CHAPTER 5 – CHEMICAL EQUILIBRIUM

Introduction

The equilibrium constant was defined in Chapter 4, and calculations were done to establish the relationship between it and the standard free energy change of the reaction. However, the equilibrium constant is most valuable because it lets us predict the composition of an equilibrium mixture or to adjust the reactant concentrations so as to obtain an equilibrium mixture with the desired composition. These calculations are so important that they form the basis of this chapter and much of Chapters 6, 7, and 8, where the principles established in this chapter are applied to proton transfer, solubility, and electron transfer processes, respectively.

5.1 The Equilibrium Constant

Introduction

The thermodynamic equilibrium constant discussed in Chapter 4 is unitless because it is defined in terms of unitless activities. However, equilibrium constants can be defined in terms of partial pressures or molar concentrations. These equilibrium constants typically, but not always, have units. In this section, we introduce both types of equilibrium constants, show how to convert from one to the other, and demonstrate some of their properties.

Objectives

- Determine the value of K for a reaction given the value of K for a related reaction that differs only by a multiple or in direction.
- Determine the equilibrium constant of a reaction that is the sum of several other reactions.
- Convert between K_p and K_c.

K_p Versus K_c

5.1-1. K_p and K_c Defined

An equilibrium constant in which partial pressures are used for activities is called K_p, while one in which molar concentrations are used for activites is called K_c. For a reaction that involves only gases, K_p equals K (the thermodynamic equilibrium constant that has no units) if the partial pressures are in atmospheres because the activity of a gas is numerically equal to its partial pressure in atmospheres. For a reaction that involves only solutes in a liquid solution, K_c equals K because the activity of a solute is numerically equal to its molar concentration.

Consider the following equilibrium:

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$
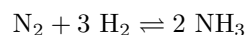
The units of K_p would be determined as follows:

$$K_p = \frac{(P_{NH_3})^2 \text{ atm}^2}{(P_{N_2}) \text{ atm} \cdot (P_{H_2})^3 \text{ atm}^3}$$

which would have units of atm^{-2}. The exponent of the units equals the sum of exponents in the numerator minus the sum of exponents in the denominator or the number of moles of products minus the number of moles of reactants, which is Δn_g. This is true for any equilibrium, so we can state that for a gas phase equilibrium,

- the units of K_p are $\text{atm}^{\Delta n_g}$
- the units of K_c are $M^{\Delta n_g}$

For solution equilibria, the units of K_c are $M^{\Delta n}$, where $\Delta n =$ the number of moles of solute products minus the number of moles of solute reactants.

5.1-2. Converting Between K_p and K_c

Since the thermodynamic K equals K_p for gas phase equilibria, K_p values are a common way to discuss their equilibria. However, there are times when it is more convenient to consider gas phase equilibria in terms of molar concentrations; i.e., in terms of K_c. In such cases, the K_p would have to be converted into a K_c. The conversion involves converting the partial pressures of the gases into molar concentrations, which is done with the ideal gas law. We first express the partial pressure of gas A in terms of its pressure as follows:

$$P_A = \frac{n_A RT}{V} = \frac{n_A}{V} \times RT$$

where P_A is the partial pressure of A, n_A is the number of moles of gas A. n_A/V is the number of moles of A per liter of gas, which is [A], the molar concentration of A. Substitution of $n_A/V = [A]$ into the above equation yields Equation 5.1, which relates the concentration of a gas to its partial pressure.

$$P_A = [A]RT \qquad \text{Pressure-Concentration Relationship} \tag{5.1}$$

Substitution of $[A]RT$ for P_A into a K_p expression converts the expression from one of pressures to one of concentrations; i.e., it converts the K_p into a K_c. Equation 5.2 summarizes the relationship.

$$
\begin{aligned}
K_p &= K_c \times (RT)^{+\Delta n_g} \\
K_c &= K_p \times (RT)^{-\Delta n_g}
\end{aligned}
\qquad \text{Relationship of } K_p \text{ and } K_c \tag{5.2}
$$

5.1-3. Converting with the Factor Label Method

If remembering which sign of Δn_g to use is a problem, then $K_p \rightleftharpoons K_c$ conversions can be done as factor label conversions in which units of $(\text{atm}^{\Delta n_g})$ are converted into units of $(M^{\Delta n_g})$ using RT as the conversion factor. R, which is the ideal gas law constant, equals 0.08206 L·atm·K^{-1}·mol^{-1}. However, it can be made more useful for converting between atm and M by recognizing that L·mol^{-1} = M^{-1}, so the units of R can be expressed as atm·K^{-1}·M^{-1}, so

- RT has units of atm·M^{-1} = atm/M.

EXAMPLE:

If $\Delta n_g = -2$, then K_p has units of atm^{-2}, so the conversion would be

$$K_c = \frac{K_p}{\text{atm}^2} \times \frac{(RT)^2 \text{ atm}^2}{M^2} = \frac{K_p(RT)^2}{M^2} = K_p(RT)^2 M^{-2}$$

Thus, $K_c = K_p(RT)^2 = K_p(RT)^{-\Delta n_g}$, consistent with Equation 5.2.

Finally, note that when $\Delta n_g = 0$, $K_c = K_p = K$. Thus, using either molarities or partial pressures in the equilibrium constant expression of a reaction consisting only of gases yields the same value of K, which is unitless and numerically equal to the thermodynamic equilibrium constant, so long as the number of moles of gas phase products equals the number of moles of gas phase reactants.

5.1-4. Thermodynamics and K Exercise

EXERCISE 5.1:

What are K, K_p, and K_c for the following at 298 K if $\Delta G° = -31.0$ kJ?

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

$\Delta n_g = $ _____
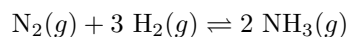
	Value	Units
K		
K_p		
K_c		

5.1-5. Exercise

EXERCISE 5.2:

Convert the given K_p to K_c at 298 K.

	Reaction	K_p
(a)	$H_2O(l) \rightleftharpoons H_2O(g)$	0.031 atm
(b)	$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$	622
(c)	$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$	6.1e5 atm^{-2}

$RT = $ _____ atm·M^{-1}

|	Δn_g		K_c	
(a)		mol		M
(b)		mol		
(c)		mol		M^{-2}

Properties of the Equilibrium Constant

5.1-6. Properties

We will use the following two aqueous equilibria for our discussions of the properties of the equilibrium constant:

$$A(aq) \rightleftharpoons B(aq) \qquad K_1 = \frac{[B]}{[A]} = 5 \qquad \text{(Equilibrium 1)}$$

$$B(aq) \rightleftharpoons C(aq) \qquad K_2 = \frac{[C]}{[B]} = 0.3 \qquad \text{(Equilibrium 2)}$$

- If the coefficients of a chemical equation are all multiplied by some number n, then the equilibrium constant of the resulting chemical equation equals the original equilibrium constant raised to the nth power: $K' = K^n$. For example, multiplying Equilibrium 1 by 3, we obtain

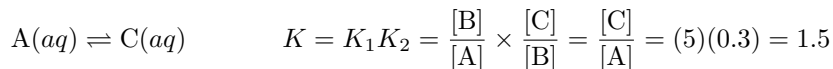$$3\,\text{A}(aq) \rightleftharpoons 3\,\text{B}(aq) \qquad K = K_1^3 = \frac{[\text{B}]^3}{[\text{A}]^3} = 5^3 = 125$$
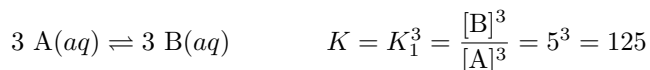
- If the direction of the equation is reversed, then the equilibrium constant of the resulting equation is the reciprocal of the original equilibrium constant: $K' = 1/K$. For example, reversing Equilibrium 1, we obtain

$$\text{B}(aq) \rightleftharpoons \text{A}(aq) \qquad K = K_1^{-1} = \frac{[\text{A}]}{[\text{B}]} = 5^{-1} = 0.2$$
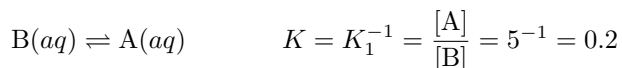
- If two chemical equations are added, then the equilibrium constant of the resulting equation is the product of the two original equilibrium constants. For example, adding Equilibria 1 and 2, we obtain $\text{A}(aq) \rightleftharpoons \text{C}(aq)$, and the equilibrium constant is then determined as follows:

$$\text{A}(aq) \rightleftharpoons \text{C}(aq) \qquad K = K_1 K_2 = \frac{[\text{B}]}{[\text{A}]} \times \frac{[\text{C}]}{[\text{B}]} = \frac{[\text{C}]}{[\text{A}]} = (5)(0.3) = 1.5$$

5.1-7. Exercise

EXERCISE 5.3:

Given the following equilibrium constants,

	Reaction	K
1	$\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{F}^{1-}(aq) + \text{H}_3\text{O}^{1+}(aq)$	7.2e$-$4
2	$\text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NO}_2^{1-}(aq) + \text{H}_3\text{O}^{1+}(aq)$	4.0e$-$4

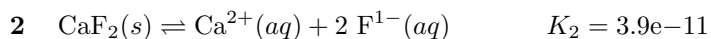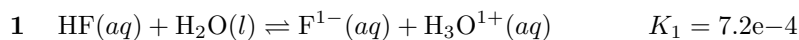Determine the value of the equilibrium constants of the following.

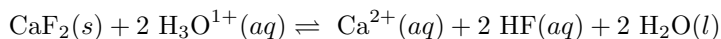| Reaction	K
$\text{F}^{1-}(aq) + \text{H}_3\text{O}^{1+}(aq) \rightleftharpoons \text{HF}(aq) + \text{H}_2\text{O}(l)$	
$\text{F}^{1-}(aq) + \text{HNO}_2(aq) \rightleftharpoons \text{HF}(aq) + \text{NO}_2^{1-}(aq)$	

5.1-8. Exercise

EXERCISE 5.4:

Given the following equilibrium constants,

1 $\quad \text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{F}^{1-}(aq) + \text{H}_3\text{O}^{1+}(aq) \qquad K_1 = 7.2\text{e}{-}4$

2 $\quad \text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\,\text{F}^{1-}(aq) \qquad K_2 = 3.9\text{e}{-}11$

Determine the equilibrium constant for the following reaction.

$$\text{CaF}_2(s) + 2\,\text{H}_3\text{O}^{1+}(aq) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\,\text{HF}(aq) + 2\,\text{H}_2\text{O}(l)$$

First determine how to sum Equations 1 and 2 to obtain the desired equation.

Which chemical equation must be reversed?

    Equation 1
    Equation 2

Equation 1 must be multiplied by what integer?

——————

Equation 2 must be multiplied by what integer?

_____

$K =$ _____

5.2 Le Châtelier's Principle

Introduction

In Chapter 4, the spontaneous direction of a reaction was predicted from known concentrations by using the fact that a reaction proceeds from left to right when $Q < K$ and from right to left when $Q > K$. We also saw that a temperature rise causes the equilibrium constants of endothermic reactions to increase and the equilbirium constants of exothermic reactions to decrease. However, the same conclusions can be drawn without calculation by applying Le Châtelier's Principle. In this section, we apply this important principle to three types of disturbances:

- changing an amount of a reactant or product
- changing the volume
- changing the temperature

Objectives

- Explain how Le Châtelier's Principle is a summary of the relationship between Q and K of the reaction.
- Use Le Châtelier's Principle and considerations of the reaction quotient and the equilibrium constant to predict the direction of the shift in equilibrium caused by stress placed on the equilibrium.

5.2-1. Statement of Le Châtelier's Principle

Le Châtelier's Principle

- If a system at equilibrium is disturbed, then the system reacts so as to counteract the disturbance.

If a substance is added, then equilibrium shifts to remove it. If a substance is removed, then equilibrium shifts to replace it. If an equilibrium is heated, then it shifts so as to remove heat. If the volume is increased, then the equilibrium shifts to produce gas to fill the increased volume.

5.2-2. Changing the Amount of a Substance

Consider Figures 5.1a–c, which show the effect of changing one concentration in an equilibrium mixture of $A + B \rightleftharpoons C + D$.

Figure 5.1a: Effect of Adding and Removing Substances from an Equilibrium Mixture
The colored rectangles represent the concentrations of each of the substances.

Figure 5.1a shows the original equilibrium in which $[A] = [B] = 0.40\ M$ and $[C] = [D] = 0.80\ M$, so

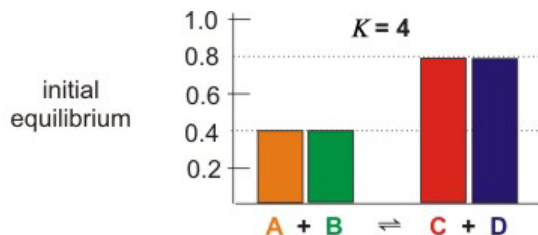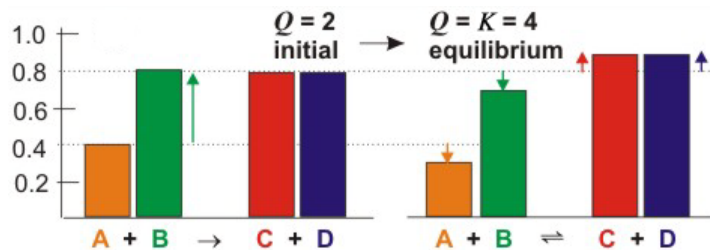$$K = \frac{[C][D]}{[A][B]} = \frac{(0.80)(0.80)}{(0.40)(0.40)} = 4.0$$

Figure 5.1b: Effect of Adding and Removing Substances from an Equilibrium Mixture
The colored rectangles represent the concentrations of each of the substances. Figures on the left correspond
to the concentrations immediately after the change occurs, while those on the right represent the resulting
equilibrium concentrations.

In Figure 5.1b, the concentration of B is increased to 0.800 M. Le Châtelier's Principle predicts that the equilibrium
should shift so as to reduce the effect of the additional B by reducing its concentration. Alternatively, we determine
that $Q = (0.80)^2/(0.40)(\mathbf{0.80}) = 2.0$ after the addition, so $Q < K$, and the reaction proceeds to the right, which
has the effect of reducing [B] as predicted by Le Châtelier's Principle. Thus, B reacts with A to produce C and D.
The changes in concentration resulting from the reaction cause Q to increase, which it does until it equals K and
equlibrium is re-established. We use the symbol Δ for the changes in concentration; i.e., [A] and [B] each decrease by
Δ, while [C] and [D] each increase by Δ. The magnitude of Δ is given by the arrows on the right side of the figure.
We will show how to determine the value of Δ in the following section, but now we simply state that a $\Delta = 0.105$ M
is required to restore equilibrium, so the new concentrations would be the following:

- [A] $= 0.400 - \Delta = 0.40 - 0.105 = 0.295$ M
- [B] $= 0.800 - \Delta = 0.80 - 0.105 = 0.695$ M
- [C] $=$ [D] $= 0.800 + \Delta = 0.80 + 0.105 = 0.905$ M

Note that we carry an extra decimal place in the concentrations to avoid rounding errors. Placing these concentrations
back into the equation for Q, we obtain

$$Q = \frac{(0.905)^2}{(0.295)(0.695)} = 4.0 = K$$

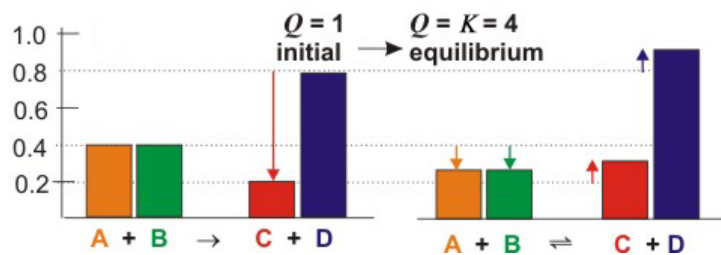Thus, $Q = K$ at these concentrations, so the system is back to equilibrium.

Figure 5.1c: Effect of Adding and Removing Substances from an Equilibrium Mixture
The colored rectangles represent the concentrations of each of the substances. Figures on the left correspond
to the concentrations immediately after the change occurs, while those on the right represent the resulting
equilibrium concentrations.

In Figure 5.1c, the concentration of C is reduced to 0.20 M, so equilibrium should shift so as to replace some
of the C; i.e., A and B must react in order to replace some of the removed C. The original conditions result in
$Q = (\mathbf{0.20})(0.80)/(0.40)^2 = 1.0$. $Q < K$, so again the reaction proceeds to the right and Q increases again until
$Q = K$ and equilibrium is re-established. Again the extent of reaction, Δ, is represented by the arrows on the right
side of the figure. In this case, $\Delta = 0.125$ M, which produces the following concentrations:

- [A] $=$ [B] $= 0.400 - \Delta = 0.400 - 0.125 = 0.275$ M
- [C] $= 0.200 + \Delta = 0.200 + 0.125 = 0.325$ M
- [D] $= 0.800 + \Delta = 0.800 + 0.125 = 0.925$ M

$$Q = \frac{(0.325)(0.925)}{(0.275)^2} = 4.0 = K$$

$Q = K$, so the new concentrations are indeed equilibrium concentrations.

5.2-3. Changing the Volume

Changing the volume changes the pressures of the gases, and Le Châtelier's Principle states that an equilibrium mixture reacts to counteract the change. At constant temperature, the only way to change the pressure is to change the number of moles of gas. Consequently, equilibrium mixtures react so as to increase the number of moles of gas when the volume of the mixture is increased or decrease the number of moles of gas when the volume is decreased.

Changing the volume changes both the pressures and the concentrations of the gases, which changes Q. The change in Q depends upon Δn_g in such a way that the same conclusions are drawn from Q and K considerations as with Le Châtelier's Principle.

5.2-4. Changing the Temperature

Changing the temperature at constant pressure changes K not Q, and Le Châtelier's Principle summarizes the effect that temperature has on the equilibrium constant. Heat can be viewed as a product of an exothermic reaction and as a reactant in an endothermic reaction. Heating an exothermic reaction is the same as adding a product, which shifts the reaction toward the reactant side ($\leftarrow$). The shift increases the equilibrium concentrations of the reactants and decreases the equilibrium concentrations of the products. The result is that the value of K is decreased in agreement with the conclusion reached using the equation $\ln(K_2) = \ln(K_1) + \dfrac{\Delta H^\circ}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$.

5.2-5. Exercises

EXERCISE 5.5:

Consider the following equilibrium:

$$3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g) \qquad\qquad \Delta H^\circ = -46\ \text{kJ}$$
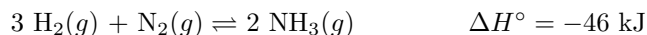
Apply Le Châtelier's Principle to determine the effect on the equilibrium pressure of N_2.

Adding H_2:
    increase
    decrease
    no change
Increasing the volume:
    increase
    decrease
    no change

Removing NH_3:
    increase
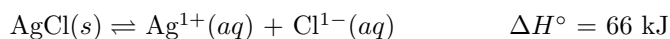   decrease
    no change
Increasing the temperature:
    increase
    decrease
    no change

EXERCISE 5.6:

Consider the following equilibrium:

$$AgCl(s) \rightleftharpoons Ag^{1+}(aq) + Cl^{1-}(aq) \qquad \Delta H^\circ = 66 \text{ kJ}$$

Indicate the effect on the equilibrium concentration of Ag^{1+} caused by the following.

Dissolving solid $AgNO_3$ in the solution:
    increase
    decrease
    no change
Increasing the temperature:
    increase
    decrease
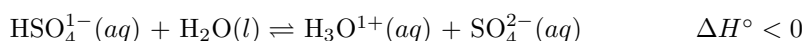   no change

Adding solid AgCl to the solution:
    increase
    decrease
    no change
Adding water:
    increase
    decrease
    no change

EXERCISE 5.7:

Consider the equilibrium:

$$HSO_4^{1-}(aq) + H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + SO_4^{2-}(aq) \qquad \Delta H^\circ < 0$$

Indicate the effect on the hydrogen sulfate ion concentration of the following.

Adding $Pb(NO_3)_2(aq)$, which precipitates $PbSO_4$ from the solution:
    increase
    decrease
    no change
Warming the solution:
    increase
    decrease
    no change

Adding hydrochloric acid to increase $[H_3O^{1+}]$:
    increase
    decrease
    no change

5.3 Using the Equilibrium Constant

Introduction

The stoichiometry problems of Chapter 1 all assumed that the limiting reactant disappeared completely during reaction. However, this assumes that the equilibrium constant is very large. In this section, we address problems in which the equilibrium constant is not very large, so the limiting reactant does not disappear completely. We will again use a reaction table as introduced in Chapter 1. The reaction table consists of three lines: the initial, change, and final. In equilibrium problems, the unknown can lie on any one of these lines or it can require filling in the table to determine the value of the equilibrium constant. In this section we show how to solve equilibrium problems.

Objectives

- Calculate the concentrations of one substance in an equilibrium mixture from the other concentrations and the equilibrium constant.
- Determine the equilibrium constant for a reaction given the initial amounts and one equilibrium amount.
- Determine the equilibrium composition from the initial composition and the equilibrium constant.
- Calculate the amount of one reactant required to react with a given amount of another reactant to produce a given amount of product.
- Determine the extent of the change caused by the addition of known amounts of reactants or products to an equilibrium mixture, given K and the initial equilibrium concentrations.

- Calculate the amount of one substance that would have to be added to an equilibrium to change the concentration of another substance in the equilibrium by a given amount.

Solving for One Concentration when K and the Other Concentrations are Known

5.3-1. Determining an Unknown Concentration

We begin with the easiest of equilibrium problems: determining an unknown concentration when all other concentrations and the equilibrium constant are known. Solving this type of problem involves setting up the equilibrium constant expression, solving it for the unknown, and substituting the known values into the resulting expression. The next two exercises demonstrate the process.

5.3-2. Exercise

EXERCISE 5.8:

What is the acetate ion concentration in a solution in which $[CH_3COOH] = 0.10$ M and $[H_3O^{1+}] = 1.0e{-}5$ M? Recall that K_a is the equilibrium constant for the reaction of an acid with water and is referred to as the acid dissociation constant.
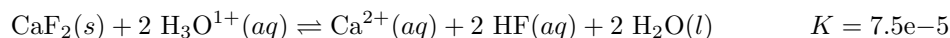
$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^{1-}(aq) + H_3O^{1+}(aq) \qquad K_a = 1.8e{-}5$$
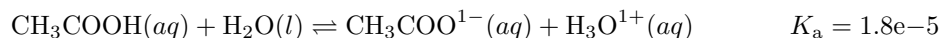
$[CH_3COO^{1-}] = $ _____ M

5.3-3. Exercise

EXERCISE 5.9:

What is the maximum calcium ion concentration that can exist in equilibrium with $[H_3O^{1+}] = 0.10$ M and $[HF] = 0.20$ M?

$$CaF_2(s) + 2\ H_3O^{1+}(aq) \rightleftharpoons Ca^{2+}(aq) + 2\ HF(aq) + 2\ H_2O(l) \qquad K = 7.5e{-}5$$

$[Ca^{2+}] = $ _____

Using Reaction Tables in Equilibrium Problems

5.3-4. Filling in the Reaction Table

The amount of a substance present in an equilibrium mixture is determined from the concentrations of all reactants and products, not just a single limiting reactant, and the reaction table is again the best way to track the changes. However, the label of the last line is changed from "final" to "eq" to emphasize that equilibrium is established. The Δ line represents the amount of each substance that must form or react in order to change from initial to equilibrium concentrations. When making entries into it, remember the following:

- It is the only line to which stoichiometry applies. If one entry on the Δ line is known, then all other entries can be determined by stoichiometry.
- If the initial system must shift to the right ($\rightarrow$, $Q < K$), the concentrations of everything on the right (product) side of the reaction must increase ($\Delta > 0$), while all concentrations on the left side must decrease ($\Delta < 0$).
- If the shift is to the left ($\leftarrow$, $Q > K$), the concentrations of everything on the left side must increase ($\Delta > 0$), while the concentrations of everything on the right side must decrease ($\Delta < 0$).

5.3-5. Types of Equilibrium Problems

We will be doing equilibrium problems in most of the remaining chapters as we examine acid-base, solubility, and redox equilibria. However, there are only three different kinds of equilibrium problems:

1. Determine K from the equilibrium concentrations. If K is the unknown, then the reaction table can contain no unknowns.

2. Determine the equilibrium concentrations from K and a set of initial concentrations. The unknown is in the Δ line and therefore also in the equilibrium line. We will use x as our unknown identifier.

3. Determine the amount of substance that must be added (removed) to (from) a known amount of another reactant to produce a desired equilibrium concentration. The unknown is in the initial line.

You should realize that the methods set forward in the remainder of this chapter will be used repeatedly in subsequent chapters. We examine each of these types in the following exercises.

Determining K

5.3-6. Method

In order to determine K, you must be given sufficient information to determine the equilibrium concentrations. This information can be given directly, but many times only the initial concentrations and the final concentration of just one of the substances are given. Setting up a reaction table is the easiest way to establish the other concentrations.

In these cases, use the following method:

1. Enter the given concentrations into the reaction table.

2. Determine the entry on the Δ line of the substance whose final concentration is given by subtracting the initial concentration from the equilibrium concentration: $\Delta = \text{eq} - \text{initial}$.

3. Determine the other entries on the Δ line by applying stoichiometry to the entry determined in Step 2.

4. Determine the other equilibrium concentrations by adding the initial and Δ lines.

5. Use the equilibrium concentrations determined in Step 4 to determine K.

5.3-7. K_c for a Gas Phase Reaction

EXERCISE 5.10:

At some temperature, 6.0 moles of hydrogen and 4.0 moles of nitrogen are added to a 10.0 L flask and allowed to react. At equilibrium, there is 1.0 mole of hydrogen remaining. What is the value of K_c for the following reaction at this temperature? Fill in the reaction table in molar concentrations, then determine K. **Include the signs in the Δ line, even when positive.**

	$N_2(g)$	+	$3\ H_2(g)$	$\rightleftharpoons$	$2\ NH_3(g)$	
initial						M
Δ						M
eq						M

$K_c = \underline{\hspace{2cm}} M^{-2}$

5.3-8. Aqueous Reaction

EXERCISE 5.11:

10. mmol of NH_4Cl and 15 mmol of KCN are dissolved in enough water to make 200. mL of solution. What is the value of the equilibrium constant of the following reaction if $[NH_4^{1+}] = 0.018\ M$ at equilibrium? Fill in the reaction table and then use the equilibrium values to determine K. The entries in the Δ line must include the sign.

	$NH_4^{1+}(aq)$	+	$CN^{1-}(aq)$	$\rightleftharpoons$	$NH_3(aq)$	+	$HCN(aq)$	
initial								M
Δ								M
eq								M

$K = $ _____

Determining Equilibrium Amounts

5.3-9. Method

If you are asked for an equilibrium concentration or pressure, you must be given the value of K and the initial conditions. The unknown (x) is in the reaction table. To find equilibrium concentrations or pressures given the equilibrium constant and the initial concentrations, use the following method.

1 Put the initial quantities in the reaction table.

2 If both reactants and products are present, calculate Q and determine the direction in which the reaction is proceeding by comparing Q and K. This will help you decide upon the signs to use with the entries on the Δ line.

3 Use x's to complete the Δ line. To simplify stoichiometry considerations, the coefficient of x in each entry should be the same as the coefficient in the balanced equation for that substance. Be sure to include the proper sign.

4 Add the initial and final lines to get the equilibrium line.

5 Substitute the equilibrium line entries into the equilibrium constant expression and solve for x.

6 Use the value of x determined in Step 5 and the expressions for the equilibrium concentrations to determine the equilibrium concentrations or pressures.

5.3-10. Hints to Simplify the Problems

Equilibrium problems involving gas phase reactions in which $\Delta n_{\mathrm{g}} = 0$ can be done in moles rather than molarities because the volumes cancel.

K_{c} depends upon the equilibrium concentrations, which depend upon the volume of the container and the number of moles of each species present. However, if $\Delta n_{\mathrm{g}} = 0$, the volumes in the numerator and denominator cancel, so K_{c} depends only upon the number of moles. In other words, equilibrium problems on gas phase reactions in which $\Delta n_{\mathrm{g}} = 0$ can be done in moles rather than molarities. However, if Δn_{g} is not zero, you must convert to molarities in order to use a K_{c}.

Taking the square root of both sides of the equilibrium expression will often simplify the algebra.

Solving an equilibrium expression can be very difficult because many expressions contain high order terms. However, the problems in this course have been constructed to simplify the algebra, so you can focus on the equilibrium.

Many of the problems involve squares and can be solved with the quadratic equation, but most of these can be simplified because the equilibrium expression is a perfect square. In these cases, take the square root of both sides of the equation before solving for x.

5.3-11. Equilibrium Moles

EXERCISE 5.12:

0.80 mol N_2 and 0.80 mol O_2 are mixed and allowed to react in a 10 L vessel at 2500 °C. How many moles of nitric oxide would be present when the equilibrium is established? Use x as the unknown identifier.

Hint: You are given moles and are asked for moles, and $\Delta n_g = 0$, so the problem can be done in moles with the given equilibrium constant.

	N_2	+	O_2	$\rightleftharpoons$	2 NO	$K = 2.1e{-}3$
initial						mol
Δ						mol
eq						mol

The equilibrium constant expression is a perfect square, so take the square root of both sides and solve for x.

$x =$ _____ mol   moles of NO = _____ mol

5.3-12. Determining Equilibrium Pressures

EXERCISE 5.13:

What are the equilibrium pressures in a mixture if the initial pressures of CO and H_2O are each 0.200 atm?

	$CO(g)$	+	$H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$H_2(g)$	$K = 10.0$
initial								atm
Δ								atm
eq								atm

The equilibrium constant expression is a perfect square, so take the square root of both sides and solve for x.

$x =$ _____ atm

$P_{CO} = P_{H_2O} =$ _____ atm $P_{CO_2} = P_{H_2} =$ _____ atm

5.3-13. Re-establishing Equilibrium After an Addition

EXERCISE 5.14:

At a temperature near 450 °C, an equilibrium mixture in a 1.0 L flask contains 0.70 mol of HI(g) and 0.10 mol each of $I_2(g)$ and $H_2(g)$. If 0.30 mol of H_2, 0.30 mol of I_2, and 0.10 mol of HI are injected into this equilibrium mixture, how many moles of each gas will be present when equilibrium is re-established?

	H_2	+	I_2	$\rightleftharpoons$	2 HI		
initial equilibrium						mol	$K =$
injected						mol	
initial						mol	$Q =$
Δ						mol	
eq						mol	

The equilibrium constant expression is a perfect square, so take the square root of both sides and solve for x.

$x =$ _____ mol

moles of HI = _____ mol

moles of H_2 = moles of I_2 = _____ mol

Determining the Amount to Add or Remove

5.3-14. Method

Another important calculation involves determining how much of one substance to add or remove in order to get a desired amount of one of the substances. In these cases, the unknown lies in the initial line. Sometimes, you add or remove the substance from an equilibrium mixture, but the equilibrium mixture cannot be the initial line because nothing would happen if it were at equilibrium. However, adding or removing a substance from an equilibrium line makes it an initial line. Remember that you will have only one unknown in each problem, so there are no other unknowns if one is already in the initial line.

5.3-15. Percent Yield

EXERCISE 5.15:

At 700 K, the equilibrium constant for $H_2 + I_2 \rightleftharpoons 2$ HI is 49.0. How many moles of H_2 would have to be added to 1.00 mol I_2 in a 1.00 L flask to get a 90.0% yield? Use x for the number of moles to be added.

	H_2	+	I_2	$\rightleftharpoons$	2 HI	$K = 49.0$
initial						mol
Δ						mol
eq						mol

$x =$ _____ mol H_2 must be added

5.3-16. Adding Reactants to Shift Equilibrium to Desired Position

EXERCISE 5.16:

An equilibrium mixture in a 1.00 L flask at some temperature was found to contain 0.0500 mol of SO_2, 0.0250 mol of O_2, and 0.0180 mol of SO_3. How many moles of O_2 should be added to this equilibrium mixture to double the number of moles of SO_3 at equilibrium?

Note that Δn_g does not equal zero, so the problem must be done in molarity. However, the reaction takes place in a 1.00 L flask, so the molarity of each gas equals the number of moles.

	2 SO_2	+	O_2	⇌	2 SO_3	
initial						M
Δ						M
eq						M

$K_c =$ _____ M^{-1}

The number of moles of O_2 that must be added = _____ mol

Putting it Together

5.3-17. Mixing an Acid and a Base

EXERCISE 5.17:

100. mL of a 0.10 M solution of KF and 100. mL of a 0.10 M solution of HNO_2 are mixed.

What are the equilibrium concentrations in the final solution?

	$F^{1-}(aq)$	+	$HNO_2(aq)$	⇌	$HF(aq)$	+	$NO_2^{1-}(g)$	$K = 0.56$
initial								M
Δ								M
eq								M

The equilibrium constant expression is a perfect square, so take the square root of both sides and solve for x.

$x =$ _____ M

$[F^{1-}] = [HNO_2] =$ _____ M $[HF] = [NO_2^{1-}] =$ _____ M

EXERCISE 5.18:

The equilibrium mixture in the previous exercise was $[\text{F}^{1-}] = [\text{HNO}_2] = 0.029\ M$ and $[\text{HF}] = [\text{NO}_2^{1-}] = 0.021\ M$. By how much should the fluoride ion concentration be increased to increase the HF concentration to $0.040\ M$?

	$\text{F}^{1-}(aq)$	+	$\text{HNO}_2(aq)$	$\rightleftharpoons$	$\text{HF}(aq)$	+	$\text{NO}_2^{1-}(g)$	$K = 0.56$
initial								M
Δ								M
eq								M

Solve the equilibrium expression for x.

$x =$ _____ mol/L fluoride ion must be added

5.4 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.