

Faculty of Science

**Unit 3:
Equilibrium**

CHEM 1523
Principles of Chemistry

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Unit 3: Equilibrium

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Unit 3: Equilibrium

Overview

In 1811, Napoleon led his military expeditionary force into North Africa. The chemist Bertholet, whom Napoleon had brought along as scientific advisor, noticed that the composition of the crystallized salts in the partly dried salt lakes of the Egyptian desert seemed to vary in a curious way—the amount of one kind of crystalline salt present appeared to depend on the concentration of another salt in the remaining solution. Bertholet's attempts to explain this relationship were the beginning of the scientific study of chemical equilibrium.

Nearly one hundred years passed before the development of thermodynamics led to a real understanding of equilibrium. In this unit, you will learn how to determine the *extent* of change that will have occurred when no further change is possible. This is essentially what **chemical equilibrium** is all about.

The relative quantities of reactants and products present at equilibrium define the equilibrium state of a reaction. You will learn in this unit how to describe this **equilibrium state**. Equally important, you will learn how this equilibrium state can be altered by adding or removing substances, or by changing the temperature or pressure. You will see that a chemical reaction is as much characterized by its equilibrium properties as by the identities of the products and reactants.

Since chemical equilibria involve numeric relationships between concentrations or pressures, you will encounter a lot of mathematics in this unit. In many cases, you will have to put your questions and statements in the language of algebra, such as “let x be the concentration of...” One of the aims of this unit is to get you into the habit of thinking in this way. A lot of examples of equilibrium calculations are provided, so you will have plenty of guidance. Remember that mathematics by itself cannot work magic—you are applying it as a *tool* to help you organize data and draw conclusions about the real world. It is important to keep the chemistry in mind along with the mathematics, and to make sure you understand the chemical meaning of any unknown you calculate.

The actual mechanics of the algebraic manipulations required, including the solution of second-degree (quadratic) equations, are fairly straightforward. Even if you are quite rusty in this area, the examples should get you to the point where you can practise on your own. In this unit, more than in any other, such practice is quite important, since much of the remainder of this course will be concerned with equilibrium in one form or another.

In chemistry, the “systems” considered are chemical reactions. In such systems, the total amounts of the various elements present must, of course, be constant. But the way in which they are distributed amongst the reactants and products will vary with the extent of the reaction. When a chemical reaction reaches equilibrium, there will be a definite relation between the relative amounts of products and reactants present. This fact is of great importance to you as a chemist, because it allows you to treat equilibrium in terms of chemically meaningful quantities, such as concentrations of substances in solution or partial pressure of gases. This unit deals mainly with this aspect of equilibrium.

When a reaction is at equilibrium, the quantities of the various substances present will not change. When the reaction is *not* at equilibrium (as, for example, when reactants alone are present), it will tend to approach equilibrium and can only reach it as fast as the mechanics of the process allow; observed time scales range from a millionth of a second to hundreds of years.

You probably think of a chemical reaction as going from left to right, with reactants being converted into products until the equilibrium state is attained. One important feature missing from this *macroscopic* view of a reaction is the **dynamics** of the process. If you could obtain a microscopic view of a reaction, you would always see *two* processes taking place: reactants being converted into **products**, and products being converted back into **reactants**. It is the balance between these two processes that changes between the time the reaction starts and the time the equilibrium state is reached. When these two rates are identical, there will be no net change in concentrations of substances. The reaction will be in equilibrium. This amounts to a *kinetic* definition of equilibrium.

Although the equilibrium state is characterized by no *net* change, this does not mean that no change at all is occurring. The forward and reverse steps are still taking place, and individual atoms are continually being exchanged between reactant molecules and product molecules. However, since these steps are in perfect balance, there is no change in the total quantities of substances. In other words, equilibrium is a *dynamic* process, not a static one.

An appreciation of this last point is essential if you are to understand what happens when something is done to upset a system in equilibrium. Consider first a simple example—a covered container of water. When the water is first placed in the container, molecules of H_2O begin evaporating from the surface of the liquid and enter the vapour space. Gradually, as the concentration of vapour H_2O builds up, more and more of these molecules will hit the surface of the water and re-enter the liquid phase. Eventually, equilibrium is reached at a partial pressure of H_2O given by the vapour pressure of water at a given temperature (review Unit 1 on gases). Now the lid is taken off the container.

This enables vapour H_2O molecules to disperse away from the container and never return. The equilibrium is upset. How does the system respond? The level of the water gradually falls until it is eventually all evaporated. How did this come about? Did the liquid start sending out molecules of vapour faster than before? Certainly not; the liquid has no way of “knowing” that the lid has been removed from the container! What happened is that the liquid just kept on vaporizing at the same rate as formerly (the forward reaction), but with the lid off the reverse reaction (condensation) was essentially “turned off,” allowing a net change (evaporation) to occur.

The same kind of reasoning can be applied to explain many other physical equilibria, such as the lowering of the freezing point of water by addition of a solute. More important, chemical reactions can be treated in essentially the same way. If more reactant is added to a chemical reaction already in equilibrium, the rate of the forward step will increase. This will bring about a net increase in the concentration of the product, which will in turn cause the rate of the reverse process to increase. Eventually the equilibrium state will again be reached, with larger quantities of both reactant and product present than before. Later in this unit, you will see how this behaviour constitutes a simple example of the important concept known as **Le Chatelier’s principle**.

Knowledge of systems at equilibrium is necessary to understand many industrial, biological, geological, and physical processes. Although the title of this unit is “Equilibrium,” it does not mean that all equilibrium processes are confined to this unit. Unit 4, “Acids and Bases,” contains many applications of equilibrium principles. In fact, almost every unit in this course mentions equilibrium in some way. So widespread in chemistry is the concept of equilibrium that it has prompted a bumper sticker that reads:

“Old chemists never die, they just reach equilibrium!”

Learning Outcomes

When you reach the end of Unit 3, you should be able to:

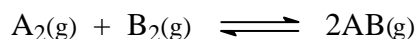
- Write an equilibrium expression from an equilibrium equation.
- Determine if a system is in equilibrium, given the value of the appropriate equilibrium constant and the equilibrium concentrations or pressures.
- Predict, using Le Chatelier’s principle, the direction in which an equilibrium will move if perturbed.
- Calculate the equilibrium constant from equilibrium concentration or pressure data.

- Calculate the concentration or pressure of reactants and products at equilibrium, given the numerical value of the equilibrium constant and data on initial or starting conditions.
- Calculate K_c from K_p and vice versa.
- Calculate K_{sp} from solubility data.
- Calculate the solubility in g/L or in mol/L of sparingly soluble ionic salts from K_{sp} data.
- Use the common ion effect in solubility product calculations.
- Perform calculations, based on K_{sp} data, where sparingly soluble salts precipitate under specified conditions.

The Concept of Equilibrium

Study Section 14.1 of your textbook.

Consider the following schematic reaction:



This equation can be read either forward or backward. If A_2 and B_2 are mixed, some AB will be formed. If, on the other hand, you start with pure AB, some of this will decompose to form A_2 and B_2 . Figure 3.1, below, shows what happens if a mixture of A_2 and B_2 are placed in a container. In order to react, two kinds of molecules must somehow collide. As they react, the concentrations of A_2 and B_2 decrease. At lower concentrations there will be fewer collisions, so the rate of the forward reaction will decrease. This is shown as a slowing of the decrease in the concentration of A_2 or B_2 with time.

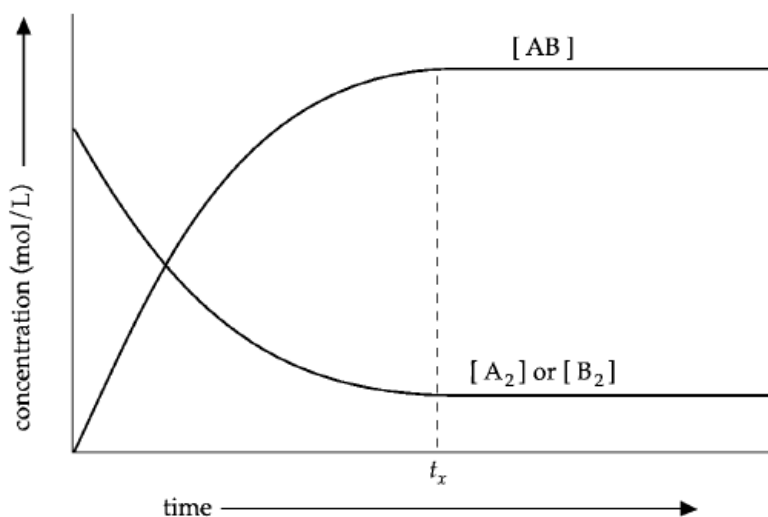
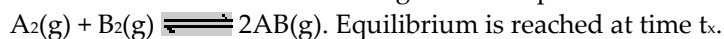


Figure 3.1: Curves show concentration changes for the species in the reaction



At the beginning of the experiment only the forward reaction occurs. There are too few molecules of AB for a backward reaction to be noted. Eventually the concentration of AB increases to the point that the backward reaction is also occurring. The rate of the backward reaction increases as long as the concentration of AB is increasing. The rate of the forward reaction drops until it reaches the point where it is the same as the increasing backward reaction—the reaction has reached equilibrium. In Figure 3.1 you can see that the net concentration of product (AB) and reactants (A_2 or B_2) remains constant at equilibrium.

You should understand two very important consequences of this view of the attainment of equilibrium. First, notice that the equilibrium state is the same, whether started with pure products, or with pure reactants, or with some arbitrary mixture. The rates of the forward and reverse steps must ultimately come into balance at the same equilibrium point.

The second important point to understand is that at equilibrium the system is not static but constantly changing. An external observer, however, is unable to distinguish this, since the ratios of the components of the equilibrium remain the same. Equilibria are dynamic, indicating the changing microscopic nature of the system.

You should know what is meant by the **law of mass action** and how the extent of a chemical reaction relates to the magnitude of the equilibrium constant.

Ways of Expressing Equilibrium Constants

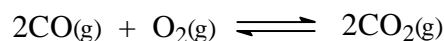
Study Section 14.2. Make sure you understand when to use K_c and when to use K_p .

If the number of moles of gas is the same on both sides of the equation, then K_c and K_p have the same numerical value. If the number of moles of gas differs on each side of the equation, then K_c and K_p are related by

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

where Δn is the change in the number of moles of gas, that is, the number of moles on the right minus the number of moles on the left.

Problem: At 1205°C, K_c for



is 7.09×10^{12} . Calculate K_p at this temperature.

Solution: Substitute in

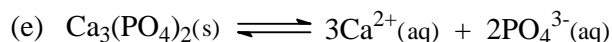
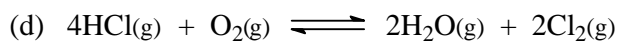
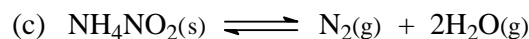
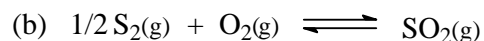
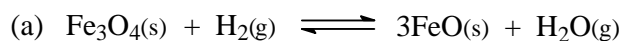
$$K_p = K_c (RT)^{\Delta n}$$

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

$$\begin{aligned} K_p &= 7.09 \times 10^{12} (0.0821 \times 1478)^{-1} \\ &= 5.84 \times 10^{10} \end{aligned}$$

For the rest of this unit and in the practice exercise and Assignment 3, you should designate the equilibrium constant as K_c or K_p , as appropriate. Note the differences between homogeneous and heterogeneous equilibria.

Problem: Write the expressions for the equilibrium constants for each of the following. Use K_p for gaseous reactions and K_c for aqueous reactions.



Solution:

(a) Solids do not appear in the expression for K_p . Only $\text{H}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are included.

$$K_p = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$$

(b) All three components of this equilibrium system are gases, so all appear in the equilibrium expression. The coefficient of $\text{S}_2(\text{g})$, that is, $\frac{1}{2}$, appears as an exponent, meaning the square root of the pressure of $\text{S}_2(\text{g})$.

$$K_p = \frac{P_{\text{SO}_2}}{(P_{\text{S}_2})^{1/2} P_{\text{O}_2}}$$

(c) In this example only $\text{N}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ appear in the equilibrium expression. The pressure or the concentration of a pure liquid or solid is a constant and does not appear. You can think of it as being represented mathematically as "1."

$$K_p = P_{\text{N}_2} \times (P_{\text{H}_2\text{O}})^2$$

(d) All species are found in the equilibrium expression. Note that the coefficients become exponents.

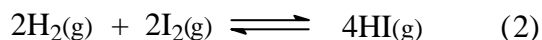
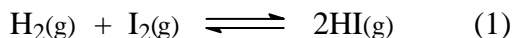
$$K_p = \frac{(P_{\text{H}_2\text{O}})^2 \times (P_{\text{Cl}_2})^2}{(P_{\text{HCl}})^4 \times (P_{\text{O}_2})}$$

(e) The concentrations of the aqueous ionic species are given as moles per litre, signified by the square brackets []. The concentration of the solid does not appear in the equilibrium expression.

$$K_c = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2$$

You should know and be able to use the rules for writing equilibrium constant expressions, given at the end of Section 14.2 in the textbook.

Remember that the equilibrium expression relates to a particular equation. The following two equations represent the same chemical reaction.



There is a difference in their equilibrium expressions. The first would be

$$K_1 = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2}) \times (P_{\text{I}_2})}$$

and the second would be

$$K_2 = \frac{(P_{\text{HI}})^4}{(P_{\text{H}_2})^2 \times (P_{\text{I}_2})^2}$$

These two expressions are *not* the same. In fact, $K_2 = (K_1)^2$. You can check this out by substituting mathematical values for the pressures. Assume that the pressure of HI is 1 atm and the pressure of H₂ and I₂ are each 2 atm at equilibrium at a particular temperature. Then

$$K_1 = \frac{1.0}{2.0 \times 2.0} = \frac{1.0}{4.0} = 0.25$$

and

$$K_2 = \frac{(1.0)^4}{(2.0)^2 \times (2.0)^2} = \frac{1.0}{16} = 0.063$$

and

$$(0.25)^2 \text{ is } 0.063.$$

(You would get $K_1 = K_2$ if the value of K_1 happened to be 1, since $1^2 = 1$.) Overall, if you write the equation as doubled, then the equilibrium expression and the value of the equilibrium constant, K , are squared. If you write the equation tripled, then the equilibrium expression and K are raised to the power 3. This is an important point to remember. *The equilibrium expression and equilibrium constant refer to a particular chemical equation with fixed coefficients* and not to that equation halved, doubled, and so on.

If you have not already done so, turn to your textbook and work through Examples 14.1, 14.2, 14.3, 14.4, 14.5, 14.6, and 14.7, as well as their related practice exercises. The answers to the practice questions are at the very end of the chapter.

Equilibrium and Kinetics

Study Section 14.3. You do not have to memorize the derivation of the relationship between equilibrium constant and reaction rate constants, but you should understand how the law of mass action can be derived for either a single-step or a multi-step reaction.

Using the Equilibrium Constant

Study Section 14.4.

The Reaction Quotient

It is very important to understand the difference between the equilibrium constant, K , and the **reaction quotient**, Q . Very simply, it is this: Q is the value you get when you substitute actual concentrations or pressures into the equilibrium expression. Thus, Q can have any positive value from zero to infinity. (It will be zero when there are no products present, and infinity when only products are present.) Of all these possible values, only one describes the equilibrium state. This one special value of Q is the equilibrium constant, K .

At equilibrium, $Q = K$. Work through Example 14.8 and its practice exercise in your textbook, where you can see how a value for Q enables you to predict in which direction a reaction must move for equilibrium to become established.

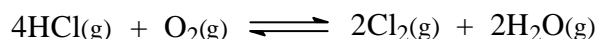
Calculation of the Equilibrium Constant

In these calculations you are given the equilibrium concentrations or pressures and are asked to find K . The first step is always to write the relevant equilibrium equation and then the equilibrium expression from that equation. The question might go into detail about the process. Often such detail is interesting but is not at all necessary to the calculation of K . This is not to say that such data should not be

included in a chemistry course—it is important that you be exposed to such topics—however, you should be able to pick out the relevant parts of a calculation. Example 14.2 in the textbook and its practice exercise involve finding K values. Note that once you have written the equation and the equilibrium expression it is only a matter of substituting the given equilibrium concentration or pressure values.

Now try the following problem.

Problem: HCl gas and O₂ gas were introduced into a container and allowed to come to equilibrium at a set temperature. The equation for the equilibrium is



The initial pressure of the HCl gas was 2.50 atm and of the O₂ gas was 1.65 atm. At equilibrium the partial pressure of the Cl₂ gas was found to be 0.350 atm. Calculate K_P for the equilibrium at this temperature.

Solution: The equilibrium equation is given. The equilibrium expression is

$$K_P = \frac{(P_{\text{Cl}_2})^2 \times (P_{\text{H}_2\text{O}})^2}{(P_{\text{HCl}})^4 \times (P_{\text{O}_2})}$$

The reaction proceeds from left to right.

	HCl	O ₂	Cl ₂	H ₂ O	
Start	2.50	1.65	0	0	(atm)
Equilibrium	2.50 – 4y	1.65 – y	0.350	0.350	(atm)

In this case, you have to calculate the value of y where y is the change in the pressure of O₂. The equation tells you that for every 1 mole of O₂ reacted, 2 moles of Cl₂ and 2 moles of H₂O are formed. Since pressure is proportional to the number of moles of gas, the change in the pressure of O₂ is $0.350 \div 2 = 0.175$ atm. Thus at equilibrium the pressure of HCl will be $2.50 - 4(0.175) = 1.80$ atm. The equilibrium pressure of O₂ will then be $1.65 - 0.175 = 1.48$ atm.

Substituting in the equilibrium expression,

$$K_P = \frac{(0.350)^2 (0.350)^2}{(1.80)^4 (1.48)} = 9.66 \times 10^{-4}$$

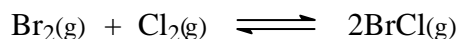
Calculation of Equilibrium Concentrations

These calculations are started in exactly the same manner as the previous type. That is, you write down the appropriate equilibrium equation and equilibrium expression.

Go over Example 14.9 in the textbook and its practice exercise carefully. Note that x is introduced and always is considered to be the amount of a reactant consumed or the amount of product generated.

Example 14.9 and the following problem have the form of a perfect square.

Problem: For the equilibrium



At 127°C , K_p is 7.0. If 0.0400 moles of $\text{Br}_2(\text{g})$ and 0.0400 moles $\text{Cl}_2(\text{g})$ are introduced into a one-litre container at 127°C , what is the partial pressure of $\text{BrCl}(\text{g})$ when equilibrium is established at this temperature?

Solution: The equation has been given. The equilibrium expression is

$$K_p = \frac{(P_{\text{BrCl}})^2}{(P_{\text{Br}_2}) \times (P_{\text{Cl}_2})}$$

Use the ideal gas law to find the starting partial pressure of Br_2 and Cl_2 .

$$P = \frac{nRT}{V} = \frac{0.0400 \text{ mol} \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 400 \text{ K}}{1.00 \text{ L}} = 1.31 \text{ atm}$$

Thus the starting partial pressure of both Br_2 and Cl_2 is 1.31 atm.

	BrCl	Br₂	Cl₂	
Start	–	1.31	1.31	(atm)
Equilibrium	$2x$	$1.31 - x$	$1.31 - x$	(atm)

Here x is the change in the partial pressure of Br_2 (and of Cl_2). Substitute in the equilibrium expression:

$$7.0 = \frac{(2x)^2}{(1.31 - x)(1.31 - x)}$$

Since the right-hand side of this equation is $\frac{(2x)^2}{(1.31 - x)^2}$, a perfect square, we have

$$\sqrt{7.0} = \frac{(2x)}{(1.31 - x)}$$

so $x = 0.75 \text{ atm}$.

Thus, the equilibrium partial pressure of BrCl is $2 \times 0.75 = 1.5 \text{ atm}$.

Check: Using these equilibrium values,

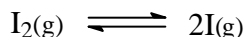
$$K_p = \frac{(1.5)^2}{(1.31 - 0.75)^2} = 7.2$$

Example 14.10 in the textbook requires you to solve a quadratic equation. You should be able to do this using the formula

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

Where a is the coefficient of the x^2 term, b is the coefficient of the x term, and c is the numerical term in the quadratic. It is not too difficult to solve a quadratic equation using this formula (and a calculator). Your graphing calculator can be programmed to perform this calculation very easily. You can often make a simplification and avoid the quadratic altogether. This is possible when the value for K is reasonably small, as shown in the following calculation.

Problem: The equilibrium constant, K_c , for the dissociation of molecular iodine into atomic iodine is 3.80×10^{-5} at 727°C . If 0.200 moles of I_2 is placed in a 1.00 L container and allowed to reach equilibrium, calculate the concentration of iodine atoms at this temperature.



Solution:

$$K_c = \frac{[\text{I}]^2}{[\text{I}_2]}$$

	I_2	I	
Start	0.200	0	(mol L ⁻¹)
Equilibrium	$0.200 - x$	$2x$	(mol L ⁻¹)

Here, for every mole of I_2 that dissociates, 2 moles of I atoms are formed. Substituting into the equilibrium expression,

$$K_c = \frac{(2x)^2}{0.200 - x} = 3.80 \times 10^{-5}$$

You could rearrange this to a quadratic equation. However, in this case, as K_c is reasonably small, the equilibrium lies very much to the left. Very little molecular iodine dissociates at this temperature. So,

$$x \ll 0.200 \quad \text{and} \quad 0.200 - x = 0.200$$

Note: That we are *not* saying that x equals 0, but that compared to 0.200, x is negligible. The calculation now becomes

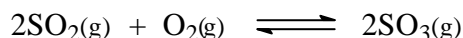
$$\frac{(2x)^2}{0.200} = 3.80 \times 10^{-5}$$

and, on solving, x is found to be 1.38×10^{-3} .

Was it reasonable to use this approximation? You should remember that any time you use approximations such as this, you should check the final answer. If the value of x obtained makes a difference of less than 5%, then the approximation is considered valid. In this case, 5% of 0.200 is 1.00×10^{-2} . Since 1.38×10^{-3} is less than 1.00×10^{-2} , the approximation is valid and thus the concentration of atomic iodine at equilibrium is $2 \times (1.38 \times 10^{-3} \text{ mol L}^{-1}) = 2.76 \times 10^{-3} \text{ mol L}^{-1}$.

You should spend enough time on equilibrium calculations like this (including those at the end of Chapter 14) to ensure that you really understand them. They demonstrate important equilibrium principles and methods of doing equilibrium calculations. The practice exercise in this unit will give you further examples. Very occasionally, an equilibrium problem leads you to a cubic equation. There is no simple formula for solving a cubic equation; you have to be able to make an approximation. A calculation where such an approximation is not valid means that you would have to use the method of successive approximations. This can be done (often chemists will use a computer program for this purpose), but in this course you are not expected to solve a cubic equation. If you do end up with a cubic equation, it will be an equilibrium system where simplification by approximation is valid. The following example illustrates this.

Problem: At a set temperature, the equilibrium constant for the reaction



is 3.00×10^{-2} . SO_2 , originally at a partial pressure of 0.02 atm, and O_2 , originally at partial pressure of 0.010 atm, were allowed to come to equilibrium at this temperature. Calculate the equilibrium partial pressure of SO_3 .

Solution: The equation is given. The equilibrium expression is

$$K_p = \frac{(P_{\text{SO}_3})^2}{(P_{\text{SO}_2})^2 \times (P_{\text{O}_2})}$$

	2SO₂(g)	+	O₂(g)	⇌	2SO₃(g)	
Start	0.020		0.010		–	(atm)
Equilibrium	0.020 – 2x		0.010 – x		2x	(atm)

Here the change in the pressure of O_2 is x . For every one O_2 molecule used, two SO_2 molecules are used and two SO_3 molecules are formed. Thus, at equilibrium the pressures of SO_2 and SO_3 are as shown. Substituting into the equilibrium expression,

$$0.030 = \frac{(2x)^2}{(0.020 - 2x)^2 (0.010 - x)}$$

gives

$$0.030 (0.00040 - 0.080x + 4x^2) (0.010 - x) = 2x^2$$

which, on expansion, has the form of a cubic. But if you go back to the equation

$$0.030 = \frac{(2x)^2}{(0.020 - 2x)^2 (0.010 - x)}$$

and make the assumption that, since the equilibrium lies very much to the left, x is small compared to 0.010 and $2x$ is small compared to 0.020, then

$$0.010 - x = 0.010 \quad \text{and} \quad 0.020 - 2x = 0.020$$

so the equation becomes

$$0.030 = \frac{(2x)^2}{(0.020)^2 (0.010)}$$

This simplifies to

$$x^2 = 3.0 \times 10^{-8}$$

so

$$x = 1.7 \times 10^{-4}.$$

Since $0.010 - 0.00017$ does approximately equal 0.010, the assumption is valid. (By the 5% rule, x should be less than 0.00050, and it is.) So the equilibrium pressures are

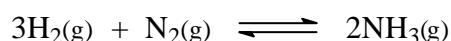
$$P_{SO_3} = 3.4 \times 10^{-4} \text{ atm}, \quad P_{SO_2} = 0.020 \text{ atm}, \quad \text{and} \quad P_{O_2} = 0.010 \text{ atm}$$

Note: To check an answer to a calculation like this, substitute the values you obtained in the equilibrium expression and make sure that you get the given K value.

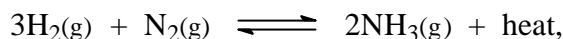
$$\frac{(3.4 \times 10^{-4})^2}{(0.020)^2 \times (0.010)} = 0.030$$

Le Chatelier's Principle

Study Section 14.5 in your textbook. Le Chatelier's principle says that a system in equilibrium will move so as to offset any applied stress. All this means is that the reaction will go more to the left or more to the right, depending on which way uses up the added (or subtracted) component. This component can be one of the chemical species involved, it can be heat if the temperature is increased, or it can be increased pressure. We will use the Haber process for the production of ammonia as an example of changes in a gas phase equilibrium. Note that an increase in either, or both, of $\text{H}_2(\text{g})$ or $\text{N}_2(\text{g})$ causes the equilibrium reaction



to move to the right. The addition of $\text{NH}_3(\text{g})$ moves the equilibrium to the left. These adjustments use up the extra component added. If one of the species is removed, then the equilibrium adjusts to produce more of that substance. If you consider heat as part of the chemical reaction, for example, for the exothermic reaction ($\Delta H^\circ = -92.6 \text{ kJ}$),



then you can use the same logic to decide which way the equilibrium moves with increased or decreased temperature. For a change in pressure, remember that increased pressure favours the side of the reaction that has the smaller number of gas molecules.

Test your grasp of the principle of Le Chatelier by working through the following example.

Problem: The following equilibrium is established.

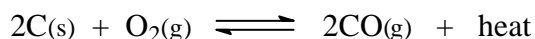


What will be the effect on the equilibrium if:

- CO is added?
- O_2 is removed?
- C is added?
- The container volume is increased?
- The temperature is lowered?

Solution: You have to consider what effect each action would have on the equilibrium and then use Le Chatelier's principle. That is, deduce what the equilibrium would do to minimize this effect.

- If CO is added to the system, the equilibrium moves so as to use up as much of this extra CO as possible. The reaction would go to the left until equilibrium is re-established.
- If O₂ is removed, then the equilibrium moves so as to replace as much of the O₂ as possible until equilibrium is re-established. The only way that the equilibrium can replace O₂ is for some of the CO to decompose. The equilibrium moves to the left.
- Since the concentration of a pure solid, such as C, does not appear in the equilibrium expression, the addition of more carbon does not cause any movement of the equilibrium.
- If the container volume is increased, then the pressure is decreased (review Boyle's law in Unit 1). Decreased pressure favours the side of the equilibrium with the greatest number of moles of gas. In this case, the right-hand side of the equilibrium is favoured and the reaction moves to the right.
- The reaction can be written to include heat as if it is one of the reacting species



This is an exothermic reaction, so heat is written as being given off on the right-hand side. If you lower the temperature, you can consider that heat is being used up. C and O₂ will then combine to form more CO and generate more heat to replace that removed by lowering of the temperature. The net result is that the equilibrium moves to the right.

Now turn to your textbook and work through Examples 14.11, 14.12, and 14.13, as well as their practice exercises. Use the summary at the end of Chapter 14 in your textbook to check your understanding of the equilibrium concepts discussed so far.

Solutions of Sparingly Soluble Ionic Solids

Study Section 16.6 in your textbook. Since you will not cover acid-base concepts until Unit 4, you are not expected to do problems involving pH or anion hydrolysis in this unit.

Solubility equilibria are applicable only to sparingly soluble ionic solids (sometimes referred to as slightly soluble or even insoluble ionic solids). You follow the same series of initial steps as for other equilibrium calculations: write an equation and

then the appropriate equilibrium expression. Since the ionic solid, on the left-hand side of the equation, is always a solid, it does not appear in the equilibrium expression. Therefore, the equilibrium constant for sparingly soluble ionic salts consists of just a numerator. The K_c value is known as the **solubility product** and is written as K_{sp} . Table 16.2 in your textbook gives a number of such K_{sp} values. You are not required to memorize such values; they will be given to you, if necessary.

Note the difference between solubility and solubility product. Solubility is often given as grams per litre. You must convert this to moles per litre when you substitute in the K_{sp} expression.

The K_{sp} expression is always written with the [] notation (meaning moles per litre). There are two other points to remember when you are doing K_{sp} calculations. First, you must have the correct stoichiometry for the ionic equation. This means you have to know what ions are obtained from the ionic solids. If necessary, review Table 2.3 in your textbook and Unit 1 of CHEM 1503. The second point to remember is to substitute exactly as written in the equilibrium expression. As an example, K_{sp} for $\text{CaF}_2(\text{s})$ is written as

$$[\text{Ca}^{2+}][\text{F}^-]^2$$

The solubility of CaF_2 in water is 2.2×10^{-4} mol/L. This means that there will be 2.2×10^{-4} moles of Ca^{2+} in one litre of water. Since you get two F^- ions for every one Ca^{2+} ion, the concentration of F^- is 4.4×10^{-4} mol/L. These are the values that you substitute in the K_{sp} expression.

$$K_{sp} = (2.2 \times 10^{-4})(4.4 \times 10^{-4})^2 = 4.2 \times 10^{-11}$$

Sometimes students are bothered by the fact that not only is the $[\text{F}^-]$ double that of the $[\text{Ca}^{2+}]$ but the $[\text{F}^-]$ is also squared. This seems as if the $[\text{F}^-]$, since it is being both doubled and squared, is somehow accounted for twice. *But the definition of K_{sp} requires this.* Substitute exactly as the K_{sp} expression dictates. This is demonstrated again in the following example.

Problem: The solubility of $\text{Cr}(\text{OH})_3$ is 3.25×10^{-8} mol/L. Calculate the K_{sp} for $\text{Cr}(\text{OH})_3$.

Solution: First give the appropriate equation



and the equilibrium expression

$$K_{sp} = [\text{Cr}^{3+}][\text{OH}^-]^3$$

For every $\text{Cr}(\text{OH})_3$ unit that dissolves there will be one Cr^{3+} ion and three OH^- ions. So in solution there will be 3.25×10^{-8} moles of Cr^{3+} and $3 \times 3.25 \times 10^{-8}$ moles of OH^- in each litre. Substituting into the K_{sp} expression

$$K_{sp} = (3.25 \times 10^{-8})(3 \times 3.25 \times 10^{-8})^3 = 3.01 \times 10^{-29}$$

Work through Example 16.8 and its practice exercise in your textbook.

If you are given the value of K_{sp} , use a similar method to calculate the solubility of the salt. Even if you are asked for the solubility as a number of grams in a certain volume, remember that K_{sp} calculations require you to work out solubilities in moles per litre first. Go over Example 16.9 and its practice exercise in your textbook. Then work through the following example.

Problem: K_{sp} of $\text{Al}(\text{OH})_3$ is given as 1.80×10^{-33} . Calculate the mass of $\text{Al}(\text{OH})_3$ that dissolves in 780 mL of water.

Solution: First give the equilibrium equation and expression,



$$K_{sp} = 1.80 \times 10^{-33} = [\text{Al}^{3+}][\text{OH}^-]^3$$

	$[\text{Al}^{3+}]$	$[\text{OH}^-]$	
Start	0	0	(mol L ⁻¹)
Equilibrium	x	$3x$	(mol L ⁻¹)

The value of x is the solubility of $\text{Al}(\text{OH})_3$. Thus

$$1.80 \times 10^{-33} = (x)(3x)^3$$

$$x^4 = \frac{1.80 \times 10^{-33}}{27}$$

and

$$x = 2.86 \times 10^{-9}$$

The solubility of $\text{Al}(\text{OH})_3$ is 2.86×10^{-9} mol/L. The molar mass of $\text{Al}(\text{OH})_3$ is 78.8 g/mol, so in one litre the mass of $\text{Al}(\text{OH})_3$ that dissolves is

$$2.86 \times 10^{-9} \text{ mol L}^{-1} \times 78.0 \text{ g mol}^{-1} = 2.23 \times 10^{-7} \text{ g L}^{-1}$$

Therefore, in 780 mL (0.780 L) the amount of $\text{Al}(\text{OH})_3$ dissolved will be

$$0.780 \text{ L} \times 2.23 \times 10^{-7} \text{ g L}^{-1} = 1.74 \times 10^{-7} \text{ g}.$$

This is a very small mass, as we would expect from such a sparingly soluble ionic salt such as $\text{Al}(\text{OH})_3$.

In problems where you are calculating solubility from a given K_{sp} , you need to find square roots, or cube roots, or fourth roots, and so on. This can be done easily on a scientific calculator. The following sequence demonstrates this. To find the cube root of 8,

enter $\boxed{8}$
press $\boxed{\text{INV}}$ key (or $\boxed{\text{2nd F}}$ key)
press $\boxed{y^x}$ key
enter $\boxed{3}$
press $\boxed{=}$.

This should give you the correct answer of 2. Not all calculators work in the same way so, if in doubt, consult the instruction manual for *your* calculator!

When the solubility product is exceeded, some of the ionic solid tends to precipitate out of solution. It is possible to calculate whether or not this will happen under certain conditions. It is also possible to calculate the conditions necessary for precipitation. Example 16.10 in your textbook demonstrates a problem of this type. The arithmetic involved is fairly straightforward. You have to be able to calculate concentrations and deal with dilutions (review Unit 6, CHEM 1503). The rest of the problem involves applying the principle of not exceeding the solubility product.

Fractional Precipitation

Study Section 16.7 of your textbook.

If there is more than one possible ionic salt that can precipitate, then a procedure called **selective** or **fractional precipitation** may be possible. Example 16.11 and its practice exercise deal with solutions containing more than one sparingly soluble ionic salt. Make sure you understand the reasoning discussed and method followed in these examples. Then consider the following problem.

Problem: A solution contains SO_4^{2-} at $1.0 \times 10^{-5} \text{ M}$ and some F^- ions. When some solid BaCl_2 is added, BaF_2 and BaSO_4 precipitate simultaneously. Calculate the fluoride ion concentration before precipitation.

Solution: The K_{sp} values for BaSO_4 and BaF_2 are given in Table 16.2 of your textbook. First, write the appropriate equations and equilibrium expressions for each solid.



$$K_{\text{sp}} = 1.7 \times 10^{-6} = [\text{Ba}^{2+}][\text{F}^{-}]^2$$

and



$$K_{\text{sp}} = 1.1 \times 10^{-10} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

The concentration of SO_4^{2-} is given as $1.0 \times 10^{-5} \text{ M}$, so substituting in the BaSO_4 solubility product expression,

$$1.1 \times 10^{-10} = [\text{Ba}^{2+}](1.0 \times 10^{-5})$$

$$[\text{Ba}^{2+}] = \frac{1.1 \times 10^{-10}}{1.0 \times 10^{-5}} = 1.1 \times 10^{-5}$$

Since simultaneous precipitation occurs, this is also $[\text{Ba}^{2+}]$ when the K_{sp} for BaF_2 is exceeded. So, in the BaF_2 solubility product expression

$$1.7 \times 10^{-6} = (1.1 \times 10^{-5})[\text{F}^{-}]^2$$

and

$$[\text{F}^{-}]^2 = \frac{1.7 \times 10^{-6}}{1.1 \times 10^{-5}}$$

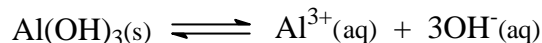
$$[\text{F}^{-}] = 3.9 \times 10^{-1} \text{ M}$$

This is the concentration of F^{-} ions at the point where precipitation just starts.

The Common Ion Effect

Study Section 16.8 of your textbook.

In addition to being used in calculating the solubility of these salts in water, K_{sp} can be used to calculate the solubility in a solution already containing one of the ions. This is an example of the **common ion effect**. The solubility of the sparingly soluble salt is lowered even further. The common ion effect is an application of Le Chatelier's principle, for example, in the case of $\text{Al}(\text{OH})_3$



The addition of either Al^{3+} or OH^{-} from another source would force the equilibrium to the left. This would mean that solid $\text{Al}(\text{OH})_3$ would precipitate out of solution. $\text{Al}(\text{OH})_3(\text{s})$ would be even less soluble than in pure water.

Work through Example 16.12 and its practice exercise in your textbook. The same type of approximation assumption is used here as was used in previous equilibrium calculations. However, you do not need to check the assumption using the 5% rule in these cases. The equilibrium constant value (K_{sp}) is so small and the equilibrium lies so far to the left that the approximation is almost always valid.

Section 16.9 of your textbook will be covered in the next unit. Section 16.10 covers another application of equilibria concepts—read this section on complex ions, but you do not need to study this material.

Qualitative Analysis by Selective Precipitation

Read Section 16.11 of your textbook. For this unit, you are not required to know any special qualitative analysis scheme but you should understand that the traditional method of separating inorganic cations is based on differences in solubilities of their salts. If you encounter laboratory time separating and identifying metallic cations, it would be useful to reread this section of the textbook.

Self-Assessment

Having reached the end of Unit 3, you should be able to:

- Write an equilibrium expression from an equilibrium equation.
- Determine if a system is in equilibrium, given the value of the appropriate equilibrium constant and the equilibrium concentrations or pressures.
- Predict, using Le Chatelier's principle, the direction in which an equilibrium will move if perturbed.
- Calculate the equilibrium constant from equilibrium concentration or pressure data.
- Calculate the concentration or pressure of reactants and products at equilibrium, given the numerical value of the equilibrium constant and data on initial or starting conditions.
- Calculate K_c from K_p and vice versa.
- Calculate K_{sp} from solubility data.
- Calculate the solubility in g/L or in mol/L of sparingly soluble ionic salts from K_{sp} data.
- Use the common ion effect in solubility product calculations.
- Perform calculations, based on K_{sp} data, where sparingly soluble salts precipitate under specified conditions.

Practice Exercise 3

Finish working through Unit 3 before starting this practice exercise which is found listed under the Practice Exercises section of course. The material in this unit is integrated throughout the practice exercises. The solutions to these problems will be provided once you have completed this practice exercise.

You may first want to try some of the supplementary exercises suggested under the next heading. However, if you feel that you have a reasonable understanding of the material, you can begin the practice exercise immediately. If you have no problems with this practice exercise, begin Assignment 3. If you feel that you need more practice, go to the Suggested Supplementary Exercises.

You should make a serious attempt to solve the practice exercises by yourself, using as a guide similar exercises from the textbook and from this unit. If your attempt is serious, you will learn a lot from the worked solutions in the Solutions to Practice Exercise 3.

Suggested Supplementary Exercises

At the end of each chapter in your textbook are further exercises on the material covered. We suggest that you do as many of these exercises as necessary. Doing such problems helps you understand and apply the principles involved in the concepts discussed. Fully worked solutions for most of the following exercises are given in the *Student Solutions Manual*. Other exercises at the ends of the chapters may have their answers in the back of the textbook, or a solution method is described in the *Student Solutions Manual*.

You should make a serious attempt to solve the problem by yourself before looking at a worked solution.

From Chapter 14:

14.7, 14.13, 14.15, 14.17, 14.19, 14.20, 14.25, 14.26, 14.28, 14.29, 14.33, 14.34, 14.37, 14.39, 14.41, 14.42, 14.43, 14.46, 14.48, 14.52, 14.58, 14.59, 14.60, 14.64, 14.67, 14.70, 14.71, 14.72, 14.74, 14.75, 14.76, 14.82

From Chapter 16:

16.50, 16.53, 16.56, 16.58, 16.60, 16.62, 16.63, 16.64, 16.65, 16.103, 16.105

Assignment 3

Now refer to your *Assignments* and complete Assignment 3. Consult your Course Guide for the week this assignment is due. Send the assignment to your Open Learning Faculty Member. You may send the assignment to your Open Learning Faculty Member using the assignment tool in Blackboard or by mail with a Marked Assignment Form. Be sure to keep a copy of the assignment—it will be useful if you wish to discuss your work with your Open Learning Faculty Member.