICE chart with the information from the question. You may need to make calculations before you fill in the chart.

In order to find concentration, use the formula:

$$c = \frac{n}{V} = \frac{0.50 \text{ mol}}{2.0 \text{ L}} = 0.25 \text{ mol/L}$$

ICE	$[N_2]$ in mol/L	$[O_2]$ in mol/L	[NO] in mol/L
Initial	0.25	0.25	0
Change			
Equilibrium			

Step 3: Since there is no product present initially, product must be formed. The concentration of the reactants will decrease and the concentration of the product will increase. According to the balanced equation for each mole of N_2 reacted and for each mole of O_2 reacted, two moles of NO are produced. The product will go up by twice the amount that each reactant goes down. You don't know how much this is, so you use "$-x$" to represent the decrease in the reactants and "$+2x$" to represent the increase in the products.

It cannot be emphasized enough that the "Change" line in the ICE table is directly related to the mole ratios in the balanced chemical equation. The coefficients in the balanced equation show that the reacting mole ratio of N_2:NO is 1:2. Therefore, comparing the "Changes" in these two chemicals, we would write X:2X. The change in N_2 is shown as –X since it is decreasing.

To get the equilibrium concentrations, combine the initial concentration and the change in concentration.

ICE	$[N_2]$ in mol/L	$[O_2]$ in mol/L	[NO] in mol/L
Initial	0.25	0.25	0
Change	$-x$	$-x$	$+2x$
Equilibrium	$0.25 - x$	$0.25 - x$	$2x$

Step 4: Now substitute the equilibrium concentrations into the equilibrium expression. Since K_{eq} has no units, units can be omitted at this step. However, they must be included in your final answer, whether you are asked to find the concentration or the number of moles.

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

$$0.0025 = \frac{(2x)^2}{(0.25 - x)(0.25 - x)}$$

Step 5: Solve for x and calculate the concentration and the number of moles of each gas at equilibrium.

$$0.0025 = \frac{(2x)^2}{(0.25 - x)(0.25 - x)}$$

$$0.0025 = \frac{(2x)^2}{(0.25 - x)^2}$$

The algebra required to solve this may look complex, but if you notice that the right side of this equation is a perfect square, then you would realize that this can be simplified by taking the square root of both sides of the equation.

$$\sqrt{0.0025} = \sqrt{\frac{(2x)^2}{(0.25 - x)^2}}$$

Take the square root of both sides. This eliminates the squared terms and makes the remaining calculations much easier.

$$0.05 = \frac{2x}{0.25 - x}$$

$$0.05(0.25 - x) = 2x$$

$$0.0125 - 0.05x = 2x$$

$$0.0125 = 2.05x$$

$$x = \frac{0.0125}{2.05} = 0.0060975 = 0.0061$$

Now that you've solved for x, you can calculate the equilibrium concentrations of all three gases:

$[N_2] = [O_2] = 0.25 – x = 0.25 – 0.0061 = 0.24$ mol/L

$[NO] = 2x = 2(0.0061) = 0.012$ mol/L

To solve for the number of moles, use:

$n = c \times V$

For N_2 and O_2, find the number of moles as follows:

$n = 0.24$ mol/L $\times$ 2.0 L = 0.48 mol

and for NO, find the number of moles as follows:

$n = 0.012$ mol/L $\times$ 2.0 L = 0.024 mol

Example

Next, take a look at the second example.

Hydrogen gas and chlorine gas react together to form hydrogen chloride gas, according to this balanced equation:

$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$ $\qquad K_{eq} = 2.15$

If 1.00 mol of hydrogen chloride is placed in a 750. mL container, determine both the concentration and the number of moles of each gas, when the reaction is at equilibrium.

Solution

Step 1: $K_{eq} = \dfrac{[HCl]^2}{[H_2][Cl_2]}$

Steps 2 and 3: First, calculate the concentration of the known amount, in this case, HCl. There is 1.00 mole in 750. mL, so

$$c = \frac{n}{V} = \frac{1.00\text{ mol}}{0.750\text{ L}} = 1.33\text{ mol/L}$$

Initially there are no reactants, only product. Some of the product has to change into reactants. One mole of each reactant forms when two moles of product are reacted, so each reactant increases by x, to $0 + x$, and the product decreases by $2x$, to give an equilibrium concentration of $1.33 - 2x$.

This information comes from the coefficients in the balanced equation. The equilibrium can be reached from either the reactant or product side. This system of change begins with only the product, HCl, being present in the container. In this situation, the reverse reaction begins the process of change and no forward reaction occurs, initially. Because we begin this with only product materials (right-side materials), we say that the system "comes to equilibrium from the right."

ICE	$[H_2]$ in mol/L	$[Cl_2]$ in mol/L	[HCl] in mol/L
Initial	0	0	1.33
Change	$+ x$	$+ x$	$- 2x$
Equilibrium	x	x	$1.33 - 2x$

Steps 4 and 5:

$$2.15 = \frac{(1.33 - 2x)^2}{(x)(x)}$$

$$2.15 = \frac{(1.33 - 2x)^2}{(x)^2}$$

$$\sqrt{2.15} = \sqrt{\frac{(1.33 - 2x)^2}{(x)^2}}$$

$$1.47 = \frac{(1.33 - 2x)}{(x)}$$

$$1.47x = 1.33 - 2x$$

$$3.47x = 1.33$$

$$x = \frac{1.33}{3.47} = 0.383$$

Now that you've solved for x, you can calculate the equilibrium concentrations of all three gases:

$[H_2] = [Cl_2] = x = 0.383$ mol/L

$[HCl] = 1.33 - 2x = 1.33 - 2(0.383) = 0.564$ mol/L

You can check these answers by substituting them into the equilibrium expression from Step 1 and completing the calculation. You will see that the result is close to the given K_{eq} of 2.15. Any very small difference would be attributed to rounding errors.

To solve for number of moles, use:

$n = c \times V$

For H_2 and Cl_2, find the number of moles as follows:

$n = 0.383$ mol/L $\times$ 0.750 L = 0.287 mol

and for HCl, find the number of moles as follows:

$n = 0.564$ mol/L $\times$ 0.750 L = 0.423 mol

Example

Now, take a look at the third example. In this example, you will learn about some more complicated mathematics that can be used to solve equilibrium problems, as well as a shortcut that you can often use.

Nitrogen dioxide decomposes into nitrogen gas and oxygen gas, according to this balanced equation:

$2NO_{2(g)} \rightleftharpoons N_{2(g)} + 2O_{2(g)}$ $\qquad K_{eq} = 3.5 \times 10^{-5}$

If 0.150 mol of NO_2 is initially placed in a 500. mL container, determine the concentration of each gas when the reaction is at equilibrium. Note that the K value here is considered small.

Recall in the discussion about magnitude of K that this small value implied that, at equilibrium, we should expect to have small amounts of product.

Solution

Step 1: $K_{eq} = \dfrac{[N_2][O_2]^2}{[NO_2]^2}$

Steps 2 and 3: First, calculate the concentration of the known amount and enter it in the table.

$$c = \frac{n}{V} = \frac{0.150 \text{ mol}}{0.500 \text{ L}} = 0.300 \text{ mol/L}$$

Second, use the stoichiometric coefficients from the balanced equation to determine the change. Here, NO_2 decreases by $2x$, N_2 increases by x, and O_2 increases by $2x$.

ICE	$[NO_2]$ in mol/L	$[N_2]$ in mol/L	$[O_2]$ in mol /L
Initial	0.300	0	0
Change	$-2x$	$+x$	$+2x$
Equilibrium	$0.300 - 2x$	x	$2x$
Revised equilibrium	0.300	x	$2x$

Again, think about the magnitude of K. Our product concentrations, x and $2x$, should be very small numbers.

Steps 4 and 5:

$$3.5 \times 10^{-5} = \frac{(x)(2x)^2}{(0.300 - 2x)^2}$$

There is no perfect square in this example. You will be left with "x^2" terms, which means that, in order to solve for x, you would have to use the quadratic formula:

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

This calculation can be complicated, though it is not all that difficult as long as you keep your work tidy and your variables straight. An example is given later on. However, in this particular example, there is a way to avoid using the quadratic equation. If you recall, a small K_{eq} value means that very few reactants have become products. This means that the value of x in the ICE chart is very small. In fact, it is so small that when $2x$ is subtracted from 0.300 mol/L, the answer with the correct number of significant figures is still 0.300 mol/L.

In other words, $(0.300 - 2x)$ can be assumed to have a value of 0.300. When K is small in value, this kind of assumption can often be made, making the algebra simpler.

Checking the Assumption

Now that the algebraic solution has been derived for x (and $2x$), the assumption should be checked to see if it was valid. We had assumed that $2x$ was very small compare to 0.300. The value of $2x$ is 1.84×10^{-2}. We must see if it truly is much smaller than 0.300. Generally, if it is approximately 5% of 0.300 or less, we will accept the assumption. This is because the assumption actually creates an algebraic error compared to accurately solving using the quadratic formula. That 5% value is the error created by the assumption. Determining the percentage in our case then:

$$\frac{1.84\times10^{-2}}{0.300} \times 100\% = 6.13\%$$

This is borderline to being an acceptable error since it is slightly above the 5% rule of thumb. However, as a demonstration of the concept, we will accept our answer. If the error had been unacceptably high, then we would have had to go back and complete the algebra using the quadratic formula.

The 100 Rule

Is there a quick way of knowing that the simplifying assumption will be valid, avoiding the quadratic formula? One way to do this is to use what is termed "the 100 rule." Compare the initial concentration, in this case 0.300, to the K value. If the result is greater than 100, then the assumption will be acceptable. The calculation in this case would be

$$\frac{0.300}{3.5\times10^{-5}} = 8571$$ This is greater than 100, so the simplifying assumption is acceptable.

$$3.5\times10^{-5} = \frac{(x)(2x)^2}{(0.300)^2}$$ Substitution of the revised equilibrium concentrations

$$3.5\times10^{-5} = \frac{(x)4x^2}{(0.0900)}$$

$$3.5\times10^{-5} = \frac{4x^3}{(0.0900)}$$ Only the x is cubed, not the 4, in this case.

$$\frac{3.5\times10^{-5}(0.0900)}{4} = x^3$$

$$x^3 = 7.88\times10^{-7}$$

$$x = \sqrt[3]{7.88\times10^{-7}}$$

$$x = 9.2\times10^{-3}$$

The concentrations of all of the gases at equilibrium are:

$[NO_2] = 0.300$ mol/L

$[N_2] = x = 9.2 \times 10^{-3}$ mol/L

$[O_2] = 2x = 2 \times 9.2 \times 10^{-3} = 1.8 \times 10^{-2}$ mol/L

In other words, almost all of this reaction stays as reactants in these conditions! This is expected since the *K* value was reasonably small.

Example

Finally, take a look at the fourth example.

SO_2Cl_2 decomposes into sulfur dioxide gas and chlorine gas, according to the following balanced chemical equation:

$SO_2Cl_{2(g)} \rightleftharpoons SO_{2(g)} + Cl_{2(g)}$ $\qquad K_{eq} = 0.0410$

In this example, 0.0370 mol of $SO_2Cl_{2(g)}$ is placed in a 2.00 L container and allowed to reach equilibrium. What are the concentrations of all three gases at equilibrium?

Solution

Step 1:

$$K_{eq} = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]}$$

Steps 2 and 3:

$$c = \frac{n}{V} = \frac{0.0370 \text{ mol}}{2.00 \text{ L}} = 0.0185 \text{ mol/L}$$

ICE	$[SO_2Cl_2]$ in mol/L	$[SO_2]$ in mol/L	$[Cl_2]$ in mol/L
Initial	0.0185	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.0185 - x$	x	x

$$\frac{[initial]}{K_{eq}} = \frac{0.0185}{0.0410} = 0.451 \qquad 0.451 < 100$$

You cannot discount the "*x*" term in this situation. It must be included in the calculation. As a result, you will have to use the quadratic equation, when you solve for *x*. This result should be predicted, without calculation for the 100 rule, since the *K* value for this system is not small. We should expect that concentration of products formed at equilibrium, *x*, should be significant in size.

Steps 4 and 5:

$$0.0410 = \frac{(x)(x)}{(0.0185 - x)}$$

$$0.0410 = \frac{(x)^2}{(0.0185 - x)}$$

This is a second-degree equation that must be solved using the quadratic formula. The equation must be rearranged.

$$0.0410(0.0185 - x) = x^2$$

$$0.0007585 - 0.0410x = x^2$$

$$x^2 + 0.0410x - 0.0007585 = 0$$

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

$$a = 1$$

$$b = 0.0410$$

$$c = -0.007585$$

Substitute the values of a, b, and c into the quadratic formula.

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

$$x = \frac{-0.0410 \pm \sqrt{0.0410^2 - 4(1)(-0.0007585)}}{2(1)}$$

$$x = \frac{-0.0410 \pm \sqrt{0.004715}}{2}$$

$$x = \frac{-0.0410 \pm 0.0687}{2}$$

$$x = \frac{-0.0410 - 0.0687}{2} = \frac{-0.1097}{2} = -0.0549$$

$$\textbf{or } x = \frac{-0.0410 + 0.0687}{2} = \frac{0.0277}{2} = 0.0139$$

The value of x must be positive, so the first answer is discarded. Using the negative value for x would result in a negative concentration, which is not possible. Therefore, the answer you must use is $x = 0.0139$.

At equilibrium, the concentrations of each of the gases are:

$[SO_2Cl_2] = 0.0185 - x = 0.0185 - 0.0139 = 0.00460$ mol/L

$[SO_2] = [Cl_2] = x = 0.0139$ mol/L

Note that the value of x is significant in comparison to the initial concentration of reactant (0.0185). Because K was NOT small, a significant portion of that reactant was converted to product, in coming to equilibrium.

You will practise this problem-solving strategy in the Support Questions that follow.

- The first strategy to use is to see if you can solve for a squared variable, such as x^2, by taking the square root of both sides.
- If that will not work, see if you can use the 100 rule. If neither of these work, then use the quadratic formula.

If you cannot use the square root to eliminate the "x^2" terms, use the 100 rule to see if you can simplify the calculations and avoid using the quadratic formula. You will have to use the quadratic formula in one of the Support Questions, and may have to use it in one of the Key Questions at the end of this lesson as well, but you will not have to use it in the Final Test.

Support Questions

32. Solve the following problems. Your solutions should be in the proper format, and your final answers should use the correct units and the correct number of significant figures. As you work through these Support Questions, practise the ICE strategy. Reminder: When the equilibrium constant is small, the 100 rule will confirm that a simplifying assumption can be made that avoids the use of the quadratic formula. Scan the four problems below for the *K* value and note where the 100 rule will probably work.

a) In an experiment, 0.35 mol of $H_{2(g)}$ and 0.35 mol of $I_{2(g)}$ are added to a 5.0 L reaction container in order to synthesize hydrogen iodide gas. The balanced equation for this reaction is:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

The K_{eq} value for this reaction is 7.8. Calculate the concentration and the number of moles of all gases in the system at equilibrium.

Suggested answer

b) In another experiment, 0.500 mol of $SO_{3(g)}$ was introduced to a 750 mL container and allowed to reach equilibrium according to the reaction:

$$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$$

If the K_{eq} value for this reaction is 4.5×10^{-8}, calculate the concentrations of all gases in the system at equilibrium.

Suggested answer

c) Consider the equilibrium:

$$2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)} \qquad K_{eq} = 2.63 \times 10^{-9}$$

If 2.50 mol of ammonia is placed in a 2.00 L container, calculate the equilibrium concentrations of all gases.

Suggested answer

d) In another experiment, 0.35 mol of $H_{2(g)}$ and 0.25 mol of $I_{2(g)}$ are added to a 2.0 L reaction container. Use the same balanced equation as you used in part (a). The K_{eq} value for this reaction is 7.8. Calculate the concentration of all gases at equilibrium.

Suggested answer

Key Questions

Now work on your Key Questions in the online submission tool. You may continue to work at this task over several sessions, but be sure to save your work each time. When you have answered all the unit's Key Questions, submit your work to the ILC.

53. Solve the following problems. Your solutions should be in the proper format, and your final answers should use the correct units and the correct number of significant figures. Use the following ICE strategy. The marking scheme is based on this strategy.

The initial–change–equilibrium (ICE) strategy

1. Write the equilibrium expression for the reaction given in the question.
2. Record the initial concentrations using an ICE chart. ICE stands for initial, change, and equilibrium concentrations.
3. Use the balanced equation and the ICE chart to determine the changes in concentrations of reactants and products.
4. Substitute the equilibrium concentrations into the equilibrium expression.
5. Solve for unknown values.

a) Nitrosyl chloride, $NOCl_{(g)}$, decomposes to form nitrogen monoxide gas and chlorine gas, according to the following equation:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

At a certain temperature, the equilibrium constant is 1.60×10^{-6}. Calculate the equilibrium concentrations of all gases if 0.800 moles of $NOCl_{(g)}$ are placed in a 2.00 L container. **(10 marks)**

b) Hydrogen bromide is formed by a reaction between hydrogen gas and bromine vapour, according to the following equation:

$$H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)} \qquad K_{eq} = 3.5$$

Calculate the equilibrium concentrations of all gases if 0.40 mol of $H_{2(g)}$ and 0.60 mol of $Br_{2(g)}$ are placed in a 4.0 L container. **(14 marks)**

Now go on to Lesson 16. Send your answers to the Key Questions to the ILC when you have completed Unit 4 (Lessons 13 to 16).